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Environmental Quality and Technology Program

Treatment and Management of Closed or Inactive Small Arms Firing Ranges

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Abstract: This document provides environmental professionals and project managers with information on the effect of range type and soil type on technology selection for one-time cleanup of closed Small Arms Firing Ranges (SAFRs). The one-time cleanup of closed SAFRs typically differs in purpose, environmental context, and applicable regulations from environmental operation and maintenance (O&M) of active SAFRs. This report summarizes and evaluates available technical information relevant to cleanup of lead and other metals when a SAFR is closed. SAFRs include military small arms training ranges, law enforcement (military police, Federal law enforcement, etc.) training ranges, and recreational rifle, pistol, trap, skeet, and sporting clay ranges. Each type of SAFR uses different types of ammunition with different physical distributions, chemical compositions, and environmental behaviors. In the context of this document, the definition of SAFRs does not include indoor ranges and is limited to outdoor ranges on which no explosives or rounds more powerful than .50-caliber armor-piercing ammunition are used. Although this document only considers cleanup of closed SAFRs, the technologies considered here might be useful under some circumstances in environmental O&M of active SAFRs.

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Preface

This document provides environmental professionals and project managers with information on the effect of range type and soil type on technology selection for one-time cleanup of closed Small Arms Firing Ranges (SAFRs). This report summarizes and evaluates available technical information relevant to cleanup of lead and other metals when a SAFR is closed. This document is intended for SAFRs on property owned or controlled by the U. S. Army or Department of Defense (DoD), although it can be applied to other outdoor SAFRs such as law enforcement (military police, Federal law enforcement, etc.) training ranges, and recreational rifle, pistol, trap, skeet, and sporting clay ranges. It is also limited to ranges on which no explosives or rounds more powerful than .50-caliber armor-piercing ammunition are used.

This study was conducted by the Environmental Laboratory (EL), U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, under the Environmental Quality and Technology Program, Inorganics in Soils Focus Area, Dr. M. John Cullinane, Jr., EL, Program Manager.

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This study was conducted under the direct supervision of Dr. Patrick Deliman, Chief, Environmental Engineering Branch, and under the general supervision of Dr. Richard E. Price, Chief, Environmental Processes and Engineering Division, and Dr. Elizabeth C. Fleming, Director, EL.

Commander and Executive Director of ERDC was COL Richard B. Jenkins. Director was Dr. James R. Houston.

Unit Conversion Factors

Multiply	By	To Obtain
acres	4,046.873	square meters
acre-feet	1,233.5	cubic meters
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
degrees (angle)	0.01745329	radians
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
feet	0.3048	meters
square feet	0.092903	square meters
gallons (U.S. liquid)	3.785412 E-03	cubic meters
hectares	1.0 E+04	square meters
inches	0.0254	meters
inch-pounds (force)	0.1129848	newton meters
microns	1.0 E-06	meters
miles (U.S. statute)	1,609.347	meters
tons (force)	8,896.443	newtons
tons (force) per square foot	95.76052	kilopascals
tons (2,000 pounds, mass)	907.1847	kilograms
tons (2,000 pounds, mass) per square foot	9,764.856	kilograms per square meter
yards	0.9144	meters

Notation

AA	atomic absorption
ADA	N-2(acetamido)iminodiacetic acid
ATF	Armaments Technology Facility
ASTM	American Society for Testing and Materials
CCA	coated chelating agent
CCME	counter-current metal extraction
CDTA	1,2 cyclohexylene diamine tetraacetic acid
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CEC	cation exchange capacity
CMRI	Colorado Minerals Research Institute
COPC	contaminants of potential concern
cu	cubic
DA	Department of the Army
DDI S&S	distilled de-ionized water suspend and settle
DFOB	siderophore desferrioxamine B
DOD	Department of Defense
DOE	Department of Energy
DTPA	diethylenetriamine pentaacetic acid
DV	dual view
DW	dry weight
EDDS	ethylene diamine disuccinnic acid
EDTA	ethylene diamine tetraacetic acid
Eh	redox potential
EMF	electromotive force
EPA	Environmental Protection Agency
ERDC	Engineer Research and Development Center
ESEM	environmental scanning electron microscope
FFCA	Federal Facility Compliance Act
ft	feet

g	gram
h	hour
ha	hectare
HAFB	Hamilton Air Force Base
HAP	hydroxyapatite
HBED	<i>N,N'</i> -di-(2-hydroxybenzyl)ethylenediamine <i>N,N'</i> -diacetic acid
H-EDTA	hydroxyethyl-ethylenediamine-triacetic acid
ICP-OES	inductively coupled plasma optical emission spectroscopy
in	inch
INERT	In-place Inactivation and Natural Ecological Restoration Technologies
ITRC	Interstate Technology and Regulatory Council
kg	kilogram
KHP	potassium phosphate
KJ	Kilojoule
lbs	pounds
L	liter
m	meter
mM	milli-molar
M	molarity
meq	milli-equivalent
mg	milligram
min	minute
mL	milliliter
mm	millimeter
MPCA	Minnesota Pollution Control Agency
N	normality
NFESC	Naval Facilities Engineering Service Center
NTA	nitroacetic acid
OM	organic matter
O&M	operations and maintenance
oz	ounce
PBET	physiologically based extraction test

PEI	polyethylenimine
PDA	pyridine-2,6-dicarboxylic acid
RCRA	Resource Conservation and Recovery Act
rpm's	revolutions per minute
RO	reverse osmosis
ROD	Records of Decision
ROS	Remedial Options Study
RTDF	Remediation Technology Development Forum
SAFR	small arms firing range
SBRC	Solubility/Bioavailability Research Consortium
SEP	sequential extraction procedure
SIT	Stevens Institute of Technology
SITE	Superfund Innovative Technology Evaluation
SPLP	synthetic precipitation leaching procedure
S/S	solidification/stabilization
TCAAP	Twin Cities Army Ammunition Plant
TCLP	toxicity characteristic leaching procedure
TOC	total organic carbon
TSF	tons per square foot
TSS	total suspended solids
TVA	Tennessee Valley Authority
PAH	polycyclic aromatic hydrocarbon
ppb	parts per billion
ppm	parts per million
r ²	coefficient of determination
μm	micrometer (micron)
USAEC	U.S. Army Environmental Center
USEPA	United States Environmental Protection Agency
UTS	universal treatment standard
vol	volume
w	weight
XRD	x-ray diffraction
yd	yard

1 Introduction

Purpose and objectives of report

The objective of this document is to provide environmental professionals and project managers with the information required to understand the effect of range type and soil type on technology selection for one-time cleanup of closed Small Arms Firing Ranges (SAFRs). This report summarizes and evaluates available technical information relevant to cleanup of lead and other metals when a SAFR is closed. This document is intended for SAFRs on property owned or controlled by the U. S. Army or Department of Defense (DoD). SAFRs include military small arms training ranges, law enforcement (military police, Federal law enforcement, etc.) training ranges, and recreational rifle, pistol, trap, skeet, and sporting clay ranges, each of which is characterized by use of different types of ammunition with different physical distributions, chemical compositions, and environmental behaviors. In the context of this document, the definition of SAFRs does not include indoor ranges and is limited to outdoor ranges on which no explosives or rounds larger than .50-caliber armor-piercing ammunition are used.

The one-time cleanup of closed SAFRs typically differs in purpose, environmental context, and applicable regulations from environmental operation and maintenance (O&M) of active SAFRs. This document considers only one-time cleanup of closed SAFRs, although the technologies considered here might be useful to varying degrees in environmental O&M of active SAFRs under some circumstances.

Why range cleanup?

Closed ranges generally have to undergo decommissioning, which, in most cases, involves some treatment approach. There are essentially two reasons for this requirement. First, the lead and other metals associated with the range may pose environmental risks. Second, Federal regulations generally classify a closed range as subject to remedial action.

Possible environmental contamination resulting from SAFR

Lead in SAFRs differs from lead from most other sources (such as mining or industrial sources) in that it is primarily metallic in form. SAFR lead is

less mobile, in general, compared to these other sources. Still, metallic lead can corrode, increasing the mobility of the lead. Chen et al. (2002) characterized the lead content and distribution in a 14-year-old SAFR berm in central Florida. A majority of the lead was found in the top 10 cm of the berm soil (Figure 1). Lead levels were essentially at background levels (9 mg/kg) below about 30 cm. The authors then examined the lead concentration in the top 10 cm but in samples taken at increasing distance from the firing line (Figure 2). They found lead was distributed evenly (until the sample locations reached the berm). Lead reached maximum levels in the middle of the backstop berm). TCLP tests of all samples exceeded the 5-mg/L critical level. Most of the collected bullets were visibly corroded and partially covered by a crust of white, gray, or brown material. Sequential extraction and X-ray diffraction (XRD) analysis of the berm soil determined that the predominant form of lead (>90 percent) was hydrocerussite $[(\text{Pb}_3(\text{CO}_3)_2(\text{OH}))]$, which appeared to control the overall lead solubility in the soil. Small amounts of massicot (PbO) and cerussite (PbCO_3) were also present. Less than 1 percent of the lead was found in the exchangeable fraction. These studies suggest that elevated pH in the berm soil (Figure 2) was caused by the oxidation and transformation of the elemental lead in the lead bullets followed by the carbonation of the lead oxide.

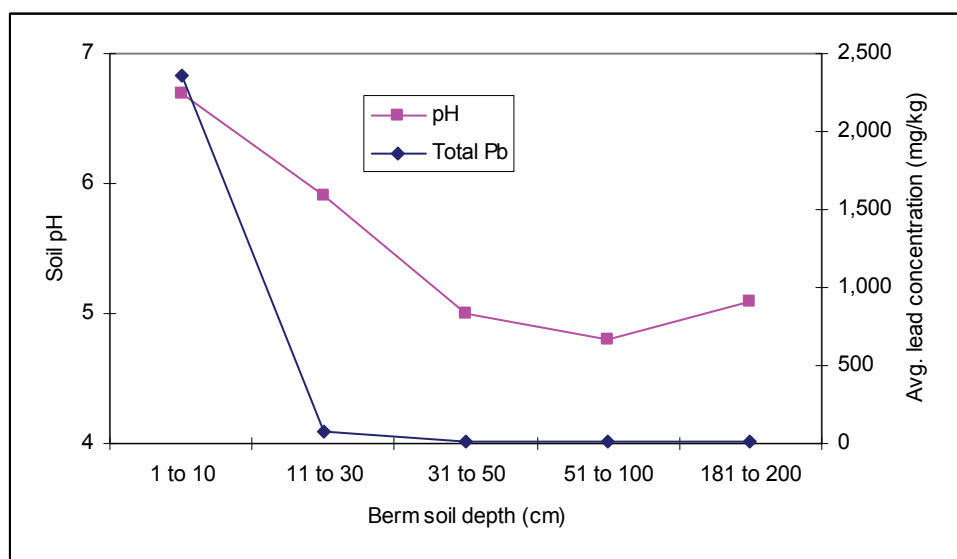


Figure 1. Average lead concentration and backstop berm soils pH at various depths (from: Chen et al. 2002).

Such corrosion can result in surface water or, more rarely, groundwater contamination. Stormwater runoff can erode and transport contaminated

soil and lead particles away from the firing range. Rainfall intensity, ground slope, soil type, and obstructions such as vegetation and fabricated structures influence the potential transport of the lead with surface runoff. Dissolved lead can also be found in some surface waters. Groundwater contamination is less frequent, but can occur in areas with unfavorable soil pH, particularly in acidic conditions, or, as occasionally found in desert environments, conditions that are too basic.

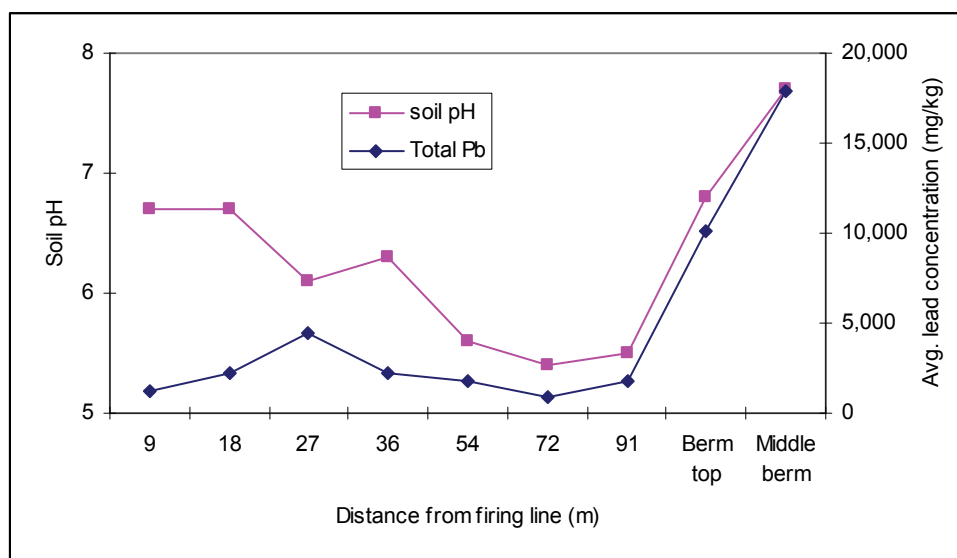


Figure 2. Average lead concentration and soil pH at different distances from the firing range on a 91-m range (from: Chen et al. 2002).

Regulatory

Active SAFRs generally do not fall under Federal solid or hazardous waste regulations, such as RCRA or CERCLA. For example, according to the U.S. Environmental Protection Agency (USEPA) Region 2 manual (USEPA 2001), lead is not considered a hazardous waste subject to RCRA at the time it is discharged from a firearm because it is used for its intended purpose. As such, shooting lead shot (or bullets) may not be regulated nor is an RCRA permit required to operate a shooting range. However, once a range is closed, the impact areas may potentially fall under these regulations, particularly RCRA. Lead bullets and shot, if abandoned, may be a solid and/or hazardous waste and may present an actual or potential imminent and substantial endangerment.

Several major reports suggest that the best management practice (BMP) for an operating range is periodic removal of the lead (U.S. Army Envi-

ronment Center (USAEC) 1998, USEPA 2001, Interstate Technology and Regulatory Council (ITRC) 2005). The soil, if then placed back on the range, is exempt from RCRA. However, if the soil were to be removed off-site, it would then require testing to determine if it is an RCRA hazardous waste. The lead, if recycled or reused, is considered a scrap metal and is, therefore, excluded from RCRA. Since individual range conditions differ, and some State laws may be more stringent than RCRA, it is advisable to seek the advice of a regulatory specialist in most cases.

Steps prior to cleanup

Regulatory interface

A critical step prior to remediation, or even characterization, is to proactively seek contact, direction, and eventual buy-in from the installation environmental staff and the regulatory agency responsible for the site. The responsible agency can vary from the Federal Environmental Protection Agency, State regulatory agencies, or even, in some cases, local organizations. The appropriate agency should be identified and a working, professional relationship should be established with a case manager to investigate all options for the site.

Consultant assistance

Even if the range manager has reliable in-house technical expertise on his staff, it is still advisable in many cases to contract with a third party consultant. Consultants often have well-established relationships with regulatory agencies and with remediation contractors, which can ease dealings with these entities. Consultants can also bring a third party perspective to characterization, cleanup, and closure.

Characterization

The site should be completely delineated in terms of concentration and area/extent of metal contamination and identification of hot spots. In addition, soil in the areas of concern should be characterized for grain size, pH, organic matter content/total organic carbon (OM/TOC), cation exchange capacity (CEC), etc. These procedures are discussed in detail in Chapter 2.

Analysis of options

Prior to any cleanup, all options should be considered. This includes the possibility of upgrading and continuing to use the range, or the recycling of contaminated soils for new berm construction.

General SAFR characteristics affecting cleanup

Each type of SAFR is characterized by a particular style of shooting and ammunition suited to the purposes of the SAFR. The implications of the general characteristics of each type of SAFR for cleanup are summarized in this section.

Military rifle and machine gun ranges

Military ranges in the United States include M-16 and M249 – SAW, which fire a 5.56-mm bullet; M-60 and M240B weapons, which fire a 7.62-mm bullet; and 50-caliber machine gun ranges. In general, these are all high-powered, high-velocity bullets. Some of these bullets have a full metal jacket, and some with steel penetrators allowing for deeper penetration into the backstop material and potentially greater agglomeration and fragmentation in the backstop. Range types include zero ranges and qualification ranges where bullets are fired into a backstop. The qualification range can use zero range using paper targets, but typically use popup target range with no backstop. Targets range from 50 to 600+ yd depending on range and weapon systems.

Much of the shooting at military small arms training ranges is with rifles fired at popup targets at varying distances from 50 yd to greater than 600 yd, which means that most targets are far in front of the backstop, if the SAFR has a backstop. Most shooting is from standing, kneeling, sitting, and prone positions, so that shots are fired essentially horizontally from 5 ft, or less, above the ground. This results in many bullets striking the ground on the range floor well in front of the backstop. In some cases, bullets have been known to ricochet at shallow angles and pass over the backstop. At SAFRs without backstops, bullets are scattered on the ground surface within approximately one-half mile downrange and with a fan of 45 deg to either side of the shooting positions. On ranges with backstops, many bullets are buried up to several feet deep in the backstop and the remainder are distributed behind the backstops in a pattern generally similar to ranges without backstops. Bullets in backstops tend to be

concentrated in pockets behind the targets. Bullets impacting on bullets already present in backstops causes both agglomeration into ragged masses of metal and fragmentation of bullets into particles of all sizes, including microscopic particles. In summary, at military rifle and machine gun ranges many bullets are found in the surface of the range floor between the shooter and the targets, many are distributed on the surface over a large area downrange, and if a backstop is present, many are buried up to several feet deep in the backstop. Occasional errant shots are fired into the air and these individual bullets may be scattered as far as several miles from the shooter.

