Available online at www.sciencedirect.com
SCIENCE DIRECT®
Applied Geochemistry 21 (2006) 1288–1300
Applied Geochemistry
www.elsevier.com/locate/apgeochem

An Apatite II permeable reactive barrier to remediate groundwater containing Zn, Pb and Cd

James L. Conca [a,*], Judith Wright [b]

[a] *New Mexico State University at CEMRC, 1400 University Drive, Carlsbad, NM, USA*
[b] *PIMS NW Inc., 403 W. Riverside Drive, Carlsbad, NM, USA*

Abstract

Phosphate-induced metal stabilization involving the reactive medium Apatite II™ [$Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$], where $x < 1$, was used in a subsurface permeable reactive barrier (PRB) to treat acid mine drainage in a shallow alluvial groundwater containing elevated concentrations of Zn, Pb, Cd, Cu, SO_4 and NO_3. The groundwater is treated *in situ* before it enters the East Fork of Ninemile Creek, a tributary to the Coeur d'Alene River, Idaho. Microbially mediated SO_4 reduction and the subsequent precipitation of sphalerite [ZnS] is the primary mechanism occurring for immobilization of Zn and Cd. Precipitation of pyromorphite [$Pb_{10}(PO_4)_6(OH,Cl)_2$] is the most likely mechanism for immobilization of Pb. Precipitation is occurring directly on the original Apatite II. The emplaced PRB has been operating successfully since January of 2001, and has reduced the concentrations of Cd and Pb to below detection (2 μg L^{-1}), has reduced Zn to near background in this region (about 100 μg L^{-1}), and has reduced SO_4 by between 100 and 200 mg L^{-1} and NO_3 to below detection (50 μg L^{-1}). The PRB, filled with 90 tonnes of Apatite II, has removed about 4550 kg of Zn, 91 kg of Pb and 45 kg of Cd, but 90% of the immobilization is occurring in the first 20% of the barrier, wherein the reactive media now contain up to 25 wt% Zn. Field observations indicate that about 30% of the Apatite II material is spent (consumed).

1. 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, and Pb and Cd are the contaminants of concern with respect to human health and wildlife. In 1995, the site of the Success mine and mill was identified as the largest remaining metals loader in the Ninemile Creek drainage (Golder, 2000). 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. On the basis of 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 load to this drainage at high- and low-discharge periods, respectively. The primary source of the metals loading was identified as groundwater discharge from the toe of the Success tailings and waste-rock pile to the East Fork of Ninemile Creek (Golder, 2000). Up to this time, the removal of metal sources within this area had relied primarily on the excavation and transporta-

---

* Corresponding author.
E-mail address: jconca@cemrc.org (J.L. Conca).

0883-2927/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.apgeochem.2006.06.008

tion of materials to hydraulically isolated repositories. Because of the large volume of source materials in the region, it was decided to investigate the use of permeable reactive barriers to treat waters as they emerged from these sources. A permeable reactive barrier (PRB) was installed at the Success site in 2001, and the objective of this study was the evaluation of its performance over the next 4 years.

PRBs consist of a water-permeable material that has specific chemical reactivities towards one or more chemical constituents via mechanisms such as adsorption, exchange, oxidation–reduction, or precipitation. These barriers can have various ranges of specificity, e.g., adsorption of Sr and microbes by modified zeolite (Bowman, 2003), precipitation of metals by apatite (Bostick et al., 1999; Conca et al., 2000, 2003; Fuller et al., 2002; Matheson et al., 2002; Wright et al., 2004a), or reduction by zero-valent Fe, other Fe phases, or microbial activity (Starr and Cherry, 1994; Benner et al., 1997; Tratnyek et al., 1997; Puls et al., 1999; Goldstein et al., 2000; Naftz et al., 2000). The results of previous and ongoing work demonstrate that stabilization of contaminated soils and groundwater by apatite-group minerals has the potential to be a successful and widely applicable remediation strategy for metals and radionuclides (McArthur et al., 1990; Ma et al., 1993, 1995; Ruby et al., 1994; Stanforth and Chowdhury, 1994; Xu and Schwartz, 1994; Chen et al., 1997a, 1997 b; Eighmy et al., 1997; Zhang et al., 1998; Manecki et al., 2000; Wright et al., 2004a,b, 2005).

Apatite-group minerals form naturally and are stable across a wide range of geological conditions for hundreds of millions of years (Nriagu, 1974; Wright, 1990a,b). Work by Wright and others (Wright et al., 1984, 1987a,b, 1990) investigated the trace-element composition of fossil apatite (teeth and bones) and sedimentary phosphorite deposits of various geological ages. It was observed that sedimentary and biogenic apatite deposited in seawater not only concentrates metals and radionuclides from the seawater to millions of times the ambient concentration, but also locks 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 and pH, temperatures of more than 500 °C, and tectonic disruptions. Including isostructural species, more than 300 apatite-type minerals exist, with elements from the entire periodic table replacing Ca, P, and OH in the fundamental apatite crystal structure (Skinner, 1989). Their solubility products (K_{sp}) vary from about 10^{-20} to 10^{-150} (Nriagu, 1974; Manecki et al., 2000).

2. Materials and methods

The reactive medium used for the PRB at the Success site is Apatite II™ (US Patent #6,217,775), a biogenically precipitated apatite material that is derived from fish bones and has the general composition $Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$, where $x < 1$, along with 30–40% by weight of associated organic materials in the internal porosity of the inorganic structure. Apatite II was chosen because in Success mine site-specific feasibility tests its performance with respect to metal-loading capacity and ability to reduce metal concentrations in solution below regulatory limits was better than various other materials, among which were phosphate rock, cow bone, C-sorb (a polymer used in remediation of mine wastes), the zeolites clinoptilolite and chabazite (Carbsorb), Fe^0 filings, compost, and activated charcoal (Conca, 1997; Conca et al., 2000). Because Apatite II is derived from fish-bone waste, its production does not cause environmental degradation, unlike the mining of phosphate rock and the production of phosphate fertilizers (Florida Institute of Phosphate Research, 2003).

Water samples were collected in the field during regular monitoring activities and were 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^-, NO_3–N and SO_4^{2-} were measured using Method 300.0, NH_3 was measured using Method 350.1, $NO_3^+ + NO_2^-$ was measured using Method 353.2, total and dissolved orthophosphate 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. Through the courtesy of Neal Yancy of the Idaho National Laboratory (INL), various portable field probes were used periodically by personnel from INL to test waters in the field for dissolved O_2 and Eh.

