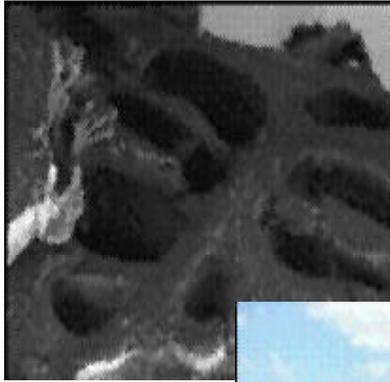


# ESTCP Cost and Performance Report

(ER-0020)



## PIMS™: Remediation of Soil and Groundwater Contaminated With Metals

June 2006



ENVIRONMENTAL SECURITY  
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

# COST & PERFORMANCE REPORT

## ESTCP Project: ER-0020

### TABLE OF CONTENTS

		Page
1.0	EXECUTIVE SUMMARY .....	1
2.0	TECHNOLOGY DESCRIPTION .....	3
2.1	TECHNOLOGY DEVELOPMENT AND APPLICATION .....	3
2.2	PROCESS DESCRIPTION .....	4
2.3	PREVIOUS TESTING OF THE TECHNOLOGY .....	6
2.4	ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY .....	8
3.0	DEMONSTRATION DESIGN .....	9
3.1	PERFORMANCE OBJECTIVES .....	9
3.2	TEST SITE SELECTION .....	9
3.3	TEST SITE/FACILITY HISTORY/CHARACTERISTICS .....	9
3.4	PHYSICAL SETUP AND OPERATION .....	13
3.5	SAMPLING/MONITORING PROCEDURES .....	14
3.6	ANALYTICAL PROCEDURES .....	15
4.0	PERFORMANCE ASSESSMENT .....	17
4.1	PERFORMANCE DATA .....	17
4.2	PERFORMANCE CRITERIA .....	20
4.3	DATA ASSESSMENT .....	22
4.4	TECHNOLOGY COMPARISON .....	24
4.4.1	Contaminant Removal Technologies .....	24
4.4.1.1	Bioremediation/Phytoremediation .....	24
4.4.1.2	Physical Separation/Acid Leaching .....	25
4.4.1.3	Electrokinetic Remediation .....	25
4.4.2	Waste Treatment Technologies .....	25
4.4.2.1	Pozzolan/Portland Cement .....	25
4.4.2.2	Phosphate Rock and Mineral Apatites .....	25
4.4.2.3	Emulsification Fixation and Reuse .....	26
5.0	COST ASSESSMENT .....	27
5.1	COST REPORTING .....	27
5.2	COST ANALYSIS .....	29
5.2.1	Cost Basis .....	29
5.2.2	Cost Drivers .....	29
5.2.3	Life-Cycle Costs .....	29
5.3	COST COMPARISON .....	30
5.3.1	No Treatment and Off-Site Disposal .....	31

## TABLE OF CONTENTS (continued)

	<b>Page</b>
5.3.2 Grouting and Off-Site Disposal .....	31
5.3.3 Phytoremediation .....	31
5.3.4 Electrokinetic Remediation.....	32
5.3.5 Physical Separation/Acid Leaching .....	32
6.0 IMPLEMENTATION ISSUES .....	33
6.1 COST OBSERVATIONS.....	33
6.2 PERFORMANCE OBSERVATIONS.....	33
6.3 SCALE-UP .....	34
6.4 OTHER SIGNIFICANT OBSERVATIONS.....	34
6.5 LESSONS LEARNED.....	34
6.6 END-USER ISSUES .....	34
6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE.....	35
7.0 REFERENCES .....	37
APPENDIX A: POINTS OF CONTACT	

## FIGURES

		<b>Page</b>
Figure 1.	HR-TEM Image of Apatite II Shows Random Nanocrystals. ....	1
Figure 2.	Photomicrograph of Apatite II Showing the Internal Porosity. ....	2
Figure 3.	Mixing Apatite II into Lead-Contaminated Soil.....	2
Figure 4.	IMS Application and Monitoring Schematics .....	5
Figure 5.	IMS Photo Schematic of Demonstration Steps.....	7
Figure 6.	Sieving to Remove UXO and Large Metal Debris .....	8
Figure 7.	Full Field Scale Demonstration Site .....	11
Figure 8.	Monitoring Lysimeter .....	11
Figure 9.	Soil Sample Collection from Treatment Zone.....	12
Figure 10.	Lognormal Distribution Graph of Pb Concentrations.....	19
Figure 11.	Bioaccessibility Results for Pb-Contaminated soils, unamended and amended with Apatite II.....	20
Figure 12.	Photomicrograph of Apatite II-Amended Camp Stanley Range Soil with ~1 Micron-Wide Pb Grain on Surface of Apatite II and Pb X-ray map. ....	23
Figure 13.	Photomicrograph of Apatite II-Amended Camp Stanley Range Soil with ~1 Micron-Wide Pb Grain on Surface of Apatite II and Pb X-ray map. ....	23
Figure 14.	Technology Cost Comparison at CSSA.....	32

## TABLES

	<b>Page</b>
Table 1. Performance Objectives.....	9
Table 2. Summary of Metal Levels Above Background in Sieved Soil.....	12
Table 3. Leachate Monitoring Results.....	18
Table 4. Expected Performance and Performance Observations.....	21
Table 5. Demonstration Costs.....	28

## COVER PHOTOS

Sieving of Camp Stanley Range Soils for UXO/Metal Removal .....	<i>Bottom left</i>
Mixing Apatite II into Pb-Contaminated Soil.....	<i>Right</i>
SEM Image of Apatite II Grain Shows Internal Porosity from 1 $\mu$ to 100 $\mu$ .....	<i>Top left</i>

## ACRONYMS AND ABBREVIATIONS

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ACC	Air Combat Command
AFCEE	Air Force Center for Environmental Excellence
APPL	Agriculture & Priority Pollutants Laboratories, Inc.
Ba	barium
Cd	cadmium
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
Cr	chromium
CSSA	Camp Stanley Storage Activity
Cu	copper
DoD	Department of Defense
DOE	Department of Energy
EPA	Environmental Protection Agency
EPCRA	Emergency Planning and Right-to-Know Act
ESTCP	Environmental Security Technology Certification Program
FIPR	Florida Institute of Phosphate Research
IDEQ	Idaho State Department of Environmental Quality
MCL	maximum contaminant level
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
MSL	mean sea level
NCP	National Contingency Plan
NWF	National Wildlife Federation
OB/OD	open burn/open detonation
O&M	operations and maintenance
Pb	lead
PIMS	phosphate-induced metal stabilization
ppb	parts per billion
PPE	personal protective equipment
ppm	parts per million
PRB	permeable reactive barrier

## ACRONYMS AND ABBREVIATIONS (continued)

---

RCRA	Resource Conservation and Recovery Act
RDX	Royal Demolition Explosives
RRAD	Red River Army Depot
RRS	Risk Reduction Standard
SAFR	small arms firing range
SBIR	Small Business Innovative Research
SCS	Soil Conservation Service
SEM	Scanning electron microscopy
SERDP	Strategic Environmental Research and Development Program
SPLP	synthetic precipitation leaching procedure
SVOC	semivolatile organic compound
SW	solid waste
SWMU	Solid Waste Management Unit
TAC	Texas Administrative Code
TCE	trichloroethylene
TCEQ	Texas Commission on Environmental Quality
TCLP	toxicity characteristic leaching procedure
TNT	trinitrotoluene
TRI	Toxic Release Inventory
TRRP	Texas Risk Reduction Program
USDA	U.S. Department of Agriculture
UXO	unexploded ordnance
VOC	volatile organic compound
XRD	x-ray diffraction
Zn	zinc

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## PREFACE-ACKNOWLEDGEMENTS

Phosphate-induced metal stabilization (PIMS™) using Apatite II™ is a simple, environmentally sustainable technology. It uses a natural, benign material derived from processing fishbone waste products to treat waste by stabilizing heavy metals in situ. In the sense of biodynamics and under the principles of recycle and reuse, PIMS using Apatite II exemplifies another step in the process of restoring and renewing the surface of our planet.

Fortunately, Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) have believed in and supported the development of PIMS using Apatite II, starting in 1993 with bench scale proof-of-principle research, and concluding in 2003 with the results of a full-scale field demonstration that has become an Interim Measure Corrective Action. Our first acknowledgements and great appreciation go to these two organizations and their dedicated and visionary staff who have served as mentors and guides to us throughout this decade-long process.

This demonstration and field activity succeeded because of the whole-hearted support and commitment of Camp Stanley Storage Activity (CSSA), particularly the environmental officer, Brian Murphy, and the base commander, Colonel Jason Shirley, as well as the site contractor, Parsons, Inc., and especially the project manager, Ken Rice, and the field team leader, Kyle Caskey. There are other organizations and companies to whom we express our appreciation: Eagle Environmental & Construction Services, L.P.; Agriculture & Priority Pollutants Laboratories, Inc.; Parsons, Inc.; Three Rivers Internet; and the U.S. Environmental Protection Agency (USEPA).

There are many individuals to thank: Xiaobing Chen, Dale Counce, Joel Cowger, Paul Didzerekis, Carlos Garcia, Paula Heller, Rene Jones, Jill Noel, Mike Ruby, and Margaret Snow.

Lastly, we thank Rob Hinchee for facilitating the collaboration between CSSA, Parsons, and UFA Ventures.

*Technical material contained in this report has been approved for public release.*

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## 1.0 EXECUTIVE SUMMARY

Lead-contaminated soils are prevalent in the United States, particularly at Department of Defense (DoD) sites, which have more than 3,000 small arms firing ranges (SAFR). Private SAFRs and police practice SAFRs constitute an additional 9,000 sites. Estimates of lead-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, with costs estimated at more than \$10 billion to dispose of them with existing baseline technologies, even if sufficient landfill space did exist. Additionally, large quantities of lead-contaminated leachates generated by rainfall and irrigation at many military sites flow into lakes or storm water drain systems, or provide contaminated recharge to shallow aquifers. The phosphate-induced metal stabilization (PIMS™) technology discussed in this report is an in situ stabilization or sequestration technology that uses a natural, benign material, Apatite II™, which is mixed into the contaminated soil to immobilize lead (Pb) without changing the basic nature of the soil, e.g., the permeability, porosity, or density. This technology allows the soil to function in the future as a soil to be left in place, or disposed of as a nonhazardous material if desired. Apatite II™ is a natural phosphate material that incorporates metals into new stable phosphate phases that are nonleachable. 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 in itself generate any hazard or environmental problem.

This demonstration included treating 3,000 yd<sup>3</sup> of Pb-contaminated range soil at Solid Waste Management Unit (SWMU) B-20 at the Camp Stanley Storage Activity (CSSA) by mixing the soils with 3% Apatite II™, spreading the amended soils out over an acre site, covering the amended soils with a layer of uncontaminated surface soil, and seeding with native grasses and wildflowers. Shallow lysimeter monitoring wells were emplaced beneath the treatment zone.

Both original performance objectives were met: (1) to determine suitable emplacement methodologies for the PIMS™ in situ treatment of Pb-contaminated soils and (2) to determine actual field implementation costs. A further objective was to actually treat all of the Pb-contaminated soils at an ordnance treatment unit at CSSA so the soil could be released back to the site in a manner consistent with pending regulatory approval and future site use plans. This demonstration transferred the technology to an end user (CSSA), by: (a) remediating the Pb-contaminated soil at SWMU B-20 at CSSA; (b) determining the degree of regulatory acceptance; (c) providing the base with an acceptable in situ alternative to off-site disposal, and (d) reducing off-site disposal costs through treatment of soil to a lesser waste classification if disposal is a desired action.

The regulatory drivers at this site include the Environmental Protection Agency (EPA) and Texas state regulators. First, leachate from amended soils by natural waters must be below the maximum contaminant level (MCL) for Pb in drinking water (0.015 milligrams per liter [mg/L]). Second, the amended soil should meet the State of Texas class 2 nonhazardous waste classification criteria of 1.5 mg/L (per 30 Texas Administrative Code [TAC] chapter 335 subchapter R), as indicated by results from batch toxicity characteristic leaching procedure (TCLP) tests. Finally, treatment should reduce the bioavailability or bioaccessibility of the Pb in the soil.

The demonstration achieved these goals. The soil contained an average total Pb concentration of 1,942 mg/kg parts per million (ppm), with an upper confidence limit calculated at 2,402 mg/kg. Waste classification results from batch TCLP tests indicated that the unamended soil did not meet State of Texas class 2 nonhazardous waste classification criteria of 1.5 mg/L Pb (per 30 TAC chapter 335 subchapter R), and required treatment. After treatment with PIMS™, the soils did meet these criteria with an average TCLP concentration of 0.46 mg/L Pb.

Field leachate monitoring results from the demonstration site after treatment average 0.0065 mg/L (ppm) Pb, well below the 0.0150 mg/L USEPA standard for Pb in drinking water. Bioaccessibility data showed that treatment reduced Pb bioavailability. PIMS™ using Apatite II™ is both a successful in situ remediation technology and a successful waste treatment technology for landfill disposal, if needed. A U.S. patent (#6,217,775) was awarded for PIMS™ using Apatite II™ during the course of this demonstration.

This demonstration was a full-scale remediation of SWMU B-20 costing less than \$22/yd<sup>3</sup> of soil which includes a variable cost of \$19/yd<sup>3</sup>. No scale-up is needed for this technology. All costs are actual, not projected. The process chemicals (the Apatite II material) and the shipping charges represent the largest portion of the costs for the field-scale demonstration. This results from the ease of application of the Apatite II material. Process equipment consisted of a front-end loader and a maintainer which were used to move and mix materials.

Other technologies demonstrated at the CSSA site gave reliable cost comparisons for the soil under similar conditions. Compared to PIMS™ using Apatite II™ at a cost of \$22/yd<sup>3</sup>, no treatment with off-site disposal cost \$118/yd<sup>3</sup>; grouting (cement solidification) with off-site disposal cost \$104/yd<sup>3</sup>; electrokinetic remediation cost \$475/yd<sup>3</sup>; and phytoremediation cost \$175/yd<sup>3</sup>. Because grouting with off-site disposal is the alternative baseline technology at SAFRs and would have been the technology utilized to remediate this site in the absence of PIMS™ using Apatite II™, the cost avoidance/savings of this demonstration was  $(\$104/\text{yd}^3 - \$22/\text{yd}^3) \times 3,000\text{yd}^3 = \$246,000$ .

The end users of this technology include all DoD sites with SAFRs. The purpose of this demonstration was to establish a remediation technology that is potentially more cost effective and efficient than other remediation processes, positively addressing stakeholder decision-making factors. As a result, PIMS™ using Apatite II™ is now being applied at other sites at CSSA and is being implemented at other DoD sites.

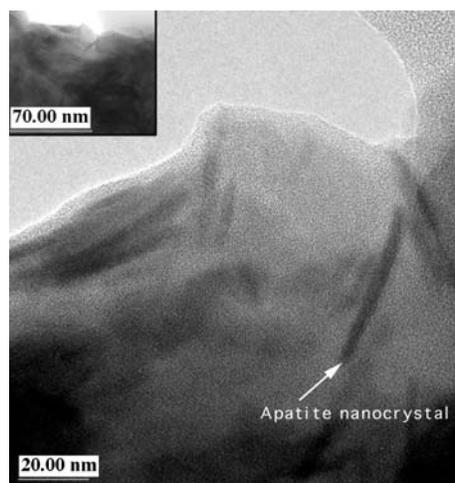
## 2.0 TECHNOLOGY DESCRIPTION

### 2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

The phosphate-induced metal stabilization (PIMS™) technology is ideal for remediating metal-contaminated systems, particularly Pb, uranium, manganese (Mn), copper (Cu), zinc (Zn), and cadmium (Cd) (Ma et al, 1993; 1995; Eighmy et al, 1998; Lower et al, 1998; Conca et al, 2000; Matheson et al, 2001; Kaplan et al, 2002; Knox et al, 2003; Thomson et al, 2003). PIMS™ using Apatite II™ is suitable for all types of soils and waters, and all contaminant concentrations from parts per billion (ppb) to percent levels. This technology is not affected by most environmental conditions and will work within most media from pH 2 to 12, at all moisture contents, and in the presence of organics and a thriving ecology. PIMS™ will not adversely affect existing biota, is not hazardous or toxic, and is ecologically beneficial.

PIMS™ uses a special reactive form of the mineral apatite, Apatite II™, chemically binds soluble metals into new insoluble solid phases (Wright et al, 1995; Chen et al, 1997a,b; Conca, 1997; 1998; Conca and Wright, 1999; Wright et al, 2003). Apatite II™ is manufactured from fish cannery waste products, producing a fish bone and fish hard part material that is primarily hydroxy calcium phosphate with residual organics of 25-35%. Apatite II™ binds Pb into Pb-pyromorphite, an insoluble phase that is stable over all environmental conditions for hundreds of millions of years (Wright et al, 1987a,b; Wright, 1990; Wright, 2005). Pb-pyromorphite has an extremely low solubility product,  $K_{sp} \ll 10^{-80}$  (Nriagu, 1974; Manecki et al, 2000) and will not dissolve under most environmental conditions. Apatite II will stabilize about 20 percent of its weight in Pb (Conca, 1997). Similar performance occurs with uranium, plutonium, and other metals.

