

Remediation of Groundwater Contaminated with Zn, Pb and Cd using a Permeable Reactive Barrier with Apatite II

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Introduction

Phosphate-Induced Metal Stabilization (PIMS) using Apatite II stabilizes a wide range of metals, especially Pb, Cd, Zn, U and Pu, *in situ* or *ex situ*, by chemically binding them into new stable phosphate phases and other low-solubility phases that are stable over geologic time. The concept resulted from paleochemical oceanographic and chemostratigraphic studies, in the 1970s and 1980s, of phosphatic sedimentary materials from the Cambrian period (570 million years ago) to the Present [1,2]. These studies showed that apatite hard parts of marine animals, and even abiotic phosphorite deposits, developed identical trace metal signatures of the seawater with which they were in contact, but with concentrations enriched by six or seven orders of magnitude. The chemical reactions were relatively fast and the chemical signatures were retained over geologic time, even in the face of multiple destructive events such as burial, lithification, heating, and weathering. Recent laboratory and field studies have demonstrated the applicability of this concept towards remediation of metal-contaminated waters and soil. Results are presented from a field site at Success Mine in Idaho, where a permeable reactive barrier (PRB) filled with Apatite II has been operating for just under two years to remediate Zn, Cd and Pb [3]).

Some form of mineral apatite is necessary for efficient metal remediation, especially for instigating the heterogeneous nucleation of metal-apatite phases necessary for remediation under environmental conditions [4]. A special form of biogenic apatite, Apatite II, has been developed that is the most reactive and the most cost-effective apatite available. Unlike any other apatite, Apatite II has the optimal structural and chemical characteristics for metal and radionuclide remediation: 1) no substituted fluorine, 2) a high degree of substituted carbonate ion, 3) low initial trace metal concentrations, 4) extremely poor crystallinity (basically amorphous) coupled with random nanocrystallites, and 5) high microporosity. The ultimate driving force for the robust performance of reactive phosphate with respect to metals is the extreme stability of these metal-phosphate phases, some of which are listed in Table 1. These metal phosphates are twenty to seventy orders of magnitude more insoluble than quartz. Combined with this stability, the rapid kinetics of the metal-phosphate precipitation ensures immobilization of the metals in the face of most possible transport mechanisms. Non-apatite phosphate and mixtures of precursor constituents will not perform as well, if at all, under most environmental conditions. The apatite can be emplaced down-gradient as a permeable reactive barrier (PRB) to capture

TABLE 1

<i>Mineral Phase</i>	<i>Solubility Product (log K_{sp})</i>	<i>Mineral Phase</i>	<i>Solubility Product (log K_{sp})</i>
Pb ₅ (PO ₄) ₃ (OH,Cl)	-76.5	Am(PO ₄)	-24.8
Ca(UO ₂) ₂ (PO ₄) ₂ •10H ₂ O	-49.0	Pu(PO ₄)	-24.4
Sr ₅ (PO ₄) ₃ (OH)	-51.3	UO ₂ (HPO 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

RESULTS FROM FIELD SCALE STUDY (acid mine drainage)