3. Geological setting

The Success site is in Shoshone County, approximately 8 km NE of Wallace (Fig. 1), and is underlain by the Belt series of Precambrian age (Hobbs et al., 1965). The site, incorporating the mine, mill foundations, and a ~300,000 m^3 tailings and waste-rock pile, covers an area of about 4 ha 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 a relatively wide (120 m), almond-shaped alluvial flat on the east side of an otherwise narrow V-shaped canyon. The waste pile (360 m in length, about 45 m high with side slopes of up to 40°) occupies the lower half of the almond-shaped flat (SAIC, 1993). There are 6 to 18 m of ground between the creek and toe of the pile. The EFNC, with a gradient between 7 and 8% from 1152 m to 1082 m above sea level across the site, flows into the main stem of Ninemile Creek about 2.1 km downstream of the Success site. The confluence of Ninemile Creek with the South Fork of the Coeur d'Alene River occurs 6.9 km down-stream of Success. The EFNC basin receives an average of 1270 mm precipitation/a. The average annual flow for the EFNC is estimated at 0.45 $m^3\ s^{-1}$, with a 2-a peak flow of 4.78 $m^3 s^{-1}$, a 50-a peak flow of 12.0 $m^3 s^{-1}$, and a 100-a peak flow of 13.6 $m^3 s^{-1}$. Peak flows typically occur in April and May (SAIC, 1993).

The Success deposit, discovered in 1885, was mined from 1886 to 1932 and was reworked from 1934 to 1956, producing about 717,000 tonnes of ore. In 1993, the EPA completed a time-critical response action at Success that involved relocation of the EFNC into an armored 500-a channel (Fig. 2), 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. After the site was 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. The team decided on emplacement of a PRB as the preferred alternative because 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). Installation of the PRB was completed in January of 2001.

4. Sequestration mechanisms in apatite

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 geological time. The stabilization efficiency comes from the extremely low solubility products (K_{sp}) of the resultant metal-apatite, e.g.,

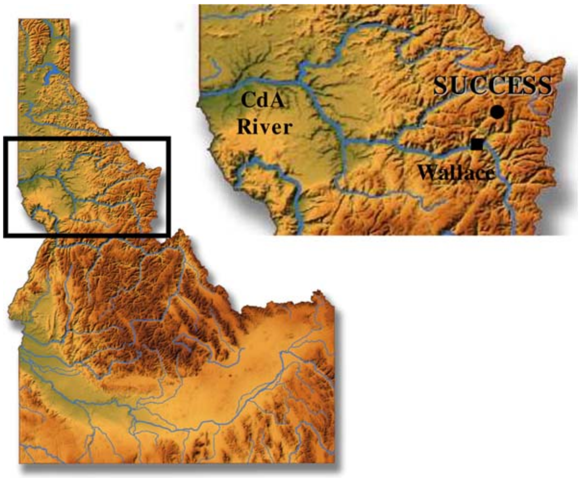

Fig. 1. Location map for the Success mine and mill site, Idaho.

Fig. 2. Success mine tailings and waste-rock pile, with the East Fork of Ninemile Creek in the foreground.

for the Pb-dominant member [pyromorphite, $Pb_5(PO_4)_3Cl$] $K_{sp} < 10^{-80}$ (Nriagu, 1974; Geochem Software Inc., 1994; Ruby et al., 1994; Manecki et al., 2000). 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 transport mechanisms (Koeppenkastrop and De Carlo, 1990; Lower et al., 1998). The solubility of unreacted Apatite II, $K_{sp} = \sim 10^{-20}$, means that Apatite II will persist in the environment for a long time without causing phosphate loading.

Apatite II works to sequester metals by 4 general, non-mutually-exclusive processes depending upon the metal, concentration and aqueous chemistry. First, Apatite II continuously supplies a small, but sufficient, amount of PO_4^{3-} to solution to exceed the solubility limits of various metal-phosphate solids such as pyromorphite. Depending upon the metal concentration and other solution conditions, the metal-phosphate will precipitate via homogeneous nucleation directly from solution at higher metal concentrations, or by heterogeneous nucleation onto a pre-existing phase of similar structure at lower concentrations, i.e., a seed crystal (Wright et al., 1995; Lower et al., 1998). Under environmental conditions, heterogeneous nucleation dominates for Pb and most other metals, and a seed crystal of apatite is necessary to precipitate pyromorphite. Homogeneous nucleation in the absence of a seed crystal of apatite or autunite [$Ca(UO_2)_2(PO_4)_2 \cdot nH_2O$] will not occur unless Pb concentrations exceed about 10 mg kg^{-1} (Xu and Schwartz, 1994; Lower et al., 1998), which is a condition rarely achieved in the environment, even for acid mine drainage. This observation is 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.

The reaction between the apatite and metals is too rapid to be measured accurately (Koeppenkastrop and De Carlo, 1990; Ma et al., 1993, 1995; Wright et al., 1995; Chen et al., 1997a, 1997 b), 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 and rate with which dissolved metals come into contact with the surfaces of the reactive media.

For Pb, the overall reaction is a two-step dissolution reaction of the Apatite II and precipitation of pyromorphite:

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

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

The degree of protonation of the phosphate and carbonate in the intermediate reactions depends upon the pH. The above example is for the typical range of acid mine drainage, i.e., pH between 3 and 6. Reaction (1) does not necessarily lead to reaction (2). However, because the apatite provides a small but constant supply of phosphate to solution, if Pb^{2+} is in solutions contacting the apatite, then reaction (2) will take place. Apatite II dissolution is a strong pH buffering reaction, buffering around neutral (6.5–7) through its PO_4^{3-}, OH^- and substituted CO_3^{2-} groups. This pH increase alone is effective at precipitating many metal-bearing phases, particularly of Al and Fe. This is the second of the 4 processes by which Apatite II sequesters metals. Sulfate reduction (reaction (3) below) also provides strong pH buffering in this particular system. 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, and was observed to adsorb up to 5% of its weight by this mechanism (Conca, 1997).

The fourth process is precipitation of insoluble metal phases as a result of chemical changes induced by biological activity. Biological stimulation of SO_4-reducing bacteria by the Apatite II, followed by precipitation of ZnS, is the primary mechanism of Zn sequestration in the PRB at the Success site. Apatite II supplies both P and readily bioavailable organic material at low but optimal concentrations for stimulating microbial communities (Martinez et al., 2005), especially SO_4- and NO_3-reducing bacteria and others important to biodegradation of contaminants such as TNT and perchlorate. Apatite II contains between 30% and 40% organic material by weight, mostly collagen with various amounts of more soluble proteins, fats, and lipids, such as cholesterol, that remain after processing of the fish bone

(Martinez et al., 2005). The organic substances are slowly leached from the capillary pores and other microporosity of the Apatite II, and the equilibrium concentration of P from dissolution of the Apatite II is usually between 1 and 10 mg L^{-1}, but is as low as 0.5 mg L^{-1} and as high as 50 mg L^{-1}, depending upon pH and major solution chemistry. Martinez et al. (2005) hypothesized that Apatite II reduces metal concentrations, whose toxicity might otherwise prevent or limit microbial activity. The 90 tonnes of Apatite II within the PRB can sustain these biologically favorable conditions for 10–20 a, depending upon flow rate and solution chemistry.