Pistol ranges

Pistol ranges generally have a backstop at 50 yd or less. Most bullets are caliber of 9 mm, moderate velocity, and soft composition. They are deposited in the top foot or two of the backstop. Substantial quantities of pistol bullets are scattered on the surface of the range floor. Or, they can skip over the backstop, and are scattered on the surface within a few hundred yards behind and within the range fan to the sides of the backstop. Bullets in backstops tend to be concentrated in pockets behind the targets, where both agglomeration and fragmentation particles of all sizes occur.

Shotgun ranges

Trap, skeet, and sporting clays, and their variations are collectively referred to as shotgun sports. Although these sports are recreational, they are common at military facilities. All are based on clay targets thrown into the air and shot at with a charge of several shot pellets approximately 2 mm in diameter, in contrast to the single bullet approximately $\frac{1}{4}$ to $\frac{1}{2}$ in. in diameter fired by rifles and pistols. The shot is distributed widely across the range due to the different angles at which targets are thrown relative to the shooter. Some shot falls near the shooter. This increases in density to a point 375 to 600 ft from the shooter, and then gradually decreases again out to 680 ft in skeet and 770 ft in trap and sporting clays (National Shooting Sports Federation (NSSF) 1997). These distances assume flat ground, and will increase if shooting is downhill and decrease if shooting is toward a hillside, due to the pellet trajectory. Each trap field deposits shot in a funnel-shaped pattern covering approximately 4 acres (assuming flat ground), and about $1\frac{3}{4}$ acres are added for each adjacent overlapping trap field on a trap range. The shotfall zone of a single skeet field covers approximately 14 acres (assuming flat ground), and about

2 acres are added for each additional overlapping skeet field on a skeet range. In all the shotgun sports, shot are fired into the air and fall to the ground only with the force of gravity, so the shot pellets are found within the top few inches of soil.

A shotgun range of moderate size and use can easily throw 250,000 or more targets per year. At an average of approximately 28.35 grams (1 oz) of pellets in each shotgun shell, this would result in deposition of 7087 kg or 15,625 lb (7.8 tons), or more, of shot in the shotfall zone annually.

Composition of bullets and shot

A wide variety of ammunition types and compositions are used on the different kinds of SAFRs. However, each type of range is characterized by ammunition of the composition indicated in Table 1. These may usually be considered the primary metal contaminants of potential concern (COPC) at SAFRs. Bullets and shot are typically thought of as “lead.” However, bullets often contain copper and zinc in jackets around the lead, antimony as a hardening alloy with lead, and arsenic for malleability. Some military bullets contain iron in hard steel cores.

Table 1. Metallic makeup of various bullet sources.

Range Type	Typical metal concentration range in percent					
	Lead	Copper	Iron	Zinc	Arsenic	Antimony
Military Small Arms ¹	50-67	31-35	0-13	0	0	0.4-1
Pistol	14-79	16-82	0	6-28	<0.5	0.1-2
Shotgun	50-92	8-65	0	0	0.3-1.4	0.1-5.5
¹ ITRC 2003						

Lead in SAFR soils

Regardless of the type of SAFR, lead in SAFR soils differs from most industrial or mining lead contamination in that a large proportion of the lead is present in metallic, zero-valent form. Although this metallic lead is itself not very active environmentally, if left in place it can provide a potential long-term source of soluble lead.

Transport of metals from an SAFR is influenced by many factors including soil chemistry, soil acidity, water chemistry, metal speciation, atmospheric

precipitation, site topography, wet and dry cycles, freeze and thaw cycles, groundwater depth and velocity, and bullet type. Once the metal is dissolved, factors such as the soil organic content, metal oxides, metal carbonates and metal sulfides, soil clay content, and soil cation exchange capacity can affect metal solution chemistry. Each factor contributes to the retention or release of the metals by the soils. Lead in soils at SAFRs can be transported through several mechanisms.

Organization of report

This report has six subsequent chapters. Chapter 2 presents a detailed study on the characteristics of range soils and how these affect contaminant properties in the soils. Chapter 3 discusses the use of phytoremediation to treat range-contaminated soils, and summarizes several field studies. Chapter 4 describes the use of physical separation as a treatment approach, and details several field applications. Chapter 5 discusses the use of chemical stabilization, covering the literature in detail, and then summarizing laboratory studies. Chapter 6 covers the use of soil washing. Chapter 7 summarizes the report and provides a decision matrix.

2 SAFR Backstop Materials

Introduction

Soil characteristics, heavy metals contamination, and federal and local regulatory requirements each play a key role in the technologies used to remediate closed SAFR sites. In order to evaluate the relationship between soil type and metals contamination, 29 soils were prepared and evaluated. These were:

- eight reference soils (generated under controlled conditions)
- twenty-one range soil specimens (collected from SAFR backstop material).

These soils were characterized physically and chemically. The laboratory procedures included:

- Baseline soil chemistry and evaluation
 - soil particle size distribution
 - total metals concentrations
 - soil pH
 - soil total organic carbon (TOC)
- Three different leaching procedures
 - Toxicity characteristic leaching procedure (TCLP)
 - Distilled, de-ionized water suspend and settle (DDI S&S) leaching procedure
 - Synthetic precipitation leaching procedure (SPLP)
- Sequential metals extraction from the soils
- X-ray diffraction (XRD)
- Environmental scanning electron microscope (ESEM)
- Earthworm bioassay

Reference soil characterization

The eight reference soils were selected based on their different physical and potentially different chemical properties. They were collected from locations that were not associated with range activity and contained only background concentrations of metals. The pre-firing reference soils were

sieved to remove particles greater than 26.5 mm and were then placed into tared, plastic-lined, 55-gal drums for transport and storage. The chemical and physical properties of the reference soils, prior to the soil being impacted with lead bullets (excluding sand red river 02), are summarized in Table 2. The pre-firing soils were classified according to ASTM procedure D-2487 (ASTM 2000) as CL (clay), SM (sandy clay, glacial till, and sand), MH (muck), ML (loess), and SW (Red River 02).

Table 2. Reference soil properties prior to firing upon with lead bullets.

Property	Clay	Sandy Clay	Glacial Till	Sand	Muck	Loess
Specific gravity	2.72	2.65	2.52	2.62	2.58	2.73
Percent fines	88.9	24.2	47.6	22.3	91.5	98.9
Percent sand	8.3	75.8	48.8	77.2	8.5	1.1
Percent gravel	2.8	0.0	3.6	0.5	0.0	0.0
Unified soil classification	CL	SM	SM	SM	MH	ML
	Fine-grained clay, low plasticity	Coarse-grained silty sand, low plasticity	Coarse-grained silty sand, low plasticity	Coarse-grained silty sand, low plasticity	Fine-grained silt, high plasticity	Fine-grained silt, low plasticity
Percent total organic carbon (TOC)	0.427	0.134	1.8	1.24	5.16	0.87
Cation exchange capacity (CEC) meq/100g	11	9	20	8	27	5
pH	5.12	5.51	4.96	5.48	6.75	8.67
CA (mg/kg)	227	412	730	152	3200	2780
FE	3.17	1.76	8.68	1.88	5.87	2.36
MG	113	61	58.1	26.4	602	466
MN	1.58	0.26	2.67	0.4	0.37	1.97
K	27.7	61.4	61.1	12.7	210	17
NA	10.4	<4.00	32.9	<4.00	224	59.3
SO-4	31	20	66	19	168	21
CL	46	42	60	36	227	60
TKN	6.4	18	53	1.6	110	1
TP	4.7	8	15	1.5	43	13
OPO4	<0.3	<0.3	<0.3	<0.3	1.5	1.2
NH3-N	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
NO2/NO3	0.93	32	49	2.2	28	0.93

The pre-firing reference soils were microwave digested following USEPA SW 846 (1999) Method 3051 (2001). A modified version of EPA Method 200.7 was used to analyze the digestate samples for metals concentrations typically found in the M855 bullet composition using the Perkin-Elmer Optima 4300 Dual View (DV) Inductively Coupled Plasma (ICP) Optical Emission Spectroscopy (OES) (USEPA 1999). Table 3 presents the metals concentrations in the reference pre-firing soils. Loess Pb1 and Loess Pb2 came from the same location or borrow pit, so their chemical and physical properties prior to firing upon with lead bullets were essentially the same.

Table 3. Pre-firing reference soil metals concentrations.

Soil Type	Total metals concentration of bulk soil in ppm (mg/kg)					
	Antimony (Sb)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)
Clay	<0.600	20.70	10.500	12.00	25.90	53.30
Sandy clay	<0.600	18.60	20.000	16.30	18.50	34.50
Glacial till	<0.600	10.40	9.870	7.41	13.60	33.00
Sand	<0.600	6.80	8.150	42.80	1.86	7.09
Muck	<0.600	28.40	12.400	19.10	18.40	101.00
Loess Pb1/Pb2	<0.600	2.18	0.436	1.27	1.27	<2.00
Sand Red River 02	1.039	5.01	1.800	9.96	2.18	4.97
Soil Type	Iron (Fe)	Manganese (Mn)	Molybdenum (Mo)	Vanadium (V)	Tungsten (W)	
Clay	37,800	146.00	0.384	26.10	<40.0	
Sandy clay	15,600	284.00	0.234	30.30	<40.0	
Glacial till	13,600	562.00	0.471	15.70	<40.0	
Sand	5,190	26.60	0.218	11.60	<40.0	
Muck	33,200	913.00	0.392	36.20	<40.0	
Loess Pb1/Pb2	1,210	8.80	<0.200	3.27	<40.0	
Sand Red River 02	3,335	77.77	0.270	6.91	<40.0	

In order to produce simulated berm soils using these eight pre-firing reference soils, sufficient rounds were fired into a known mass of each soil to produce post-firing soils that contained approximately 10,000 mg/kg lead delivered through bullet impact with the soil (Table 4). The pre-firing reference soils were loaded into a catch box positioned at a dedicated test range. The soils were then subjected to M-16 (M855 bullets) rifle fire at a distance of approximately 25 m (82 ft) to 98.5 m (323 ft) into the catch

boxes, with lead bullets impacting the soils. The post-firing reference soils or “simulated berm soils” were produced in separate studies (Armament Research, Development and Engineering Center (ARDEC) Picatinny Arsenal, unpublished, and ERDC-Vicksburg, unpublished) and made available for the research described in this report. The metal concentrations in the post-firing reference soils are experimental values that are not intended to replicate conditions at any particular site. Instead, they are intended to provide eight different soils types that have been subjected to similar bullet loading conditions. The reference soils were then used in laboratory studies and experiments to generate data and knowledge to assist with understanding the physical and chemical interactions within the post-fired-on soil matrix and if possible compare and understand the relationships in SAFR soils.

Table 4. Reference soil preparation to achieve 10,000 mg/kg lead in the soil after being fired upon with lead bullets.

Soil	Bullet Type	Range to Target (m)	Dry Mass (kg)	Rounds Fired	Calculated Lead Concentration (mg/kg)
Loess Pb1	Lead	98.5	222.6	1113	10,000
Muck	Lead	98.5	500.8	2504	10,000
Clay	Lead	98.5	350.8	1754	10,000
Glacial till	Lead	98.5	581.6	2908	10,000
Sandy clay	Lead	98.5	628.2	3141	10,000
Sand	Lead	98.5	253.2	1266	10,000
Loess Pb2	Lead	25.0	222.6	1113	10,000
Sand Red River 02	Lead	<25.0	1270.1	5800	9,133

After generating reference soils that had lead concentrations of approximately 10,000 mg/kg, the reference soils were again microwave digested (EPA SW 846 Method 3051) after passing them through a 1.7-mm (No. 12) sieve (USEPA 1999). The digestates were analyzed for metals associated with the M-16 bullet using the ICP spectroscopy (USEPA 1999). Throughout the report, the metals concentrations of copper, antimony, zinc, and manganese are provided in tables and figures separate from the lead, since the lead concentrations were typically much higher than the other metals (Figures 3 and 4). At a minimum, triplicates were used in the metals digestion procedure, and outlier data values were removed from average metals concentrations.

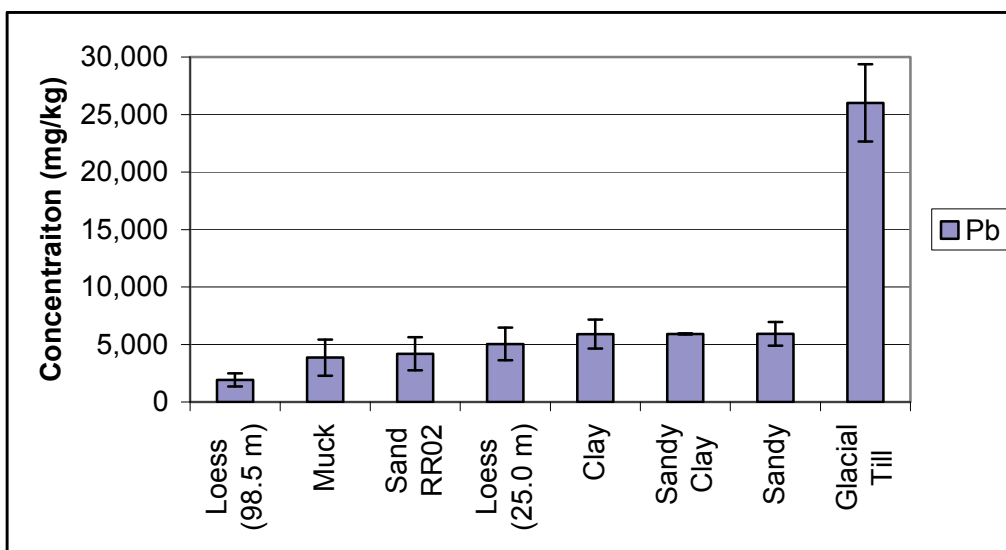


Figure 3. Total lead (mg/kg) in the digested reference soils passing through a 1.7-mm sieve.

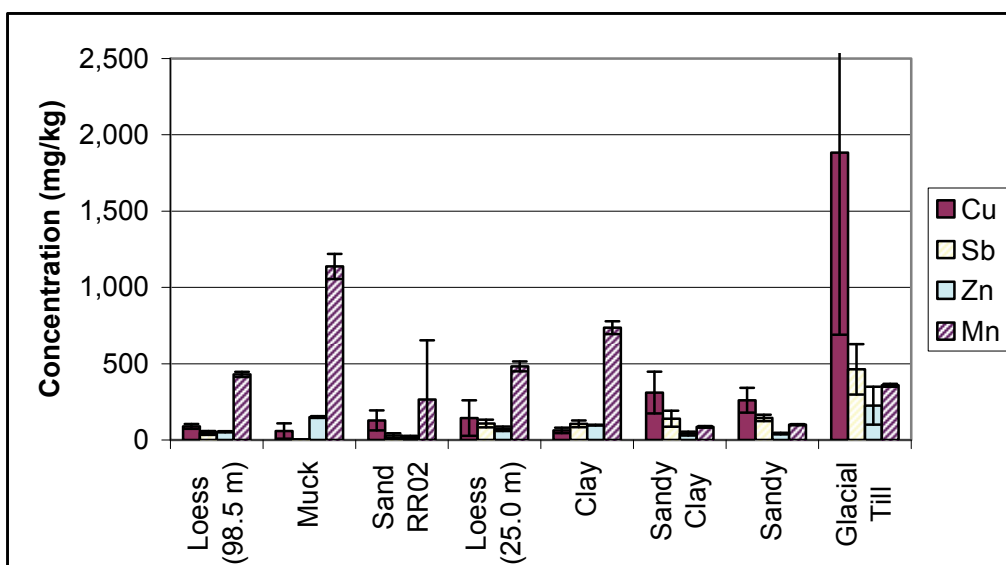


Figure 4. Total copper, antimony, zinc, and manganese (mg/kg) in digested reference soils passing through a 1.7-mm sieve.

The coarseness of the soil must be taken into account when determining the metals concentration. This is done by analyzing the soil fraction that passes through a 1.7-mm sieve. The calculated lead concentrations in the soils were based on the number of rounds fired, their lead compositional mass, and the amount of soil that the bullets were fired into. The expected lead concentration for the reference soils was calculated at approximately 10,000 mg/kg.

Soil that has large rocks associated with it, such as glacial till, will skew the results in two ways:

1. Bullets hitting rocky soil will fragment more than bullets hitting non-rocky soil; therefore a larger quantity of fragmented bullet material will pass through the sieve, raising the metals concentration in the less than 1.7-mm fraction.
2. In addition, the rocks in the soil will themselves be less likely to pass through the 1.7-mm sieve, thus decreasing the mass of soil present in the less than 1.7-mm fraction and further increasing the metals concentration.

To correct for this skewing effect, the soil fraction retained on the 1.7-mm sieve was weighed and that mass was divided by the total mass prior to sieving in order to determine the percentage of the soil that did not pass through the sieve. The percentage for each soil was then used to normalize the actual less than 1.7-mm metal concentrations to produce the "mass adjusted" metal concentrations (Table 5). The estimated lead concentration of 10,000 mg/kg and the "mass adjusted" metal concentrations were used in order to arrive at an estimate of the percentage of lead that passed through the 1.7-mm sieve. This percentage of lead passing through the 1.7-mm sieve is also an indicator of the degree of fragmentation associated with the different soil types. In general, the fine-grained soils fragmented the bullets less than the coarse-grained soils.

Table 5. Estimated percentage of lead passing through the 1.7-mm sieve.

