

PIMS USING APATITE II: REMEDIATION OF Pb-CONTAMINATED RANGE SOIL AT CAMP STANLEY STORAGE ACTIVITY, TX

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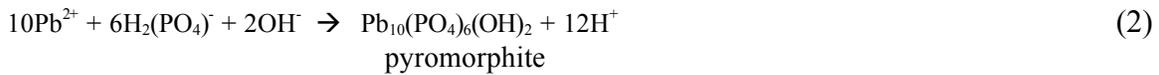
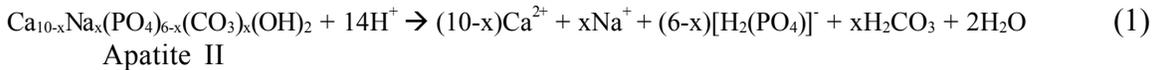
ABSTRACT: Phosphate-Induced Metal Stabilization (PIMS™) using Apatite II™ was implemented at Camp Stanley Storage Activity (CSSA) in Boerne, Texas to remediate lead(Pb)-contaminated range soils at Solid Waste Management Unit (SWMU) B-20, a former open burn/open detonation (OB/OD) area. The full-scale field operation remediated 3,000 yd³ by soil mixing and placement back onsite. The Apatite II treatment reduced the average leaching of Pb from 0.373 mg/L in untreated soil to 0.003 mg/L in treated soil, as observed from lysimeter wells, eliminating potential impacts to groundwater and surface water run-off. Waste classification results from Toxicity Characteristic Leaching Procedure (TCLP) tests gave an average of 0.46 mg/L Pb for treated soils which meets the State of Texas class 2 non-hazardous waste classification criteria of 1.5 mg/L Pb making the treated soil non-hazardous, while the untreated soil did not meet these criteria. The Apatite II treatment also reduced the Pb bioaccessibility of the soil. CSSA has achieved acceptable levels of lead at SWMU B-20 by the PIMS treatment using Apatite II and expects to obtain closure on this site. A 100-year flooding event occurred one year after emplacement with no adverse effects. The total actual costs of the remediation were \$22/yd³ and represented a significant cost savings relative to all other technologies tested at this site.

INTRODUCTION

Pb-contaminated soils are prevalent in the United States, particularly at Department of Defense sites that have small arms firing ranges, detonation sites or testing facilities. Estimates of Pb-contaminated soil from range use in the United States are 100 million cubic yards, far exceeding that which can be disposed to landfills. These soils pose one of the costliest environmental issues facing the DoD, estimated at over ten billion dollars to dispose with existing baseline technologies, if sufficient landfill space existed. Large quantities of Pb-contaminated leachates generated by rainfall and irrigation at many military sites (Cao et al., 2003) flow into lakes or stormwater drain systems, or provide contaminated recharge to shallow aquifers. The Phosphate-Induced Metal Stabilization (PIMS™) technology is an *in situ* stabilization or sequestration technology that uses an amendment, Apatite II™, to the contaminated soil that immobilizes the metal or renders it non-toxic, but does not change the basic nature of the soil, e.g., the permeability or porosity. This technology allows the soil to function in the future as a soil to be left in place, or disposed of as a non-hazardous material if desired. Apatite II™ is a natural phosphate material produced from fish bones that incorporates metals into new stable phosphate phases that are non-leachable. Only simple mixing into the soil is required. The advantages over other technologies are that PIMS with Apatite II is inexpensive, fast,

long-lasting, and does not generate any hazard or environmental problem as a result of its production (Florida Inst. Phosphate Res., 2003; Nat'l. Wildlife Fed., 2003).