Within the Success mine PRB, SO_4-reduction using organic C from the Apatite II can be represented as (Benner et al., 1997; Scherer et al., 2000):

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \qquad (3)$$

$$Zn^{2+} + HS^- \rightarrow ZnS + H^+ \qquad (4)$$

The CH_2O represents the organic C from the Apatite II that serves as both electron donor and C source for the SO_4-reducing bacteria (Scherer et al., 2000). There are no other sources of organic C within this system. As will be discussed below, the SO_4 reduction within the Success PRB is being microbially mediated by *Entercocci*. The solubility of the sphalerite, represented by the reverse reaction in (4), is still very low, $K_{sp} < 10^{11}$ (Geochem Software Inc., 1994); therefore, the stability of the resulting product from a remediation standpoint is good, and concentrations of Zn and S exiting the PRB should be low, as is the case for the PRB at the Success site.

For Pb, U, Ce, Pu, Mn and other metals for which precipitation into an apatite mineral structure is the primary mechanism of removal from solution, e.g., reaction (2), the solubility of the new phase controls the equilibrium concentration of the metal in solution (Geochem Software Inc., 1994; Eighmy et al., 1997; Lower et al., 1998; Manecki et al., 2000). Differences in the performance among various apatite members results 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 (the presence of carbonate decreases crystal-structure stability, thereby increasing solubility and dissolution rate; in contrast, F increases the stability and therefore decreases the solubility and dissolution rate. However, for Zn, Cd, Cu, and other transition metals, adsorption and (or) precipitation onto non-apatite minerals, such as sulfides, are the primary mechanisms. Therefore, the performance with respect to these metals, and their equilibrium concentrations, depends upon the adsorption characteristics of the apatite and on properties such as the amount and type of organic material, solution chemistry, surface properties, grain size, degree of crystallinity and competing ions.

Studies by Wopenka and Pasteris (2005) have shown that the nanocrystalline apatite mineral in bone material is mineralogically unique relative to abiotic hydroxylapatite [$Ca_5(PO_4)_3(OH)$], and it may be misleading to consider bone as hydroxylapatite (Wopenka and Pasteris, 2005). The OH does not occupy a significant fraction of the hydroxyl positions in bone apatite, and only occurs in high concentrations in tooth enamel and less so in dentin (Pasteris et al., 2004). It is unclear how charge balance is maintained in living bone, although biomolecular processes probably control this condition in order for the organism to tailor bone structure and composition to specific biological functions. It is important to note these discrepancies because predictive modeling of reactive media uses thermodynamic data from well-defined solids and may not reflect the behavior of special materials like Apatite II. Fish-bone apatite is different even than mammalian bone as it is not weight-bearing, and is even less crystalline. Fig. 3 shows some high-resolution transmission electron microscopy images (HR–TEM, Lu et al., 2001) comparing the structural properties of the Apatite II, cow bone, and mineral apatite. The Apatite II shows a poorly to non-crystalline matrix (no lattice structure evident) with dispersed thin nanocrystals. The cow bone and the apatite from phosphate rock show well-developed lattice structures associated with a high degree of crystallinity. For remediation of metals, the cow bone is a less effective apatite, on average having only 1/10 to 1/100 the metal uptake capacity of Apatite II per mass (Conca, 1997; Bostick et al., 1999; Conca et al., 2000), presumably because of its higher crystallinity (results were similar for charred and uncharred cow bone). The apatite in all phosphate rock is less effective still, with only 1/100 to 1/10,000 of the metal uptake capacity of Apatite II, because of its high crystallinity, large amount of F substitution, the lack of carbonate substitution, the low internal porosity, and the high content of trace metals (Bostick et al., 1999; Conca et al., 2000, 2003).

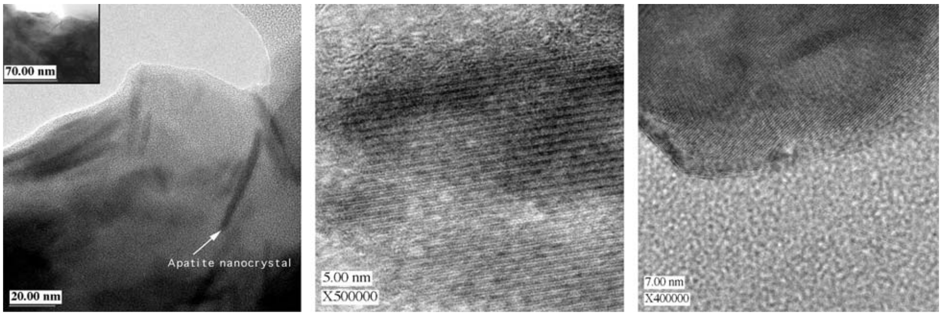

Fig. 3. HR-TEM images of three different apatite types. Left: Apatite II, Showing the X-ray amorphous nature of the matrix with random nanocrystal inclusions of cryptocrystalline apatite embedded throughout. Center: Cow bone, showing the highly crystalline nature of the apatite. Right: North Carolina phosphate rock (mineral apatite), showing the highly crystalline nature of the apatite.

5. Results and discussion

5.1. PRB installation

Pre-installation site investigations included excavation of test pits, installation of piezometers and five pairs of deep/shallow groundwater monitoring wells 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 5 and 6.8 m below ground surface, with an average downgradient surface slope of 7.5%. The unconsolidated material above bedrock comprises fill material, including a layer of mixed tailings and alluvium that is 0.6–2.1 m thick and overlies a poorly sorted alluvium. The concentrations of Cd, Pb and Zn within soils and groundwater between the tailings pile and the EFNC are summarized in Tables 1 and 2, along with the EPA's 1999 risk-based guidance levels and water standards. As shown in Table 2, samples taken from the shallow monitoring wells indicate that the groundwater within the unconsolidated aquifer between the tailings pile and the EFNC significantly exceeds the criteria for drinking water and aquatic life.

Table 1
Cd, Pb and Zn in soils between the tailings pile and the EFNC

Analyte	Concentration range ($\mu g\ kg^{-1}$)	Guidance level[a] ($\mu g\ kg^{-1}$)
Total Cd	10.5–125	5700
Total Pb	1690–90,800	2000
Total Zn	1600–9060	57,000

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

Table 2
Cd, Pb and Zn concentrations ($ng\ L^{-1}$) in groundwater between the tailings and EFNC

Analyte	Concentration range	Drinking-water criteria[a]	Aquatic criteria[b]
Dissolved Cd	8–1250	5	1
Dissolved Pb	70–1440	15	2.5
Dissolved Zn	4850–177,000	5000	100

[a] Federal maximum contaminant level (MCL) for protection of drinking water.