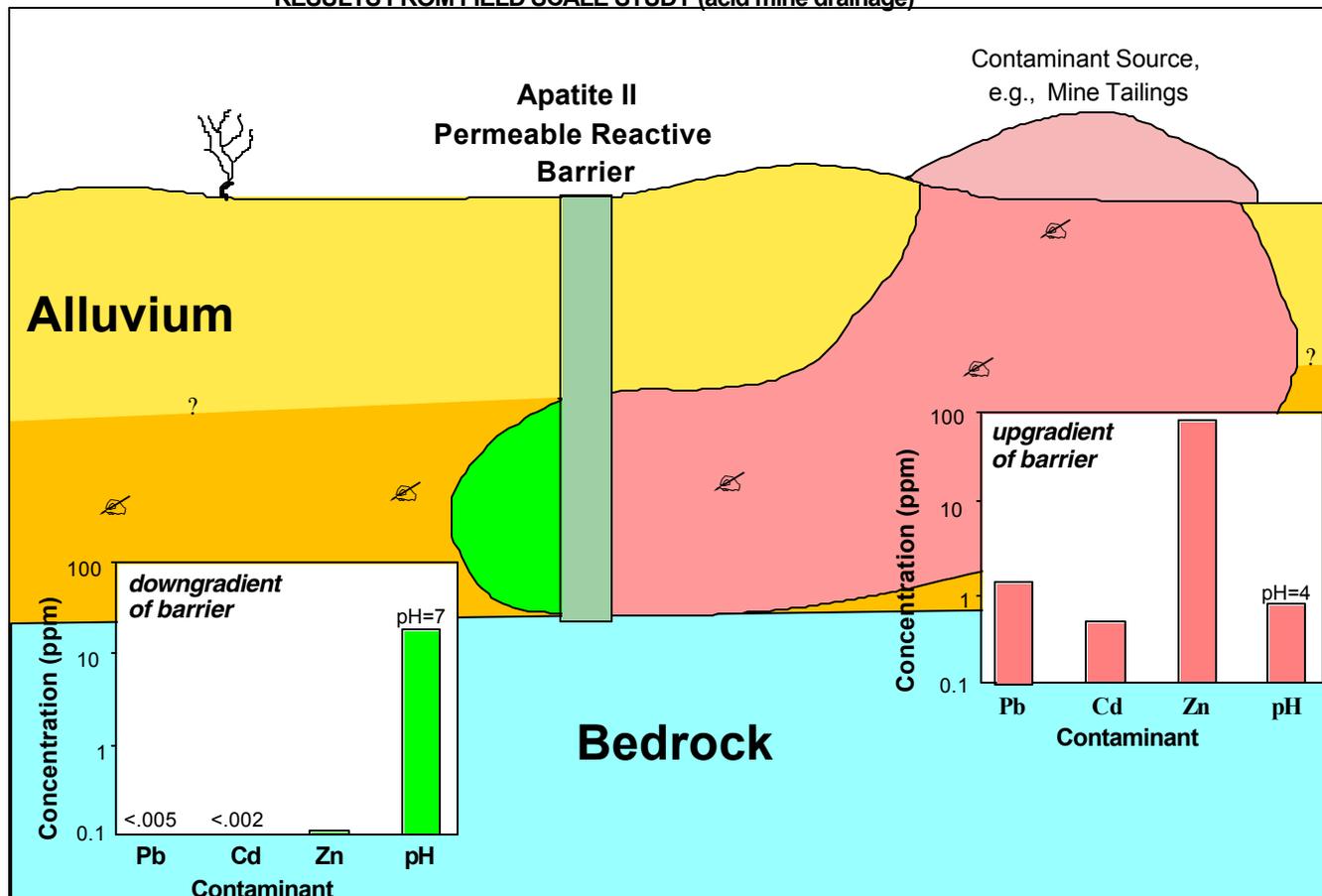


FIGURE 1. Schematic of a permeable reactive barrier showing actual results from the field.

groundwater or seeps, mixed into contaminated soil or waste, used as a disposal liner, or emplaced by any method that brings the soluble metal into contact with the apatite surface. Figure 1 shows the concept of a PRB along with actual monitoring results from the field (Success Mine, Idaho).

Material and Methods

Various reactive media were investigated to remove metals and radionuclides from groundwater and soils [2,5]. Analytical techniques included Ion Chromatography, Inductively-Coupled Plasma (ICP) Emission and Mass Spectroscopy, Liquid Scintillation Counting, Transmission Electron Microscopy, and Potentiometric Stripping, plus standard methods for measuring pH, dissolved oxygen and other field and laboratory parameters. Batch tests and flow-through column tests were used to determine relative performance and to provide media for solids characterization. Batch sorption studies were performed on materials to determine the reactive sorption or distribution coefficient (K_d), which is a ratio of the amount of contaminant sorbed onto the media to the amount remaining in solution [6]. Column studies are run until the contaminant begins to appear in the column effluent, referred to as breakthrough.

Results and Discussion

The metal-stabilization potential of reactive phosphates from different sources was investigated along with other materials for remediation of contaminated soil and groundwater from the Bunker Hill/Success Mine Site in northern Idaho [7,8,9]. Materials included zeolites (clinoptilolite and chabazite), compost,