Soil	Percent Soil Mass Passing 1.7 mm sieve	Pb in < 1.7 mm Soil Fraction (mg/kg)	Adjusted Pb in < 1.7 mm Soil Fraction (mg/kg)	Expected Pb in Soil Based on Number of Bullets per Soil Mass (mg/kg)	Estimated Percent of Pb Passing Through 1.7 mm Sieve
Loess Pb1	100	1,918	1,918	10,000	19
Muck	100	3,857	3,857	10,000	39
Sand Red River 02	86.7	4,198	3,639	9,133	40
Clay	76.2	5,911	4,504	10,000	45
Loess Pb2	100	5,050	5,050	10,000	51
Sandy Clay	100	5,924	5,924	10,000	59
Sandy	99.7	5,930	5,912	10,000	59
Glacial Till	47.6	26,011	12,381	10,000	124

The weapon and bullet type fired into an impact area can affect the amount of lead that is potentially released from a range. For instance, a shotgun skeet range will contain mainly small pellets associated with the shot that falls to the ground, thus primarily providing a corroded form of lead to the surrounding environment. Similarly, the M-9 round fired from a handgun has potentially less fragmentation than the high velocity rounds of the M-16 and/or M-60 type weapons systems (M-249, M240B, and M-60). The M-9 bullets introduced into the berm soil will be primarily a source of corroded lead, but may also introduce particulate lead into the berm. Conversely, the high velocity M-16 and M-60 rounds will be a source of both corroded and particulate lead associated with the bullets and bullet fragments. The intent here is not to provide a lesson on ballistics, but to demonstrate that different rounds will impact the ground and fragment in different ways depending on the impact berm soil conditions. Fragmentation or lack of fragmentation can directly affect the rate at which bullets corrode and their subsequent soluble or particulate release of metals into the environment.

The results of metals digestion and ICP analysis indicate that the metals concentrations varied by range (Figures 5 and 6). The Barksdale 03 soil, M-16 SAFR, was obtained after the berm had been reworked and there was minimal opportunity for training to occur on the range. This may explain why the total lead concentrations in this soil are not very high (Figure 5). The Hamilton SAFR lead concentrations will be discussed within the earthworm bioassay section of this chapter. Because three replicates (minimum) were used in determining the metals concentration, outlier data values were removed from the average metals concentrations.

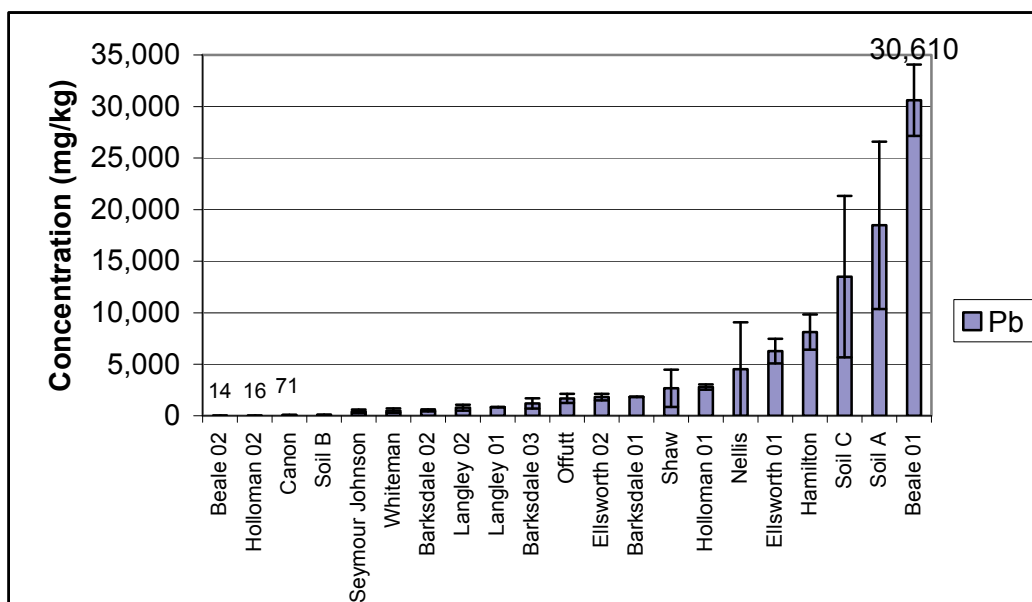


Figure 5. Total lead concentration (mg/kg) in the SAFR digested soils.

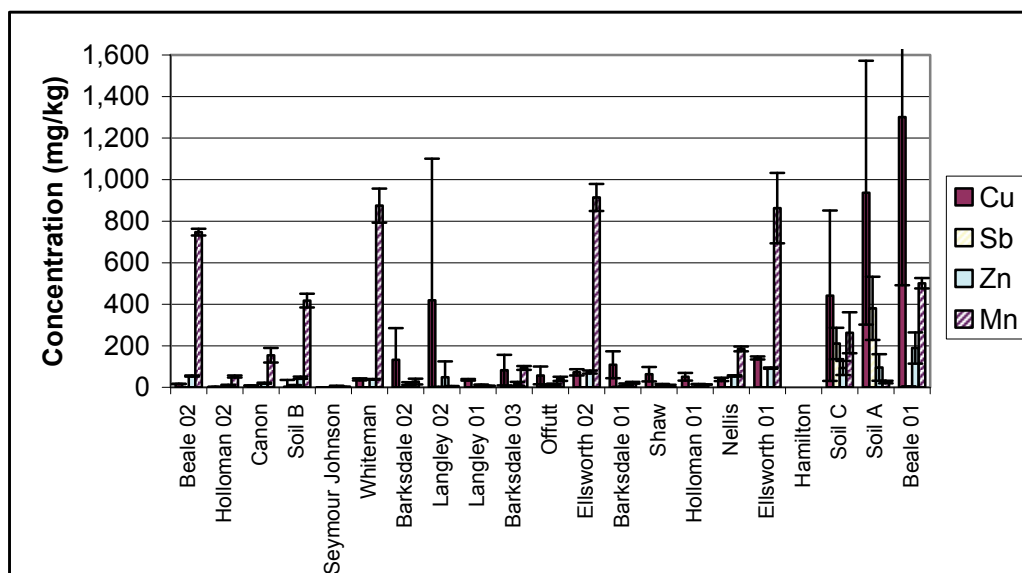


Figure 6. Total copper, antimony, zinc, and manganese concentrations (mg/kg) in the SAFR digested soils.

Soil and associated lead particle size distribution

There are many different ways that one can separate a soil by sieve size fractions. For this study, two sieve sizes common to all the studies were the 75- μm (No. 200) sieve and the 250- μm (No. 60) sieve. Most of the results presented in this chapter are based on the No. 60 sieve separation.

Soil classification based on the No. 200 sieve

The soils were subjected to particle size distribution analysis following a modified version of ASTM C136-01 (2001) using standard sieve sizes ranging from 6.5 mm to 63 μm (No. 230). A soil is typically classified into one of two categories (coarse-grained or fine-grained) relative to the percentage of soil that either passes through or that is retained on a 75- μm (No. 200) sieve. A coarse-grained soil will retain more than 50 percent of the soil on the No. 200 sieve, while a fine-grained soil will pass more than 50 percent of the soil. Both the reference and range soils provided fine and coarse-grained soils, as shown in Table 7.

Table 7. Soil classification based on No. 200 sieve.

Soil Type	Coarse-Grained Soil	Fine-Grained Soil
Reference Soil	Sandy Clay	Clay
	Glacial Till	Muck
	Sand	Loess Pb1
	Sand Red River 02	Loess Pb2
Range Soil	Barksdale 02	Barksdale 01
	Beale 01	Barksdale 03
	Beale 02	Ellsworth 01
	Canon	Ellsworth 02
	Holloman 01	Holloman 02
	Langley 01	Offutt
	Langley 02	Whiteman
	Nellis	
	Seymour Johnson	
	Shaw	

Soil classification based on No. 60 sieve

Another common sieve size, 250 μm (No. 60), was used to discriminate between fine and coarse soil particles associated with SAFR soils. For the purpose of this study, the 250- μm sieve was used to separate the reference and range soils into two categories:

Category 1. 50 percent passing: Greater than 50 percent passing through the No. 60 sieve.

Category 2. 50 percent retained: Greater than 50 percent retained on the No. 60 sieve.

Four of the reference soils fall into Category 1 and four fall into Category 2 (Figures 7 and 8).

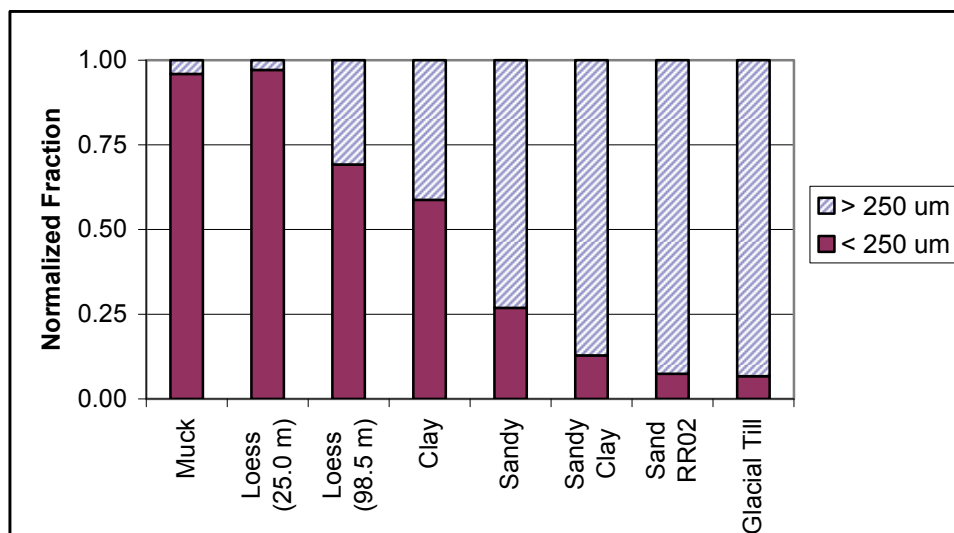


Figure 7. Reference soils particle size distribution with respect to the percent soil retention on and passing through the 250- μ m sieve.

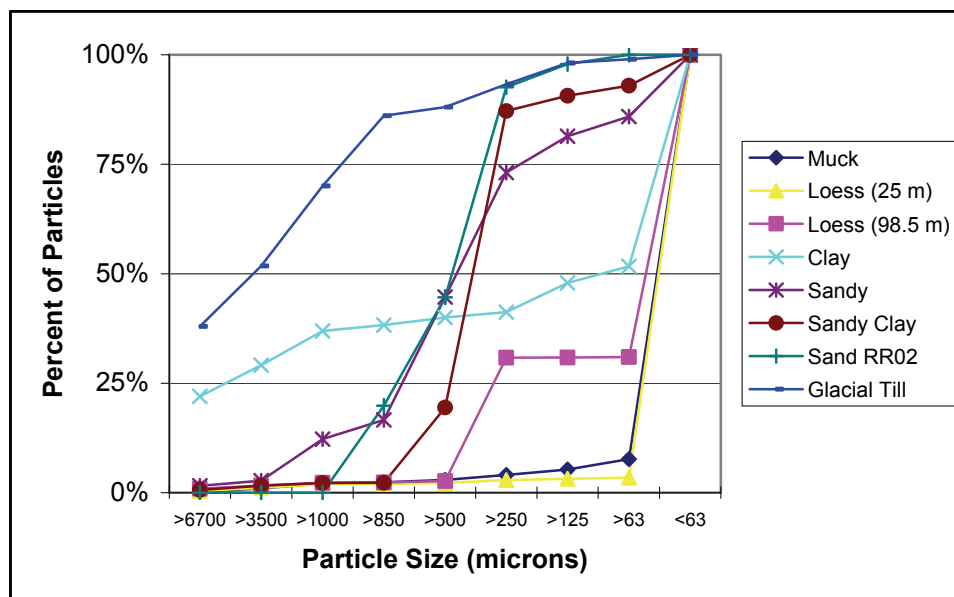


Figure 8. Particle size distribution for reference soils.

Twenty of the SAFR soils were also compared by using the 250- μ m particle size reference point. Fifteen of the range soils fell into Category 1 and five

fell into Category 2, having greater than 50 percent retained on the No. 60 sieve (Figure 9). The general trend evident from this study is that active range berm soil tends to have a smaller particle size distribution than the reference soils, possibly due to continuous loading of bullets into the impact berm area.

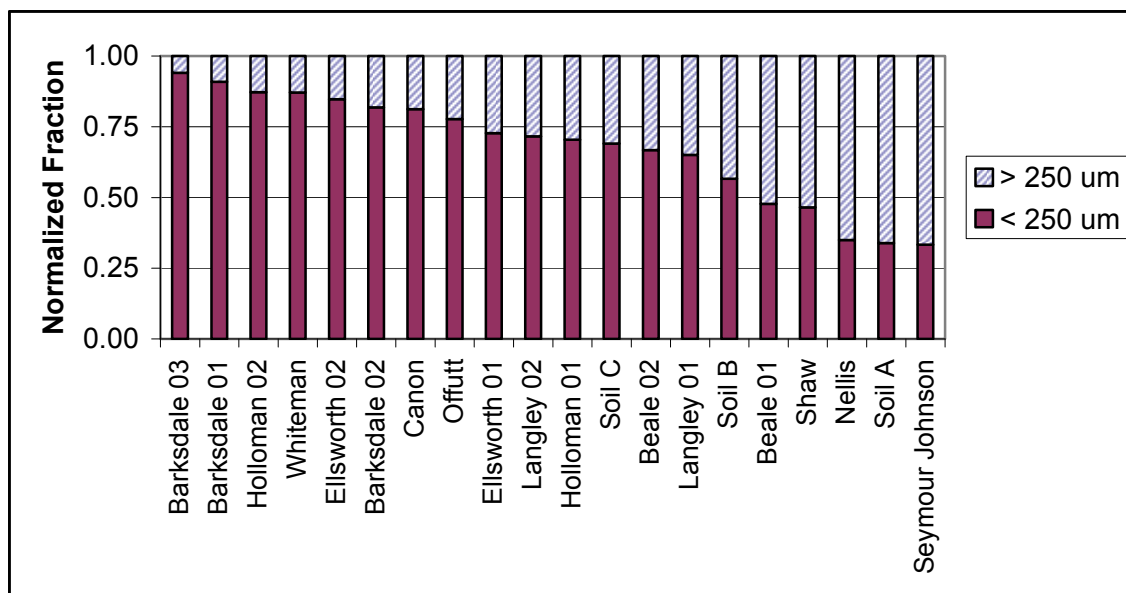


Figure 9. SAFR soils particle size distribution with respect to the percent soil retention on and passing through the 250- μm sieve.

Lead particle size distribution

The reference soils were also analyzed for metals by particle size using USEPA SW 846 Method 3051 (USEPA 1999). The particle size fraction was digested and analyzed using the ICP. In general, for the reference soils, as the particle size shifts from the smaller to larger particles, there is also a shift in lead (Figure 10).

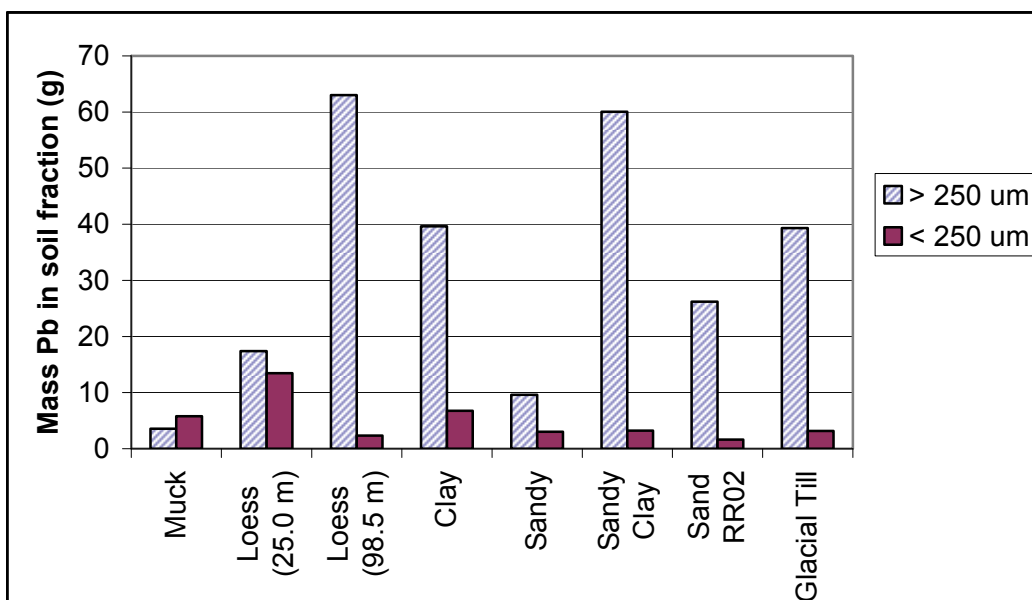


Figure 10. Reference soil lead concentration distribution associated with the 250-μm size fractions.

For the range soils, unlike the reference soils, there is no apparent relationship between the fraction of lead in the > 250 μm and the < 250 μm size (Figure 11). The weapons type and unknown loading at the range does not allow for a good comparison between these systems.