[b] State chronic criteria for the protection of fresh water aquatic life.

Over the lower portion of the site, where the tailings pile is within 18 m of the creek, the contaminated groundwater within the alluvial aquifer discharges directly to the creek (Fig. 2). The hydraulic conductivity of the alluvial aquifer averaged $0.61 \times 10^{-3}\ m\ s^{-1}$ (TerraGraphics, 1998; Golder, 2000). The hydraulic conductivity of the shallow bedrock averaged $2 \times 10^{-5}\ m\ s^{-1}$. Flow estimates based on the site geometry, ranges of hydraulic conductivity, and water levels measured in May 2000, indicate that between 0.68 and 23 $m^3\ h^{-1}$ (3 and 100 gpm) of shallow groundwater flows out of the alluvial aquifer at the downgradient end of the site, strongly dependent upon seasonal precipitation (Golder, 2000).

Extrapolation of the feasibility results indicated that 90 tonnes of Apatite II could reduce concentrations of dissolved Zn to below 5 $\mu g\ L^{-1}$, and could neutralize the pH and buffer it to around 6.5 for about 3 a assuming a flow-through rate of 1.1 $m^3\ h^{-1}$ (5 gpm) and an inflow dissolved-Zn concentration of 155 $mg\ L^{-1}$ (TerraGraphics, 1998). Feasibility results also indicated that concentrations of dissolved Cd and Pb would be reduced to below 15 $\mu g\ L^{-1}$ for many years. The PRB design included construction of a pressure-grouted wall, 441 m long, between the waste pile and the EFNC (Golder, 2000); the wall extends vertically from the upper 0.3 m of bedrock to about 0.6–1 m above the spring groundwater high. 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 PRB vault, 4.1 m high and 4.5 m wide by 15.2 m long with two separately plumbed cells (East and West), was poured into rebar-reinforced forms using Type V (corrosion resistant) Portland cement.

The vault was designed with an inflow port, two side-by-side baffled PRB treatment cells (each consisting of five connected chambers) and two outflow ports with a head drop of 2.3 m from the inflow. The plumbing was installed inside the vault and about 103 m^3 of Apatite II (about 90 tonnes at \$330 t^{-1}) were placed within all of the chambers of the two cells. The West cell has 100% Apatite II and the East cell has 50% gravel and 50% Apatite. Interior cell dimensions measured about 2.7 m in height, 3 m in width, and 13.7 m in length. A compartment containing clean, rounded gravel was designed as the up-gradient front to the two PRB treatment cells. Groundwater entering the vault through the inlet flows downward through the gravel and enters the two PRB treatment cells at their base, thence passing through each of the series of baffled chambers that makes up a cell, moving up and down through the barrier to maximize contact with the reactive media. 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 control flow. The vault outflow discharges to the EFNC via a rock-apron outfall. Construction was completed between September 2000 and January 2001 (Fig. 4). Emplacement used traditional trenching and earth-moving equipment.

Fig. 4. The emplaced Apatite II PRB at the Success mine, between the East Fork of Ninemile Creek and the tailings pile, September 2002.

5.2. Monitoring and performance

Monitoring began in January 2001, a few days after the vault valves were opened. Observations were made on the composition, volume, pH, and temperature of the water flowing into and out of the vault, and on the water levels in front of and within the vault were measured. 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 in February 2002, the operation, maintenance and monitoring of the PRB was taken over by the Idaho DEQ. The monitoring results to date are presented in Table 3 as an average of the two cells. Generally, concentrations of dissolved metals are greatly reduced and the pH is buffered to between 6 and 7. The rise in metal concentrations exiting the PRB in June and August 2001 resulted from

Table 3
Dissolved metal concentrations entering and exiting the Apatite II PRB

Date	Entering barrier (μg L^{-1})				Exiting barrier (μg L^{-1})			
	pH	Cd	Pb	Zn	pH	Cd	Pb	Zn
1/20/01	–	–	–	–	7.0	<2	<5	14
3/23/01	4.5	333	1230	44,700	6.0	<2	<5	27
6/1/01	5.0	413	1400	58,500	7.0	8	65	900
8/20/01	4.5	379	1290	53,700	6.5	6	11	775
10/27/01	5.0	437	1110	71,300	6.5	<2	<5	74
1/10/02	5.0	779	1210	116,000	6.5	<2	<5	66
6/27/02	4.8	726	1450	57,230	6.9	<2	<5	243
8/02/02	4.2	430	1185	64,600	7.1	<2	<5	83
10/19/02	4.5	414	1030	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	1190	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	1310	122,000	6.9	<2	<5	19
7/1/03	4.5	749	1350	146,900	6.8	<2	<5	59
10/3/03	4.6	587	1330	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

hydraulic problems (flooding and circumvention around one of the PRB cells). Maintenance activities, including additional grouting, in September 2001 corrected the hydraulic problem and, in October 2001, metal concentrations were again reduced to very low levels. In general, the two cells behaved similarly, with the West Cell performing slightly better with respect to flow and metal sequestration, presumably because the West Cell contained 100% Apatite II instead of the 50/50 mix with gravel. Although the subsequent discussions and specific numbers are from the West Cell, the trends are the same for both cells.

The barrier was designed to treat 1.1 $m^3 h^{-1}$ (5 gpm), and flow through the barrier has been between 0.2 and 1.1 $m^3 h^{-1}$ (1 and 5 gpm) for most of the 5 a. Flow from the tailings pile ranges from <0.2 $m^3 h^{-1}$ to >11 $m^3 h^{-1}$ (<1 to >50 gpm) ahead of the PRB. Overflow is directed around the barrier.

On the basis of periodic daily metal-loading averages, the PRB has sequestered about 45 kg of Cd, 91 kg of Pb and 4550 kg of Zn over the 5 a since it was emplaced. The barrier was estimated to last for at least 30 a with respect to Cd, Pb and pH, but Zn should begin its breakthrough within 10 a if the results of the feasibility study are an accurate indication of performance (Conca, 1997; TerraGraphics, 1998). Judging from visual examination of the cells with respect to precipitation of sphalerite, dissolution of Apatite II, and loss of organic content, about 30% of the Apatite II in the PRB appears to be spent. This is mostly evident in the first two cells of the PRB.