Some form of apatite mineral is necessary for this technology in order to provide an optimal concentration of phosphate to soil water solutions to precipitate Pb-pyromorphite. Non-apatite phosphate and mixtures of precursor constituents will not work as well or over as long a time period. Apatites, other than Apatite II™, do not have the optimal chemical and structural properties for metal remediation in the environment, that is: (a) Apatite II™ has no fluorine substitution in the hydroxyl position; (b) Apatite II™ has a high degree of carbonate substitution; (c) Apatite II™ is generally poorly crystalline with random nanocrystals of crystalline apatite (Figure 1); (d) Apatite II™ has few trace metals; and (e) Apatite II™ has a high degree of microporosity and surface area. Figure 2 is a photomicrograph of Apatite II™ showing the internal porosity from 1-10 micron ( $\mu$ ) (upper) to 100 nanometer (nm) (lower). Apatite II™ has other advantageous properties; e.g., under acidic conditions it buffers the pH to neutral and provides an ideal chemical environment for many other beneficial processes, such as sulfate and nitrate reduction that degrade trinitrotoluene (TNT), royal demolition explosives (RDX) and perchlorate (Conca et al, 2003; Martinez et al, 2005). PIMS™ using Apatite II™ is typically emplaced into

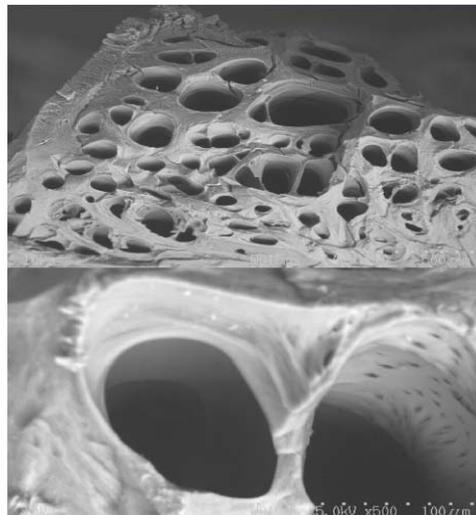


**Figure 1. HR-TEM Image of Apatite II Shows Random Nanocrystals.**

contaminated areas using soil mixing, in permeable reactive barriers (PRB), in filter systems, or used as an additive to waste streams, emplaced as a liner, or injected as a slurry.

## 2.2 PROCESS DESCRIPTION

For soil mixing, as with range soils, PIMS™ has minimal mobilization requirements, no installation requirements, and minimal operational requirements. There are no key design criteria other than effectively mixing the soil with the Apatite II™ and emplacing it appropriately so it is stable from a slope-stability/soil-stability standpoint, e.g., it will not wash away in a flooding event. An actual 100-year flooding event did occur ten months after field emplacement, and no adverse effects were observed. Mobilization is limited to bringing the Apatite II™ material on site and having the appropriate earth moving equipment available. Operational requirements include sufficiently dry conditions to allow mixing, i.e., not during or immediately after rain events and not during frozen conditions. Throughput is limited only by mixing capacity, and labor is limited to a few personnel. There are no operational sampling requirements. As an example, for this 3,000 yd<sup>3</sup> soil demonstration, process equipment consisted of a front-end loader and a maintainer, which were used to move and mix materials (Figure 3). Labor consisted of a construction supervisor, two heavy equipment operators, and an independent observer/health and safety site monitor. Actual mixing and field activities took 2 weeks. All in all, this technology is extremely easy to implement.

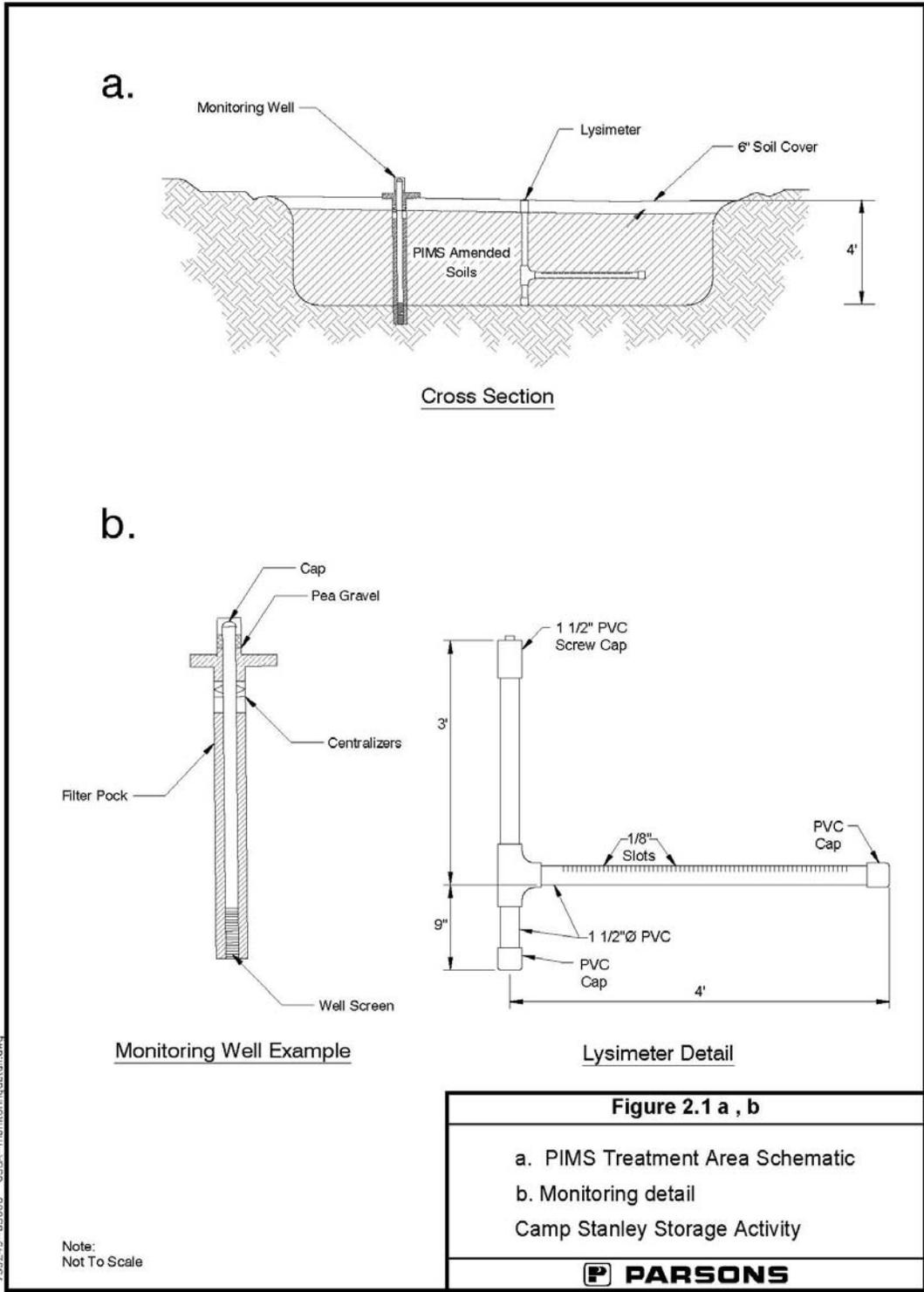


**Figure 2. Photomicrograph of Apatite II™ Showing the Internal Porosity.**

Figure 4 shows a process schematic of the technology as applied in this demonstration at CSSA. The contaminated soil existed as six 500 yd<sup>3</sup> piles that had been sieved for unexploded ordnance (UXO) removal. A 1-acre site was prepared by removing all surface debris and vegetation from the treatment site where the amended soils would be spread out. The Apatite II™ was delivered to the site in 750-kg supersacks. The soil piles were roughly mixed with the Apatite II™ by the front-end loader in an approximate ratio of 3% Apatite II™ by weight. The mixed soil was spread out over the prepared 1-acre site.



**Figure 3. Mixing Apatite II™ into Lead-Contaminated Soil.**



**Figure 4. IMS Application and Monitoring Schematics.**

The treated soil was covered with a 6-inch layer of clean soil and seeded with wildflowers and grasses. Shallow lysimeter wells were installed at three positions around the site to collect leachate leaving the treatment zone for post-emplacment monitoring (Figure 4). Figure 5 shows a photo schematic of the steps of the demonstration effort.

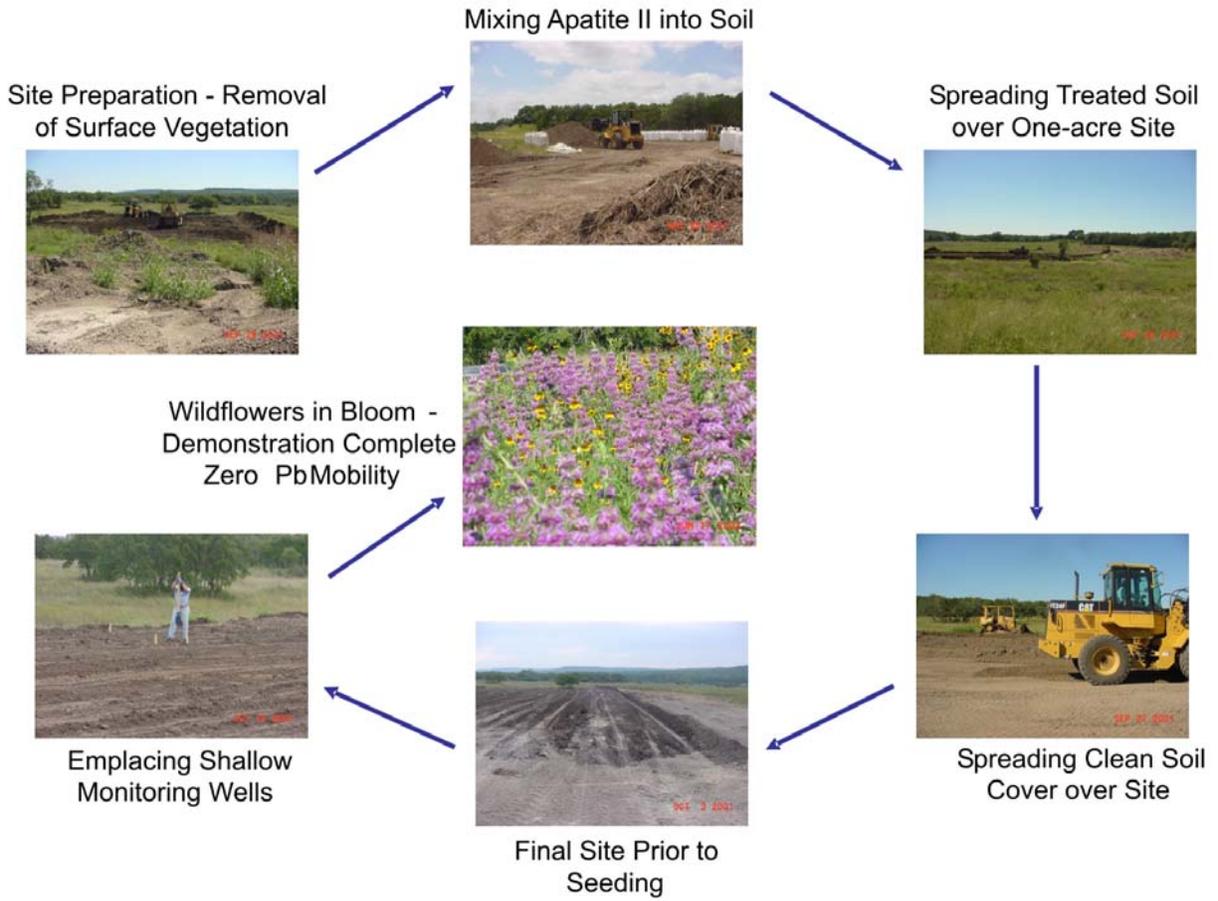
The performance of this technology is measured in several ways depending upon the target regulatory standards to be met. First, leachate from amended soils by natural waters should be below the MCL for Pb in drinking water (0.015 mg/L). This is demonstrated using monitoring wells beneath or around the treatment site. Second, the amended soil should meet the State of Texas class 2 non-hazardous waste classification criteria of 1.5 mg/L Pb (per 30 TAC chapter 335 subchapter R) as indicated by results from batch TCLP tests.

There are no technology-specific personnel or training requirements for this technology. Personnel and training requirements are those required by the site or the installation for any soil moving/heavy equipment operations, and those required by the site quality assurance project plan, sampling analysis plan, or other site-specific requirements. There are also no technology-specific health and safety requirements for this technology other than the general requirements of the site.

### **2.3 PREVIOUS TESTING OF THE TECHNOLOGY**

Previous work with Pb, Zn, Cd, aluminum, Cu, nickel, cobalt, uranium, americium, and plutonium has shown successful performance of Apatite II™ under a variety of environmental conditions. Under SERDP, EPA, Small Business Innovative Research (SBIR) and other projects, UFA Ventures, Inc. investigated the metal-stabilization potential of reactive phosphates and other sorptive media in soil mixing and PRBs at the Bunker Hill Mining District in northern Idaho. Soil was contaminated with Pb up to 4,000 ppm, and groundwater had concentrations of Pb, Zn, Cd, and Cu up to 10 ppm, 250 ppm, 1 ppm and 20 ppm, respectively. Treatability studies using columns of soil mixed with various amounts of apatite showed that PIMS™-amended soils did not leach any metal above detection limits of 5 ppb for Pb and Cd, and 25 ppb for Zn. Even as little as 1 percent apatite by weight was effective. In PRBs, Apatite II™ was orders of magnitude more effective than any other media, including bone char, mineral apatite, iron filings, zeolites, CabSorb, C-Sorb, and activated charcoal (Wright et al, 1995; Chen et al, 1997a; Conca, 1997, 1998; Conca et al, 2000).

As a result of these studies, the Idaho State Department of Environmental Quality (IDEQ) proceeded with emplacement of an Apatite II™ PRB at the Success Mine site. Monitoring results from the field have shown excellent performance: Apatite II™ has kept Pb and Cd below the detection limits of 0.005 mg/L and 0.002mg/L, respectively, and Zn below background. From 2001 to 2005 the PRB removed over 10,000 pounds of these metals from the acid mine drainage entering the adjacent stream.



**Figure 5. IMS Photo Schematic of Demonstration Steps.**

Similar results were obtained for uranium during treatability studies of remediation of uranium-contaminated soils from a depleted-uranium firing range at Los Alamos, New Mexico. A full-scale water treatment system with Apatite II™ is operating at Paducah, Kentucky, to treat over 100,000 gallons of uranium-contaminated water from flooding of a Department of Energy (DOE) processing facility. Apatite II™ was also successfully tested as a liner in treatability studies to prevent plutonium from leaching and escaping waste disposal drums (Conca et al, 2000).

## **2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY**

The advantages of this technology include (a) the capability to be used as an in situ treatment technology; (b) the relatively low cost compared to other stabilization technologies; and (c) the ease of application and lack of operations and maintenance (O&M) requirements.

Additionally, Apatite II™ is environmentally sustainable because it is generated as a waste product from the fishing industry, and its use as a remediation product further enhances the advantages of the PIMS™ technology over other phosphate technologies. This is in part because other agricultural grade or reagent grade phosphates require production from phosphorite deposits and, as such, create excessive waste and environmental hazards through their production. As an example, central Florida is experiencing an environmental crisis stemming from phosphoric acid and phosphate production from open pit mining of mineral apatite in phosphorite deposits (see the Florida Institute of Phosphate Research at <http://www.fipr.state.fl.us/publications>). Planned additional phosphorite mining activities threaten the Everglades and the last habitat of the remaining Florida panthers, which will cause extinction of the species, an effect that must be factored into costs for any technology (National Wildlife Federation [NWF], 2003, <http://www.nwf.org/panther>). There are no negative environmental impacts from using or producing Apatite II™.

The main limitation of this technology is that Pb is not removed from the system, but stabilized within the system. This technology is applicable to risk-based closures because of the reduction in Pb leachability and bioavailability. Only sites with frozen soils or other unusual soil conditions that make mixing impossible or prohibitively difficult are not appropriate for this technology. Apatite II, because it is derived from fish bones, has a fish odor associated with it, and should be stored under cover and kept dry until used. If the fish odor is undesirable, it can easily be removed by thermal pretreatment; however, the organic fatty acids decompose naturally after a few weeks in the soil.

### 3.0 DEMONSTRATION DESIGN

#### 3.1 PERFORMANCE OBJECTIVES

Performance objectives were to determine suitable emplacement methodologies for the in situ treatment of Pb-contaminated soils so the soil poses no further health threat or environmental hazard, and to determine actual field implementation costs. Both of these objectives were met. The approach for using PIMS™ at Camp Stanley Storage Activity (CSSA) was to take Pb-contaminated soils and mix them with 3% Apatite II™, then spread the amended soils back on site in a swale or slight topographic depression.