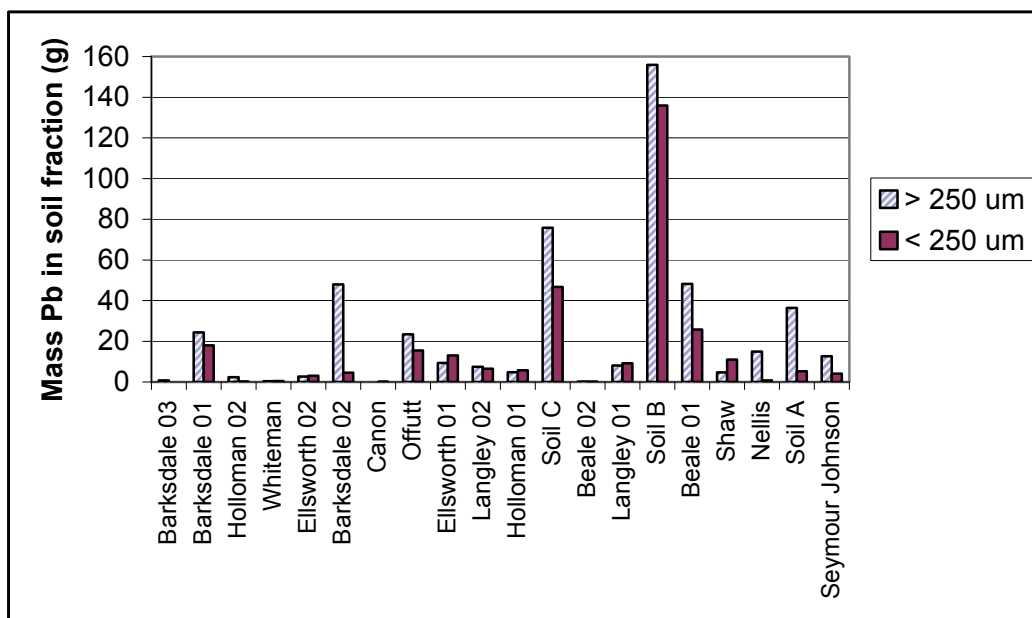


Figure 11. SAFR soil lead distribution associated by different size fractions for the 250-μm sieve.

Fort Lewis particle size distribution

The majority of lead in about one third of the soil was retained on a 37.5-mm (1-1/2-in.) sieve; this portion contained only background lead contamination and was capable of reuse on site. The soil that passed through a 37.5-mm sieve and was retained on a 11.2-mm (7/16th-in.) sieve contained bullet fragments that were large enough to be separated with a magnet. This portion of the soil was also left on site after the physical separation of the bullets from the soil. The remaining soil that passed through the 11.2-mm sieve was chemically stabilized with an amendment and was reused in SAFR berm construction projects. Understanding the particle size characteristics of the berm soil and the type of rounds present can influence the scope of cleanup at a SAFR.

Metals leachability

Three metals leachability tests were performed on the reference and range soils: TCLP, SPLP, and DDI S&S. These leachability tests help to determine the metals' leaching characteristics from the soils under buffered acidic conditions, non-buffered simulated acid rain conditions, and neutral water conditions, respectively. Weathering (aging) of the soils also affects the leachability. The range soils are naturally weathered under different temperature ranges and rainfall amounts at their respective geographical locations throughout the United States. In order to compare the effects of weathering on leaching, seven of the reference soils, excluding sand red river 02, were artificially aged. To accelerate the aging process, the soils were treated for 90 days in an environmental chamber at a temperature of 55 °C. They were wetted with 23 to 42 L of DDI water (1:2, w:vol) and an additional 6 to 8 L of DDI water was poured into the aging vessel every week for the 90-day treatment. These artificially aged soils could then be used to investigate the differences between leaching from weathered soils and leaching from freshly fired-upon soil.

TCLP

The TCLP (USEPA SW 846 Method 1311, 1999) was designed to determine the mobility, under specific conditions at a MSW landfill, of both organic and inorganic analytes present in liquid, solid, and multiphase wastes. The focus of this project was to investigate the inorganic analytes present in the reference and range soils. Because of the heterogeneity of these soils, a significant mass of soil was required in order to reduce statistical

deviation in replicate samples. Each TCLP was performed in triplicate (minimum). Forty grams of soil was mixed with 400 mL of the TCLP extraction solution (glacial acetic acid and 1N sodium hydroxide) at a pH of 4.93 ± 0.05 in a large-mouth, plastic bottle. The samples were placed on a tumbler for 18 ± 2 hr. After tumbling, an aliquot of the aqueous portion was decanted and then centrifuged at 4000 revolutions per minute (rpm's) for 20 minutes. Approximately 60 mL of supernatant was filtered using a 0.45- μm syringe filter and analyzed for metals by using the ICP method for liquids.

For the reference soils, as less soil passed through the No. 60 sieve, there was a tendency for more lead to be leached out of the soil under TCLP conditions (Figure 12). An $r^2 = 0.73$ was obtained after fitting a linear relationship for the increased TCLP lead associated with the increase in soil retained on the No. 60 sieve (Figure 12). The increased TCLP Pb concentration associated with particle size can be a factor of many soil conditions such as CEC and TOC. This phenomenon may also be associated with the manner in which bullets make impact with the different soils and how they fragment and/or break up differently. It is more likely that a bullet will break apart or fragment when fired into a coarser soil than a finer soil, notwithstanding that dry clay soil types can also fragment bullets. In addition, the smaller-sized soil particles will have relatively more surface area that can potentially react with and/or adsorb soluble metals.

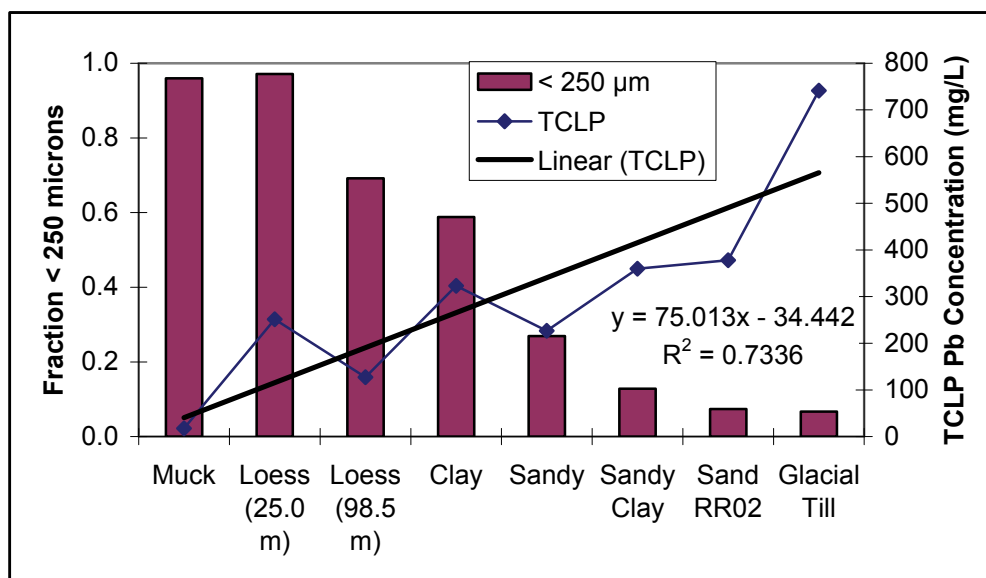


Figure 12. Reference soil TCLP lead concentrations compared to the fraction of soil passing through the 250- μm sieve.

For the SAFR soils, there was no apparent relationship between particle size and the TCLP lead concentration (Figure 13) as there was for the reference soils. Normalizing the lead concentration in both the TCLP and Total Pb assays did not provide any additional information and confirmed that site-specific soil geochemistry (TOC, CEC) is the limiting parameter in leachability.

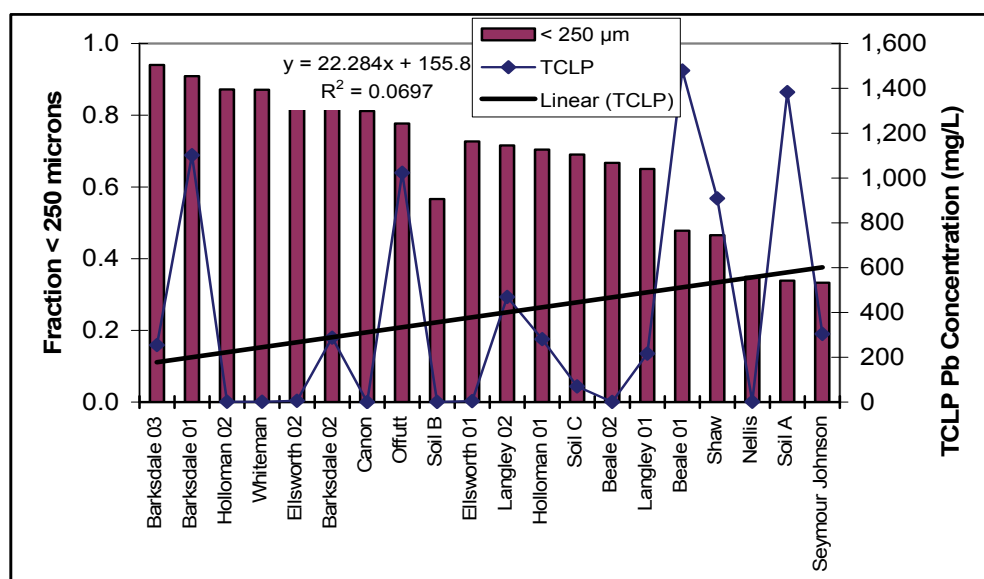


Figure 13. Range soil TCLP lead concentrations compared against the fraction of soil passing through the 250-μm sieve.

Both the reference and range soils showed an increase in TCLP lead concentration as the total lead in the soil increased (Figures 14 and 15), although this relationship was stronger in the reference soils ($r^2 = 0.5311$). Other factors that affect the TCLP lead concentration are the soil chemistry, soil pH, soil buffering capacity, and the soil particle size distribution.

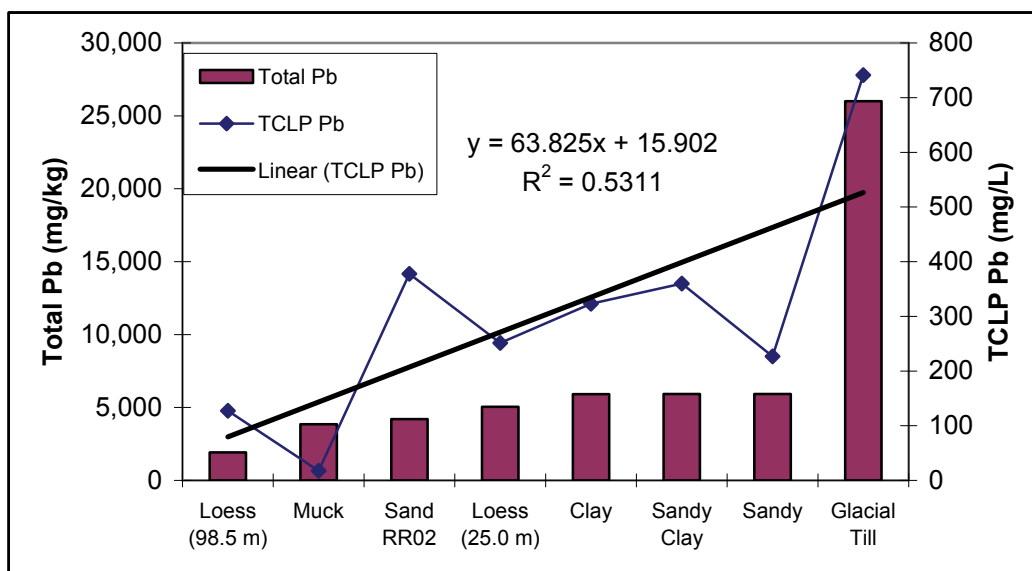


Figure 14. Total lead vs. TCLP lead concentration for reference soils.

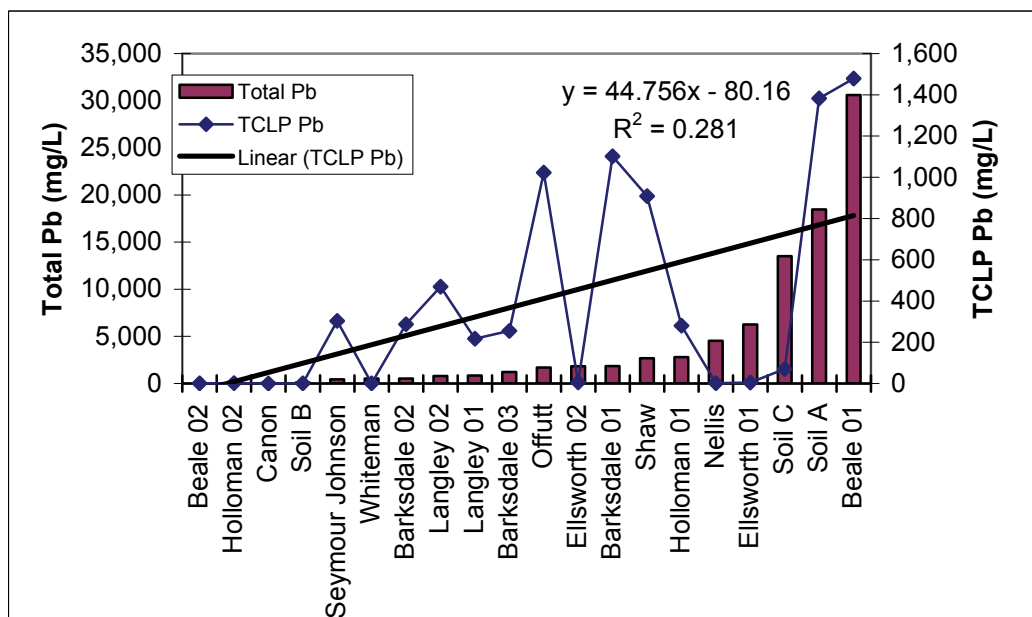


Figure 15. Total lead vs. TCLP lead concentrations for range soils.

Two trends were noted concerning the reference soil TOC and CEC (Table 2). In general, as the soil TOC increases, both the potential sorption capacity of the soil for lead and the buffering capacity of the soil also increase. Both of these effects combine to reduce lead removal by TCLP extraction. Therefore, as the TOC of the soil increased, the TCLP lead concentration decreased (Figure 16). The exceptions to this trend are glacial till and muck. Glacial till had an average TCLP lead concentration of 741-mg/L. Glacial till is different from the other soils due to the large

rocks in the soil that increase the bullet fragmentation upon impact. This makes more lead available for attack by the aggressive TCLP solution.

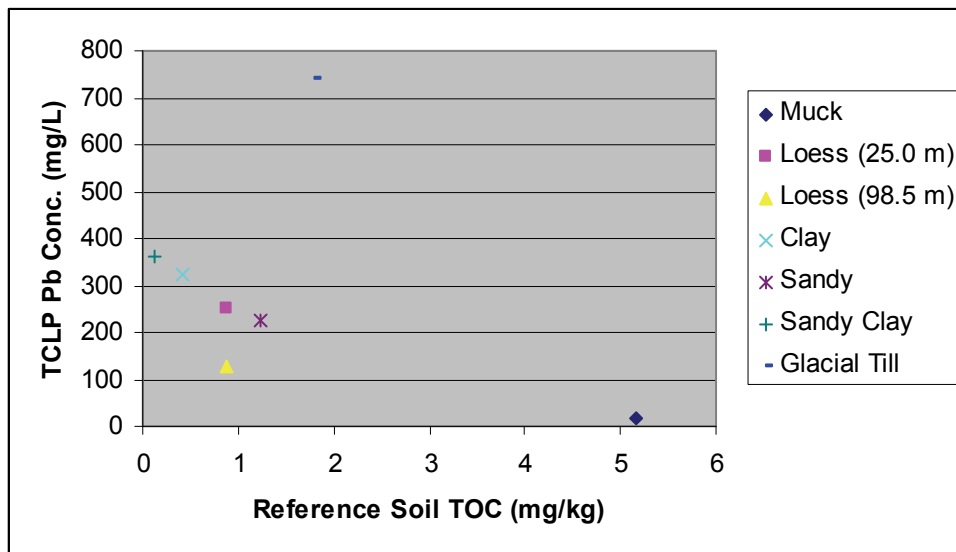


Figure 16. Reference soil TCLP lead concentration (mg/L) vs. soil TOC (mg/kg).

In contrast, as the reference soil CEC increased, so did the TCLP lead concentration (Figure 17). The exceptions are, again, glacial till and muck. Muck has a high CEC of 27-meq/100 g. In addition, muck has a high TOC content of 5-mg/kg that also affects the TCLP lead concentration, as mentioned above. Potentially, the TOC capacity for either Pb sorption and/or buffering capacity of the TCLP greatly reduces Pb solubility.

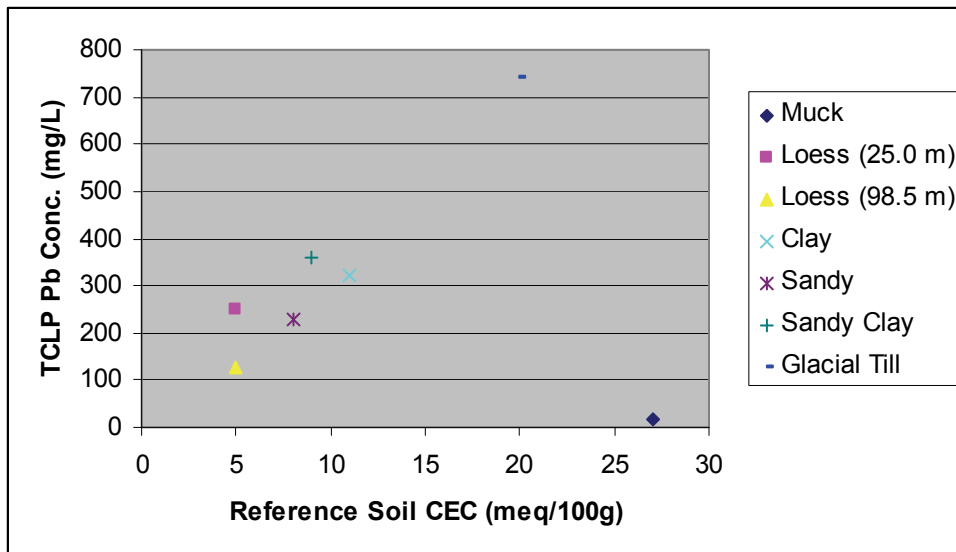


Figure 17. Reference soil TCLP lead concentration (mg/L) vs. soil CEC (meq/100g).