In the case of Pb-contaminated range soils, Apatite II binds Pb into pyromorphite, an insoluble phase that is stable for hundreds of millions of years (Wright *et al.*, 1987; Wright, 1990; Chen *et al.*, 1997). Pyromorphite has an extremely low solubility product ($K_{sp} = 10^{-80}$) and will not dissolve under most environmental conditions. Apatite II works to sequester metals by continuously supplying a small, but sufficient, amount of phosphate to solution to exceed the solubility limits of various metal-phosphate phases such as pyromorphite and autunite. For Pb, the mechanism is dissolution of the Apatite II followed by precipitation of pyromorphite:



where $x < 1$. The degree of protonation of the phosphate and carbonate in the reactions depends upon the pH. Reaction (1) does not necessarily lead to reaction (2). However, whenever Pb^{2+} is in solutions contacting the apatite, the apatite provides a constant supply of phosphate to solution to induce reaction (2). Under almost any environmental condition conceivable, Pb-pyromorphite will precipitate only by heterogeneous nucleation, i.e., a seed crystal with the apatite crystal structure is necessary for precipitation to occur. Homogeneous nucleation (precipitation directly from solution without a seed crystal) will not occur unless Pb concentrations exceed about 10 ppm (Lower *et al.*, 1998a, 1998b), a condition rarely achieved in the environment, even for acid mine drainage. This observation is absolutely 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. Without apatite, other Pb-phases will form that have much higher solubilities (Nriagu and Moore, 1984). The Apatite II grains serve as an optimal seed crystal as well as an optimal source of phosphate.

Therefore, with the use of Apatite II, over the course of time all migrating Pb in the system precipitates as Pb-pyromorphite. These microscopic Pb-pyromorphite mineral phases will grow and coalesce according to the processes of Ostwald ripening (Morse and Casey, 1988) eventually forming larger mineral clusters. During this process, which can take many years, the concentration of Pb in solution is kept extremely low, <15 ppb, by the presence of the Apatite II-supplied phosphate, so that no leaching of Pb occurs above drinking water limits, the material is no longer hazardous according to TCLP tests, and bioavailability is reduced. Studies with soluble phosphates on range soils show that the soluble phosphates actually cause greater Pb and phosphate migration both vertically through the soil and horizontally in the suspended load during runoff. However, with Apatite II vertical Pb migration was reduced to below 8 ppb in solution. Furthermore, Apatite II stabilization did not allow transport of Pb in runoff because precipitated Pb-pyromorphite as well as small Pb particles adhered to the silt and sand size Apatite II. Our recent electron microscopy studies have shown attachment of micron-sized Pb particles to the Apatite II surfaces (see associated paper in this volume,

PIMS Using Apatite II™: How It Works to Remediate Soil and Water, Wright et al.). Apatite II is also an ideal material for non-specific metal adsorption, particularly of the transition metals, through its uncompensated phosphate and hydroxyl surface groups, and will adsorb up to 5% of its weight by this mechanism (Conca et al., 2000).

MATERIALS AND METHODS

PIMS uses a special reactive form of the mineral apatite, Apatite II, which chemically binds soluble metals into new insoluble solid phases (Conca *et al.*, 2000; Manecki *et al.*, 2000; Chen *et al.*, 1997a,b; Wright *et al.*, 1995; Ma *et al.*, 1993; Wright, 1990). Apatite II is manufactured from fish cannery waste (U.S. Patent #6,217,775), producing a fish bone and fish hard part material that is primarily hydroxy calcium phosphate with residual organics of 25-35%.

Process equipment consisted of a front-end loader and a scraper which were used to move and mix materials. Actual mixing and field activities took two weeks. Soil characterization samples were collected as a one time sampling event. Leachate samples were collected for monitoring the Apatite II-amended soil as grab samples employing the use of a peristaltic pump and 0.45 micron filters. Samples were collected into one liter amber jars for further filtering efforts, if necessary, or in 250 mL plastic containers which contained pre-measured nitric acid to preserve the sample. Each soil and water sample collected was analyzed for lead using USEPA methods SW846, SW7421, SW7420, or SW1311 (TCLP extraction). Bioaccessibility tests were performed on PIMS treated soils from SWMU B-20 using SOP_110499, approved by EPA Region 8, which measures bioaccessibility as an *in vitro* indicator of *in vivo* bioavailability (Ruby et al., 1996).

