

## REMEDICATION OF GROUNDWATER CONTAMINATED WITH Zn, Pb AND Cd USING APATITE II

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Phosphate-Induced Metal Stabilization (PIMS) using Apatite II stabilizes a wide range of metals (Pb, Cd, Zn, Cu, U, Pu) *in situ* or *ex situ*, by chemically binding them into new stable phosphate minerals and other low-solubility minerals that are stable over geologic time. The concept resulted from paleochemical oceanographic studies, in the 1970s and 1980s, of phosphatic sedimentary materials from the Cambrian period (570 my ago) to the Present (WRIGHT *et al.*, 1987). 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 after burial, lithification, heating, and weathering. Recent laboratory and field studies have demonstrated the applicability of apatite towards remediation of metal-contaminated waters and soil. Some form of mineral apatite is necessary for efficient metal remediation under environmental conditions. A special form of biogenic apatite, Apatite II, has been developed that, unlike any other apatite, 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 driving force for the robust performance of reactive phosphate is the extreme stability of metal-phosphate phases, e.g., pyromorphites [ $\text{Pb}_5(\text{PO}_4)_3(\text{OH},\text{Cl})$ ;  $\log K_{sp} = -76.5$ ] and autunites [ $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$ ;  $\log K_{sp} = -49.0$ ]. Non-apatite phosphate will not perform as well, if at all, under environmental conditions. The apatite can be emplaced as a permeable reactive barrier (PRB) to capture 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.

A PRB was emplaced in the field at the Success Mine site in Idaho State to treat groundwater contaminated with Zn, Pb, Cd and Cu up to concentrations of 250 ppm, 10 ppm, 1 ppm and 20 ppm, respectively. Various reactive media were investigated to determine which would be most effective at this site for removing Pb, Cd and Zn. Materials included zeolites (clinoptilolite and chabazite), compost, various polymers, iron filings and oxides, and apatites [cowbone, phosphate rock, and three different formulations of Apatite II]. 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 (CHEN *et al.*, 1997). The bioavailability of the metals from the contami-

nated soil was also greatly reduced using Apatite II even when the metal was not in an apatite phase. Pb precipitated as pyromorphite while Zn and Cd both sorbed onto particles and precipitated as hopeite, zincite, hydrocerussite, and otavite. 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 over two years. 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 averages 500 ppb Cd, 1,000 ppb Pb and 100,000 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 100 ppb Zn. The exiting pH has been between 6.5 and 7.0. Flow rates are seasonal and vary between 1 gpm and 50 gpm. Based on periodic daily metal-loading averages over the 2.2 years since it was emplaced, the Apatite II barrier has sequestered over 75 lbs of Cd (both sorbed onto the Apatite II as well as precipitated as CdS), over 125 lbs of Pb (precipitated as pyromorphite), and over 6,000 lbs of Zn (both sorbed onto the Apatite II as well as precipitated as ZnS). The second half of the barrier is anaerobic and supports a robust *Enterococci* population that also reduces Zn to ZnS. This results from the residual organics on the Apatite II, the small amount of P released, and the buffering capacity of the Apatite II. The effluent is able to be released back into the river with no further treatment. Performance was successfully predicted using MINTEQA2, a thermodynamic speciation model. This barrier is estimated to last over thirty years for Cd and Pb, but Zn should begin to breakthrough in a few years based upon the feasibility results. Either the Apatite II can be replaced, or 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 \$350/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. This technology should work for most acid mine drainage problems with most metals under most field conditions.

### References

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Remediation of groundwater contaminated with Zn, Pb and Cd using a permeable reactive barrier with apatite II. June 2006. DOI: 10.21000/JASMR06022514. Phosphate-Induced Metal Stabilization (PIMS) using 100 tons of the reactive media, Apatite II,  $(Ca_{10-x}Na_x(PO_4)_6-x(CO_3)_x(OH)_2)$  where  $x < 1$ , was used in a permeable reactive barrier (PRB) to treat shallow alluvial groundwater from acid mine drainage. The groundwater is treated in situ before it enters the East Fork of Ninemile Creek, a tributary to the Coeur d'Alene River. Microbially-mediated sulfate reduction and the precipitation of sphalerite (ZnS) is the primary mechanism occurring for immobilization of Zn and Cd. While PRBs were initially used to treat groundwater contaminated with organic solvents, their use has broadened so that they are now used to remediate a variety of contaminants. Although ZVI has been used to treat some metals, other materials including zeolites, apatite, oxides, organic matter, limestone, alkaline materials, and sulfate have also been used in PRBs for remediating metal contaminated groundwater (Obiri-Nyarko et al., 2014). The use of recycled materials is also becoming more prevalent in reactive barrier development. Another recycled material that is potentially useful for groundwater remediation is water treatment residuals (WTR). This material has also been found to remove or immobilize cations such as Cu, Pb, and Zn, (Hardy... Cd, Pb and Li stresses may negatively affected Na and K uptake and transport in *S. europaea* to affect plant growth. In addition, the antioxidant enzyme system synergistically responded to resist the oxidative toxicity of different ions. The contents of Cd, Pb, Li in roots and shoots of *S. europaea* also increased with the increase of treatment concentration. Furthermore, Cd and Pb contents in roots were significantly higher than in shoots, while more Li accumulated in shoots than in roots. The aforementioned results showed that *S. europaea* had strong tolerance along with a high accumulate ability to Cd, Pb and Li, indicating its application potential in restoring Cd, Pb and Li contaminated saline soil. 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 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). 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.