Analytical results obtained in August 2002 as part of the quarterly monitoring program are given in Table 4 for most of the dissolved constituents entering and exiting the West Cell. Results from other monitoring events give similar results, although total PO_4 is usually <10 mg L^{-1}. Unfortunately, because volatiles such as H_2S were not monitored, it is not possible to complete the mass balance for S or to discuss its relative contribution to pH buffering; the contribution is assumed to be in the order of that of the apatite dissolution, given no other reasonable explanation of the fate of the excess S. Noting the influent and effluent SO_4, NO_3, NH_3, PO_4 and HCO_3 concentrations, it is evident that most of the Zn is being incorporated into sulfide phases in concert with the reduction of all SO_4 in the groundwater. Denitrification is also occurring, thus reducing all NO_3. Note the lack of Fe within the system. The Fe was removed upgradient by precipitation of oxyhydroxides during evolution of the acid mine drainage.

Table 4
Groundwater constituents entering/exiting the PRB West Cell 8/2002

Species	Entering PRB (mg L^{-1})	Exiting PRB (mg L^{-1})
pH	4.18	7.13
Alk ($CaCO_3$)	0	243
TDS	344.9	466.9
Cond., μS cm^{-1}	421	556
Al	3.16	0.020
As	<0.001	<0.001
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	<0.002
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	0.002
Na	3.54	5.06
NH_4	<0.02	43.1
Ni	0.015	0.002
NO_3	0.58	<0.02
Pb	1.16	<0.001
PO_4	<0.05	49.1
SiO_2	22.7	21.6
SO_4	216	68.2
U	0.0043	<0.001
Zn	64.5	0.086

A cross-section through the PRB showing conditions measured during July of 2003 is given in Fig. 5. Portable probes were used to measure pH, Eh, dissolved O_2 (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^{-1} within the barrier, and >4.0 mg L^{-1} upgradient and downgradient of the barrier. Eh values within the first cell of the barrier were >550 mV, whereas most of the barrier interior was between -100 and -300 mV. The pH rises to neutral in the first chamber of the barrier. Lead and Cd disappear completely from solution within the first chamber, and Zn concentrations decrease from chamber to chamber, finally dropping to $\leqslant 0.1$ mg L^{-1} before exiting the barrier. Concentrations of Mn, Cu, Al and U are also being reduced to the μg kg^{-1} level or below detection (Table 4).

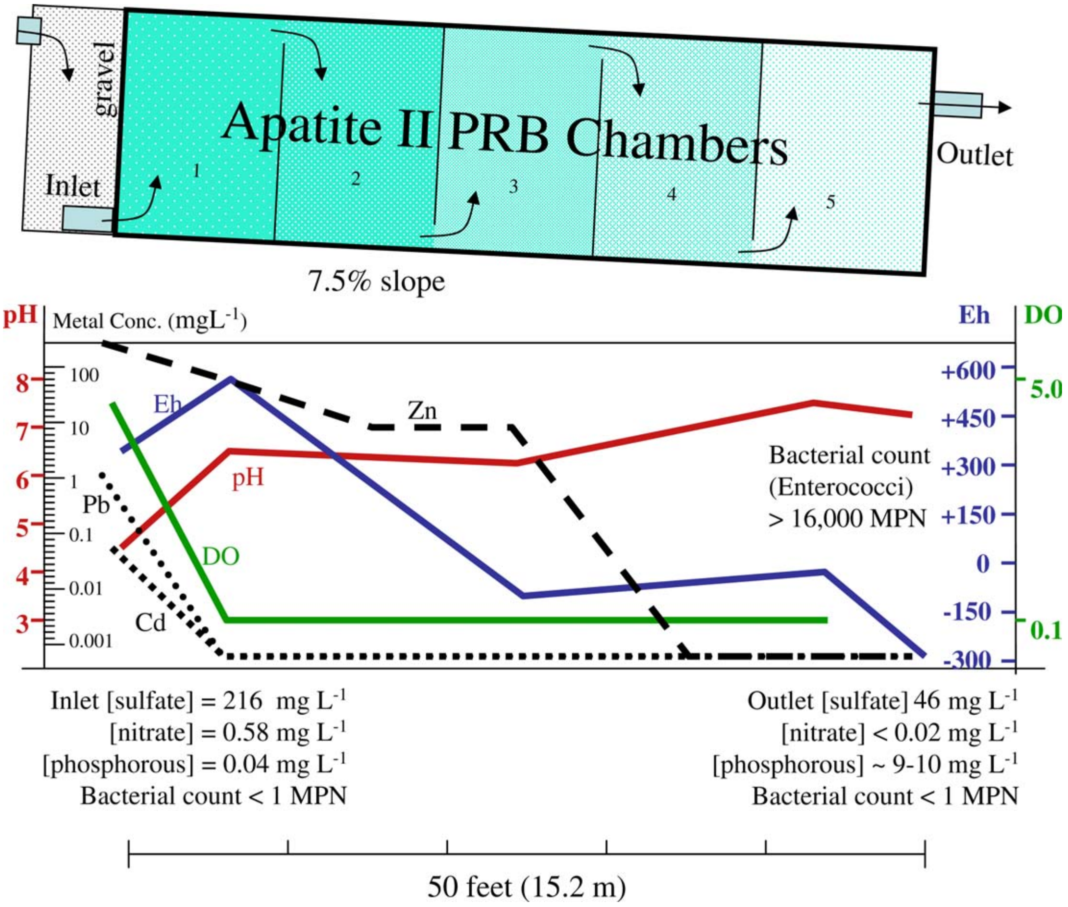

Fig. 5. Schematic cross-section of the Apatite II PRB, and the chemistry within the West Cell. Results are similar for the hydraulically separate but parallel East Cell.

Because Apatite II stimulates biological activity, bacterial sampling 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 Dobson Pass culvert, where the greatest possibility exists for public contact with water that has exited the PRB. The water samples were analyzed for *E. coli*, *Entercocci*, *Pseudomonas* and *Salmonella*. This distribution of sampling provided a background value for bacteria relative to the PRB itself in order to determine the effects of the PRB on microbial communities, especially for these four bacterial groups which are important to public health. All samples were at non-detectable concentrations at all points except for *Entercocci* at the PRB outflow in March 2001, which was measured at 16,000 MPN 100 mL^{-1}, where MPN represents the most probable number. In the outflow of the PRB, this number decreased rapidly to non-detectable by the time water reached the East Fork – West Fork confluence at the Dobson Pass culvert. However, detection of bacteria occurred only during the first sampling event in 2001; samplings in 2002, 2003, and 2004 showed non-detectable values for all bacteria, even for *Entercocci* at the PRB outflow. The recreational guideline for *Entercoccci* in fresh water is 30 MPN 100 mL^{-1}, and culturing of samples from within the barrier is ongoing.