SITE DESCRIPTION AND HISTORY

CSSA is located in south-central Texas, 25 miles north of San Antonio, on the Balcones Escarpment and has a modified subtropical climate, predominantly marine during the summer months, and continental during the winter months. Summers are hot with daily temperatures above 90°F over 80 percent of the time, and winters are mild with below freezing temperatures occurring on an average of only about 20 days per year. Average annual rainfall of approximately 29 inches is fairly well distributed throughout the year. CSSA is characterized by a rolling terrain of hills and valleys in which nearly flat-lying limestone formations have been eroded and dissected by streams draining primarily to the east and southeast. Physiography of the SWMU B-20 33.5-acre site is influenced by native topography, underlying geology, and artificial terrain modifications caused by explosive demolition and earth-moving activities. The predominant physiographic features are hills and saddles which lead to stream valleys. Elevations at the SWMU B-20 unit range from 1,360 ft on the west to about 1,300 ft on the east.

The geology of the site is essentially high-angle normally-faulted Cretaceous deposits comprised of alternating beds of limestone, marly limestone, blue shale, and occasional gypsum beds of the Glen Rose formation with its upper Trinity aquifer whose recharge is from direct precipitation on outcrops and stream flow losses. Drainage at the SWMU B-20 site is generally to the northeast in two ephemeral runoff channels within the Cibolo Creek watershed. Generally, soil types at CSSA are dark-colored, gravelly clays and loams. The soil horizon at the SWMU B-20 site is typically thin, ranging from 0.5 to 6 feet in thickness across the site, and include the Brackett-Tarrant association,

Crawford and Bexar stony soils, and Krum complex. All soils are underlain by limestone and are generally grayish-brown, loamy to various degrees, and with various amounts of clay and limestone gravel. The pH of the soils ranges from 7.5 to 8.0.

The land on which CSSA is located has been used for maneuvers since 1906. In addition to ammunition storage, CSSA lands were used to test, fire, and overhaul ammunition components. SWMU B-20 was used periodically between 1946 and 1987 to treat and dispose of waste ordnance. During that period, ordnance and other waste was detonated, buried, and disposed of on the ground surface at the site. The field remediation using Apatite II was conducted on soils primarily impacted with lead from the OB/OD activities (SWMU B-20).

At the time the site investigations began, inert metal scrap and UXO were scattered across the entire site. In addition, waste was buried and on the surface of the ground in the northern portion of the site. During a 1997 waste and UXO removal action over 3,000 yd³ of material were sieved. A total of 100,280 pounds of metal debris was removed and recycled. The sifted soils were stockpiled into five piles of approximately 500 to 750 yd³ each, which became the piles remediated using Apatite II. A total of 18 samples were collected from the sieved soil material. Semi-volatile organic compounds and explosives were not detected in the samples. All volatile organic compounds were below analytical reporting limits (RLs).

However, one or more metals concentrations in every sieved soil sample exceeded CSSA background levels, particularly barium (Ba), copper (Cu), lead (Pb), and zinc (Zn). Concentrations as high as 314 mg/kg Ba, 1,268 mg/kg Cu, 40,509 mg/kg Pb, and 479 mg/kg Zn were detected. A one-acre site was prepared for placement of Apatite II-treated soils by removing all surface debris and vegetation from the treatment site where the treated soils would be spread out. The Apatite II was delivered to the site in one-hundred and thirty-five 1,650-lb supersacks (100 metric tonnes). The soil piles were roughly mixed with 80 metric tonnes of the Apatite II by the front-end loader in an approximate ratio of 3% Apatite II by weight (Figure 1). The mixed soil was spread out over the prepared one-acre site, covered with a six inch layer of clean soil, and the site was seeded with wildflowers and grasses. Shallow lysimeter wells were installed at three positions around the site to collect leachate leaving the treatment zone, and in one position in an area of untreated soil, for post-emplacement monitoring. A total of fifty soil samples were collected from the treatment site for determination of total Pb. The average total Pb concentration was 1,942 mg/kg.



FIGURE 1. Soil mixing of Apatite II into Pb-contaminated soil at CSSA SWMU B-20.