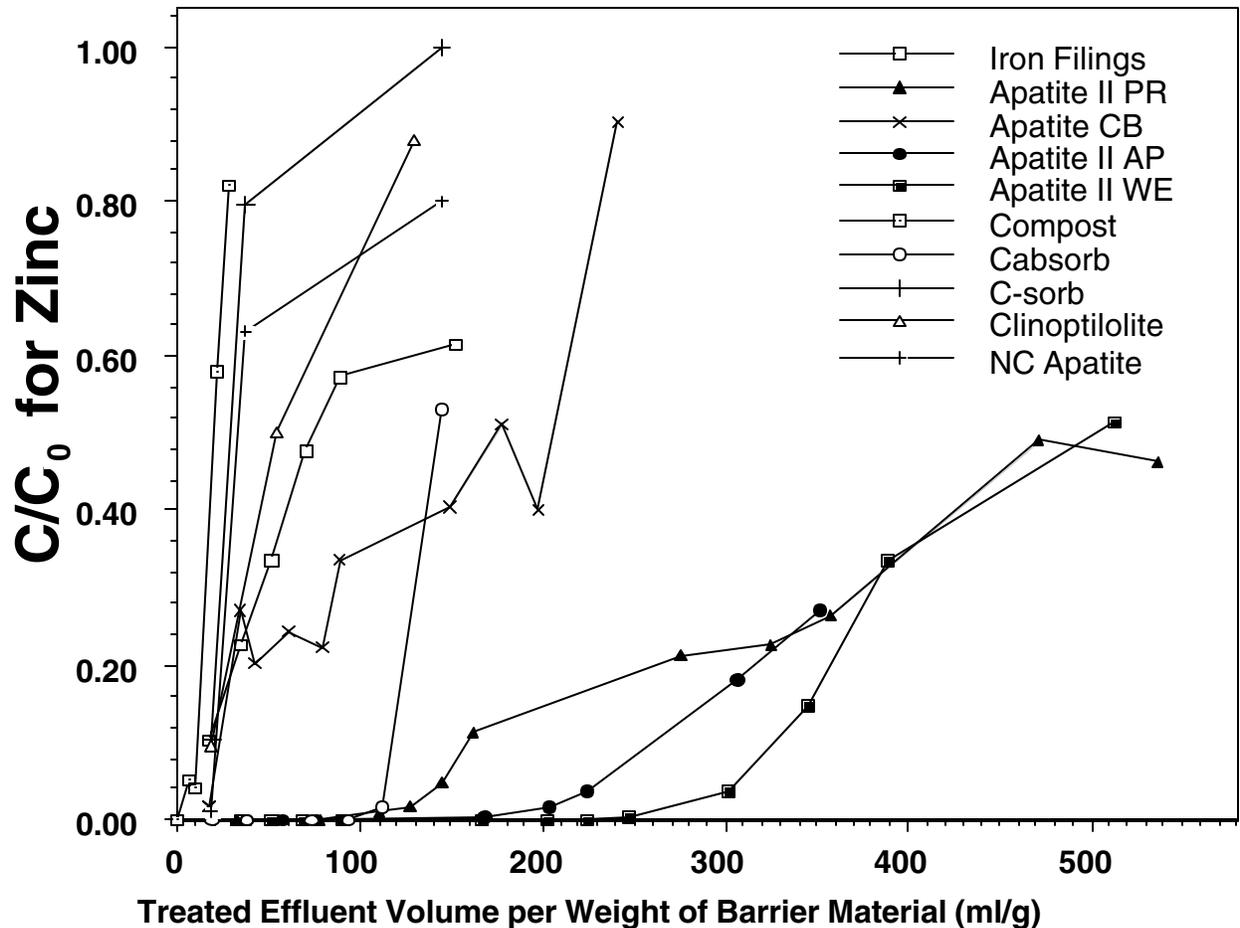


FIGURE 2. Breakthrough of dissolved Zn through various permeable reactive barriers using contaminated groundwater from the Success Mine Site. $C_{0zn} = 250$ ppm.

various polymers, iron filings and oxides, and apatites [different formulations of Apatite II (WE, PR, and AP), cowbone (CB) and phosphate rock (NC)]. Soils in this area are contaminated with 1000–4000 mg kg^{-1} (ppm) of Pb, Zn, Cd and Cu, and groundwaters are contaminated with Zn, Pb, Cd and Cu up to concentrations of 250 ppm, 10ppm, 1 ppm and 20ppm, respectively. Apatite II performed best with respect to stabilization of these three metals, sequestering almost 20% of its weight in Pb, and about 5% of its weight in Zn and Cd. The bioavailability of the metals from the contaminated soil was also greatly reduced using Apatite II even when the metal was not in an apatite phase [8]. Pb precipitated as lead-pyromorphites while Zn and Cd both sorbed onto particles and precipitated as hopeite, zincite, hydrocerrusite, otavite and other phases [7,8,9]. Results showed that the leachates from untreated soils were 100 to 1000 ppm for Pb and Zn, and hundreds of ppm for Cd, well in excess of regulatory Maximum Contamination Levels for drinking water. However, leachates from Apatite II-treated soils showed Pb, Zn and Cd below the detection limits of 5 ppb. Performance was successfully predicted using MINTEQA2, a thermodynamic speciation model [10], was substantiated by XRD results on the contaminated soils after apatite treatment [9] and was also consistent with results by other researchers [4,11]. The results for Zn are shown in Figure 3 which plots 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 barrier material. Similar results occurred for Cd [8]. As a result of these tests, a PRB of

Apatite II was emplaced between the Success Mine Tailings pile and Nine Mile Creek and has been operating for almost two years [3]. It is a 13.5-ft high, 15-ft wide and 50-ft long baffled vault filled with 100 tons of Apatite II that reaches down to bedrock and is designed to capture most of the subsurface drainage from the 500,000-ton tailings pile. The concentrations of metals entering the barrier over this time period has averaged 780 ppb Cd, 1,210 ppb Pb and 116,000 ppb Zn. The pH has been between 4.5 and 5.0. The average concentrations of metals leaving the barrier has been < 2 ppb Cd, < 5 ppb Pb and about 115 ppb Zn. The exiting pH has been between 6.5 and 7.0 [3]. Flow rates are seasonal and vary between 1 gpm and 50 gpm. Based on periodic daily metal-loading averages, it is estimated that the Apatite II barrier has sequestered over 1000 lbs of Cd, over 2,500 lbs of Pb and over 20,000 lbs of Zn over the 1.7 years since it was emplaced. This barrier is estimated to last over ten years for Cd and Pb, but Zn should begin to breakthrough in another year because of the higher-than-expected Zn loading. Either the Apatite II can be replaced, or more desirable, a second 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. The cost of the Apatite II was about \$500/ton for the approximately 100 tons used in this barrier. Emplacement used traditional backhoe and earth-moving equipment to trench the vault. The Apatite II was gravel-sized for easy flow.

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