Table 1 provides an assessment of the performance objectives. Results of leachate monitoring show that Pb leachate concentrations at SWMU B-20 are consistently below the MCL of 0.015 mg/L (ppm). Therefore, emplacement of the Apatite II material using common field equipment, e.g., backhoe/front-end loader, represents the actual field implementation costs.

**Table 1. Performance Objectives.**

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance Objective Met
Qualitative	Reduced Pb mobility	<15 ppb Pb in leachate from amended site soils (EPA)	Yes
	Faster remediation	< 2 week field implementation	Yes
	Ease of Use	Easy soil mixing	Yes
Quantitative	Meet regulatory standard	<15 ppb Pb in leachate from amended site soils (EPA)	Yes

#### 3.2 TEST SITE SELECTION

As this technology is ideally suited for Pb-contaminated media, the test site was chosen because of its Pb contamination. The site is also very representative of many other DoD sites, both in contaminant type and field characteristics. The site was also chosen because of enthusiasm by key players including site personnel, the EPA representative, stakeholders, and the existing infrastructure at CSSA.

#### 3.3 TEST SITE/FACILITY HISTORY/CHARACTERISTICS

The land on which CSSA is located was used for ranching and agriculture until the 1900s. During 1906 and 1907, six tracts of land were purchased by the U.S. government and designated the Leon Springs Military Reservation. The reservation was used for maneuvers by Army and National Guard units, and the lands included campgrounds and cavalry shelters. In October 1917, the installation was redesignated CSSA. U.S. involvement in World War I spurred extensive construction of temporary cantonments and installation support facilities. In 1931, CSSA was selected as an ammunition depot, and construction of standard and igloo magazines began in 1938 (Army, 1990). CSSA was transferred to the jurisdiction of the Red River Army Depot (RRAD) in 1947. 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 demonstration was conducted on soils primarily impacted with Pb from the former open burn/open detonation (OB/OD) waste management unit (SWMU B-20). Other metals (barium [Ba], Cd, Cu, Zn, etc.) are also present in the site soils at above-background concentrations. The PIMS™ using Apatite II™ demonstration also amended these other metals, particularly Ba, which is high at this site. SWMU B-20 consists of approximately 33.5 acres surrounded by wooded areas in the northeastern portion of CSSA.

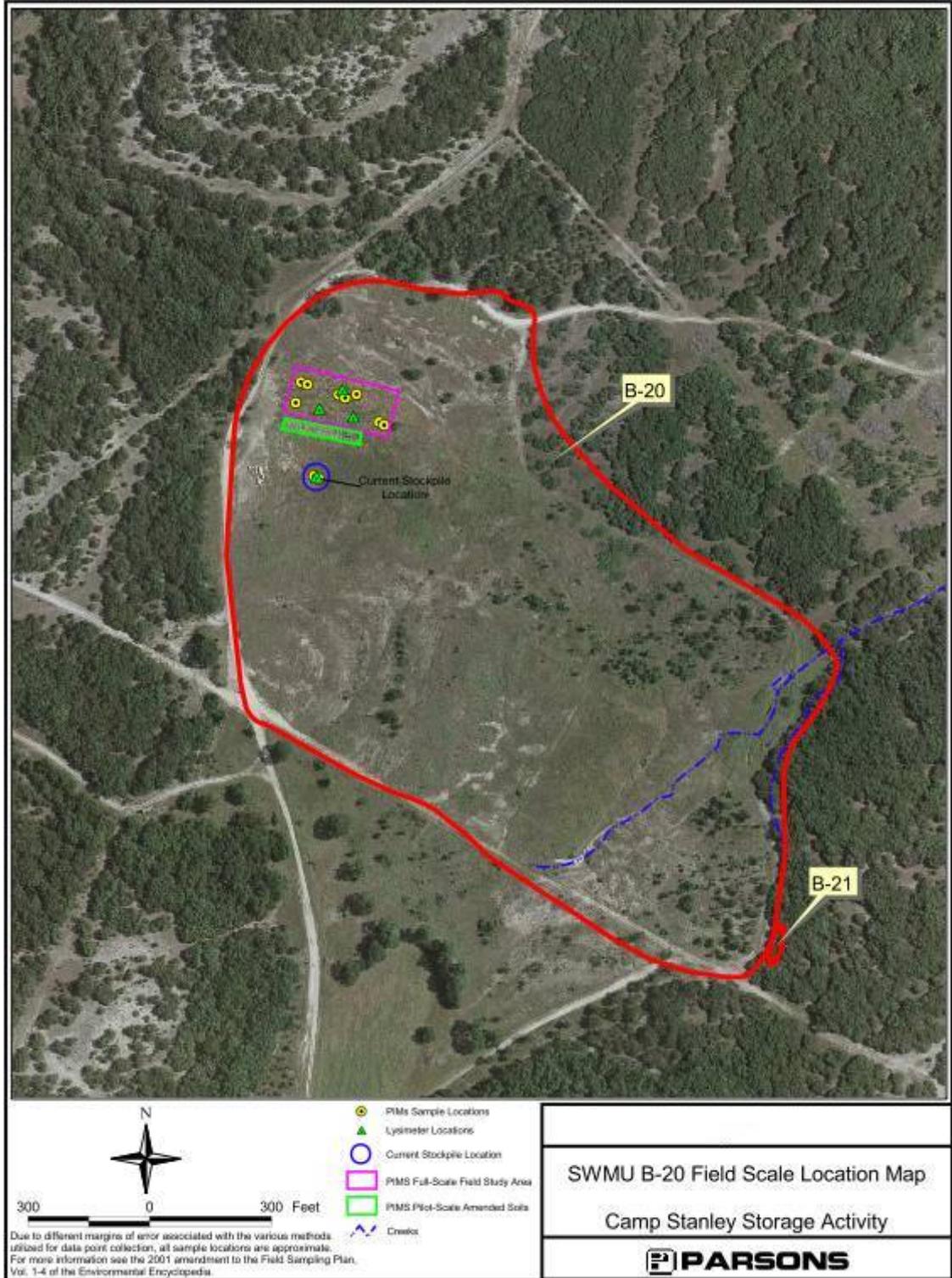
At the time the site investigations began, inert metal scrap and UXO were scattered across the entire site. Waste was buried and on the ground surface in the northern portion of the site. During a 1997 waste and UXO removal action, over 100,000 pounds of metal debris was removed and recycled by particle separation (Figure 6). The sifted soils were stockpiled into six piles of approximately 500 yd<sup>3</sup> each and became the piles remediated in the PIMS™ demonstration using Apatite II™. Figure 7 shows the field demonstration location within SWMU B-20. For characterization of sieved soils, a total of 18 samples were collected from the sieved soil material for volatile organic compounds (VOC), semivolatile organic compounds (SVOC), explosives, and metals analysis. Analytical results of the samples indicated that VOCs and metal constituents were present in the stockpiled soils. SVOCs and explosives were not detected in the samples. Methylene chloride, toluene, and trichlorethylene (TCE) were detected at very low concentrations in the three sifted soil samples that were analyzed for VOCs. All VOC results were below analytical reporting limits.



**Figure 6. Sieving to Remove UXO and Large Metal Debris.**

However, one or more metals concentrations in every sieved soil sample exceeded CSSA background levels. As shown in Table 2, Ba, Cu, Pb, and Zn concentrations most often exceeded background. Concentrations as high as 314 milligrams per kilogram (mg/kg) Ba, 1,267 mg/kg Cu, 40,500 mg/kg Pb, and 478 mg/kg Zn were detected.

The PIMS™ technology is unaffected by most geology, hydrogeology, and physiological features of any site, as long as simple soil mixing can be accomplished. Therefore, the setting of CSSA was neither hostile nor advantageous to this technology. However, the alkaline soil did present a worse-case scenario.



**Figure 7. Full Field Scale Demonstration Site.**

**Table 2. Summary of Metal Levels Above Background in Sieved Soil.**

<b>Metal</b>	<b>Background Concentration (mg/kg)</b>	<b>Frequency of Above-Background Detection</b>	<b>Minimum Concentration (mg/kg)</b>	<b>Maximum Concentration (mg/kg)</b>	<b>Sample IDs with Maximum</b>
Arsenic	19.6	0/20 (0%)	3.3	15.1	B20-SIFT15
Barium	186	15/20 (75%)	117	314	RW-B20-SIFT21
Cadmium	3.0	1/20 (5%)	0.52	131	B20-SIFT15
Chromium	40.2	0/20 (0%)	12.3	24.1	RW-B20-SIFT19
Copper	23.2	20/20 (100%)	31.9	1,268	RW-B20-SIFT22
Lead	84.5	19/20 (95%)	65.3	40,500	B20-SIFT14
Mercury	0.77	0/20 (0%)	0.024	0.69	RW-B20-SIFT21
Nickel	35.5	0/20 (0%)	7.17	14.6	RW-B20-SIFT19
Zinc	73.2	19/20 (95%)	42.2	479	RW-B20-SIFT19

CSSA is located in south-central Texas 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% of the time, and winters are mild with below freezing temperatures occurring only about 20 days per year on average. Average annual rainfall is approximately 29 inches, 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 site is influenced by native topography, underlying geology, and artificial terrain modifications caused by explosive demolition and earth-moving activities. Resistive limestone beds outcrop as topographic highs, but none form buttes or mesas. Rather, the predominant physiographic features are hills and saddles which lead to stream valleys. Topographic relief across CSSA ranges from 1,100 ft to 1,500 ft above mean sea level (MSL). Elevations at the SWMU B-20 unit range from 1,360 ft above MSL on the west to about 1,300 ft above MSL on the east.

The geology of the site is essentially high-angle, normally-faulted Cretaceous deposits composed of alternating beds of limestone, marly limestone, blue shale, and occasional gypsum beds of the Glen Rose formation. As a result of the regional faulting, many fracture systems have developed in the deposits underlying the site. The upper Trinity aquifer is located within the upper member of the Glen Rose formation. The upper Glen Rose is exposed over much of the SWMU B-20 site, and recharge to the upper Trinity aquifer is from direct precipitation on outcrops and stream flow losses. Movement of groundwater in the upper Trinity aquifer is restricted to lateral flow along bedding planes between marl and limestone, where dissolution has enhanced permeability of the limestone. Occurrence of groundwater in this aquifer is sporadic and dependent on precipitation and secondary porosity features, indicating that beds within this aquifer are perhaps not hydraulically connected by avenues of vertical permeability. The upper Trinity aquifer is under water table conditions, is generally of poor quality, and most wells achieve only low production.

All streams are intermittent at CSSA. 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, according to the U.S. Department of Agriculture (USDA) Soil Conservation Service (SCS) soil survey for Bexar County, Texas. 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.

### 3.4 PHYSICAL SETUP AND OPERATION

The general approach for demonstrating PIMS™ using Apatite II™ at CSSA was to remediate soils from SWMU B-20 that had been sieved to remove UXO pieces greater than three-quarters of an inch. The remaining soils were mounded into piles of approximately 500 yd<sup>3</sup> each. During the demonstration efforts 3,000 yd<sup>3</sup> of contaminated soil were amended with the Apatite II™ material in August 2002. The demonstration site was prepared by removing the surface



**Figure 8. Monitoring Lysimeter.**

vegetation. The field mixing efforts consisted using nonspecialized equipment (front-end loader and a maintainer) to effectively mix approximately 3% by weight of Apatite II™ material into the Pb-contaminated soil from the SWMU B-20 site at a rate of about 500 yd<sup>3</sup> per day. Mixing efforts were conducted as batch treatments of 10 yd<sup>3</sup> lots with a 3% by weight mixture of Apatite II™ material added to the contaminated soil. The soil was mixed with a maintainer, which folded the Apatite II™ material into the soil matrix in passes within the treatment area. The front-end loader then removed the amended material to a separate designated location for staging before final emplacement by spreading over the site. Three field lysimeters were installed in the treatment

zone to monitor leachate (Figure 8). Labor requirements included two heavy equipment operators, a site supervisor, and a health and safety officer to monitor safety conditions of the operations. A small portion of the remaining soils, approximately 10 yd<sup>3</sup> was left unamended and spread over a 20 ft x 20 ft plot. A lysimeter was also installed in this unamended plot to evaluate baseline conditions and compare performance between the unamended and amended soils.

Although this demonstration was completed in batches, it is envisioned that continuous mixing efforts could be utilized if a much larger amount of soil is to be amended. This could be accomplished with the use of a pug mill or other flow-through mixing units.

It is not anticipated that any residual handling will be required during the use of this technology at almost any site.

The operating parameters for the field demonstration included the application (mixing) of Apatite II™ into the contaminated soil (mixing operations). Preliminary observations provided data that showed that leachates from Apatite II™-amended soils were below the MCL for Pb and

indicated that there were no concerns from surface water runoff and leachate generated from the amended soils. All analytical and sampling methods that were used in supporting the experimental design are provided in the Environmental Security Technology Certification Program (ESTCP) Final Report for this project, which includes the CSSA Sampling and Analysis Plan, the associated Quality Assurance Project Plan, and the Health and Safety Project Plan.

### 3.5 SAMPLING/MONITORING PROCEDURES

For this project, soil and water samples were collected for chemical analysis. Most analysis and sampling efforts used during the demonstration activities have recognized standard procedures, such as the EPA Solid Waste (SW) 846 method, while others allowed some latitude in techniques, such as the use of lysimeters for collection of leachate samples. Sample media included soil (Figure 9) and water (leachate) samples (Figure 8). Soil characterization samples were collected as a one-time sampling. Monitoring samples were collected on a quarterly schedule, weather permitting. Sieved soils were sampled by randomly selecting locations in an unbiased manner, with sample locations randomly selected based on a reference point. No composite samples were used.



**Figure 9. Soil Sample Collection from Treatment Zone.**

In general, leachate samples were collected 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 premeasured nitric acid to preserve the sample. Some of the leachate samples were further filtered using a syringe with 0.1 micron filter to ensure that very small Pb particulates were removed and only dissolved Pb was analyzed. There are no known site characteristics or physical characteristics of the site which may have affected the sampling equipment during monitoring of the demonstration.

Recent studies (Pasteris et al, 2005) have shown that the first precipitates of Pb-pyromorphite formed from solution are extremely small,  $\ll 0.1$  microns, thus great care must be taken when sampling leachates for dissolved Pb. To ensure analysis of only the dissolved metal component centrifugation, additional filtering to remove the extremely fine Pb-pyromorphite crystallites from the leachates is recommended. Over time, the fine-grained crystallites will coalesce into larger particles as a result of the process of Ostwald ripening (Morse and Casey, 1988).

### **3.6 ANALYTICAL PROCEDURES**

Each soil and water sample collected was analyzed for Pb using EPA methods SW-846, SW7421, or SW7420. Additional parameters analyzed included the CSSA metals as determined through site characterization activities prior to this demonstration. These metals include As (SW7060A), Cd (SW7131A), Hg (SW7471A), and Ba, chromium (Cr), Cu, Nickel (Ni), and Zn analyzed by SW6010B. TCLP extraction method SW1311 and the synthetic precipitation leaching procedure (SPLP) extraction method SW1312 were used during this demonstration. All samples were collected by Parsons, Inc. employees and analyzed by Agricultural & Priority Pollutants Laboratory, Inc. (APPL) in Fresno, California.