Total dissolved P (P_{total}) upstream of the PRB is $<$0.04 mg L^{-1}. Loading of P_{total} to the creek from the PRB was found to be between 2 and 20 mg L^{-1}, mostly as orthophosphate, at a flow of 1.1–6.8 $\mathrm{m}^3\ \mathrm{h}^{-1}$. This is similar to the background range of P_{total} observed in other drainages downstream, such as the Coeur d'Alene River at Pinehurst (20–130 mg L^{-1}) and St Joe at Calder (3–10 mg L^{-1}).

Photographs and micrographs of the Apatite II placed into the West cell illustrate the primary (Fig. 6a), secondary (Fig. 6b), and tertiary

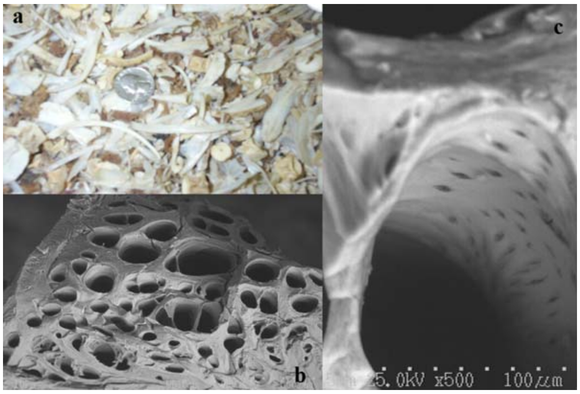

Fig. 6. Images of Apatite II from the West Cell of the Apatite II PRB after three years. (a) Gravel-type primary porosity of the bulk material; the diameter of the coin near the center is 2.3 cm. (b), Secondary porosity of the internal bone structure; the image width is 1 mm. (c) Tertiary porosity of the capillaries in the walls of the bone; image is 40 μm in width.

(Fig. 6c) porosity that makes Apatite II a good permeable reactive medium. After 5 a in the PRB, the bone is in excellent condition physically, still competent and able to support high flow. Initial MINTEQ modeling results (Geochem Software Inc., 1994) using the compositions in Table 4 indicate pyromorphite and sphalerite to be the most stable solids within the barrier with regard to Pb and Zn (saturation index, SI > 1). Chloraptite also had a SI > 1. Other potential secondary precipitates, such as carbonates, gypsum and hydroxides, had SI values of <1. Modeling is uncertain with regard to Cd, which could be both adsorbing onto the Apatite II and coprecipitating as a sulfide with Zn.

Samples collected from the first chamber of each of the two PRB cells have a whitish solid that covers most of the original Apatite II and shows little residual organic material 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. 7). These observations, together with the results in Table 4 and the MINTEQ modeling, are consistent with reactions (1)–(4), e.g., SO_4 enters at $>200\ mg\ L^{-1}$ and exits at $50–150\ mg\ L^{-1}$, HCO_3 enters at below detection and exits at just under $300\ mg\ L^{-1}$, Zn enters at $64\ mg\ L^{-1}$ and exits at below detection, Ca enters at $26\ mg\ L^{-1}$ and exits at $44\ mg\ L^{-1}$, P enters below detection and exits at $49\ mg\ L^{-1}$, and pH at the exit is neutral. 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 the groundwater. Possibly because Pb and Cd occur in concentrations between 100 and 1000 times lower than that of Zn, no discrete Pb- or Cd-bearing solids have been identified in hand specimens or by SEM. Although thermodynamically and kinetically favored to form pyromorphite in the presence of apatite (Lower et al., 1998), Pb could be co-precipitated in the sulfide or secondary chlorapatite phases.

Compared with the Apatite II in the front two cells of the PRB, that in the rear 3 cells is relatively unreacted, does not exhibit secondary mineral coatings, and still has a large complement of the original organic material. The estimate from visual inspection is that <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 because it will not be a hazardous waste (spent Apatite II from previous studies passed EPA TCLP tests) and can be disposed for about US $\$18\ t^{-1}$. The first chamber of the PRB has removed so much metal

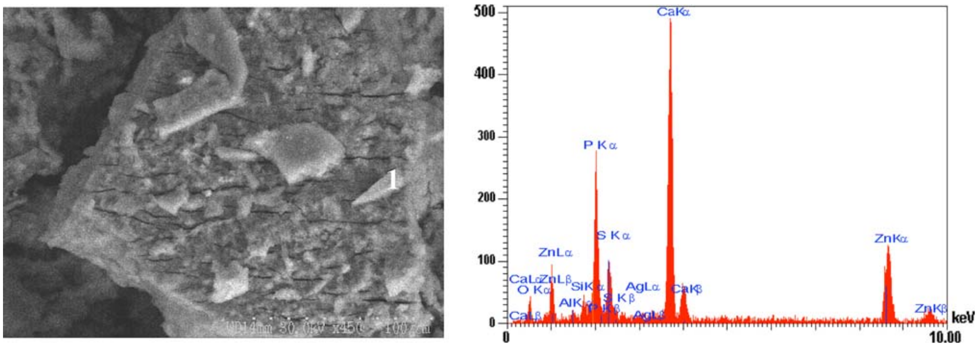

Fig. 7. Photomicrograph of Apatite II from the first chamber, showing biologically mediated formation of μm-size sphalerite crystals that formed on the surface of the Apatite II within the PRB; the image is 200 μm in width. The EDS analysis is for the crystal labeled 1.

that the hydraulic conductivity has declined; removal of the material is planned to occur at about the time of publication. The chamber can be refilled or left empty to serve as a sediment trap for the subsequent chambers.

The average residence time of water flowing through the barrier depends upon flow rate, but at 1.1 $m^3 h^{-1}$ the residence time is between 10 and 15 h. However, the average residence time in the first chamber is only about 2–3 h. The results shown in Fig. 5 indicate that most of the metal removal occurs in the first chamber, thus suggesting that the controlling reactions are short and occur within about a 2 h time frame.

6. 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 4.5 m high, 5 m wide by 16.3 m long PRB vault with two cells was placed between a ~300,000 m^3 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 ng L^{-1}) and Pb (from thousands of ng L^{-1}) to below detection (2 ng L^{-1}), has reduced Zn from 100 μg L^{-1} to near background in this region (about 100 ng L^{-1}), and has decreased SO_4 by between 100 and 200 mg L^{-1} and NO_3 to below detection (50 μg L^{-1}), prior to discharge to surface water. During the 5 a of operation, the PRB, filled with about 90 tonnes of Apatite II, has removed >4550 kg of Zn, >91 kg of Pb and >45 kg 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.