Some of the range soils that had a neutral pH (between 6 and 8) had significantly greater leaching of lead under the TCLP conditions than others (Figure 18). This indicates that more than just a neutral pH is required to stabilize the lead in range soils, if TCLP is used as a measure to characterize the soils leaching capacity. In addition, while some range soils under more acidic pH conditions released large amounts of lead under the TCLP conditions, others did not.

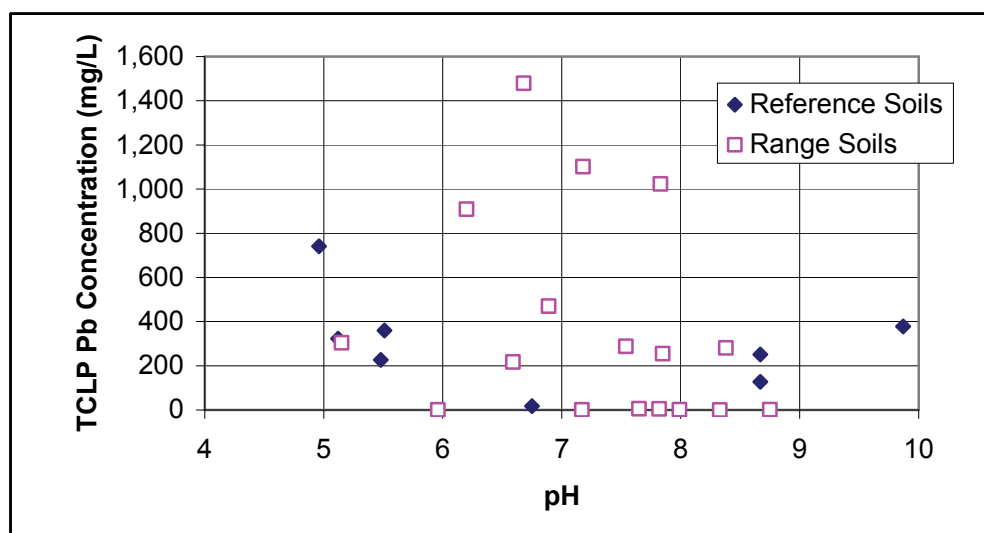


Figure 18. TCLP lead vs. pH of reference and range soils.

The reference soils had a lower TCLP Pb concentration than the range soils, 303 ± 214 mg/L and 390 ± 500 mg/L, respectively. While the average TCLP comparisons do not account for different firing range conditions such as weapons type and firing line proximity to the range berm, they do demonstrate the weathering effects on range soils and, as mentioned above, the effect of TOC and CEC on the lead released under TCLP.

Synthetic precipitation leaching procedure (SPLP)

The SPLP (USEPA SW 846 Method 1312, 1999) is a leaching procedure that is similar to the TCLP in the sample preparation and extraction process. The difference lies in the extraction fluid used. While the TCLP uses a highly buffered and mildly acidic solution (i.e. acetic acid), the SPLP uses an extraction fluid that is less buffered than the TCLP solution and is based on the physical location of the site to be characterized (east or west of the Mississippi River). This project used the eastern SPLP solution, an unbuffered solution of sulfuric and nitric acids at a slightly more acidic pH of 4.2 ± 0.05 than the TCLP solution. The SPLP typically is employed to

more closely simulate groundwater-leaching effects. SPLP extractions were carried out over an 18 ± 2 hr tumbling period. Since the SPLP solution is not as buffered as the TCLP solution, the SPLP solution tends to take on the soil pH, in a similar manner to the DDI S&S leaching solution. For this reason, the SPLP is a less aggressive leaching technique than the TCLP.

Unlike the TCLP results, there are no apparent trends associated with the particle size fractions and the SPLP Pb concentrations (Figures 19 and 20).

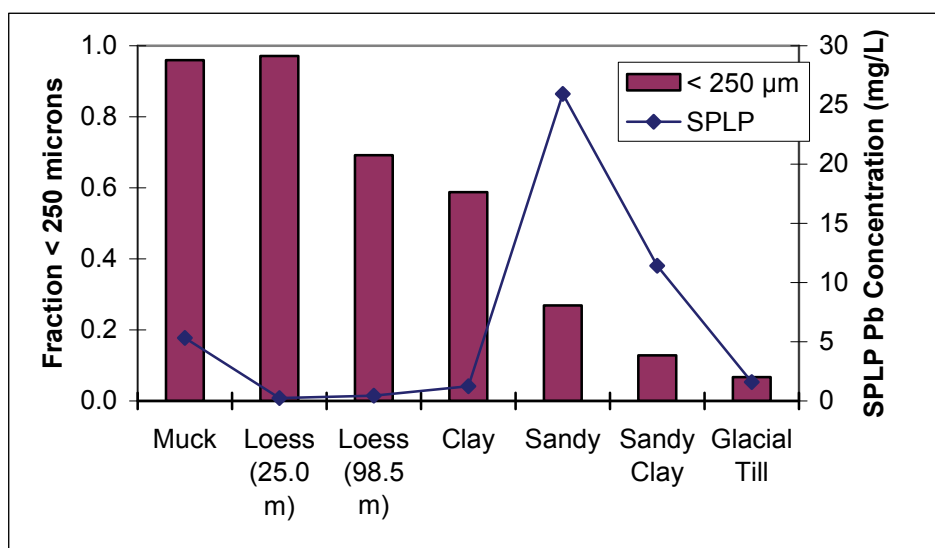


Figure 19. Reference soil SPLP lead concentrations compared to the fraction of soil passing through the 250-μm sieve.

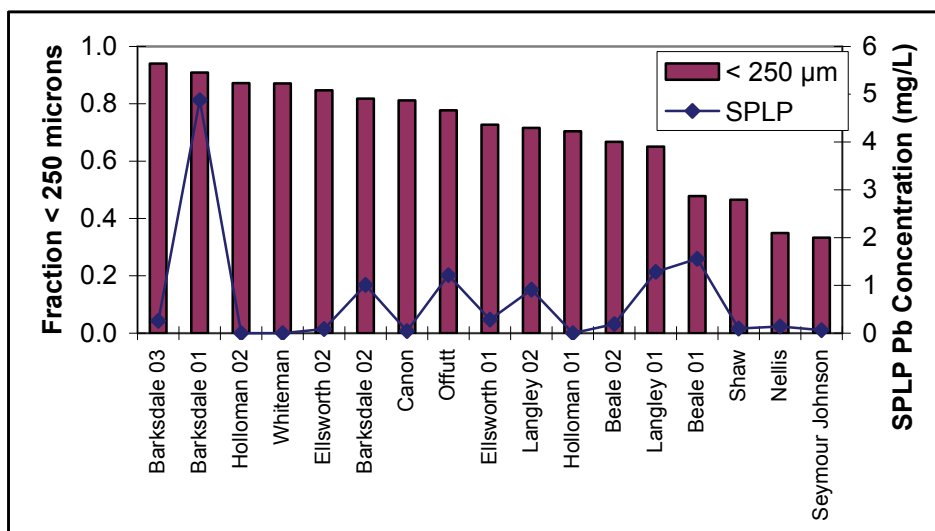


Figure 20. Range soil SPLP lead concentrations compared to the fraction of soil passing through the 250-μm sieve (no SPLP data for Soils A, B, and C).

When the SPLP lead concentration is plotted against the soil TOC and CEC (Figures 21 and 22) there are no apparent trends. The exception is a sandy soil that has both a moderately low TOC of 1.24 mg/kg and a low CEC of 8 meq/100g. With both of these low values, the sandy soil produced the highest lead concentration in the SPLP solution, with a pH just below 6.

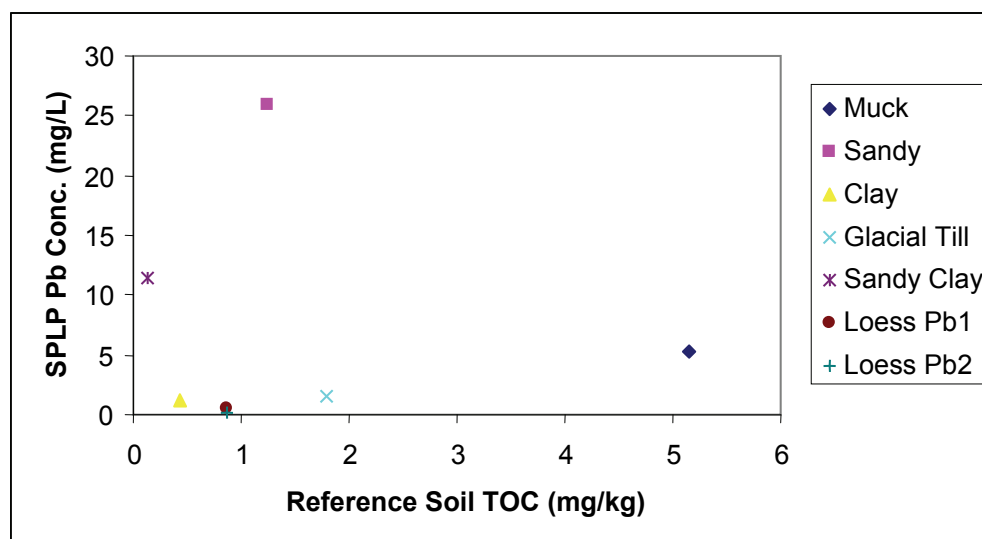


Figure 21. Reference soil SPLP lead concentration (mg/L) vs. soil TOC (mg/kg).

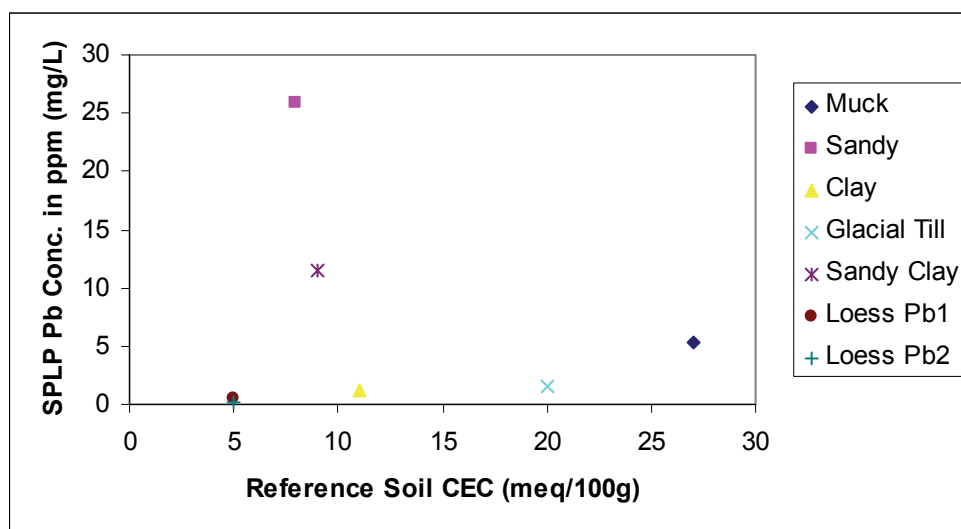


Figure 22. Reference soil SPLP lead concentration (mg/L) vs. soil CEC (meq/L).

Unlike the TCLP, the reference soils had higher SPLP lead concentrations than the range soils at 6.6 ± 9.4 mg/L and 0.6 ± 1.1 mg/L, respectively. As seen in Figure 23, the range soils were less likely to release lead into the SPLP solution than the reference soils. This is likely to be a result of soil

aging. Lead in the range soils has had more time than lead in the reference soils to form complexes with soil components. Since the SPLP solution is a less aggressive leaching solution than the TCLP solution, it is less likely to be able to remove this lead.

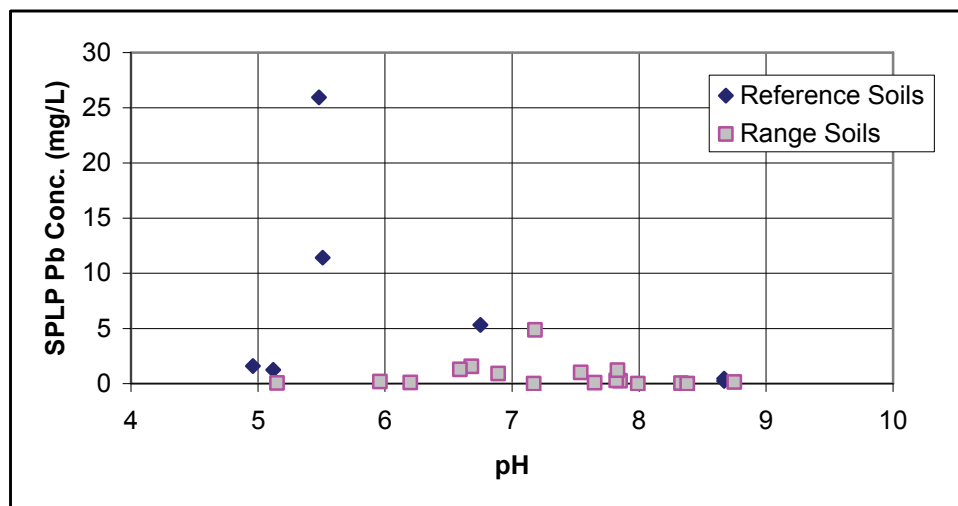


Figure 23. SPLP lead concentration vs. pH for reference and range soils.

Distilled, de-ionized water suspend and settle (DDI S&S)

The DDI S&S leaching procedure is similar to the EPA leach testing (TCLP and SPLP). DDI S&S quantifies soluble heavy metals in soils, but it does not involve continuous shaking in a sealed container or aggressive solvents. Forty grams of soil was combined with 400-mL of DDI water in a large-mouth, plastic bottle. After shaking for 1 hr on a shaker table, the bottle was removed and the soil and water mixture was allowed to settle overnight. After settling for 18 ± 2 hr, an aliquot was removed from the mixture and filtered through a $0.45\text{-}\mu\text{m}$ syringe filter. The filtered solutions were analyzed as described above for heavy metals and the solution pH was determined using a pH electrode. The DDI S&S is a less aggressive leaching procedure than either the TCLP or the SPLC due to the fact that water, not an aggressive solvent, is used and the soil and water are mixed for a short time and then allowed to equilibrate for 18 hr.

No apparent trend is associated with the particle size fractions and the DDI S&S leaching techniques (Figures 24 and 25), except for the reference soils that were roughly classified as sand. These soils had a larger lead concentration in the leachate from the DDI S&S leaching procedure.

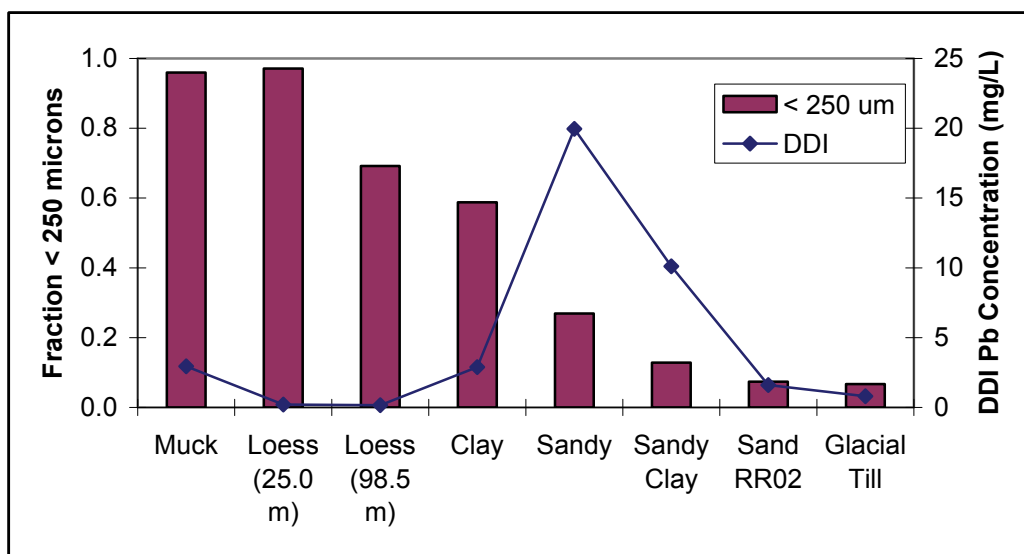


Figure 24. Reference soil DDI S&S lead concentrations compared to the fraction of soil passing through the 250-µm sieve.

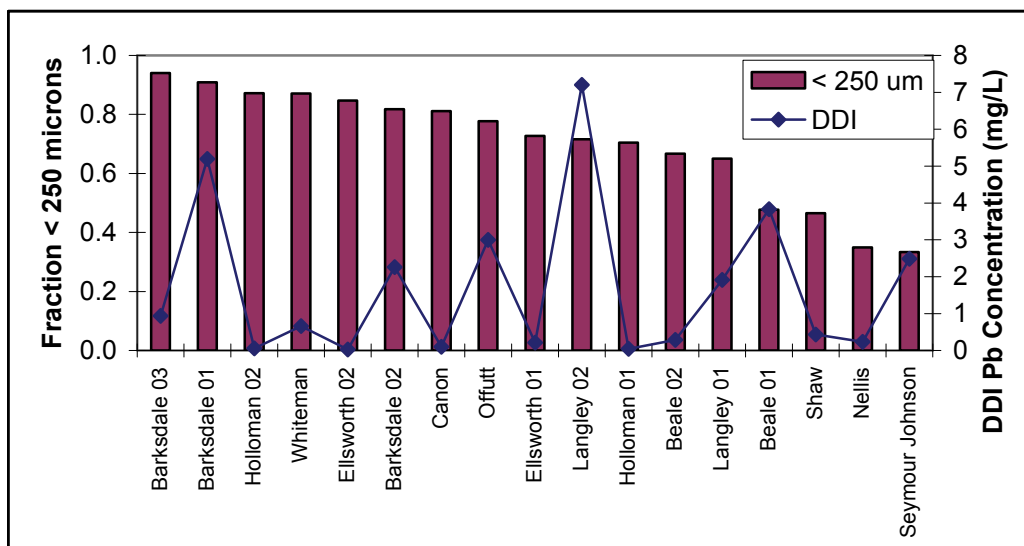


Figure 25. Range soil DDI S&S lead concentrations compared to the fraction of soil passing through the 250-µm sieve.