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## 4.0 PERFORMANCE ASSESSMENT

### 4.1 PERFORMANCE DATA

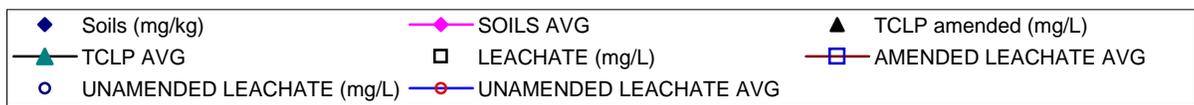
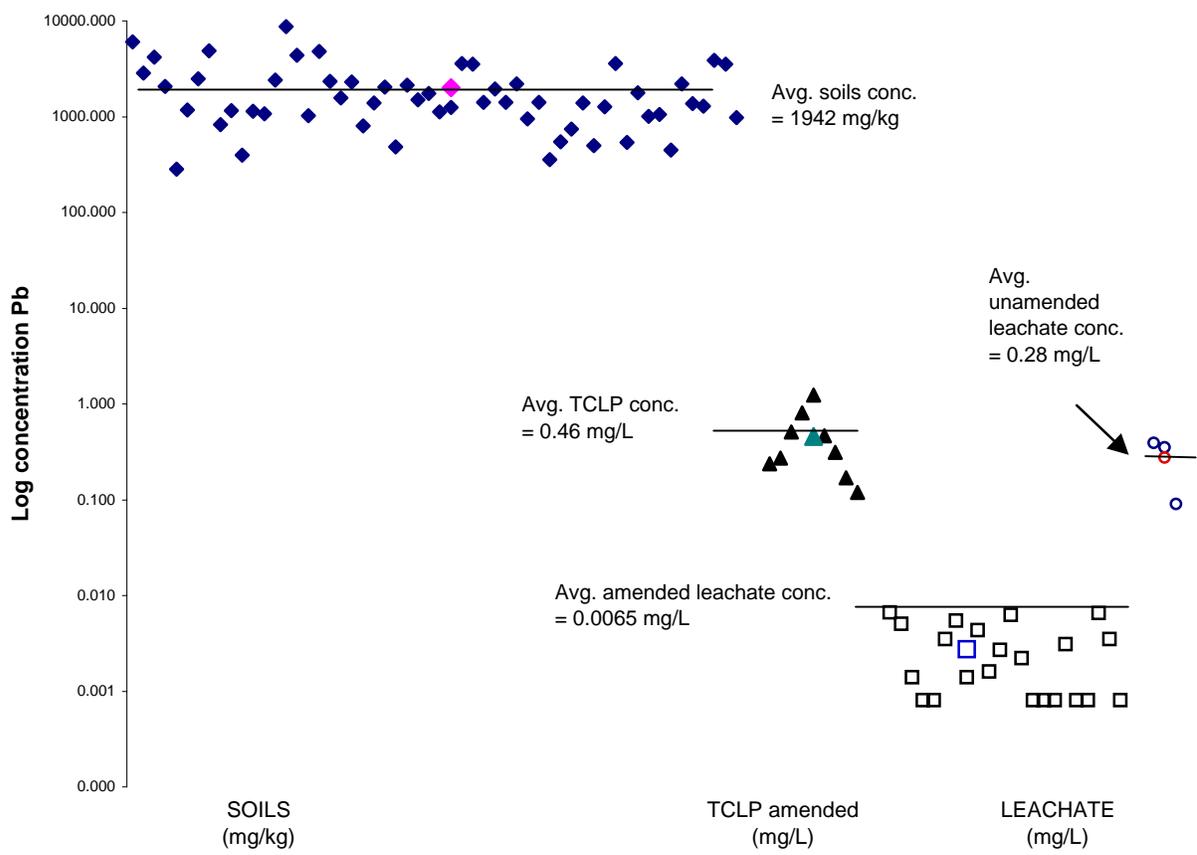
A summary of monitoring results from the demonstration are presented in Table 3, which shows the results of analyses for leachate generated from the remediated soils. In the table, L1, L2, and L3 are monitoring lysimeters in the amended soils, and L4 is the monitoring lysimeter in the unamended soil plot. The other numbers in the Sample ID are used to designate the sampling event and the filter size used. For example, Sample ID# B20-L2-1.45 indicates that the first leachate sampling event from water collected from the second lysimeter installed in the amended soils at SWMU B20 was filtered with an 0.45 micron syringe filter.

Soil amended with Apatite II<sup>TM</sup> resulted in a significant reduction of soluble Pb in the leachates exiting the site. Figure 10 graphically presents all demonstration analytical results on a log normal scale and includes total soil, TCLP, and leachate concentrations, and their arithmetic means. The average leachate concentration from the amended soils was 0.0065 mg/L (ppm), below the 0.015 mg/L drinking water standard. The results of TCLP analyses for the amended soils demonstrate that the amended soils meet State of Texas class 2 nonhazardous waste classification criteria of 1.5 mg/L (per 30 TAC chapter 335 subchapter R) with an average concentration of 0.46 mg/L. These results satisfy the performance acceptance criteria as established in the demonstration plan. There were no deviations from the expected performance.

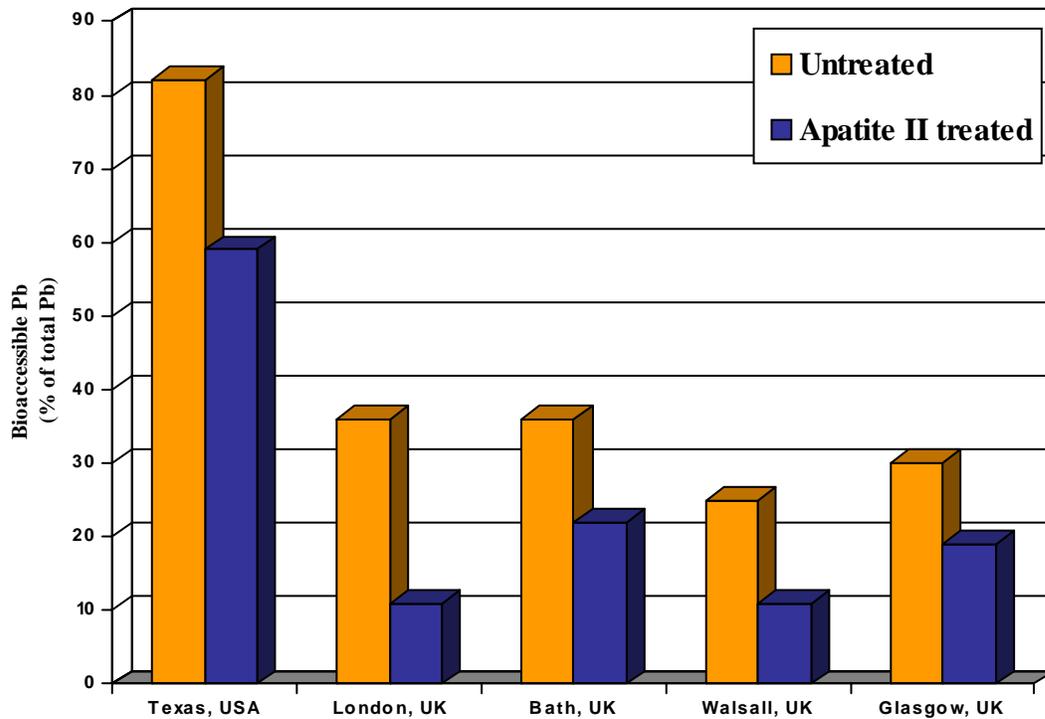
In vitro bioaccessibility tests were performed on Camp Stanley soils, both amended and unamended, to observe the reduction in bioavailability. However, there is no consensus on how to incorporate this type of data into performance assessment, much less into the regulations. Camp Stanley amended and unamended soils were analyzed using the in vitro bioaccessibility test, developed by Ruby et al (1993 and 1996) which is recognized by EPA Region VIII (see ESTCP Final Report, Appendix D, for results of the in vitro studies for this project). The studies were performed by Exponent, Inc. under Ruby's direction. Results from eleven samples (analyzed in triplicates), gathered from the unamended and amended soils at SWMU B-20 at CSSA exhibited an average reduction in bioaccessibility of 27% in the amended soils, similar to results from other phosphate amended soils (Ruby, personal communication). Results are shown in Figure 11, along with soils from several Pb-contaminated industrial sites in the United Kingdom (Wright *et al*, 2005), which were amended with Apatite II and analyzed using the Ruby *et al* in vitro bioaccessibility tests. The results indicate that Apatite II amendment reduces bioaccessibility, but that the amount of reduction strongly depends upon soil type.

**Table 3. Leachate Monitoring Results.**

DATE		Sample ID		EPA METHOD / CONCENTRATION								
				SW7421 (mg/L)	SW6010B (mg/L)					SW706 0A (mg/L)	SW713 1A (mg/L)	SW747 1A (mg/L)
					Pb	Ba	Cr	Cu	Ni	Zn	As	Cd
<b>Field Scale Data</b>												
<b>4/11/02</b>	B20-L2-1.45	0.0066										
	B20-L3-1.45	0.0050										
	B20-L3-1.10	0.0014										
<b>6/30/02</b>	B20-L1-2.45	0.0008	1.97	0.0030	0.0690	0.0150	0.0500	0.0050	0.0001	0.0001		
	B20-L2-2.45	0.0008	1.25	0.0010	0.0450	0.0080	0.0340	0.0091	0.0003	0.0001		
<b>7/10/02</b>	B20-L2-3.45	0.0035	4.14	0.0010	0.1220	0.0200	0.1350	0.0076	0.0002	0.0002		
	B20-L3-3.45	0.0054	0.623	0.0010	0.0310	0.0050	0.0340	0.0124	0.0003	0.0001		
<b>8/21/02</b>	B20-L1-4.1	0.0014	0.416	0.0010	0.0390	0.0060	0.0210	0.0010	0.0002			
	B20-L2-4.1	0.0043	0.046	0.0020	0.0110	0.0030	0.0330	0.0013	0.0003			
	B20-L3-4.1	0.0016	0.308	0.0010	0.0260	0.0050	0.0190	0.0024	0.0001			
<b>10/26/02</b>	B20-L1-5.45	0.0027										
	B20-L2-5.45	0.0062										
	B20-L3-5.45	0.0022										
	B20-L4-5.45	0.3940	15.6	0.0040	0.0810	0.0050	0.0960	0.0008	0.0003	0.0001		
<b>12/21/02</b>	B20-L1-6.45	0.0008	1.78	0.0010	0.0380	0.0070	0.0310	0.0008	0.0001			
	B20-L1-6.1	0.0008	1.80	0.0030	0.0390	0.0080	0.0280	0.0008	0.0001			
	B20-L2-6.45	0.0008	0.658	0.0040	0.0380	0.0070	0.0310	0.0008	0.0001			
	B20-L2-6.1	0.0031	0.590	0.0010	0.0360	0.0060	0.0300	0.0008	0.0003			
	B20-L3-6.45	0.0008	0.555	0.0010	0.0190	0.0030	0.0200	0.0008	0.0001			
	B20-L3-6.1	0.0008	0.534	0.0010	0.0190	0.0030	0.0210	0.0008	0.0001			
	B20-L4-6.45	0.3510	11.1	0.0010	0.0770	0.0040	0.0460	0.0008	0.0001			
B20-L4-6.1	0.0906	11.5	0.0020	0.0740	0.0080	0.0590	0.0008	0.0002				
<b>4/10/03</b>	B20-L1-7.45	0.0065										
	B20-L2-7.45	0.0035										
	B20-L3-7.45	0.0008										



**Figure 10. Lognormal Distribution Graph of Pb Concentrations.**



**Figure 11. Bioaccessibility Results for Pb-Contaminated Soils, Unamended and Amended with Apatite II<sup>TM</sup>** (Wright et al, 2005). (The results are variable and depend on soil type. From left to right, the soils are from Camp Stanley SAFR, Texas, and from the following United Kingdom sites—general urban, London, metallurgical industry, Bath, West Midlands, cattle market, Bath, Chippenham, and canal dredging, Glasgow.

#### 4.2 PERFORMANCE CRITERIA

Performance criteria and performance evaluation of the PIMS using Apatite II remediation technology are presented in Table 4. The primary criteria were decrease in contaminant mobility and ease of use. The first was confirmed by leachate monitoring and the second by the low cost and short time required to treat the 3,000 yd<sup>3</sup> of soil. Actual performance met all expectations. There were no deviations from the demonstration or sampling plan.

**Table 4. Expected Performance and Performance Observations.**

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method	Actual (post demo)
<b>PRIMARY CRITERIA (Performance Objectives)</b> (Qualitative)			
<b>Contaminant mobility</b>	The contaminant mobility is expected to be reduced such that the leachable Pb available from the amended soils meets the groundwater MCL.	Analysis of generated leachate by EPA SW-846 methods	The contaminant mobility was reduced as expected.
<b>Ease of Use</b>	This technology utilizes only typical construction type equipment for mixing and emplacement of the amended soils.	Experience from demonstration operations	Equipment included use of a backhoe/loader, maintainer, and shovel.
<b>PRIMARY CRITERIA (Performance Objectives)</b> (Quantitative)			
<b>Feed Stream</b> - Contaminant concentration	10 yd <sup>3</sup> batch process with expected Pb levels greater than 2,000 ppm	EPA SW-846 method 6010B	Approximately 600 yd <sup>3</sup> /day amended during demonstration treatment efforts
<b>Target Contaminant</b> - Regulatory standard	Reduce leachable Pb from soil to less than 15 ppb Secondary goal to reduce leachable Pb to below state of Texas Class 1 nonhazardous waste criteria of 1.5 ppm	EPA SW-846 method 7421  EPA SW-846 method 1311/6010B	Observations concluded that leachate generated from the site ranges from 2 to 7 ppb, well below the MCL for Pb (15 ppb) and reduced the leachable Pb from the soil matrix to State of Texas Class 2 nonhazardous waste criteria. Bioaccessibility as measured during in vitro tests indicated a reduction in bioavailability.
<b>Hazardous Materials</b> - Eliminated - Generated	None None	Not applicable Not applicable	
<b>Reliability</b>	None	Not applicable	
<b>Process Waste</b> - Generated	None	Observation	None
<b>Factors Affecting Performance</b> - Throughput  - Media Size	- No limit  - Large rocks may slow throughput	Analysis at high flow rate Soil sieving may be applicable	The demonstration treatment rate was 600 yd <sup>3</sup> per day. The demonstration was performed on site soil which had previously been sieved for UXO removal actions.
<b>SECONDARY PERFORMANCE CRITERIA</b> (Qualitative)			
<b>Reliability</b>	No breakdowns	Record keeping	No breakdowns within the treatment application. The monitoring phase experienced minor leachate collection problems as a result of sampling equipment failure.
<b>Safety</b> - Hazards - Protective Clothing	Dust Modified Level D PPE	Experience from demonstration operation personnel monitoring	All field efforts were conducted in Modified Level D PPE, and no significant dust was noted as being generated.
<b>Versatility</b> - Intermittent Operation  - Other Applications	Yes  Yes, may be applicable for other contaminant (chromium, cadmium, etc.)	Experience from demonstration operation EPA SW-846 method 6010B	The mixing operations could be intermittent as necessary due to operational or weather constraints. Other metals were monitored with barium, copper, and zinc showing significant reductions in soluble concentrations within amended versus nonamended leachate sample analysis.
<b>Maintenance</b> - Required	None	Experience from demonstration operation	Field treatment demonstration efforts required no efforts for maintenance. However, monitoring efforts did require leachate collection systems maintenance.
<b>Scale-Up Constraints</b> - Flow Rate - Contaminant Concentration	Largest batch unit available Toxicity levels to classify waste	Monitor during demonstration operation EPA SW-846 method 1311/6010B	Through field observations, there do not seem to be any scale-up constraints with application of this technology.

### 4.3 DATA ASSESSMENT

The performance observations given in Table 4 confirm that the performance criteria were met or exceeded: the PIMS™ technology is as easy to implement as expected and reductions in leachable Pb and in TCLP leachate Pb concentrations are below regulatory requirements. Also, there is reduction in Pb bioaccessibility. The demonstration achieved all the performance and cost goals set forth in the demonstration plan, e.g., mixing rates were even faster than expected; leachate Pb concentrations were reduced to below the desired regulatory limits; personnel, training, health, and safety requirements were as minimal as expected; operations were as easy as expected; and there were no limitations that affected the demonstration. The final actual cost for the full-scale remediation of 3,000 yd<sup>3</sup> of soil was \$21.26/yd<sup>3</sup>, even lower than expected (see Section 5). No emissions or hazardous or secondary wastes were generated.

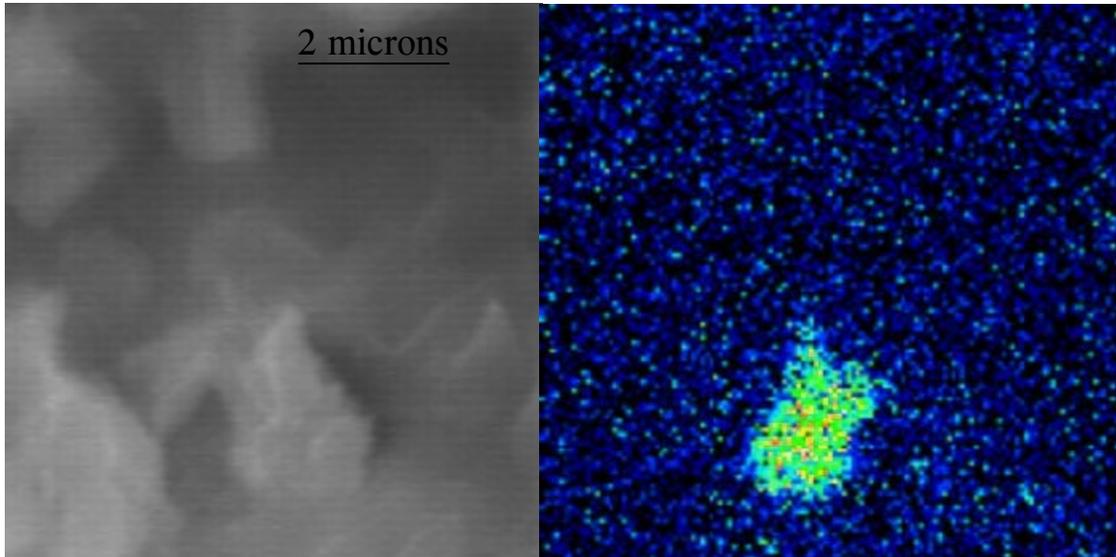
As with all technologies, it is important to demonstrate performance of the various components or aspects. The nature of the PIMS technology with respect to soil mixing and soil remediation is that it performs by continuously removing dissolved Pb from the soil pore water by precipitation with phosphate on the surface of the Apatite II and adjacent soil particles as the Pb comes into solution from the primary Pb phases. Therefore, as fresh pulses of rainwater, or other waters, infiltrate the soil and dissolve Pb from bullet fragments and weathered Pb phases such as cerussite (PbCO<sub>3</sub>) or Pb-oxihydroxides, the Pb in solution reacts with the small amount of phosphate in solution from the Apatite II, and precipitates as Pb-pyromorphite. The initial precipitates are in the nanometer range and will eventually coalesce according to Ostwald ripening (Morse and Casey, 1988) into larger crystals after many years.