RESULTS AND DISCUSSION

The performance of this technology is measured in several ways depending upon the target regulatory standards to be met. First, leachate from treated soils by natural waters should be below the MCL for lead in drinking water (0.015 mg/L), as shown by using monitoring wells beneath or around the treatment site. Second, the treated soil should meet the State of Texas class 2 non-hazardous waste classification criteria of 1.5 mg/L Pb as indicated by results from batch TCLP tests. Finally, treatment should achieve acceptable preliminary remediation goals as indicated by the USEPA Adult Lead Model using bioavailability or bioaccessibility data.

A summary of monitoring results are presented in Table 1, which shows the results from analyses of leachates generated from the treated and untreated soils. Leachates were collected from one or more shallow lysimeter wells. Multiple results for any collection date indicate different lysimeter wells. Collection from untreated soils did not begin until October of 2002. Soil amended with Apatite II resulted in a significant reduction of soluble lead in the leachates exiting the site. The average leachate concentration from the untreated soils was about 0.373 mg/L (ppm) well above the 0.015 mg/L drinking water standard, while the average leachate concentration from the treated

TABLE 1. Leachate monitoring results for Pb from Camp Stanley.

DATE COLLECTED	APATITE II TREATED SOIL	UNTREATED SOIL
4/11/2002	well #2	0.007 mg/L
	well #3	
6/30/2002	well #1	0.001
	well #2	
7/10/2002	well #2	0.004
	well #3	
8/21/2002	well #2	0.004
10/26/2002	well #1	well #4 0.394 mg/L
	well #2	
	well #3	
12/21/2002	well #1	well #4 0.351
	well #2	
	well #3	
4/10/2003	well #1	0.007
	well #2	
	well #3	

soils was 0.003 mg/L (ppm), well below the drinking water standard. TCLP results for the treated soils averaged 0.46 mg/L, which meet the State of Texas class 2 non-hazardous waste classification criteria of 1.5 mg/L (per 30 TAC chapter 335 subchapter R) and so can be disposed to an ordinary landfill as non-hazardous waste if so desired. TCLP results for untreated soils averaged 2.1 mg/L and did not meet these criteria.

Bioavailability. Bioaccessibility data were used to estimate a preliminary remediation goal using the USEPA Adult Lead Model (Maddaloni et al., 1998; Ruby et al., 1999; Graziano et al., 2001, 2003; Wright and Conca, 2004). The Apatite II amended soil

reduced the risk to adults that may potentially ingest the < 250- μ m soil size fraction at CSSA, and increased the preliminary cleanup goal at the SWMU B-20 site to over 2,300 mg/kg Pb. Therefore, because the soil contains an average Pb concentration of 1,942 mg/kg of soil, acceptable levels of Pb have been achieved at SWMU B-20 by the PIMS treatment.

Cost Analysis. Table 2 shows the total actual costs incurred for the treatment of approximately 3,000 yd³ of Pb-contaminated range soils using Apatite II, and were \$22/yd³. The overall costs should be directly comparable for other sites applying this technology. It is anticipated that when applying this technology in other *in situ* applications, the equipment could vary, e.g., use of a tractor with a disc and tiller instead of a scraper. Additionally, when firing range berms are treated for reuse as restored berms under pollution prevention applications, additional activities, e.g., earth moving, sieving, rebuilding, may need to be performed. Deep soils may require the use of augering or other methods to emplace the Apatite II.

The Apatite II material costs, including the delivery charges, provide the best basis for projecting costs of implementing this technology. The process chemicals (Apatite II material) and the shipping charges represent two-thirds of the expended costs for the remediation. This results from the ease of application of the Apatite II material. Note the lack of O&M costs.

TABLE 2. PIMS Remediation Costs at SWMU B-20, Camp Stanley.