It appears that soil pH does not have a significant effect on the DDI S&S leaching of lead (Figure 26) from the range soils. Unlike the TCLP lead concentrations, the average DDI S&S lead concentration was greater for the reference soils than for the range soils at 4.8 ± 6.9 mg/L and 1.6 ± 2.0 mg/L, respectively. Again, these average numbers provide a general comparison and support the argument that aging and soil conditions do have an effect on the leaching of Pb from the soils under the non-aggressive DDI S&S leaching procedure. It appears that the reference soils may have had more

readily available lead for leaching under the DDI S&S procedure than the range soils, probably due to the different aging that the range and reference soils were subjected to.

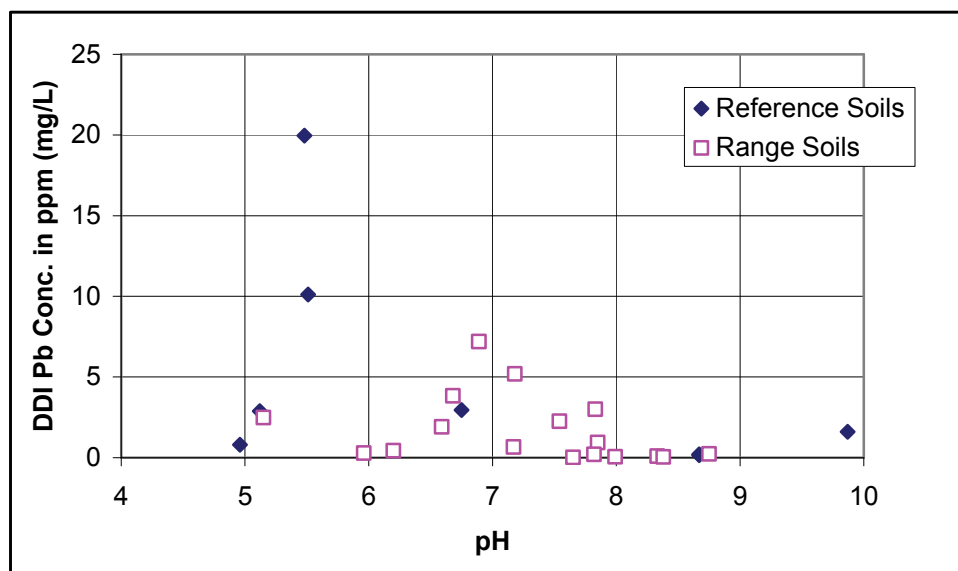


Figure 26. DDI S&S lead concentration vs. soil pH.

For the reference and range soils, there were similarities (Figures 23 and 26) for the DDI S&S and SPLP lead concentration between

- the TOC and CEC values
- the pH results

Plotting the SPLP lead concentration versus the DDI S&S lead concentration (Figure 27) for the reference soils results in an almost linear profile for the soils, with an $r^2 = 0.97$. The range soils have an $r^2 = 0.42$ and a more scattered plot (Figure 28). The reference soils are considered to be new soils that have not been weathered and/or aged for a significant amount of time under natural environmental conditions. Therefore, very little natural lead corrosion has occurred in the reference soils. The range soils have been exposed to environmental conditions and have weathered for a longer time. The different aging of the range and reference soil may help to explain why the range soils SPLP and DDI S&S results are more scattered.

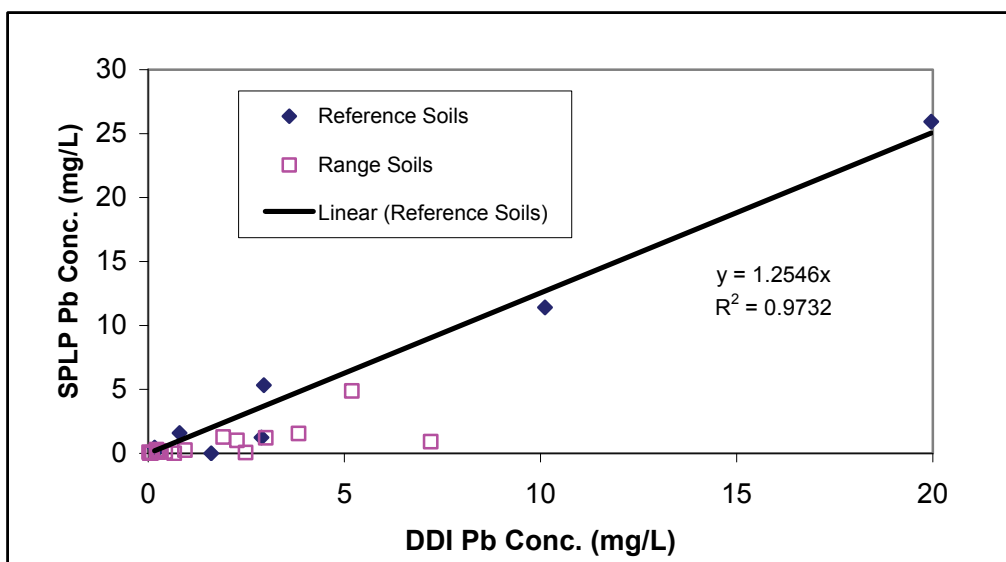


Figure 27. SPLP vs. DDI S&S lead concentrations for reference and range soils.

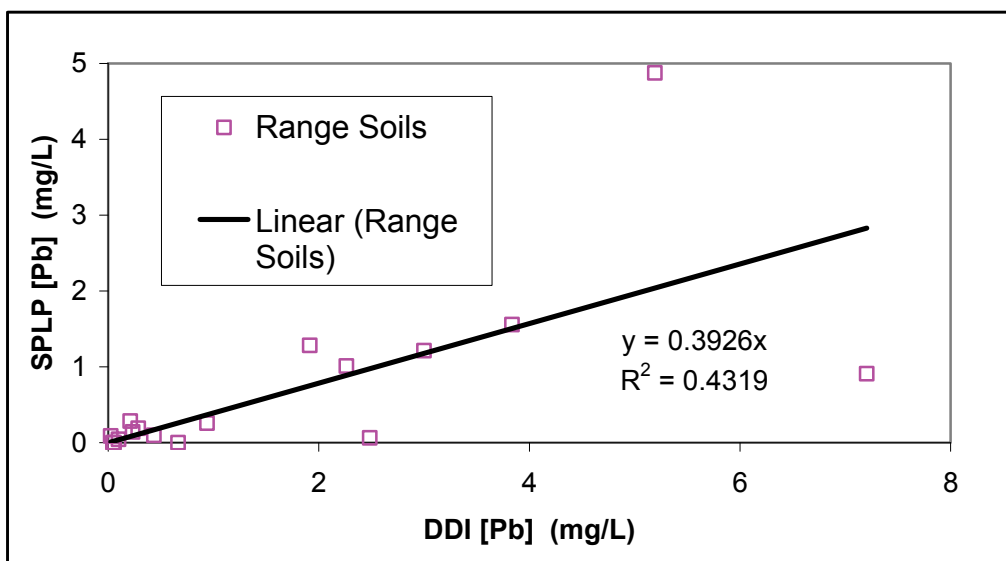


Figure 28. SPLP vs. DDI S&S lead concentrations for the range soils.

Sequential extraction

Sequential extraction separates the metals of a soil into operationally defined fractions. In this study, the sequential extraction procedure separated the metals into five fractions:

1. Exchangeable (includes metals that are reversibly sorbed to soil minerals, amorphous solids, and/or organic materials).

2. Carbonate (made up of metals that are irreversibly sorbed, or otherwise bound in metal carbonate minerals which are removed by mild acid (pH 5) dissolution).
3. Fe-Mn Oxide (comprises the metals bound to hydroxides of iron, manganese and/or aluminum, which are liberated by an acidic reducing agent).
4. Organic matter and sulfide (consists of any metal associated with sulfide minerals or that are irreversibly bound to organic groups).
5. Residual (consists of the remaining metals that are distributed between the silicates, phosphates, and refractory oxides released by total dissolution of the material).

The names of the fractions are attributed to the metal (i.e. lead) phases found in the environment. Because the definition is operational, the extraction system becomes more aggressive by using different extraction solutions (Table 8). In this way, the relative availability of the metals in each soil can be evaluated.

Sequential extraction was conducted on the reference and range soils, excluding the reference sand red river 02 and the Hamilton range soil, to determine where the metals (i.e. lead) reside within the soil matrix (Tables 9 and 10). As the soil particle size distribution went from larger to smaller passing through the 250- μm sieve, there was generally an increase in the lead present in the exchangeables, carbonates, Fe-soil fractions, and a decrease in the residual fraction. The OM and sulfide fraction displayed a slight increase with particle size, but no trend was noted. In the reference soils, no relationship was apparent between the sequential extraction fraction and the soil CEC or pH (Table 10).

Table 8. Sequential extraction general procedure used to evaluate the soils.

Sequence	Reagents	Conditions
Step 1: Exchangeable Pb	1M MgCl ₂	1. Weigh 80 g of soil into a 1000-mL centrifuge bottle
		2. Add 800 mL of 1M MgCl ₂ solution at pH 7
		3. Shake for 1 hr
		4. Centrifuge at 2000 rpm for 30 min
		5. Filter using 0.45-µm filter
		6. Collect supernatant, label "Exchangeable"
Step2: Lead Carbonates	1M NaOAc	1. To residue, add 800 mL of 1M NaOAc solution at pH 5
		2. Shake for 3 hr
		3. Centrifuge at 2000 rpm for 30 min
		4. Filter using 0.45-µm filter
		5. Collect supernatant, label "Carbonates"
Step 3: Fe-Mn Oxides	0.04M NH ₂ OH·HCl in 25 percent (v/v) HOAc	1. To residue add 800 mL of 0.04M NH ₂ OH·HCl in 25 percent (v/v) HOAc
		2. Heat in water bath at 95°C for 3 hr with occasional agitation
		3. Centrifuge at 2000 rpm for 30 min
		4. Filter using .45-µm filter
		5. Collect supernatant, label "Fe-Mn Oxides"
Step 4: Organic Matter & Sulfide	0.02M HNO ₂ and 30 percent H ₂ O ₂	1. To residue add 240 mL of 0.02M HNO ₃ and 240 mL of 30 percent H ₂ O ₂ at pH 2
		2. Warm in water bath at 85°C for 2 hr
		3. Add 240 mL of 30 percent H ₂ O ₂ at pH 2
		4. Warm in water bath at 85°C for another 3 hr with intermittent agitation
	3.2M NH ₄ OAc in 20 percent HNO ₃	5. Cool and add 400 mL of 3.2M NH ₄ OAc in 20 percent HNO ₃
		6. Dilute to 1600 mL and shake for 30 min
		7. Centrifuge at 2000 rpm for 30 min
		8. Collect supernatant, label "OM and Sulfides"
Step 5: Residual	1M HNO ₃ and 1M H ₃ PO ₄	1. Remove residue from centrifuge bottles and weigh
		2. Dry residue for 24 hr
		3. Weigh dried sample and grind for 10 min
		4. Microwave samples using method 3050B (method modified by using 8 mL of HNO ₃ and 2 mL of H ₃ PO ₄ to 2g of dried sample)
		5. Filter samples and label "Residual"

Table 9. Reference soil sequential extraction of lead (un-normalized concentration) compared to soil particle size and arranged from smallest (top - Muck) to largest (bottom - Glacial Till)

Soil	Pb in Exchangeables (mg/L)	Pb in Carbonates (mg/L)	Pb in Fe-Mn Oxides (mg/L)	Pb in OM and Sulfide (mg/L)	Pb in Residuals (mg/kg)	Total Pb <1.7mm (mg/kg)
Muck	50.07	133.33	138.67	759.33	2,200.00	3,856.89
Loess Pb1	7.85	377.33	641.67	1,432.00	2,879.67	1,917.78
Loess Pb2	49.13	1,356.67	769.00	1,581.00	2,606.00	5,050.00
Clay	176.33	1,293.33	1,655.00	2,303.33	2,723.33	5,911.43
Sandy	935.67	1,856.67	716.33	1,713.33	317.00	5,930.00
Sandy Clay	556.33	1,870.00	870.33	1,970.00	692.37	5,924.44
Glacial Till	1,380.00	6,183.33	1,189.33	1,072.33	361.00	26,011.11

Table 10. Range soil sequential extraction of lead (un-normalized concentration) compared to soil particle size and arranged from smallest (top - Barksdale 03) to largest (bottom - Seymour Johnson)

Soil	Exchangeables (mg/L)	Carbonates (mg/L)	Fe-Mn Oxides (mg/L)	OM and Sulfide (mg/L)	Residuals (mg/kg)	Total Pb <1.7 mm (mg/kg)
Barksdale 03	0.61	5.07	6.86	15.36	1,030.71	1,213.03
Barksdale 01	0.00	0.00	0.00	15.82	1,475.50	1,842.00
Holloman 02	0.00	2.61	5.26	592.57	20,516.00	15.69
Whiteman	2,445.33	12,769.67	13,973.33	7,206.33	208.50	518.60
Ellsworth 02	281.08	37,950.00	39,840.00	179,326.67	10,747.50	1,822.33
Barksdale 02	0.00	9.80	6.12	15.82	3,733.37	532.00
Canon	0.00	1,016.40	1,651.00	1,305.67	12.68	71.42
Offutt	1.06	30.35	12.76	44.79	10,491.67	1,694.00
Soil B	1.50	28.93	30.10	8.75	22.97	93.45
Ellsworth 01	4,148.33	102,450.00	143,533.33	260,100.00	13,038.67	6,272.33
Langley 02	0.00	0.00	0.00	0.00	1,742.67	798.40
Soil C	51.50	3,246.67	3,176.67	4,450.00	17,533.33	13,501.11
Holloman 01	7.38	218.47	76.28	163.07	44,500.00	2,799.00
Beale 02	0.00	0.00	0.00	0.00	61.20	13.64
Langley 01	1.23	8.61	0.00	0.00	1,736.00	848.25
Beale 01	79,723.33	1,027,300.00	0.00	631,366.67	46,466.67	30,610.00
Shaw	8.51	23.45	7.46	37.22	2,321.67	2,677.20
Nellis	0.00	3.90	3.32	10.41	6,925.90	4,518.33
Soil A	345.00	6,520.00	3,490.00	10,490.00	4,049.33	18,477.78
Seymour Johnson	12.83	4.84	6.14	92.99	4,989.00	446.55

X-ray diffraction and environmental scanning electron microscopy

X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was used to determine the effects of the metal bullet fragments on the mineralogy of the soils. The samples were run as randomly oriented packed powders. A Philips PW 1800 Automated Powder Diffractometer system was used to collect XRD patterns employing standard techniques for phase identification. The run conditions included Cu K α radiation and scanning from 2 to 65 °2 θ with collection of the diffraction patterns accomplished using the PC-based, Windows-based version of Datascan, and analysis of the patterns using the Jade program (both from Materials Data, Inc.). In preparation for XRD analysis, a portion of the sample was ground in a mortar and pestle to pass a 45- μ m mesh sieve (No. 325). The mineral species present in each pre-firing soil, marked as “x,” are shown in Table 11.

Table 11. XRD geochemical characterization of pre-firing reference soils.

Soil	Quartz	Expandable Clays	Non-expandable Clays	Feldspars	Carbonates
Clay	x	x	x	x	
Sandy Clay	x	x	x		
Glacial Till	x		x	x	
Sand	x		x		x
Muck	x	x	x	x	
Loess Pb1/Pb2	x	x	x	x	x

Environmental scanning electron microscopy (ESEM)

Characterization and base line distribution (homogeneity) of the metals in the soil provide data to determine how the metals are spread throughout the sample. Spatial distribution of the metals was determined using a low-pressure SEM (Environmental SEM, ESEM Model 2020 SEM with a GSED detector), which eliminated the need for sample preparation or application of a conductive coating. Four-quadrant, solid-state backscatter electron detectors were used to highlight the size and distribution of heavy metals in each sample. Energy-dispersive x-ray microanalysis was used to ascertain the elemental composition and mapping of elemental distributions. Scanning electron microscopy provides valuable data on the condition of the bullet fragments (Figures 29 through 32) in the soil and

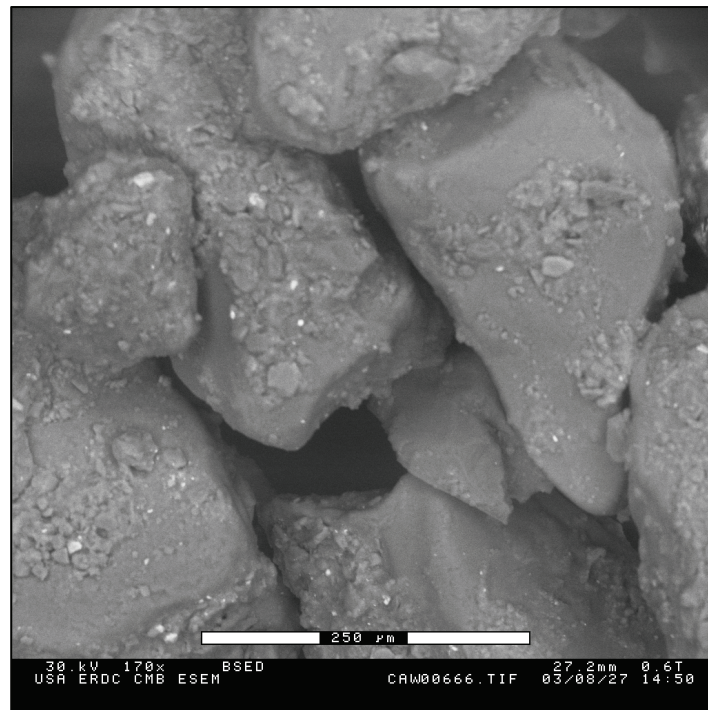


Figure 29. ESEM figure of clean soil (250-μm scale in figure).