The result over time is a build-up of Pb on the surface of the Apatite II that should be observable using imaging techniques such as scanning electron microscopy (SEM). See Figures 12 and 13. Since the rate of removal of Pb from the pore water onto the Apatite II is rapid (Koeppenkastrop and De Carlo, 1990; Lower *et al*, 1998; Ma *et al*, 1993; Pasteris *et al*, 2005), the rate of buildup of Pb on the surfaces depends on the rate of Pb entering the soil pore water. This can be estimated by the annual flux of pore water through the contaminated soil. It has been shown that Pb concentrations in pore water from Pb-contaminated soils are in the range of tens to hundreds of ppb (µg/L). Assuming a worst case of 1 ppm Pb in solution (the highest seen at Camp Stanley is about 390 ppb), and that the soil is saturated and has a porosity of 40% and a density of 1.5 g/cm<sup>3</sup> (kg/1,000cm<sup>3</sup>), then the amount of Pb in solution at any one time is:

$$0.4 \div 1.5 \text{ g/cm}^3 \times 0.001 \text{ g Pb/L} \times 1 \text{ L/1000cm}^3 = 2.67 \times 10^{-7} \text{ g Pb/g of soil}$$

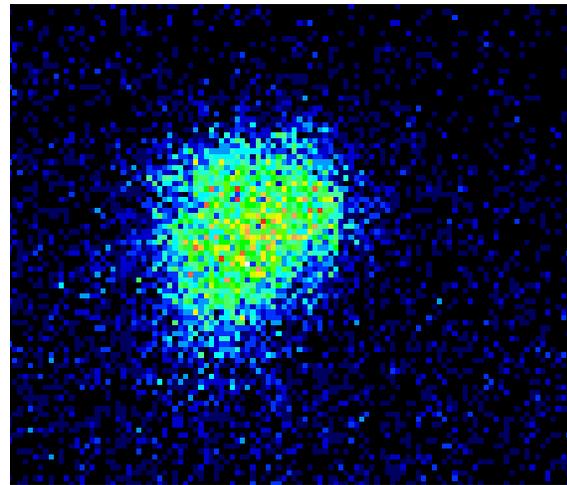
and this calculated worst case value of 267 µg Pb/g of soil is the maximum amount of Pb buildup on the surface of the Apatite II per pore volume of water. Given the following worst-case assumptions for Camp Stanley: that all precipitation infiltrates the soil, that all water entering the soil pores dissolves 1 mg/L Pb, that Camp Stanley averages 30 inches of rainfall per year (equal to two pore volumes of saturation within the 3-foot treatment zone at SWMU B-20 [30 inches ÷ 0.4 = 75 inches = 6.25 ft]), and that all of the Pb is removed as it reacts with the Apatite II (indicated by the below-MCL Pb levels in the leachate collected from the field lysimeters), then the annual amount of Pb buildup on the surface of the Apatite II and adjacent soil particles is equivalent to 534 µg Pb/g of soil. Therefore, the amount of Pb buildup on grain surfaces is so

slow that it would not be seen in x-ray diffraction (XRD) patterns of the soil for many years (XRD requires 0.5% to 1% of the mineral phase for detection). Even using SEM, it is difficult to find Pb in sufficiently high concentrations to observe in the Camp Stanley soils after the 3 years of reaction time, when samples were collected for SEM analysis.



**Figure 12. Photomicrograph of Apatite II-Amended Camp Stanley Range Soil with ~1 Micron-Wide Pb Grain on Surface of Apatite II (left) and Pb X-Ray Map (right).**

QuickTime™ and a  
TIFF (LZW) decompressor  
are needed to see this picture.



**Figure 13. Photomicrograph of Apatite II-Amended Camp Stanley Range Soil with ~1 Micron-Wide Pb Grain on Surface of Apatite II (left) and Pb X-Ray Map (right).**

Another mechanism that can operate in amended soils is the adherence of submicron-sized Pb particles to the surfaces of Apatite II. Small Pb particulates such as spalled particles in the soil may come into contact with grains of Apatite II through local migration by suspension or during the mixing process. Because there is a source of Pb in contact with a source of phosphate, the precipitation of pyromorphite/phosphate cement at the interface should occur.

After lengthy scanning of many Apatite II grains taken from the 3-year-aged amended soil, occasional submicron-sized Pb particles were observed attached to the Apatite II. Figures 12 and 13 show two examples of SEM photomicrographs. Having a large atomic mass, Pb is easy to spot using energy-dispersive analysis in Pb mapping mode. It is difficult to know whether these grains are the result of precipitation from solution or adherence to the surface through cementation, but from morphology, some appear to have grown in place (see Figure 12) while others appear to have been cemented onto the surface (see Figure 13).

Therefore, the best performance criteria for this technology in soils is the drop in Pb concentration in the pore water solutions as indicated by the consistently less than 7 ppb Pb levels in the leachate collected from the field lysimeters in the amended soils relative to the hundreds of ppb Pb concentrations in the unamended soils.

#### **4.4 TECHNOLOGY COMPARISON**

To facilitate an appropriate technology comparison, a comparison to two different and distinct criteria should be used. The first criteria are identified for technologies which have the potential to provide closure of SWMUs impacted with metals contamination. These include removal technologies such as phytoremediation, physical separation, electrokinetic remediation. The second comparison criteria are associated with waste treatment. These technologies include solidification and other stabilization technologies. The PIMS technology can be utilized in both scenarios, and a discussion of some of the competing technologies is presented below. Section 5 presents a comparison of costs for technologies that have been demonstrated through field tests or bench-scale tests at CSSA on the same soils.

##### **4.4.1 Contaminant Removal Technologies**

###### **4.4.1.1 Bioremediation/Phytoremediation**

Phytoremediation is the only bioremediation method applicable to soils at sites such as CSSA. Phytoextraction is the removal of inorganic contaminants from above-ground portions of the plant (Anderson and Coats, 1994). When the shoots and leaves are harvested, the inorganic contaminants are reclaimed or concentrated from the plant biomass. The advantages of phytoremediation are the low input costs, soil stabilization, pleasing aesthetics (no excavation), and reduced leaching of water and inorganic contaminants from the soil. The limitations of phytoremediation are: the annual O&M efforts are extended over many years; the plant must be able to grow in the contaminated soil or material; and the soil diffusion/transport of metals to the rhizosphere must be sufficiently fast and complete to allow uptake of most metals from the soil relative to leaching to groundwater. However, if working correctly the plant biomass should be contaminated above hazardous criteria and thus would necessitate proper handling and disposal, which leads to increased costs. Phytoremediation is passive and will take up to 20 years or more for contaminant concentrations to reach regulatory levels at most range sites. Therefore, phytoremediation is not appropriate for sites that pose an immediate threat or risk to human health, or for clients who require rapid cleanup. No actual Pb-contaminated range site has been successfully amended with phytoremediation.

#### **4.4.1.2 Physical Separation/Acid Leaching**

Physical separation capitalizes on density differences between metals and soil; when suspended in water, the denser metals settle out of the suspension for collection and recycling. Acid leaching processes use different strengths of acid to dissolve and wash metals from soils and subsequently treat the residual Pb in the soil to below regulatory levels. A benefit of this process is that, unlike stabilized or landfilled soil, the site incurs no liability when returning the washed soil to the site, provided the soil meets TCLP requirements and the recovered metals can be recycled. The acid leaching process is good for soils with low clay contents. However, ranges such as Camp Stanley with highly alkaline carbonate soils require huge amounts of acid and are not amenable to this technology, and implementation at CSSA failed.

#### **4.4.1.3 Electrokinetic Remediation**

Laboratory experiments using electrokinetic remediation of heavy metals have demonstrated that certain pollutants dissolved in an aqueous phase can be removed by electroosmosis and electromigration. An electric current transports dissolved metals through the soil water towards electrodes placed in the ground. Permeabilities require saturated or near-saturated soil conditions, and acidic soil-water pHs are required to keep the metals in solution, so alkaline soils, such as carbonate soils, are not amenable to this technology. The reproduction of laboratory conditions in the field has proven difficult. Only small laboratory scale and bench-scale studies have been successfully performed on metal-contaminated soils using electrokinetic remediation, and it is unlikely that large throughput volumes can be achieved at most sites. Implementation of electrokinetic remediation at Camp Stanley failed.

### **4.4.2 Waste Treatment Technologies**

#### **4.4.2.1 Pozzolan/Portland Cement**

The baseline technology, against which the PIMS performance was compared, is cement solidification with off-site disposal. Grouting (cement solidification) and off-site disposal is the presumptive technology at SAFRs and is well-researched and well-used. Grouting encapsulates the contaminated soil, renders it immobile and changes it to a solid mass or non-soil. The alkaline nature of grout also ensures that the amended material will likely pass a TCLP test. There is a significant increase in volume, depending on the formulation, that ranges from 6% to 25%. Grouting is almost always used to treat off-site disposal, so it is not considered an on-site treatment technology. Similarly, mixing soil with silicates from pozzolanic-based materials like fly ash, kiln dust, pumice, or blast furnace slag will also form a cementitious matrix upon reaction with water. Pozzolan treatment also raises the pH of the system, which may help precipitate and immobilize heavy metal contaminants. Cement solidification has been successfully used at CSSA.

#### **4.4.2.2 Phosphate Rock and Mineral Apatites**

Like Apatite II, other solid forms of natural apatite minerals can be used, primarily mineral apatites mined as phosphate rock in Florida, North Carolina, Tennessee and Montana. While relatively inexpensive, these minerals have high levels of metals already in their structure, particularly Pb, Cd, arsenic, uranium, and thorium, and their high degree of crystallinity makes

them less reactive. Open pit mining of these minerals has caused extensive environmental damage in Florida and other states, particularly with respect to radon and metal contamination in runoff and has become an important economic issue in this region (see the Florida Institute of Phosphate Research, 2003 at <http://www.fipr.state.fl.us/publications>). Continued development of new areas for mining of phosphorite deposits in the Everglades is also threatening the last habitat of the endangered Florida panther (NWF, 2003). These types of negative environmental impacts are generally not calculated into the total costs of using these materials in remediation.

Manufactured Phosphate Chemicals—Phosphate chemicals, fertilizers, and liquids can be applied to induce metal stabilization, and many have been tried successfully. They induce precipitation of the soluble Pb into stable phosphate phases and do not convert the waste into a hardened, monolithic mass. Synthetic solutions may consist of a mixture of additives containing oxygen, sulfur, nitrogen, and phosphorous. However, these phosphate materials are not long-lasting in the environment so they cannot treat future Pb that comes into solution in the soil as the primary Pb phases continue to leach Pb into the soil water. Additionally, the processes used to manufacture these soluble phosphates from mineral apatite leave a costly legacy of environmental degradation (Florida Institute of Phosphate Research [FIPR], 2003).

#### **4.4.2.3 Emulsification Fixation and Reuse**

Pb-contaminated soil can be blended with water-based asphalt emulsion (or other organic binding materials) to produce a range of solid mass cold-mix asphaltic products. These products can then be used as structural backfill, parking lot pavement, and road construction material, as well as for stabilization prior to landfill disposal as they will usually pass a TCLP test. Asphalt cements have been used to treat organic-contaminated soils in which the asphalt-cemented soil was then used on site for paving and road construction (Conca and Testa, 1994; Testa *et al*, 1992). However, the authors know of no large-scale use of this process for metal-contaminated soil, and this application would be limited because the volume of Pb-contaminated soils in the United States is vast compared to the paving needed at these sites.

## 5.0 COST ASSESSMENT

### 5.1 COST REPORTING

Cost issues are critical to the evaluation of any remediation technology. The PIMS field demonstration project developed and validated the expected operational costs of this technology. Because this demonstration was an actual full field-scale remediation at an SWMU, these costs are real and do not require scaling of any sort. This section includes a discussion of all relevant costs and related data that were tracked and documented during the demonstration so operational costs of the technology can be estimated with a high degree of accuracy.

The overall costs presented in this section should be directly comparable for other sites applying this technology for in situ remediation. While it is recognized that there were some potential cost benefits as a result of previous efforts in UXO removal actions at SWMU B-20, the application of this technology would not be any more difficult or costly than what is represented in the field-scale demonstration cost assessment of this technology. It is anticipated that when applying this technology in other in situ applications, the equipment could vary, e.g., using a tractor with a disc and tiller instead of a maintainer. Additionally, when firing range berms are amended for reuse as restored berms under pollution prevention guidelines, other activities such as earth moving, sieving, and rebuilding may need to be performed and may add costs. Deep soils may require the use of augering or other methods to emplace the Apatite II.

The Apatite II material costs, including delivery charges, provide the best basis for projecting costs of implementing this technology. The process chemicals (Apatite II material) and the shipping charges represent over 50% of the expended costs for the field-scale demonstration efforts because of the ease of application of the Apatite II material. Process equipment consisted of a front-end loader and a maintainer which were used to move and mix materials. Labor consisted of a construction supervisor, two heavy equipment operators, and an independent observer/health and safety site monitor.

Table 5 presents demonstration costs incurred for the treatment of approximately 3,000 yd<sup>3</sup> of Pb-contaminated range soil. Fixed costs include start-up costs (planning, site characterization, mobilization, and site preparation costs) and operating costs such as process chemical (Apatite II material) and raw material purchases (soil cover and vegetation). Operational costs include equipment rental, labor, and personal protective equipment (PPE) and account for nearly all the costs of implementing this technology. Re-occurring costs such as performance testing are included; however, these costs represent a small fraction of the cost and may not be required for long-term monitoring when regulatory acceptance is obtained.

**Table 5. Demonstration Costs.**

<b>Item</b>	<b>Basis</b>	<b>Field-Scale Costs (\$)</b>
<b>START-UP COSTS</b>		
<i>Planning</i>	Planning costs include 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 and grubbing of vegetation and large debris	500
Demobilization	Equipment demobilization only	550
<b>Total start-up costs</b>		<b>8,100</b>
<b>OPERATING COSTS</b>		
<i>Direct environmental activity costs</i>		
Capital equipment rental	Included front-end loader and motor grader.	2,375
Ancillary equipment rental	None	0
Supervision	Included one supervisor for 40 hrs @ \$60/hr	2,400
Operator labor	Included two operators for 40 hrs at \$35/hr	1,400
Observer/health and safety monitor	Included one observer for 40 hrs @ \$65/hr	2,600
Maintenance	None	0
Utilities	None	0
Raw materials	Includes 6-inch soil and vegetative cover	4,500
Process chemicals	Included 80 tons of Apatite II material	18,000
Consumables, supplies	Include PPE	100
Sampling and analysis	Includes performance testing	300
Long-term monitoring	Includes quarterly sampling for 5 years @ 5% inflation (estimated at \$2,500, but is not included as part of treatment cost)	0
Shipping	Included shipment from Apatite II generating plant to CSSA	24,000
<i>Indirect environmental activity costs</i>		0
Environmental and safety training	None	0
OSHA ambient environment sampling	None	0
Waste manifesting (if any)	None	0
<b>Total operational costs</b>		<b>55,675</b>
<b>Total project costs</b>		<b>8,100</b>
Total cost/yd <sup>3</sup> of soil amended		21.26
Variable cost/yd <sup>3</sup> of soil		19

## 5.2 COST ANALYSIS

### 5.2.1 Cost Basis

The basis of the costs presented in Table 5 is derived from the actual field cost for implementing the demonstration. The demonstration effort consisted of mixing 3,000 yd<sup>3</sup> of Pb-contaminated soil with 80 tons of Apatite II and providing a 6-inch clean vegetated soil cover. The field-scale amended soils were placed in an area measuring 100 ft by 200 ft with a depth of approximately 3.5 ft. Mixing and emplacement took approximately one work week, using one equipment operator and a supervisor who operated the second piece of equipment. The site observer was available to ensure that efforts complied with finalized plans and quality assurance testing, and to document field efforts.

### 5.2.2 Cost Drivers

The largest cost drivers for the PIMS remediation technology include the cost of the Apatite II material and the shipment of the material to the work site. As with any commodity, the price and supply of the PIMS Apatite II material are subject to market pressures and will change over time. The original purchase price of PIMS material in the year 2000 was approximately \$225/ton. The price has fluctuated between \$200/ton and \$500/ton over the last 5 years. However, even at a cost of \$500/ton, the total cost per yd<sup>3</sup> of soil amended (Table 5) would rise only to \$28.