ITEM	BASIS	COST
Planning	Preparation of Work Plan, Sampling and Analysis Plan, and Health and Safety Plan.	\$5,000
Site Characterization	Sampling and analysis	\$1,500
Mobilization	Mobilization of equipment only	\$550
Site Preparation	Includes clearing, grubbing of vegetation, large debris	\$500
Demobilization	Equipment demobilization only	\$550
Capital Equipment Rental	Front-end loader and scraper	\$2,375
Supervision	One supervisor for 40 hours @ \$60/hr	\$2,400
Operator Labor	Two operators for 40 hours at \$35/hr	\$1,400
Observer/Health&Safety	One observer for 40 hours @ \$65/hr	\$2,600
Maintenance	None	\$0
Utilities	None	\$0
Raw Materials	Includes 6-inch soil and vegetative cover	\$4,500
Process Chemicals	80 tons of Apatite II material	\$18,000
Consumables, Supplies	PPE	\$100
Sampling and Analyses	Performance testing	\$300
Shipping	Shipment from Apatite II generating plant to CSSA	\$24,000
ES&T Training	None	\$0
OSHA Sampling	None	\$0
Waste Manifest	None	\$0
Total costs for 3000 yd³		\$63,775
Cost/yd³ of soil		\$21.²⁶

Because material and shipping costs for Apatite II are the major cost drivers, the total cost is not sensitive to most site scenarios.

The DoD-wide savings are potentially large if this technology is adopted to treat much of the estimated 100,000,000 yd³ of Pb-contaminated soils across the Complex. The baseline alternative of grouting and off-site disposal is a firm number at \$104/yd³ at CSSA, and the cost of Apatite II is \$22/yd³, also an actual firm number from this remediation. Therefore, the potential DoD-wide savings are $(\$104/\text{yd}^3 - \$22/\text{yd}^3) \times 100,000,000 \text{ yd}^3 = \8.2 billion . Even a small fraction of this amount would constitute significant savings.

PIMS using Apatite II can be compared to both *in situ* remediation technologies used in site closure actions under TRRP Standard A Tier 1 criteria, and also to solidification/stabilization technologies used for treatment prior to offsite disposal. Grouting (cement solidification) with off-site disposal is the alternative baseline technology at small arms firing ranges and is considered the alternative baseline technology to PIMS using Apatite II. Some of these technologies have been attempted at CSSA in pilot-scale treatability studies and have directly-comparable costs and performances (Figure 2). The comparison is made on derived costs per cubic yard or reported costs per cubic yard of contaminated soil.

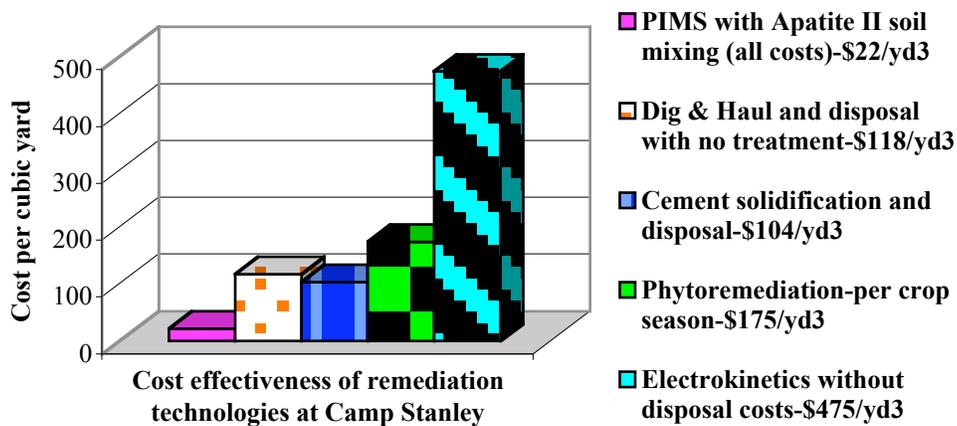


FIGURE 2. Technology cost comparison for soil remediation of Pb at CSSA.

ACKNOWLEDGEMENTS

This work was supported by the Environmental Security Technology Certification Program (ESTCP), Project CU-0020, Contract #DACA 72-00-C0007.

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