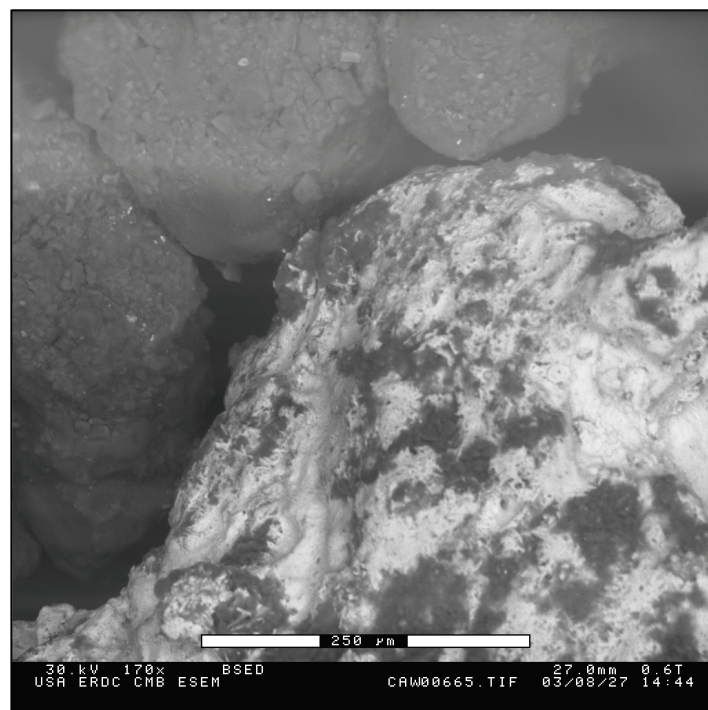


Figure 30. ESEM with large lead chunk in the soil deposited from firing lead bullets into the soil (250-μm scale in figure).

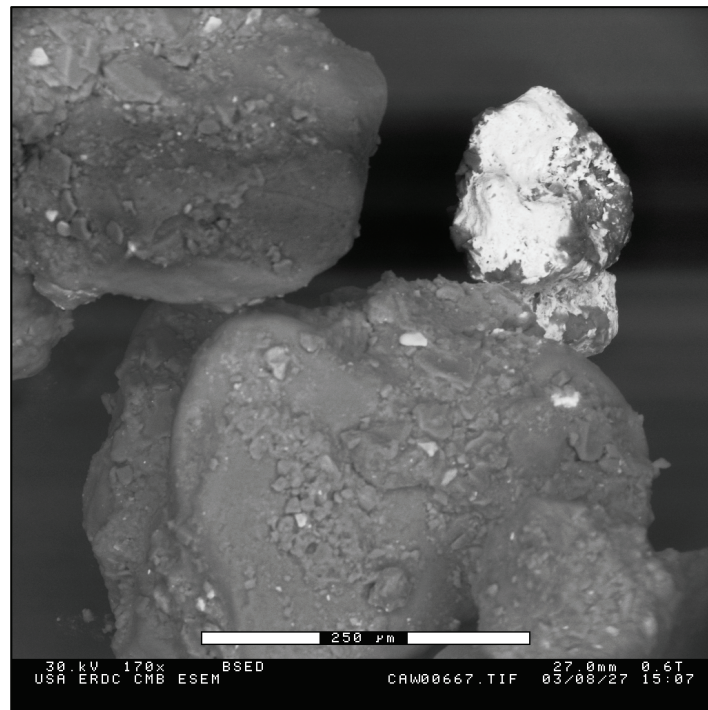


Figure 31. ESEM small lead chunk in the soil deposited from firing lead bullets into the soil (250-μm scale in figure).

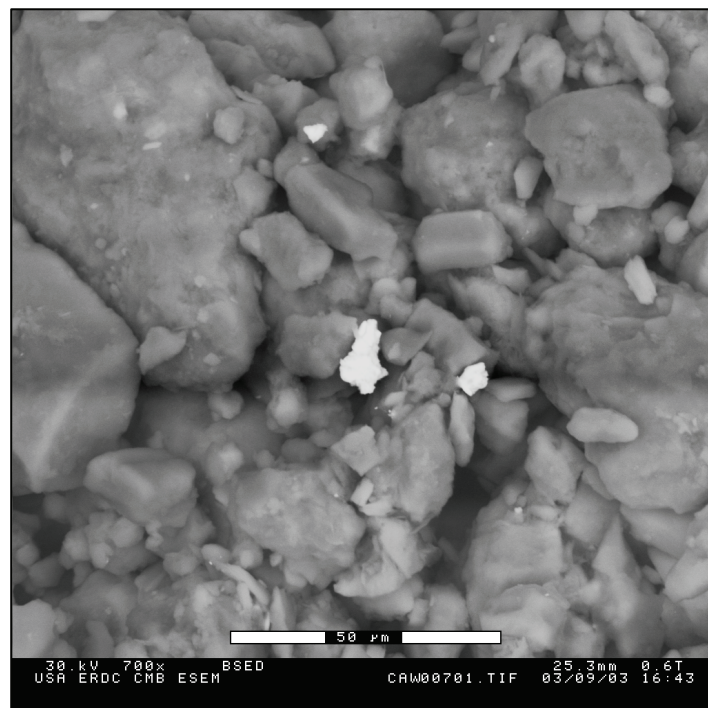


Figure 32. ESEM smaller lead chunk in the soil deposited from firing lead bullets into the soil (50-μm scale in figure).

presence of metal couples (copper jacket material attached to lead core fragments) that can accelerate corrosion and the release of metals as soluble species. Characterizing the mineralogy of each soil provides data that are used to determine the soil's ability to remove soluble metals from groundwater and ultimately trap metals, mitigating potential migration off range.

Earthworm bioassay

An earthworm bioassay was conducted for reference and range lead-contaminated soils. Earthworms were placed in samples of the soils, removed after a specified amount of time (approximately 28 days) and analyzed for lead (Figures 33 and 34). Generally, as the total soil lead concentration (< 1.7-mm sieved soil) increased, the lead concentration in the earthworms also increased.

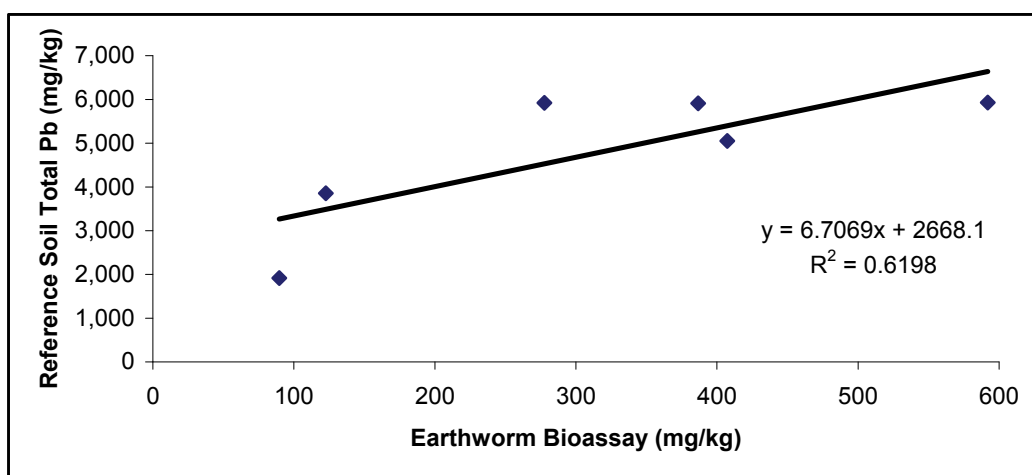


Figure 33. Reference soil earthworm bioassay.

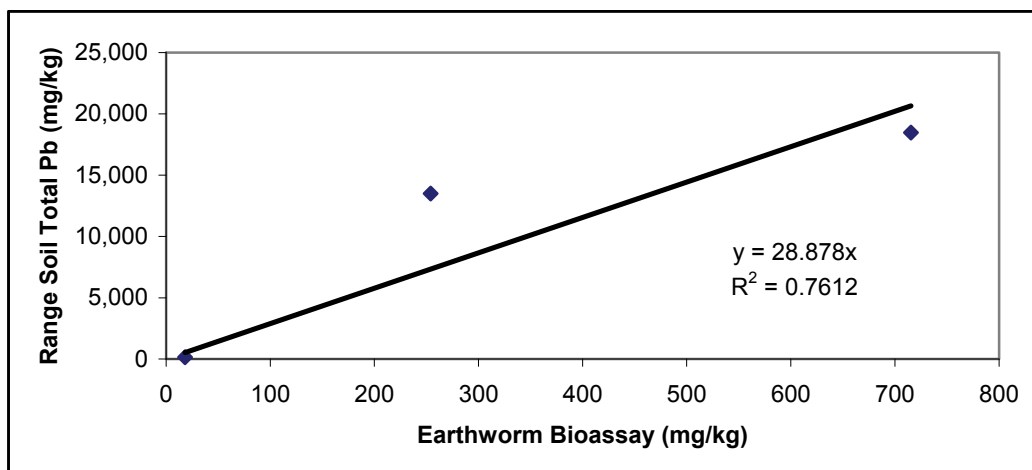


Figure 34. Range soils A, B, and C earthworm bioassay.

An earthworm bioassay was also conducted with SAFR soil collected from Hamilton AFB. This study compared total soil lead and earthworm bioassay digests. The results were similar to the observations for the reference and range soils; the more lead present in the soil, the more lead will be found in the earthworms (Figure 35).

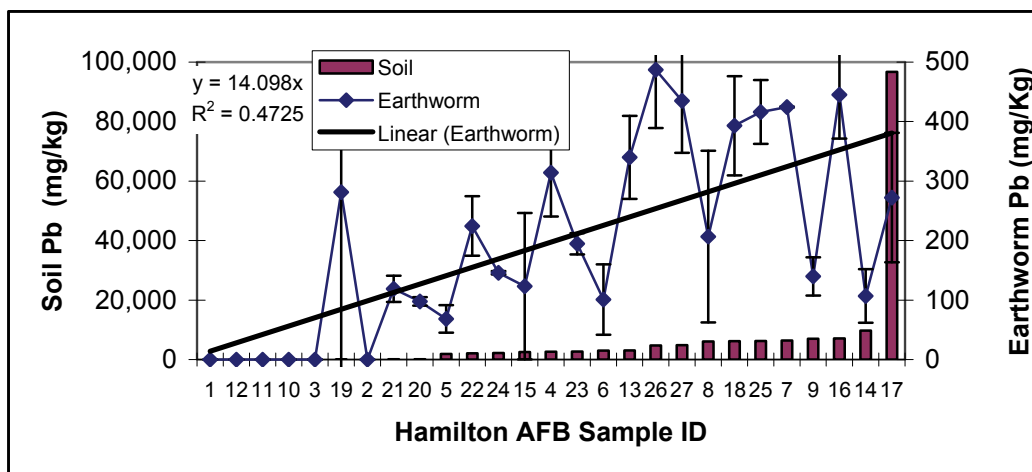


Figure 35. Hamilton SAFR soil earthworm bioassay.

Observations

1. In the reference soils, as the concentration of lead increased in the soil (for digested samples < 1.7 mm), there was an increase in the TCLP lead concentrations.
2. In the range soils, the same trend was not as apparent.
3. As the reference soil TOC increased, the TCLP lead concentration decreased.
4. As the reference soil CEC increased, the TCLP lead concentration increased. The exception is a soil with a very high CEC, at which point the TCLP lead concentration decreases.
5. The DDI and SPLP lead concentrations were very similar for the reference soils, but not as similar for the range soils.
6. As the soil lead concentration increased (< 1.7-mm digested soil), and, conversely, the amount of soil passing through the No. 60 sieve decreased, the sequential extraction resulted in an increase in

lead exchangeables and carbonates, an Fe-soil increase and a residual lead fraction decrease.

The reference and range soils are complex systems. The soil classification indicates that the physical size of the soil will generate different types of bullet fragments on SAFR impact areas. Additionally, different bullet types will impact the soil and fragment differently. Fragment size, soil conditions, and soil weathering affect the rate and amount of lead that may migrate from an SAFR. Several proposed techniques can be used to clean up closed SAFRs, such as stabilization, phytoremediation, and soil washing. The research conducted on these techniques and their effectiveness will be discussed in the following chapters. The important point is that generally a soil that has larger particles will create more bullet fragments that can affect the rate of lead transport into the environment. It is also important to understand the amount and types of ammunition used on a range, because this can also impact how remediation is conducted at a closed SAFR.

3 Phytoremediation

Introduction

Plants normally require both macronutrients and micronutrients for essential plant growth and metabolism, and they have developed highly specific mechanisms to take up, translocate, and store these nutrients. Some heavy metals, such as Zn, Mn, Ni, and Cu, are essential micronutrients. In common, non-accumulator plants, the uptake of these micronutrients does not exceed the metabolic needs (<10 ppm) of the plant. However, high metal soils often support plant species that thrive in metal-enriched environments. Some of these species, called hyperaccumulators, can retain unusually high concentrations of toxic metals to levels that far exceed the soil levels (Baker and Brooks 1989, Baker et al. (2000), Reeves et al. (2000), Raskin et al. 1994). Various hyperaccumulator species can concentrate more than 10-ppm Hg; 100-ppm Cd; 1,000-ppm Co, Cr, Cu, and Pb; and 10,000-ppm Ni and Zn. To date, approximately 400 plant species from at least 45 plant families have been reported to hyperaccumulate metals. Most hyperaccumulators bioconcentrate Ni; about 30 absorb Co, Cu, and/or Zn; even fewer species accumulate Mn and Cd; and there are very few known natural Pb-hyperaccumulators (McGrath and Baker 1994, Salt and Krämer 2000). Reasons that plants may sequester metals include defense against predation and defense against the toxicity of the metals themselves (McCutcheon and Schnoor 2003).

Lead in soils due to small arms range training is present in a spectrum of oxidation states. Intact projectiles or projectile fragments and particulates are present as metallic, or zero-valent, lead. Weathering of lead in soils at small arms ranges can result in lead that is ion exchanged onto soil particles or lead salts such as lead carbonates. The presence of many lead species and oxidation states such as occurs at SAFRs results in different exposure environments for plants, compared to high lead soils that occur naturally or as a result of anthropogenic dispersion of lead salts. The presence of ammunition residue that contains metallic lead is a unique challenge for phytoremediation of small arms firing ranges. Plants do not have the capability to take up metallic lead. The lead must be oxidized to produce a bioavailable species before it can be taken up into the plant roots and then translocated into stems and leaves, the above-ground portions of the plants. For this reason, the length of time a phytoremediation tech-

nique would be required depends on the amount of time required for oxidation of the metallic lead in the soil.

Lead and lead-alloy corrosion in the environment

Lead

Lead has two oxidation states, +2 and +4, and is toxic in both. Lead (II) is generally insoluble in groundwater. Lead carbonate (PbCO_3) and lead sulfate (PbSO_4) are less soluble Pb(II) compounds. Lead(II) monoxide (PbO), in the forms of litharge and massicot, is sparingly soluble in water, but readily dissolves in acid. Lead in its low solubility form can be found with sulfur in the mineral galena (PbS). Natural mineral deposits containing particularly large quantities of heavy metals are present in many regions of the globe. Lead (IV) is generally the more soluble ion, but is far less prevalent in the environment. PbO_2 is a lead oxide that is soluble in water.

The background lead content of agricultural soils can range from 1 mg/kg to 135 mg/kg, with a median value of 11 mg/kg (Holmgren et al. 1993). Lead in soil is classified as a weak Lewis acid, which implies a strong covalent character to many of the ionic bonds it forms in soils and plants. Aqueous phase lead may occur in either the dissolved or suspended form. Dissolved lead is generally considered bioavailable and is the form targeted by phytoremediation. The suspended particles may either be particulates of lead alloy (as is the case with SAFRs), or lead adsorbed onto soil or clay particles, and these forms may be relatively unavailable for plant uptake. Lead retention in the roots is based on binding of lead to ion exchangeable sites on the cell wall and extra-cellular precipitation, mainly in the form of lead carbonate (PbCO_3) deposited in the cell wall. Large lead particles cannot easily cross into the roots due to their size and charge characteristics.

Lead alloys

Metallic lead has good resistance to corrosion. However, it is a relatively soft metal with poor tensile strength. To overcome these problems, lead is normally alloyed with other metals, such as antimony, to give it strength and hardness. In de-mineralized water, chemical lead has a corrosion rate of 18-mdd ($\text{mg}/\text{dm}^2/\text{day}$) while a 6-percent antimonial-lead has a rate of 1.6-mdd (Revie 2000). The corrosion rate in seawater is slower than in

de-mineralized water due to the formation of lead salts on the surface of the lead or lead alloy (Revie 2000). The average corrosion rate of chemical lead and 1-percent antimonial-lead was determined for different natural outdoor atmospheres to be 0.25-mdd and 0.14-mdd, respectively (Revie 2000). This suggests that the antimony-lead alloy bullet will corrode slower in both water and under atmospheric conditions than chemical lead. The rate of oxidation of metallic lead alloy particles at small arms ranges is dependent on numerous variables including soil pH, temperature, rainfall, soil hydraulic conductivity, the type of ammunition used, the presence of other metals and the associated kinetic properties of these metals, and the extent of projectile fragmentation during soil impact. Also, when corrosion begins, it creates a coating around the lead alloy particles, which slows down the corrosion process (Scheetz 2004).