### 5.2.3 Life-Cycle Costs

An estimated life-cycle cost for the PIMS remediation technology includes the following considerations:

- Fixed costs (permitting and regulatory requirements, site characterization, site preparation, engineering and administrative support, equipment mobilization, demobilization, etc.)
- Variable costs (site excavation, equipment lease, labor, sampling and analysis, Apatite II material, shipping, etc.)
- Future liability implications and costs associated with monitoring for a period of 5 years.

The fixed costs represent a one-time cost incurred that would be similar for any size project. That is, the efforts that represent fixed cost include planning, site characterization, and mobilization/demobilization costs. For the full field-scale demonstration efforts, these costs represented only a small fraction (approximately one-fifth) of the total costs. It is expected that these costs would be stable for future efforts and their cost relative to the total cost would decrease as the amount of amended soil increases.

Variable costs represent costs that are directly dependent on the expected amount of contaminated media to be amended. The largest cost item is that of the Apatite II material and the associated shipping costs. These costs represent over 50% of the total cost for the remediation technology. Shipping costs are also variable, with shipping costs to CSSA estimated at approximately \$300/ton. However, shipment to Seoul, South Korea, has an approximate cost

of only \$180/ton because of the location of the facility producing the Apatite II material and methods of shipment. In shipping to South Korea, the material is loaded on a ship and transported directly to Seoul. In shipping to San Antonio, the material was shipped via boat and train and then completed its journey to CSSA by truck. Rising fuel costs will be an important factor in the variable costs. However, it is anticipated that as new markets are opened to provide the Apatite II material, e.g., the Mississippi delta region with its large catfish farm supply, the shipping cost will decrease with better proximity to user sites. Negotiations are on-going to open this market.

Future liability implications and costs associated with this technology are uncertain at this time. As stated earlier, this technology does not remove the contaminant but changes it into a much more stable mineral molecular form over time while preventing leaching and migration off site. Therefore, for the field-scale demonstration efforts, Pb is still in the soil matrix and would continue to be regulated by the EPA and the Texas Commission on Environmental Quality (TCEQ). However, performance data has shown that the bioavailability of the Pb is reduced and that the Pb is not leaching from the soils, thus gaining favorable closure standards where monitoring or deed recordation is not required. For estimating costs for addressing future liability, a period of 5 years of quarterly monitoring was specified per the National Contingency Plan (NCP). Upon completion of the 5 years of monitoring in 2006, an evaluation of the data is recommended to determine if further monitoring is necessary.

Because the material and shipping costs for Apatite II are the major cost drivers, the total cost is not very sensitive to most site scenarios. One scenario that will significantly affect cost is the remoteness of the site. Extreme remoteness (far from paved roads, railroad tracks or water lanes) could significantly increase the transportation cost, but most military ranges in the United States are not remote. The only other scenario is a site where soil mixing could not be carried out, such as in a permafrost area, or a site with extreme topography, but most military ranges are not located in these areas because extreme geomorphic features interfere with range activities.

The DoD-wide savings are potentially very large if this technology is adopted to treat much of the estimated 100,000,000 yd<sup>3</sup> of Pb-contaminated soils across the complex. The baseline alternative of grouting and off-site disposal is a firm number at \$104/yd<sup>3</sup> (Section 5.3) and, taking an average cost of PIMS of \$25/yd<sup>3</sup>, the potential DoD-wide savings are:

$$(\$104/\text{yd}^3 - \$25/\text{yd}^3) \times 100,000,000 \text{ yd}^3 = \$7.9 \text{ billion.}$$

Even a small fraction of this amount would constitute significant savings.

### **5.3 COST COMPARISON**

Grouting (cement solidification) and off-site disposal is the alternative baseline technology at SAFRs and is considered the alternative baseline technology to PIMS. Most solidification/stabilization technologies are not used in site closure actions where contaminant removal is specified but are used for treatment prior to off-site disposal. The PIMS demonstration provides an adequate comparison to other soil solidification/stabilization technologies because of TCLP testing of the amended soil. Therefore, to compare costs for other technologies such as solidification, the costs are compared as if they were able to treat to waste

disposal criteria. For example, in comparing the PIMS technology to cement stabilization, it is necessary to assume that the treatment can occur to the specific criteria, State of Texas Class 2 nonhazardous waste criteria, as specified in 30 TAC 335 subchapter R.

This PIMS demonstration can also be compared to in situ remediation technologies. In situ remediation technologies are used in site closure actions where contaminant removal is specified (Texas Risk Reduction Standard 1 [RRS1] or in current standard Texas Risk Reduction Program [TRRP] Standard A Tier 1 closures). These closure standards specify contamination removal to certain levels (RRS1, to background levels; TRRP Standard A Tier 1, to 1,600 mg/kg). The goal of this PIMS demonstration is to provide data to allow TRRP Standard A Tier 1 closure. Comparable technologies in this category include other stabilization technologies and extraction technologies discussed in Section 4.4. Some of these technologies have been attempted at CSSA by Parsons in pilot-scale treatability studies and have directly-comparable costs and performances.

Figure 14 compares costs of the technologies tested at CSSA to the PIMS Apatite II technology. The comparison is made on derived costs per cubic yard or reported costs per cubic yard of contaminated soil. Below is a short description of each technology demonstrated for metal remediation at CSSA in addition to PIMS with Apatite II.

### **5.3.1 No Treatment and Off-Site Disposal**

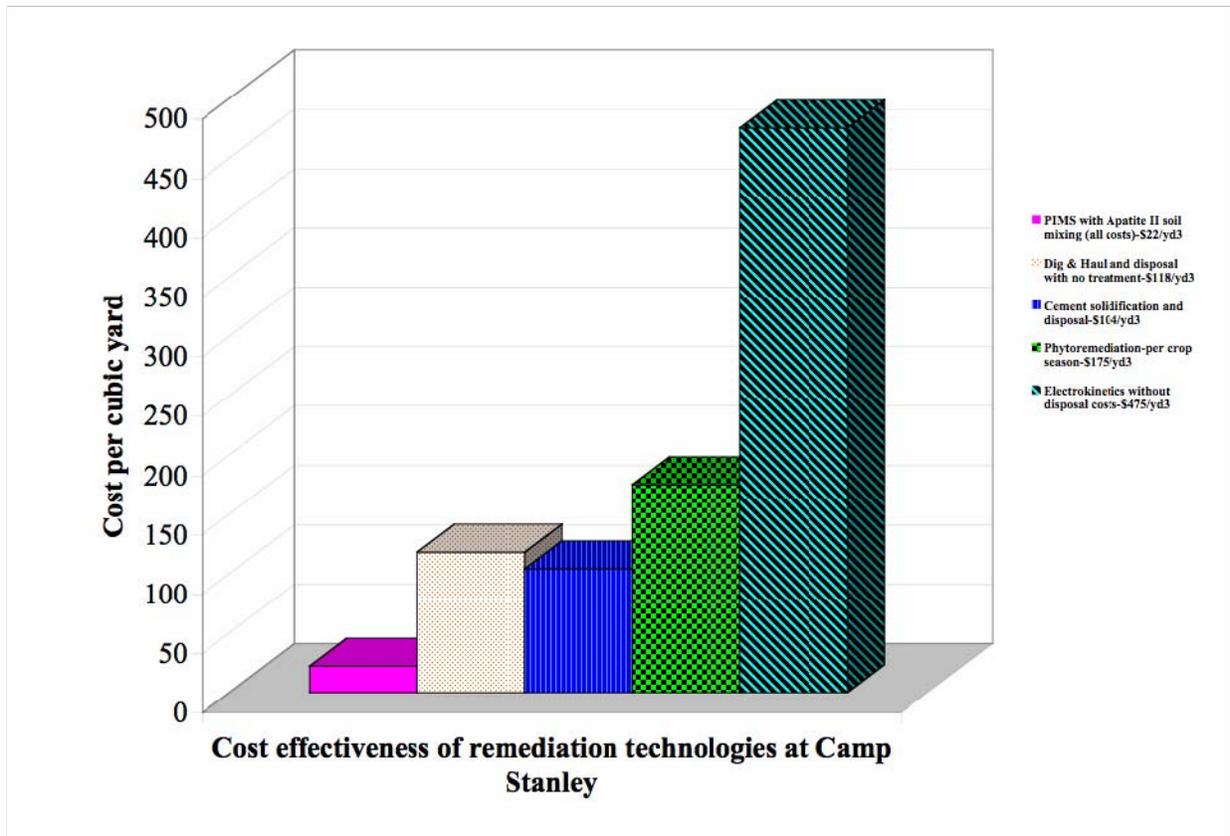
Simply excavating the contaminated soil and disposing of it off site is the presumptive remedy case and involves simple earth-moving equipment. Excavation with no treatment is \$40/yd<sup>3</sup> at Camp Stanley. Added to this is the waste disposal cost of \$68/yd<sup>3</sup>, making the total cost of disposal with no treatment \$118/yd<sup>3</sup>. This is the reference cost that must be addressed for any technology to compete at this and similar sites.

### **5.3.2 Grouting and Off-Site Disposal**

Grouting (cement solidification) and off-site disposal is the alternative baseline technology at SAFRs and is well-researched and well-used. At CSSA, grouting and off-site disposal was \$104/yd<sup>3</sup>, the next most cost-effective to PIMS.

### **5.3.3 Phytoremediation**

Parsons demonstrated phytoremediation at CSSA and found that all the issues associated with this technology occurred, e.g., slow action over many growing seasons, poor growth of necessary species, inefficient movement of contaminant from soil to the roots, contaminated biomass concentrated at the surface for dispersion or ingestion by animals, and a long-term commitment over about 20 years. Phytoremediation was not very cost beneficial at CSSA (\$175/yd<sup>3</sup> per crop season) and did not achieve clean-up goals.



**Figure 14. Technology Cost Comparison at CSSA.**

### 5.3.4 Electrokinetic Remediation

Electrokinetics also failed at CSSA because of the usual reasons of poor mobilization and permeabilities, unfavorable soil pHs, and scale-up problems. For the CSSA site, electrokinetic remediation was not cost effective (\$475/yd<sup>3</sup>) and failed to meet anticipated objectives.

### 5.3.5 Physical Separation/Acid Leaching

Bench-scale physical separation techniques were accomplished at CSSA for Pb-impacted soils from SWMU B-20. This physical separation method, referred to as density separation, uses water to separate heavy metals from the soil matrix, as traditionally used in mining industry operations. The soils used in the bench-scale test contained approximately 2,123 mg/kg of total Pb, of which 1,069 mg/kg was particulate Pb. There was a 50% decrease (1,055 mg/kg) of Pb contaminants following density treatment, which does not meet the closure criteria for the removal action. The estimated costs for physical separation of Pb from sieved soils at CSSA was \$56/ton. Physically amended soils were to be advanced to an evaluation of acid leaching. However, soils at the site were found to have too high a pH (alkaline), and acid leaching was considered cost prohibitive and technically inappropriate. This technology was not demonstrated at a field-scale level at CSSA.

## **6.0 IMPLEMENTATION ISSUES**

### **6.1 COST OBSERVATIONS**

PIMS remediation technology does not usually require any permitting efforts or special notifications if accomplished in situ. The in situ application alleviates any of the Resource Conservation and Recovery Act (RCRA) requirements normally associated with ex situ treatment of hazardous media and is a substantial cost benefit. For the full field-scale demonstration efforts, the contaminated soil media was analyzed to determine the waste classification. Results of analyses in the feasibility studies indicated that the amended soils for the PIMS field demonstration efforts met Class 1 nonhazardous criteria. Therefore, treatment of the sieved soils at SWMU B-20 could occur without the cumbersome permitting or planning requirements of RCRA.

With the in situ application of the Apatite II material, a determination as to the amount of rubble or oversize cobbles or stones is required. An overly large amount of oversized rubble or rocks could cause the mixing efforts to be difficult or incomplete. As with any in situ application, frozen soil or tundra would also hinder mixing operations.

There were no factors that caused costs to differ from projected costs. No site-specific conditions occurred in which costs were affected. The major potential area for future cost reductions is success in the ongoing development of new sources of Apatite II and reduction in shipping costs. The former is likely as development continues, and the latter is unlikely as fuel and transportation costs will probably not decrease in the near future. Because the technology is so easy to implement (no special equipment, no special training), there are few learning curve effects. Decreased soil mixing times using specialized mixing equipment could reduce the per ton cost if large amounts of soil were to be amended, but these methods are well known and do not have significant learning curves associated with them. The important procurement aspect that could reduce costs is purchasing the Apatite II early to take advantage of low points in the cost fluctuations, or stockpiling Apatite II during low-cost periods.

### **6.2 PERFORMANCE OBSERVATIONS**

The performance objectives for this project were met, as indicated in Section 4. The performance observations discussed in Section 4, particularly the reduction in leachable Pb and reduction in TCLP leaching Pb concentrations to acceptable levels, confirm that the PIMS technology is as easy to implement as expected, and achieved all the performance and cost goals set forth in the demonstration plan. This demonstration utilized the PIMS technology in sequestering Pb within the soil matrix for an evaluation of closure actions and contaminated media treatment. There were no deviations from performance goals. Because the technology requires no special equipment, redundancy measures are not necessary, e.g., a front-end loader can be replaced very easily at almost any location if it breaks down during mixing. Site-specific feasibility studies, which are required for any remediation activity, should determine whether or not contaminant breakthrough could occur after treatment, and site monitoring will detect any contaminant breakthrough so appropriate action can be taken. If desired, a greater amount of Apatite II could be used to ensure redundancy in this respect. However, Apatite II can hold up to 20% of its weight in Pb so failure is unlikely with proper mixing.

### **6.3 SCALE-UP**

The demonstration described in this report was a full field-scale test and, as such, no additional scale-up costs are expected.

### **6.4 OTHER SIGNIFICANT OBSERVATIONS**

There are no other major factors that can affect implementation of this technology, and no anticipated workaround solutions are needed. For help in contracting for the technology, contact PIMS NW, Inc. (see Appendix A, POINTS OF CONTACT).

### **6.5 LESSONS LEARNED**

In summarizing for others who may be interested in implementing the PIMS technology, there appear to be few limitations on applying PIMS to range soils in both soil characteristics, site conditions, time constraints, operational issues, and cost. This technology is simple, easy, and less costly than any alternative to date. It is important to perform site-specific feasibility studies to determine if the soil type and metal concentrations are amenable to using the PIMS technology.

### **6.6 END-USER ISSUES**

The end users have been and still are being, heavily involved with this technology at all times during the demonstration. The base environmental officer was a key player in helping design and implement PIMS, and for managing the process, contractors, and interactions with regulators. Because many of the end users for this technology will be DoD sites, this demonstration has been a good model for end-user and stakeholder involvement. Each step of the demonstration/remediation involved a decision and approval of the base environmental officer, and ultimately the base commander.

CSSA has also become a post-demonstration end user. Because of the success of the demonstration, the base environmental officer used PIMS elsewhere at CSSA and is planning to implement PIMS at several other sites at CSSA.

The concern of the end user for this technology for remediation of range soils is the applicability to close the site without contaminant removal. This technology has been proven to be competitive with other forms of waste treatment, such as off-site disposal, because of the simplicity of this technology. However, the real success will be to gain regulatory approval of this technology in all states for standards that are protective of human health and the environment with no deed recordation and/or monitoring requirements.

Because the source of the Apatite II material is presently limited to about 10,000 tons/yr, there is a concern that there will not be enough material to use at all potential application sites. However, new sources of the Apatite II material have been identified and are being developed.

Future efforts to transfer this technology to the end user include discussing results of innovative technologies at conferences where environmental professionals meet.

During review, colloids were identified as a possible issue concerning Pb mobility in these systems. Over the last decade, colloid-facilitated transport of metals has been recognized as an important process in contaminant transport, in some cases explaining higher-than-predicted migration rates in groundwater and soils. Colloids exist naturally in groundwater and soil in almost all subsurface environments with the composition and concentration of colloids being site specific and determined by the geologic nature of the subsurface. Natural colloids form in a continuous size range from 0.001  $\mu\text{m}$  to 1.0  $\mu\text{m}$ , and concentrations range from 0.1 ppm to 100 ppm (McCarthy and Zachara, 1989; Corapcioglu and Jiang, 1993; McGraw 1996). The large surface area of colloids ( $10^4$  to  $10^6$   $\text{m}^2 \text{kg}^{-1}$ ) can significantly sorb metals even for relatively low mass concentrations of colloidal particles.

Pb does not form true colloids, i.e., Pb-polymeric masses, but instead forms pseudo-colloids by attaching to existing mineral or organic colloids, e.g., humic acids, clays, oxides and silicates. (Liang and McCarthy 1995). Colloid concentration and stability is a function of pH, redox, the concentrations of Na, K, Ca, Mg, and organic carbon, as well as the status of the chemical and physical steady state of the hydrogeochemical system. Key factors affecting colloid stability have been identified as pH, redox potential, salt (Na, Ca) concentrations, the presence of dissolved organics, and the status of the system steady state (McCarthy and Degueudre, 1993).