Acknowledgements

The authors thank Bryony Stasney, Neal Yancy, Paul Didzerekis, Cheryl Ross, Lisa Hall and Terra*Graphics* for helping to get this project started at the Success mine site. This work was supported by grants from the Strategic Environmental Research and Development Program (SERDP, Department of Defense), the Unites States Environmental Protection Agency, the Idaho State Department of Environmental Quality, and the Silver Valley Natural Resource Trustees.

References

Benner, S.G., Blowes, D.W., Ptacek, C.J., 1997. A full-scale porous reactive wall for the prevention of acid mine drainage. Groundwater Monitor. Remed. 17, 99–107.

Bostick, W.D., Jarabek, R.J., Bostick, D.A., Conca, J., 1999. Phosphate-induced metal stabilization: use of apatite and bone char for the removal of soluble radionuclides in authentic and simulated DOE groundwaters. Adv. Environ. Res. 3, 488–498.

Bowman, R.S., 2003. Applications of surfactant-modified zeolites to environmental remediation. Micropor. Mesopor. Mat. 61, 43–56.

Calabretta, M., Hansen, B., Harvey, G., Morel, D., 2001. Treatment of metals-impacted groundwater with a semi-passive organic apatite system. In: Paper Presented at GeoDestiny – Resources for the Future. 107th Annual Meeting of Northwest Mining Association (December). Northwest Mining Association, Spokane, WA.

Chen, X.-B., Wright, J.V., Conca, J.L., Peurrung, L.M., 1997a. Effects of pH on heavy metal sorption on mineral apatite. Environ. Sci. Technol. 31, 624–631.

Chen, X.-B., Wright, J.V., Conca, J.L., Peurrung, L.M., tul=0?>Chen et al., 1997 b. Evaluation of heavy metal remediation using mineral apatite. Water Air Soil Pollut. 98, 57–78.

Conca, J.L., 1997. Phosphate-Induced Metal Stabilization (PIMS). Final Report to the US Environmental Protection Agency #68D60023.

Conca, J.L., Lu, N., Parker, G., Moore, B., Adams, A., Wright, J.V., Heller, P., 2000. PIMS – remediation of metal contaminated waters and soils. In: Wickramanayake, G.B., Gavaskar, A.R., Chen, S.C. (Eds.), Remediation of Chlorinated and Recalcitrant Compounds, vol. 6. Battelle Press, Columbus, Ohio, pp. 19–326.

Conca, J., Strietelmeier, E., Lu, N., Ware, S.D., Taylor, T.P., Kaszuba, J., Wright, J.V., 2003. Treatability study of reactive materials to remediate groundwater contaminated with radionuclides, metals and nitrates in a 4-component permeable reactive barrier. In: Naftz, D.L., Morrison, S.J., Davis, J.A., Fuller, C.C. (Eds.), Groundwater Remediation of Metals, Radionuclides, and Nutrients, with Permeable Reactive Barriers. Academic Press, New York, pp. 221–252.

Eighmy, T.T., Crannell, B.S., Butler, L.G., Cartledge, F.K., Emery, E.F., Oblas, D., Krzanowski, J.E., Eusden Jr., J.D., Shaw, E.L., Francis, C.A., 1997. Heavy metal stabilization in municipal solid waste combustion dry scrubber residue using soluble phosphate. Environ. Sci. Technol. 31, 3330–3338.

Florida Institute of Phosphate Research, 2003. Available from: <ttp://fipr.state.fl.us/publications>.

Fuller, C.C., Bargar, J.R., Davis, J.A., Piana, M.J., 2002. Mechanism of uranium interactions with hydroxyapatite: implications for groundwater remediation. Environ. Sci. Technol. 36, 158–165.

Geochem Software Inc., 1994. Mac MINTEQ-A2: Aqueous Geochemistry for the MacIntosh. Geochem Software Inc., Reston, VA.

Golder, 2000. Pre-design Investigation, Workplan and Monitoring Plan for Semi-passive Groundwater Treatment System, Success Mill Site. Wallace, Idaho. Prepared for the Silver Valley Natural Resource Trustees by Golder Associates Inc., August 2000.

Goldstein, K.J., O'Hannesin, S., McDonald, S., Gaule, C., Anderson, G.A., Marsh, R., Senick, M., 2000. Dual permeable reactive barrier walls remediate chlorinated hydrocarbon contamination. In: Wickramanayake, G.B., Gavaskar, A.R., Chen, S.C. (Eds.), Remediation of Chlorinated and Recalcitrant Compounds, vol. 6. Battelle Press, Columbus, Ohio, pp. 273–280.

Hobbs, S.W., Griggs, A.B., Wallace, R.E., Campbell, A.B., 1965. Geology of the Coeur d'Alene District, Shoshone County, Idaho. US Geol. Surv. Prof. Pap. 478.

Koeppenkastrop, D., De Carlo, E.J., 1990. Sorption of rare earth elements from seawater onto synthetic mineral phases. Chem. Geol. 95, 251–263.

Lower, S.K., Maurice, P.A., Traina, S.J., Carlson, E.H., 1998. Aqueous Pb sorption by hydroxylapatite: applications of atomic force microscopy to dissolution, nucleation and growth studies. Am. Mineral. 83, 147–158.

Lu, N., Xu, H., Wright, J.V., Conca, J., 2001. PIMS – remediation of metal-contaminated groundwater and soil using a special reactive form of the mineral apatite. In: Rammlmair, D., Mederer, J., Oberthür, T., Heimann, R.B., Pentinghaus, H. (Eds.), Applied Mineralogy in Research, Economy, Technology, Ecology and Culture, vol. 2. Balkema, Rotterdam, The Netherlands, pp. 603–606.

Ma, Q.Y., Logan, T.J., Traina, S.J., 1995. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol. 29, 1118–1126.

Ma, Q.Y., Traina, S.J., Logan, T.J., 1993. In situ lead immobilization by apatite. Environ. Sci. Technol. 27, 1803–1810.

Manecki, M., Maurice, P.A., Traina, S.J., 2000. Kinetics of aqueous Pb reaction with apatites. Soil Sci. 165, 920–933.

Martinez, M.N., Hightower, S.S., Smith, G.B., Mueller, W., Conca, J.L.,Wright, J., 2005. The effect of Apatite II™ on the biodegradation of TNT and perchlorate in contaminated soil samples. In: Second Conference Proceedings on Sustainable Range Mgmt. Available from: <www.battelle.org/bookstore>.

Matheson, L.J., Goldberg, W.C., Huddleston, G.J., Bostick, W.D., 2002. Remediation of metal-contaminated soil and groundwater using Apatite II. In: Gavaskar, A.R., Chen, A. (Eds.), Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press, Columbus, Ohio.