Colloids will migrate only in conditions under which they are stable and are kept suspended in solution. Factors decreasing the colloid stability are an increase of salt ( $\text{Na}^+$ ,  $\text{K}^+$ ) concentration and of water total hardness ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ). Increases of the concentration of alkali elements above  $10^{-2}$  M and of alkali-earth elements above  $10^{-2}$  M decrease colloid stability and concentration. Therefore, at pHs above 7.5 in carbonate-rich environments such as Camp Stanley, colloids are not stable and will not tend to migrate. This is seen at Camp Stanley by the absence of Pb in the leachates collected in the shallow lysimeters. If Pb-colloids were present, filtering to 0.45  $\mu\text{m}$  or 0.1  $\mu\text{m}$  would remove only a small fraction of the colloids, and Pb would be seen in the filtrate. Since Pb has not occurred above 0.015 mg/L in the filtrate over the last 3 years, colloid-facilitated transport of Pb is not an issue at this site.

## **6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE**

PIMS helps address many regulatory requirements, particularly those of RCRA, Comprehensive Environmental Response Compensation and Liability Act (CERCLA), and the Clean Water Act. The regulatory drivers at this site include EPA and Texas state regulations. First, leachate from amended soils leaving the treatment zone must be below the MCL for Pb in drinking water (0.015 mg/L). Second, the amended soil must meet the State of Texas class 2 nonhazardous waste classification criteria of 1.5 mg/L (per 30 TAC chapter 335 subchapter R), as indicated by results from batch TCLP tests. The demonstration met both these regulatory goals. EPA Region VI and Region VIII are now familiar with this technology and favorably inclined towards it because it meets regulatory goals with respect to Pb. In several meetings, representatives of both regions have verbally endorsed this technology.

The patent holder, PIMS NW, Inc., immediately after setting up the contract with Parsons granted the end user with a use license to apply PIMS at CSSA. No state or federal permits were required to apply this technology. EPA Region VI (Greg Lyssy) has been involved with this demonstration from the very first meeting at CSSA with UFA Ventures, base personnel, Parsons,

and Air Force Center for Environmental Excellence (AFCEE), and they have given their verbal approval. CSSA and Parsons have also met with the TCEQ and are negotiating how to fit this demonstration into the overall closure schedule for CSSA. A large group from TCEQ visited the CSSA in 2004 and was favorably impressed towards it. Neither EPA nor TCEQ are requiring further actions, thereby giving tacit approval to this technology. While TCEQ does not want to make a ruling at this time on this technology (and many others), wanting more time to evaluate long-term performance, this tacit approval has been taken by CSSA as favorable and no further actions are planned.

Shortly after PIMS was selected by ESTCP for this demonstration, PIMS was selected for use in a voluntary non-time-critical CERCLA removal action at the Success Mine site in Idaho by the Silver Valley Natural Resource Trustees in conjunction with the IDEQ. That action has also been successful, and IDEQ has now taken over that site and is planning further activities with Apatite II.

Other regulatory drivers may also invoke the PIMS technology, particularly through its use in pollution prevention. The EPA Toxics Release Inventory (TRI) Program was established by Congress under section 313 of the Emergency Planning and Right-to-Know Act (EPCRA) of 1986 and expanded by the Pollution Prevention Act of 1990. It requires certain facilities in covered industry sectors to file reports of their environmental releases and other waste management quantities of chemicals listed on the EPCRA section 313 list of toxic chemicals if they manufacture, process, or otherwise use more than established threshold quantities of these chemicals.

On January 17, 2001, EPA classified Pb and Pb-compounds as persistent, bioaccumulative toxic chemicals and lowered the previously existing 25,000 pound and 10,000 pound reporting thresholds for Pb and Pb-compounds to 100 pounds for calendar year 2001 and each year thereafter. For small arm ranges that meet the criteria for reporting, there are two types of release that take place during the firing of bullets from firearms. One type of release is the Pb bullet itself coming to rest after it has been fired, the other is the emission of trace amounts of Pb vapor to air. The EPCRA requirements include a pollution prevention for minimizing potential releases of the reported EPCRA compound to the surrounding environment. The PIMS technology is being considered as a pollution prevention opportunity for potential release of Pb and Pb-compounds to surface or groundwater at several military bases. PIMS NW, Inc. has completed a project with Air Combat Command (ACC) to evaluate PIMS and another technology for remediation of SAFRs at 17 ACC bases across the country.

## 7.0 REFERENCES

- Anderson, T.A. and T.R. Coats. 1994. *Innovative Site Remediation Technology Stabilization/Solidification*. Water Environment Federation, Alexandria, Virginia.
- Army. 1990. *Camp Bullis: Admirably Suited to All Purposes of Military Training. A History of the Leon Springs Military Reservation, 1890-1990*. Fort Sam Houston Museum, U.S. Army.
- Chen, X.-B., J. V. Wright, J. L. Conca, and L. M. Peurrung. 1997a. *Evaluation of Heavy Metal Remediation Using Mineral Apatite*. Water, Air and Soil Pollution. 98:57-78.
- Chen, Xiaobing, Judith Wright, James L. Conca, and Loni M. Peurrung. 1997b. *Effects of pH on Heavy Metal Sorption on Mineral Apatite*. Env. Sci. and Tech. 31:624-631.
- Conca, J., E. Strietelmeier, N. Lu, S. D. Ware, T. P. Taylor, J. Kaszuba, and J. Wright. 2003. *Treatability Study of Reactive Materials to Remediate Groundwater Contaminated with Radionuclides, Metals and Nitrates in a Four-Component Permeable Reactive Barrier*. In Groundwater Remediation of Metals, Radionuclides, and Nutrients, with Permeable Reactive Barriers, Eds. Naftz, Morrison, Davis, and Fuller, Elsevier Science, USA. p. 221-252.
- Conca, J. L., N. Lu, G. Parker, B. Moore, A. Adams, J. V. Wright, and P. Heller. 2000. *PIMS – Remediation of Metal Contaminated Waters and Soils*. In Remediation of Chlorinated and Recalcitrant Compounds, Eds., Wickramanayake, Gavaskar, Gibbs and Means, Battelle Memorial Institute, Columbus, Ohio. vol. 7, p. 319-326.
- Conca, James, and Judith Wright. 1999. *PIMS: A Simple Technology for Clean-Up of Heavy Metals and Radionuclides Throughout the World*. In Environmental Challenges of Nuclear Disarmament, Ed. T.E. Baca, Proc. NATO Adv. Res., Poland. p. 1-13.
- Conca, J. L. 1997. *Phosphate-Induced Metal Stabilization (PIMS)*. Final Report to the U.S. Environmental Protection Agency #68D60023.
- Conca, J. L. 1998. *Success Mine Apatite Remediation Project*. Report to the Idaho State Department of Environmental Quality #QC038900.
- Conca, J. L., and S. M. Testa. 1994. *Chemical Aspects of Environmentally Processed Asphalt*. In Asphaltene Particles in Fossil Fuel Exploration, Recovery, Refining, and Production Processes. Eds. Sharma and Yen. Plenum Pub. Corp., New York. p.101-113.
- Corapcioglu, M.Y., and S. Jiang. 1993. *Colloid-Facilitated Groundwater Contaminant Transport*. Water Resources Research. 29:2215–2226.
- Florida Institute of Phosphate Research (FIPR). 2003. <http://www.fipr.state.fl.us/publications>.

- Eighmy, T. T., B.S. Crannell, L.G. Butler, F.K. Cartledge, E.F. Emery, D. Oblas, J.E. Krzanowski, J.D. Eusden, Jr., E.L. Shaw, and C.A. Francis. 1997. *Heavy metal stabilization in municipal solid waste combustion dry scrubber residue using soluble phosphate*. *Env. Sci. and Tech.* 31:3330-3338.
- Kaplan, D., A. Knox, and C. Coffey. 2002. *Reduction of Contaminant Mobility at the TNX Outfall Delta Through the Use of Apatite and Zero-Valent Iron as Soil Amendments*. Report Number WSRC-TR-2002-00370, Rev. O. WTS SRC, Aiken, South Carolina.
- Koeppenkastrop, D., and E. J. De Carlo. 1990. *Sorption of rare earth elements from seawater onto synthetic mineral phases*. *Chem. Geol.*, 95:251-263.
- Knox, A.S., D.I. Kaplan, D.C. Adriano, T.G. Hinton, and M.D. Wilson. 2003. *Apatite and Phillipsite as sequestering agents for metals and radionuclides*. *J. Env. Qual.* 32:515-525.
- Liang, L., and J.F. McCarthy. 1995. *Colloidal Transport of Metal Contaminants in Groundwater*. *Metal Speciation and Contamination of Soil*, p. 86–112. Hung, P., G. W. Bailey, and A.R. Boweres, Eds. Boca Raton, Florida. Lewis Publishers.
- Lower, S. K., P. A. Maurice, S. J. Traina, and E. H. Carlson. 1998. *Aqueous lead sorption by hydroxylapatite: Applications of atomic force microscopy to dissolution, nucleation and growth studies*. *Amer. Min.* 83: 147-158.
- Ma, Q. Y., S. J. Traina, and T. J. Logan. 1993. *In Situ Lead Immobilization by Apatite*. *Env. Sci. Tech.* 27: 1803-1810.
- Ma, Q.Y., T.J. Logan, and S.J. Traina. 1995. *Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks*. *Env.Sci. Tech.* 29:1118-1126.
- Maneck, M., P.A. Maurice, and S.J. Traina. 2000. *Kinetics of aqueous Pb reaction with apatites*. *Soil Science.* 165:920-933.
- Martinez, M.N., S.S. Hightower, G.B. Smith, W. Mueller, J.L. Conca, and J. Wright. 2005. The effect of Apatite II™ on the biodegradation of TNT and perchlorate in contaminated soil samples. In *Sustainable Range Management*, Battelle Press, Columbus, Ohio.
- Matheson, L.J., W.C. Goldberg, and W.D. Bostick. 2001. *Laboratory batch and column studies to evaluate Apatite II removal of soluble uranium from contaminated groundwater*. *Amer. Chem. Soc. Nat'l. Mtg.* 41:109-113.
- McCarthy, J.F., and J.M. Zachara. 1989. *Subsurface Transport of Contaminants: Mobile Colloids in the Subsurface Environment May Alter the Transport of Contaminants*. *Environmental Science and Technology.* 23:496–502.

- McCarthy, J., and C. Degueudre. 1993. *Sampling and Characterisation of Groundwater Colloids for Studying their Role in Subsurface Transport of Contaminants*. Environmental Particles, II. Buffle, J., and H. Van Leeuwen, Eds., Chapter 6, p. 247–315. Boca Raton, Florida: Lewis Publishers. NNA.19930607.0075.
- McGraw, M. A. 1996. *The Effect of Colloid Size, Colloid Hydrophobicity and Matrix Saturation on Colloid Transport in The Subsurface*. PhD. Dissertation, University of California, Berkeley.
- National Wildlife Federation (NWF). 2003. <http://www.nwf.org/panther>.
- Nriagu, J.O. 1974. *Lead orthophosphates. IV: Formation and stability in the environment*. Geoch. Cosmoch. Acta. 38:887-898.
- Pasteris, J.D., D.E. Giammar, B. Wopenka, L. Xie, P.Scully, and J. Wright. 2005. *Fishing for lead: metal remediation through use of fish bone*. Geol. Soc Amer. Abstr. Prog.
- Rice, J.A. 1995. *Mathematical Statistics and Data Analysis*. Duxbury Press Belmont, California.
- Ruby, M.V., A. Davis, T.E. Link, R. Schoof, R.L. Chaney, G.B. Freeman, and P. Bergstrom. 1993. *Development of an in vitro screening test to evaluate the in vivo bioaccessibility of ingested mine-waste lead*. Env. Sci. Tech. 27(13):2870–2877.
- Ruby, M.V., A. Davis, R. Schoof, S. Eberle, and C.M. Sellstone. 1996. *Estimation of lead and arsenic bioavailability using a physiologically based extraction test*. Env. Sci. Tech. 30(2):422–430.
- Ruby, M.V., R. Schoof, W. Brattin, and M. Goldade *et al* 1999. *Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment*. Env. Sci. Tech. 33(21):3697–3705.
- Testa, S. M., J. L. Conca, and D. L. Patton. 1992. *Fixation of Petroleum Contaminated Soils via Cold-Mixed Asphalt for Use as a Liner*. Trans. Haz. Mat. Cont. Res. Inst. p. 30-33.
- Thomson, B.M., C.L. Smith, R.D. Busch, M.D. Siegel, and C. Baldwin. 2003. *Removal of Metals and Radionuclides Using Apatite and Other Natural Sorbents*. J. Env. Eng. 129(6): 492-499.
- USEPA. 2003. *Recommendations of the Technical Review Workgroup for Lead for an Approach to Assessing Risks Associated with Adult Exposure to Lead in Soil*. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency. EPA-540-R-03-001, OSWER #9285.7-54, January 2003. Washington, D.C.
- Wright, Judith, Hans Schrader, and W. T. Holser. 1987a. *Paleoredox Variations in Ancient Oceans Recorded by REE in Fossil Apatite*. Geoch. Cosm. Acta. 51:631-644.

- Wright, Judith, James F. Miller, and W. T. Holser. 1987b. *Chemostratigraphy of Conodonts Across the Cambrian-Ordovician Boundary: Western U.S. and SE China*. In *Conodonts: Investigative Tech. and Appl.*, Ed., R. L. Austin. Ellis Horwood, Ltd., London. pp. 259-286.
- Wright, Judith. 1990. *Conodont Apatite: Structure and Geochemistry*. In *Biom mineralization: Patterns, Processes and Evolutionary Trends*. Ed., Joseph Carter. Van Nostrand Reinhold, New York, p. 445-459.
- Wright, Judith, Loni M. Peurrung, Timothy E. Moody, James L. Conca, Xiaobing Chen, Paul P. Didzerekis, and Eric Wyse. 1995. *In Situ Immobilization of Heavy metals in Apatite Mineral Formulations*. SERDP Technical Report, Dept. of Defense. 154 p.
- Wright, J. V., and J. L. Conca. 1998. *United States Patent #6217775 STABILIZATION AND REMEDIATION OF SOIL, WATER AND WASTES CONTAMINATED WITH METALS USING FISH BONES AND HARD PARTS*, issued 2000. U.S. Patent Office, Washington, D.C.
- Wright, Judith, James L. Conca, Ken R. Rice, and Brian Murphy. 2004a. *PIMS using Apatite II™: how it works to remediate soil and water*. In *Sustainable Range Management*. Eds., R.E. Hinchee and B. Alleman. Battelle Press, Columbus, Ohio.
- Wright, Judith, Ken R. Rice, Brian Murphy, and James L. Conca. 2004b. *PIMS-remediation of Pb-contaminated soil at Camp Stanley, TX*. In *Sustainable Range Management*. Eds., R.E. Hinchee and B. Alleman. Battelle Press, Columbus, Ohio.
- Wright, J. 2005. *From conodonts and ancient oceans to fish bones and metal contaminant stabilization*. In *Goldschmidt Conference, Invited, Geochemical Society of London Abstracts*, Univ. ID, Moscow.
- Wright, J., J.L. Conca, and A.F. Slater. 2005. *PIMS with Apatite II: A field scale demonstration on a lead contaminated soil*. In *Stabilization/Solidification Treatment and Remediation Proceedings*, Cambridge University, U.K.

### **Extended Bibliography**

- Admassu, W., and T. Breese. 1999. *Feasibility of using natural fishbone apatite as a substitute for hydroxyapatite in remediating aqueous heavy metals*. *Jour. of Haz. Mat.* 69(2):187-196.
- Arey, J.S., J.C. Seaman, and P.M. Bertsch. 1999. *Immobilization of uranium in contaminated sediments by hydroxyapatite addition*. *Env. Sci. & Tech.* 33:337-342.
- Ayati, M., and H.E. Lundager-Madsen. 2000. *Crystallization of some heavy-metal phosphates alone and in the presence of calcium ion*. *Jour. of Crystal Growth*. 208:579-591.

- Basta, N.T., R. Gradwohl, K.L. Snethen, and J.L. Schroder. 2001. *Chemical immobilization of lead, zinc and cadmium in smelter-contaminated soils using biosolids and rock phosphate*. Jour. of Env. Qual. 30:1222-1230.
- Cao, X., L.Q. Ma, M. Chen, S.P. Singh, and W.G. Harris. 2002. *Impacts of phosphate amendments on lead biogeochemistry at a contaminated site*. Env. Sci. & Tech. 36:5296-5304.
- Cotter-Howells, J., and S. Caporn. 1996. *Remediation of contaminated land by formation of heavy metal phosphates*. Appl. Geoch. 11:335-342.
- Davis, A., J.W. Drexler, M.V. Ruby, and A. Nicholson. 1993. *Micromineralogy of mine wastes in relation to lead bioavailability, Butte, MT*. Env. Sci. & Tech. 27:1415-1425.
- Eighmy, T. T., B.S. Crannell, J.E. Krzanowski, L.G. Butler, F.K. Cartledge, E.F. Emery, J.D. Eusden, Jr., E.L. Shaw, and C.A. Francis. 1999. *Characterization and phosphate stabilization of dusts from the vitrification of MSW combustion residues*. Waste Management. 18:513-524.
- Ergun, C., T.J. Webster, R. Bizios, and R.H. Doremus. 2001. *Hydroxylapatite with substituted magnesium, zinc, cadmium, and yttrium. I. Structure and microstructure*. Jour. of Biomed. Mat. Res. 59:305-311.
- Farley, K.J., D.A. Dzombak, and F.M.M. Morel. 1985. *A surface precipitation model for the sorption of cations on metal oxides*. Jour. of Colloid and Interface Sci. 106:226-242.
- Fuller, C. C., J.R. Bargar, J.A. Davis, and M.J. Piana. 2002. *Mechanisms of uranium interactions with hydroxyapatite: implications for groundwater remediation*. Env. Sci. & Tech. 36:158-165.
- Gauglitz, R., M. Holterdorf, W. Franke, and G. Marx. 1992. *Immobilization of heavy metals by hydroxylapatite*. Radioch. Acta. 58-59:253-257.
- Graziano, J.H., N.J. Lolocono, M. Maddaloni, and C.C. Blum. 2001. *Assessing the oral bioavailability of lead in soil to humans*. Presentation at the 40<sup>th</sup> Annual Meeting of the Society of Toxicology. March 28, 2001.
- Graziano, Joseph H., and Jim Shine. 2003. *NIEHS/EPA Metals-Bioavailability*. US EPA Technology Innovation Office Interactive Internet Seminar Series on Metals, [http://www.clu-in.org/conf/tio/metals\\_040903/](http://www.clu-in.org/conf/tio/metals_040903/).
- Hamon, R.E., M.J. McLaughlin, and G. Cozens. 2002. *Mechanisms of attenuation of metal availability in in situ remediation treatments*. Env. Sci. & Tech. 36:2991-3996.
- Hettiarachchi, G. M., G.M. Pierzynski, and M.D. Ransom. 2000. *In situ stabilization of soil lead using phosphorus and manganese oxide*. Env. Sci. & Tech. 34:4614-4619.

- Hodson, M. E., E. Valsami-Jones, and J.D. Cotter-Howells. 2000. *Bonemeal additions as a remediation treatment for metal contaminated soil*. *Env. Sci. & Tech.* 34:3501-3507.
- Hodson, M.E., E. Valsami-Jones, J.D. Cotter-Howells, W.E. Dubbin, A.J. Kemp, I. Thornton, and A. Warren. 2001. *Effect of bone meal (calcium phosphate) amendments on metal release from contaminated soils—a leaching column study*. *Env. Poll.* 112:233-243.
- Ioannidis, T.A., and A.I. Zouboulis. 2003. *Detoxification of a highly toxic lead-loaded industrial solid waste by stabilization using apatites*. *Jour. of Haz. Mat.* 97:173-191.
- Koutsoukos, P., Z. Amjad, M.B. Tomson, and G.H. Nancollas. 1980. *Crystallization of calcium phosphates. A constant composition study*. *Jour. Amer. Chem. Soc.* 102:1553-1557.
- Laperche, V., S.J. Traina, P. Gaddam, and T.J. Logan. 1996. *Chemical and mineralogical characterizations of Pb in a contaminated soil: reactions with synthetic apatite*. *Env. Sci. & Tech.* 30:3321-3326.
- Laperche, V., T.J. Logan, P. Gaddam, and S.J. Traina. 1997. *Effect of apatite amendments on plant uptake of lead from contaminated soil*. *Env. Sci. & Tech.* 31:2745-2753.
- Lazic, S. and Z. Vukovic. 1991. *Ion exchange of strontium on synthetic hydroxyapatite*. *Jour. of Radioanal. and Nucl. Chem.* 149:161-168.
- Leyva, A.G., J. Marrero, P. Smichowski, and D. Cicerone. 2001. *Sorption of antimony onto hydroxyapatite*. *Env. Sci. & Tech.* 35:3669-3675.
- Lindsay, W.L., and E.C. Moreno. 1960. *Phosphate phase equilibria in soils*. *Soil Sci. Soc. of Amer. Proc.* 24:177-182.
- Lindsay, W.L., and P.L. Vlek. 1977. *Phosphate minerals*. In *Minerals in Soil Environments*. Eds., J.B. Dixon, S.B. Weed, J.A. Kittrick, M.H. Milford, and J.L. White. *Soil Sci. Soc. of Amer. Madison, Wisconsin.* 639-672.
- Lower, S.K., P.A. Maurice, and S.J. Traina. 1998a. *Simultaneous dissolution of hydroxylapatite and precipitation of hydroxypyromorphite: direct evidence of homogeneous nucleation*. *Geoch. Cosmoch. Acta.* 62:1773-1780.
- Lower, S.K., P.A. Maurice, S.J. Traina, and E.H. Carlson. 1998b. *Aqueous Pb sorption by hydroxylapatite: applications of atomic force microscopy to dissolution, nucleation, and growth studies*. *Amer. Mineral.* 83:147-158.
- Lusvardi, G., G. Malavasi, L. Menabue, and M. Saladini. 2002. *Removal of cadmium ion by means of synthetic hydroxyapatite*. *Waste Management.* 22:853-857.
- Ma, L.Q. 1996. *Factors influencing the effectiveness and stability of aqueous lead immobilization by hydroxyapatite*. *Jour. of Env. Qual.* 25:1420-1429.

- Ma, Q.Y., T.J. Logan, S.J. Traina, and J.A. Ryan. 1994a. *Effects of NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and CO<sub>3</sub><sup>2-</sup> on Pb<sup>2+</sup> immobilization by Hydroxyapatite.* *Env. Sci. & Tech.* 28:408-418.
- Ma, Q.Y., S.J. Traina, T.J. Logan, and J.A. Ryan. 1994b. *Effects of Aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite.* *Env. Sci. & Tech.* 28:1219-1228.
- Maddaloni, M., N. Lolocono, W. Manton, C. Blum, J. Drexler, and J. Graziano. 1998. *Bioavailability of soilborne lead in adults by stable isotope dilution.* *Env. Health Perspectives.* 106(6):1589-1594.
- Mahapatra, P.P., D.S. Safrangi, and B. Mishra. 1995. *Kinetics of nucleation of lead hydroxylapatite and preparation of solid solutions of calcium-cadmium-lead hydroxyapatite: an x-ray and IR study.* *Jour. of Solid State Chem.* 116:8-14.
- Manecki, M., P.A. Maurice, and S.J. Traina. 2000. *Uptake of aqueous Pb by Cl<sup>-</sup>, F<sup>-</sup>, and OH<sup>-</sup> apatites: mineralogic evidence for nucleation mechanisms.* *Amer. Mineral.* 85:932-942.
- Mavropoulos, E., A.M. Rossi, A.M. Costa, C.A.C. Perez, J.C. Moreira, and M. Saldanha. 2002. *Studies on the mechanisms of lead immobilization by hydroxyapatite.* *Env. Sci. & Tech.* 36:1625-1629.
- McConnell, D. 1973. *Apatite: Its crystal chemistry, mineralogy, utilization, and geologic and biologic occurrences.* In *Applied Mineralogy.* Eds., V. Herausgegeben, V.D. Fréchette, H. Kirsch, L.B. Sand, and F. Trojer. Springer-Verlag, New York. 22-32.
- Middleburg, J.J., and R.N.J. Comans. 1991. *Sorption of cadmium on hydroxyapatite.* *Chem. Geol.* 90:45-53.
- Morin, G., F. Juillot, P. Ildefonse, G. Calas, J.-C. Samama, P. Chevallier, and G.E. Brown, Jr. 2001. *Mineralogy of lead in a soil developed on a Pb-mineralized sandstone, Largentiere, France.* *Amer. Mineral.* 86:92-104.
- Morse, J.W., and W.N. Casey. 1988. *Ostwald processes and mineral paragenesis in sediments.* *Amer. Jour. of Sci.* 288:537-560.
- Nancollas, G.H. 1984. *The nucleation and growth of phosphate minerals.* In *Phosphate Minerals.* Eds., J.O. Nriagu and P.B. Moore. Springer-Verlag, Berlin. 137-154.
- Nriagu, J.O. 1972. *Lead orthophosphates. I: solubility and hydrolysis of secondary lead orthophosphate.* *Inorg. Chem.* 11:2499-2503.
- Nriagu, J.O. 1973a. *Lead orthophosphates. II: stability of chloropyromorphite at 25 C.* *Geoch. Cosmoch. Acta.* 37:367-377.
- Nriagu, J.O. 1973b. *Lead orthophosphates. III: stabilities of fluoropyromorphite and bromopyromorphite at 25 C.* *Geoch. Cosmoch. Acta.* 37:1735-1743.

- Nriagu, J.O. 1976. *Phosphate-clay mineral relations in soils and sediments*. Canadian Jour. of Earth Sci. 13:717-736.
- Nriagu, J.O. 1984. *Formation and stability of base metal phosphates in soils and sediments*. In Phosphate Minerals. Eds., J.O. Nriagu and P.B. Moore. Springer-Verlag. Berlin. 318-329.
- Nriagu, J.O., and P.B. Moore, Eds. 1984. *Phosphate Minerals*. Springer-Verlag. Berlin. 442 p.
- Ostergren, J.D., G.E. Brown, Jr., G.A. Parks, and T.N. Tingle. 1999. *Quantitative speciation of lead in selected mine tailings from Leadville, CO*. Env. Sci. & Tech. 33:1627-1636.
- Povarennykh, A.S. 1972. *Crystal Chemical Classification of Minerals*. Plenum Press, New York.
- Pujari, M., and P.N. Patel. 1989. *Strontium-copper-calcium hydroxyapatite solid solutions: preparation, infrared, and lattice constant measurements*. Jour. of Solid State Chem. 83:100-104.
- Rabinowitz, M.B. 1993. *Modifying soil lead bioavailability by phosphate addition*. Bull. of Env. Cont. and Tox. 51:438-444.
- Raicevic, S. 2001. *Remediation of uranium contaminated water and soil using phosphate-induced metal stabilization (PIMS)*. Hemijska Industrija. 55:277-280.
- Rickard, D.T., and J.O. Nriagu. 1978. *Aqueous chemistry of lead*. In The Biochemistry of Lead in the Environment. Ed., J.O. Nriagu. Elsevier/North-Holland Biomedical Press, Amsterdam. 219-284.
- Ruby, M.V., A. Davis, and A. Nicholson. 1994. *In situ formation of lead phosphates in soils as a method to immobilize lead*. Env. Sci. & Tech. 28:646-654.
- Ryan, J.A., P. Zhang, D. Hesterberg, J. Chou, and D.E. Sayers. 2001. *Formation of chloropyromorphite in a lead-contaminated soil amended with hydroxyapatite*. Env. Sci. & Tech. 35:3798-3803.
- Santillan-Medrano, J., and J.J. Jurinak. 1975. *The chemistry of lead and cadmium in soil: solid phase formation*. Soil Sci. Soc. of Amer. Proc. 39:851-856.
- Sauve, S., M. McBride, and W. Hendershot. 1998. *Lead phosphate solubility in water and soil suspensions*. Env. Sci. & Tech. 32:388-393.
- Scheckel, K.G., and J.A. Ryan. 2002. *Effects of aging and pH on dissolution kinetics and stability of chloropyromorphite*. Env. Sci. & Tech. 36:2198-2204.

- Somasundaran, P., and Y.H.C. Wang. 1984. *Surface chemical characteristics and adsorption properties of apatite*. In *Adsorption and Surface Chemistry of Hydroxyapatite*. Ed., D.N. Misra. Plenum Press, New York 129-149.
- Sposito, G. 1986. *Distinguishing adsorption from surface precipitation*. In *Geochemical Processes at Mineral Surfaces*. Eds., J.A. Davis and K.F. Hayes. American Chemical Society, Washington, D.C. 217-228.
- Stanforth, R., and J. Qiu. 2001. *Effect of phosphate treatment on the solubility of lead in contaminated soil*. *Env. Geol.* 41:1-10.
- Sugiyama, S., T. Ichii, H. Hayashi, and T. Tomida. 2002. *Lead immobilization by non-apatite-type calcium phosphates in aqueous solutions*. *Inorg. Chem. Comm.* 5:156-158.
- Tardy, Y., and P. Veillard. 1977. *Relationships among Gibbs Free Energies and enthalpies of formation of phosphates, oxides and aqueous ions*. *Contr. to Min. and Petr.* 63:75-88.
- Theodoratos, P., N. Papassiopi, and A. Xenidis. 2002. *Evaluation of monobasic calcium phosphate for the immobilization of heavy metals in contaminated soils from Lavrion*. *Jour. of Haz. Mat.* 94:135-146.
- Van Cappellen, P., and R.A. Berner. 1989. *Marine apatite precipitation*. In *Water-Rock Interaction*. Ed., D. Miles. Balkema, Rotterdam. 707-710.
- Viellard, P., and Y. Tardy. 1984. *Thermochemical properties of phosphates*. In *Phosphate Minerals*. Eds., J.O. Nriagu and P.B. Moore. Springer-Verlag, Berlin. 171-198.
- Wright, Judith, and James L. Conca. 2002. *Remediation of groundwater and soil contaminated with metals and radionuclides using Apatite II, a biogenic apatite mineral*. *Amer. Chem. Soc. Div. of Env. Chem.* 42:117-122.
- Xu, T., and F.W. Schwartz. 1994. *Lead immobilization by hydroxyapatite in aqueous solutions*. *Jour. of Cont. Hydr.* 15:187-206.
- Xu, T., F.W. Schwartz, and S.J. Traina. 1994. *Sorption of Zn<sup>2+</sup> and Cd<sup>2+</sup> on hydroxyapatite surfaces*. *Env. Sci. & Tech.* 28:1472-1480.
- Yang, J., D.E. Mosby, S.W. Casteel, and R.W. Blanchar. 2001. *Lead immobilization using phosphoric acid in a smelter-contaminated urban soil*. *Env. Sci. & Tech.* 35:3553-3559.
- Yang, J., D.E. Mosby, S.W. Casteel, and R.W. Blanchar. 2002. *In vitro lead bioaccessibility and phosphate leaching as affected by surface application of phosphoric acid in lead-contaminated soil*. *Arch. of Env. Cont. and Tox.* 43:399-405.
- Zhang, P., and J.A. Ryan. 1998. *Formation of pyromorphite in anglesite-hydroxyapatite suspensions under varying pH conditions*. *Env. Sci. & Techn.* 32:3318-3324.

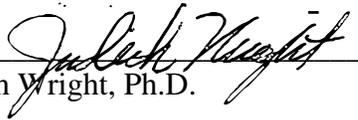
- Zhang, P., and J.A. Ryan. 1999. *Transformation of Pb(II) from cerussite to chloropyromorphite in the presence of hydroxyapatite under varying conditions of pH*. *Env. Sci. & Tech.* 33:625-630.
- Zhang, P., J.A. Ryan, and L.T. Bryndzia. 1997. *Pyromorphite formation from goethite adsorbed lead*. *Env. Sci. & Tech.* 31:2673-2678.
- Zhang, P., J.R. Ryan, and J. Yang. 1998. *In vitro soil Pb solubility in the presence of hydroxyapatite*. *Env. Sci. & Tech.* 32:2763-2768.

## APPENDIX A

### POINTS OF CONTACT

POINT OF CONTACT Name	ORGANIZATION Name/Address	PHONE/FAX/E-MAIL	ROLE IN PROJECT
Dr. Judith Wright	PIMS NW, Inc. UFA Ventures, Inc. 403 West Riverside Dr. Carlsbad, NM 88220	505-628-0916 (Work) 505-628-0915 (Fax) judith@ufaventures.com judith@pimsnw.com	Principal Investigator and Project Lead
Dr. James Conca	NMSU Carlsbad Environmental Monitoring & Research Center Carlsbad, NM 88220	505-234-5555 (Work) 505-706-0214 (Cell) 505-887-3051 (Fax) jconca@cemrc.org	Co-Investigator
Brian Murphy	CSSA 1408 Moore Place, SW Leesburg, VA. 20175	571-331-5374 (Work) murphyb@adelphia.net	Base Environmental Officer During Demonstration
Ken Rice	Parsons Inc. 8000 Centre Park, Suite 200 Austin, TX 78754	512-719-6050 (Work) 512-719-6099 (Fax) Ken.R.Rice@parsons.com	Project Manager for CSSA

**Dated Signature of Project Lead**

  
\_\_\_\_\_  
Judith Wright, Ph.D.



## ESTCP Program Office

901 North Stuart Street  
Suite 303  
Arlington, Virginia 22203  
(703) 696-2117 (Phone)  
(703) 696-2114 (Fax)  
e-mail: [estcp@estcp.org](mailto:estcp@estcp.org)  
[www.estcp.org](http://www.estcp.org)