McArthur, J.M., Sahami, A.R., Thirwall, M., Hamilton, P.J., Osborn, A.O., 1990. Dating phosphogenesis with Sr isotopes. Geochim. Cosmochim. Acta 54, 1343–1352.

Naftz, D.L., Fuller, C.C., Davis, J.A., Piana, M.J., Morrison, S.J., Freethey, G.W., Rowland, R.C., 2000. Field demonstration of PRBs to control uranium contamination in groundwater. In: Wickramanayake, G.B., Gavaskar, A.R., Chen, S.C. (Eds.), Remediation of Chlorinated and Recalcitrant Compounds, vol. 6. Battelle Press, Columbus, Ohio, pp. 281–290.

Nriagu, J.O., 1974. Lead orthophosphates, IV. Formation and stability in the environment. Geochim. Cosmochim. Acta 38, 887–898.

Pasteris, J.D., Wopenka, B., Freeman, J.J., Rogers, K., Valsami-Jones, E., van der Houwen, J.A.M., Silva, M., 2004. Lack of OH in nanocrystalline apatite as a function of degree of atomic order: implications for bone and biomaterials. Biomaterials 25, 229–238.

Puls, R.W., Blowes, D.W., Gillham, R.W., 1999. Long-term performance monitoring for a permeable reactive barrier at the US Coast Guard Support Center, Elizabeth City, North Carolina. J. Hazard. Mat. 68, 109–124.

Ruby, M.V., Davis, A., Nicholson, A., 1994. In situ formation of lead phosphates in soils as a method to immobilize lead. Environ. Sci. Technol. 28, 646–654.

SAIC, Science Applications International Corporation, 1993. Draft mine sites fact sheets for the Coeur d'Alene River basin. Prepared for Region 10, US EPA, December 1993.

Scherer, M.M., Richter, S., Valentine, R.L., Alvarez, P.J.J., 2000. Chemistry and microbiology of permeable reactive barriers for in situ groundwater clean-up. Crit. Rev. Environ. Sci. Technol. 30, 363–411.

Skinner, H.C.W., 1989. Low temperature carbonate phosphate materials or the carbonate–apatite problem. In: Crick, R. (Ed.), Origin, Evolution and Modern Aspects of Biomineralization in Plants and Animals. Plenum Press, New York.

Stanforth, R., Chowdhury, A., 1994. In situ stabilization of lead-contaminated soil. in: Federal Environmental Restoration III and Waste Minimization II Conference Proceedings, New Orleans.

Starr, R.C., Cherry, J.A., 1994. In situ remediation of contaminated groundwater: the funnel-and-gate system. Groundwater 32, 456–476.

TerraGraphics Environmental Engineering Inc., 1998. Final preliminary engineering design report Success mine site passive treatment project. Prepared for Idaho Department of Health and Welfare, Division of Environmental Quality, Coeur d'Alene, Idaho, October 1998.

Tratnyek, P.G., Johnson, T.L., Scherer, M.M., Eykholt, G.R., 1997. Remediating groundwater with zero-valent metals: kinetic considerations in barrier design. Groundwater Monitor. Remed. 17, 108–114.

US EPA, 1993. Action memorandum for a removal action at the Success mine site, Wallace, Shoshone County, Idaho. Environmental Protection Agency, Washington, DC.

Wopenka, B., Pasteris, J.D., 2005. A mineralogical perspective on the apatite in bone. Mat. Sci. Eng. C 25, 131–143.

Wright, J., 1990a. Conodont apatite: structure and geochemistry. In: Carter, J. (Ed.), Skeletal Biomineralization: Patterns Processes and Evolutionary Trends. Van Nostrand Reinhold, New York, pp. 445–459.

Wright, J., 1990b. Conodont geochemistry, a key to the Paleozoic. In: Zeigler, W. (Ed.), International Senckenberg Conference and European Conodont Symposium Contributions III, vol. 188. Courier Forschungsinstitut Senckenberg, Frankfurt, Germany, pp. 277–305.

Wright, J., Conca, J.L., Repetski, J., Clark, J., 1990. Geochemistry and microstructure of conodonts from Jilin Province, China. In: Zeigler, W. (Ed.), International Senckenberg Conference and European Conodont Symposium Contributions III, vol. 188. Courier Forschungsinstitut Senckenberg, Frankfurt, Germany, pp. 307–332.

Wright, J., Conca, J.L., Slater, A.F., 2005. PIMS with apatite II: a field scale demonstration on a lead contaminated soil. In: Al-Tabbaa, A., Stegemann, J.A. (Eds.), Stabilisation/Solidification Treatment and Remediation. Taylor and Francis Group, London, ISBN 04 1537 460 X (Chapter 4).

Wright, J., Miller, J.F., Holser, W.T., 1987a. Chemostratigraphy of conodonts across the Cambrian–Ordovician boundary: western United States and southeast China. In: Austin, R.L. (Ed.), Conodonts: Investigative Techniques and Applications. Ellis Horwood, London, pp. 259–286.

Wright, J.V., Peurrung, L.M., Moody, T.E., Conca, J.L., Chen, X., Didzerekis, P.P., Wyse, E., 1995. In situ immobilization of heavy metals in apatite mineral formulations. Technical Report to the Strategic Environmental Research and Development Program, Department of Defense, Pacific Northwest Laboratory, Richland, WA.

Wright, J., Rice, K.R., Murphy, B., Conca, J.L., 2004a. PIMS using Apatite II^{TM}: How it works to remediate soil and water. In: Proceedings of the Conference on Sustainable Range Management. Available from: <www.battelle.org/bookstore>, ISBN 1-57477-144-2, B4-05.

Wright, J., Rice, K.R., Murphy, B., Conca, J.L., 2004b. PIMS-remediation of Pb- contaminated soil at Camp Stanley, Texas. In: Proceedings of the Conference on Sustainable Range Management. Available from: <www.battelle.org/bookstore>, ISBN 1-57477-144-2, B4-04.

Wright, J., Schrader, H., Holser, W.T., 1987b. Paleoredox variations in ancient oceans recorded by rare earth elements in fossil apatite. Geochim. Cosmochim. Acta 51, 631–644.

Wright, J., Seymour, R.S., Shaw, H.F., 1984. REE and Nd isotopes in conodont apatite: variations with geological age and depositional environment. In: Clark, D.L. (Ed.), Conodont Biofacies and Provincialism. Geol. Soc. Am. Spec. Pap. 196, pp. 325–340.

Xu, Y., Schwartz, F.W., 1994. Lead immobilization by hydroxyapatite in aqueous solutions. J. Contam. Hydrol. 15, 187–206.

Zhang, P., Ryan, J., Yang, J., 1998. In vitro soil Pb solubility in the presence of hydroxyapatite. Environ. Sci. Technol. 32, 2763–2768.