These factors provide a wide timeframe for all of the metallic lead to oxidize in a given small arms range soil. Lead shot (0.5 cm) is expected to fully corrode, with some lead passing into solution, over a period of 100 to 300 years (Jorgensen and Willems 1987). However, the low end of this time range cannot be considered to be less than 20 years and could exceed 2000 years (Thornton et al. 2001), assuming linear reaction kinetics and no changes in conditions.

Phytoremediation requirements

Successful phytoremediation requires a hyperaccumulator plant species with a high biomass yield. Through a cropping scheme, suitable species can be planted in succession, ultimately leading to the reduction of soil metal concentrations to environmentally acceptable levels. In addition, the success of phytoremediation is dependent upon the availability of the toxic metal in the soil for plant uptake (Blaylock 2000, Kumar et al. 1995, Dushenkov and Kapulnik 2000).

The possible advantage of phytoremediation as an alternative method of treating heavy metals contamination is its low cost. This low cost is based on the plants' ability to reduce heavy metal concentrations in soils over a small number of growth/harvest cycles. As the number of growth/harvest cycles increases, the costs associated with planting, tending, harvesting, and disposal of plant material laden with heavy metals increases, reducing the cost-effectiveness of the technique. Additionally, phytoremediation has gained acceptance by both the public and private sectors.

Bioavailability and uptake

Plants must obtain their essential nutrients from soils through diffusion and/or the use of electrochemical metabolic pumps. Lead and other metals accumulate in the surface layers of soils. Their availability to plants depends on both soil and plant factors. Soil conditions such as pH, soil organic matter, particle size, and the cation exchange capacity (CEC) affect metal bioavailability. Important plant factors are the amount of root surface area, presence of root exudates, mycorrhization, and the rate of transpiration (Thornton et al. 2001). The soil pH effect on uptake appears to be metal specific. In general, the uptake mechanism is selective, plants preferentially acquiring some ions over others (Lasat 2000). Lead, one of the most important environmental contaminants, has limited solubility in soils and, therefore, limited bioavailability. This is due to the chemical complexes formed between lead and the soil organic matter, sorption on oxides and clays, and precipitation as carbonates, hydroxides, and phosphates (Thornton et al. 2001). Chelating agents present in root exudates desorb metals from the soil particles and increase the solubility of the metal in pore water, increasing the bioavailability and uptake (Cobbett and Goldsbrough 2000).

As part of a larger study on transport of metals off-range, research conducted by Martin et al. (2006, in preparation) used mesoscale laboratory lysimeters filled with heavy metals-contaminated range soil to determine if the metals could be stabilized with native grasses. The lysimeters were planted with a seed mixture containing red fescue (*Festuca rubra*), Kentucky bluegrass (*Poa pratensis*), and switchgrass (*Panicum virgatum*). The control lysimeter was left unplanted. The runoff and leachate water were collected from 16 simulated rain events and analyzed for lead and total suspended solids (TSS).

As shown in Figure 36, the TSS was significantly reduced in runoff from the vegetated cells ($p=0.05$). The TSS in the leachate was not significantly different between the untreated and planted cells.

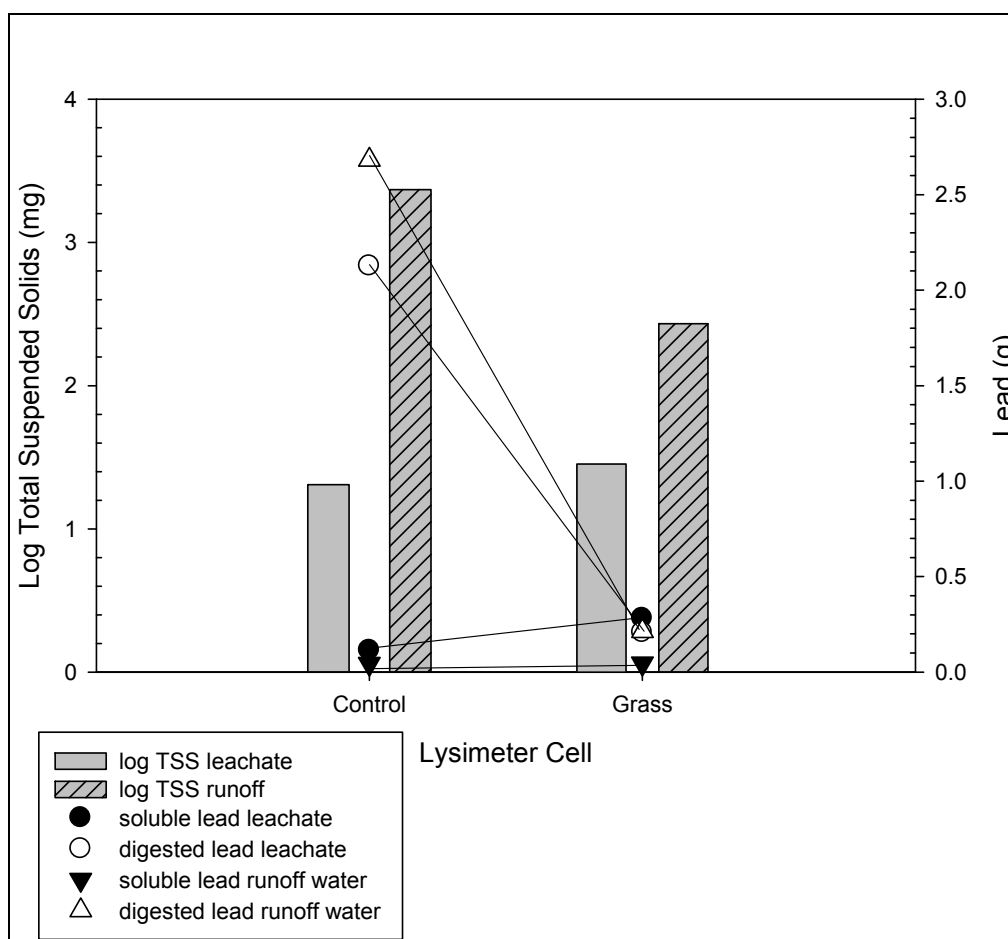


Figure 36. Comparison between planted and unplanted soils of total suspended solids (TSS) and total lead lost

The effect of grasses on transport of lead differed depending on whether the lead was associated with suspended solids or present as a soluble species. As can be seen in Figure 36 and detailed in Table 12, the mass of lead leaving the cells as particulate material was reduced in both the leachate and runoff water of the planted soil over the unplanted soil. Migration of the most mobile and bioavailable form of lead, dissolved lead, was not reduced as a result of the presence of the grasses. The grass treatment had no effect on the soluble lead in the runoff water. The presence of grasses resulted in the production of more than twice the soluble lead in leachates. The biological activity associated with the grass may produce lead chelators such as complex carboxylic acids, polyphenols, or peptides with a large amount of the sulfur containing amino acid (cysteine). These compounds can act as powerful chelators of metal cations and may be facilitating transport of soluble metals, for example lead (Cobbett and Goldsbrough 2000).

Table 12. Mass Pb released from cells as filtered and digested runoff or leachate.

Treatment	Mass Pb ¹ (g)			
	Filtered Leachate	Filtered Runoff	Digested Leachate	Digested Runoff
Control (no grass)	0.114	0.044	2.127	2.682
Grass	0.282	0.045	0.207	0.213
¹ RL of 0.05 ppb used for concentrations less than RL				

The grass roots and shoots from all three species of grass were harvested from the lysimeter cell, cleaned, digested, and analyzed for lead content in order to determine the effect of grass on the lead in the soil. The initial concentration of lead in the soil was 5303±651 mg/kg. The grass roots and shoots contained 7475±1820 mg/kg on a dry weight basis, demonstrating uptake and accumulation of the soil lead. The mobilization of soluble lead by biological activity is a further disadvantage of phytoremediation as a tool for remediation of small arms firing range soils.

Translocation

Translocation is the movement of ions (including metals) from the roots into the stems and leaves. The endodermis acts as a partial barrier to the movement of lead between the root and the shoot (Sharma and Dubey 2005). Most studies indicate that the translocation rate is much slower than the uptake rate. For example, Huang et al. (1997) found that only 30 percent of lead absorbed by roots of corn and peas is translocated. Kumar et al. (1995) evaluated six species from the Brassica family, and six crop plants that were non-Brassica. All plants tested were able to accumulate lead in the roots and the shoots to varying degrees.

Kumar et al. (1995) determined that the Brassia species had a larger phytoextraction coefficient than other species. For example *Brassia carinata* had a phytoextraction coefficient of 174.2 while *Sorghum bicolor* had a value of 13.1. The author then tested *Brassia juncea* for uptake of the toxic metals. Plants were exposed for 14 days to Cr⁶⁺, Cd²⁺, Ni²⁺, Zn²⁺, Cu²⁺, Pb²⁺, or Cr³⁺. Chromium (VI) had the highest phytoextraction coefficient, 58, followed by Cd²⁺ and Ni²⁺, Cd²⁺ and Cr³⁺ had the lowest phytoextraction coefficients of 1.7 and 0.1, respectively. Cultivar 426,308 was the most efficient shoot accumulator of lead (3.5 percent on a DW basis, phytoextraction coefficient of 55.2). *B. juncea* produced 18 ton/ha of biomass. Therefore, Cultivar 426,308 with 3.5 percent Pb in its shoots can extract 63 kg of

Pb/ha with a single harvest of the aboveground biomass. The leaves of the *Thaspi rotunifolium* ssp. *cepaefolium*, a member of the Brassicaceae family, have been reported by Reeves et al. (1983) to have lead concentrations as high as 8,200 mg/kg on a dry weight basis. Barman et al. (2000) studied the uptake and translocation of heavy metals by wheat, mustard, and weeds for metals that were in contaminated irrigation water. The pattern of best uptake of metals was $\text{Fe} > \text{Cu} > \text{Ni} > \text{Cr} > \text{Zn} > \text{Pb} > \text{Cd}$. However, a different pattern occurred regarding translocation from root to stem: $\text{Cd} > \text{Pb} = \text{Cr} > \text{Cu} + \text{Zn} > \text{Fe} = \text{Ni}$. And the pattern for translocation from root to leaves was: $\text{Cd} > \text{Fe} > \text{Zn} > \text{Cu} > \text{Ni} = \text{Pb}$.

In contrast to metal accumulation from soil, Lee et al. (1976) demonstrated that most wetland plants tend to accumulate lead in their roots. In hydroponic solution experiments with wetland plants, the authors conclusively showed that lead accumulated on the surface of the root or inside the root with limited translocation from plant roots into the above-ground plant stems and leaves. Lee et al. (1976) suggested that lead either precipitated with phosphate in or on the root surface or adsorbed onto iron oxides that formed on the root surface when oxygen was pumped from plant leaves down to plant roots to aerate the root zone around the root. Consequently, wetland plants tend to exclude lead uptake and translocation to plant tops.

Chelating agents

For some toxic metals, such as lead, a major factor limiting phytoextraction is limited solubility and bioavailability for uptake into roots. One way to increase lead solubility is to decrease the soil pH (Thornton et al. 2001). Following soil acidification, however, mobilized lead can leach rapidly below the root zone. In addition, soluble ionic lead has little propensity for uptake into roots. The use of specific chemicals, synthetic chelating agents, has been shown to dramatically stimulate the potential for Pb accumulation in plants. These compounds prevent Pb precipitation and keep the metal as a soluble chelate-Pb complex available for uptake into roots and transport within plants.

Organic chelators

In order for plants to effectively extract metals from contaminated soil into their roots and then translocate the metal into the plant tops for harvesting, the metal needs to be in a mobile form that can resist precipitation

with root phosphate or adsorption onto iron oxides. Plants perform this operation with the production of exudates containing natural chelating agents. The addition of organic chelators has been studied and shown to dramatically increase metal uptake and translocation. Chelating agents have been used to extract metals from soils (Norvell 1984) and have been widely studied and used in the fields of agriculture and plant nutrition (Albasel and Cottenie 1985). Neubauer et al. (2000) investigated the effect of three organic chelating agents (siderophore desferrioxamine B (DFOB), nitriloacetic acid (NTA), and citrate) on the uptake of zinc and cadmium. They discovered that ligand effectiveness not only depended on the contaminant, but on the soil type. NTA emerged from the study as a promising amendment. Nutrient additions might be promising methods to improve metal uptake (Sterrett et al. 1996; Ebbs et al. 1997).

Synthetic chelators

Cooper et al. (1999) examined the feasibility of phytoextraction of lead from contaminated soils using several soil types and plant species, and the addition of synthetic chelating agents. The soils were contaminated from manufacture and testing of Pb-based explosives, and total lead in the contaminated soils ranged from 1,400 to 13,000 mg Pb/kg. Several chelating agents were tested, but not EDTA (ethylene-diamine-tetraacetic-acid). The phytoenhancement studies focused on DTPA (diethylenetriamine pentaacetic acid), CDTA (1,2 cyclohexylenediamine tetraacetic acid), and H-EDTA (hydroxyethyl-ethylenediamine-triacetic acid). In an initial test, chelating agents were added to the soils to test desorption of lead. The hypothesis was that the chelating agent that desorbed the most lead would also mobilize the greatest amount of the metal for eventual plant uptake. Corn was the best performer in nutrient solution and in contaminated soil. A 2.0 mmol/kg concentration increased lead extraction for some of the chelating agents (particularly CDTA), but did not enhance lead solubility enough to make a significant impact on plant uptake and, therefore, phytoremediation. However, at 20 mmol/kg, significant increases in desorbed lead were observed for HEIDA, EGTA, DTPA, CDTA, and H-EDTA.

The chelating agents DTPA, CDTA, and H-EDTA were used in greenhouse studies to observe if these compounds would enhance lead uptake in the contaminated soils. This evaluation was complicated by the inherent phytotoxicity of the contaminated soils and the observation that the H-EDTA itself appeared to be phytotoxic. Despite the ability of H-EDTA to desorb large quantities of lead from soils, its toxicity to the plants more

than compensated and made H-EDTA an ineffective agent for enhancing plant uptake of lead. As observed in the desorption experiment, 2 mmol/kg of the chelators did not enhance lead uptake from the contaminated soils. However, 20 mmol/kg of either CDTA or DTPA significantly increased lead plant concentrations for both corn and sunflower. CDTA actually enhanced plant growth and DTPA had little effect on plant growth.

The addition of a chelating agent at a concentration of 2 mmol/kg or greater resulted in increased TCLP values from the soil, all of them higher than the EPA standard of 5 mg/L. At a chelator concentration of 20 mmol/kg, the TCLP concentrations exceeded 50 mg/l for all chelators, even after the soils had been cropped for 42 days in the greenhouse. The explanation for these observations seems to lie in the change in the exchangeable fraction of the lead upon exposure to the chelating agents. For DTPA, exchangeable (Exch-Pb) lead increased from 650 mg/kg in untreated soil to 2600 mg/kg at a DTPA concentration of 20 mg/kg. While a shift in lead distribution from more resistant forms to the most available form (Exch-Pb) might be beneficial in soil extraction, highly available lead will require careful management of lead in the field to avoid accidental contamination of nearby surface and groundwaters.

EDTA

Other chelating agents that have been studied extensively (Huang and Cunningham 1996, Huang et al. 1997) include EDTA and H-EDTA. Huang et al. (1997) presented evidence that phytoextraction of metals requires high biomass plants that can accumulate >1 percent lead in shoots. They determined that most hyperaccumulators are too small and grow too slowly for practical phytoremediation. They also had shallow root systems and many lived only in narrow ecological ranges. Accumulation of elevated lead levels is highly toxic and can cause plant death. Because of the toxic effects, it is recommended that chelators be applied only after a maximum amount of plant biomass has been produced. Prompt harvesting (within one week of treatment) is required to minimize the loss of Pb-laden shoots. Huang et al. (1997) studied the uptake of lead by corn and peas with the assistance of chelating agents. Their studies indicated the following effectiveness of chelators: EDTA>H-EDTA>DTPA>EGTA>EDDHA. The addition of EDTA increased lead shoot concentrations in both species from <500 to >10,000 mg/kg. Also, EDTA improved the translocation of metals from roots to shoots. In the second article,

Blaylock et al. (1997) studied the effect of EDTA and other chelates on improving uptake of lead and other metals (Cd, Cu, Ni, and Zn) by Indian mustard. A combination of EDTA and acetic acid was most successful. A pH range of 5 to 7.5 was tested. A pH of 5 worked the best, with or without EDTA. EDTA also improved translocation of the lead to the shoot. EDTA chelation, in combination with low soil pH, effectively prevents the cell wall retention of lead in the roots, making it available for translocation to shoots (Jarvis and Leung 2002, Kulli et al. 1999, Kayser et al. 2000, Kos and Lestan 2003, Luo et al. 2005).

Studies by Vassil et al. (1998) focused on the uptake, accumulation, and translocation of lead by Indian mustard (*B. juncea*) using EDTA solution as an amendment. Two-week-old plants (*B. juncea*, var. 426308) were grown in nutrient solution containing various concentrations of lead and EDTA for 48 hr, and the uptake of lead and EDTA was quantified. Uptake increased with increasing EDTA solutions up to a concentration of 0.4 mM EDTA. Rates then decreased with increasing EDTA concentration, perhaps due to phytotoxicity or to competition between the plant and the EDTA for the lead. EDTA and Pb-EDTA complexes were identified in the plant mixture. Similar to other studies, EDTA improved both uptake and translocation of lead within the plant.

Wu et al. (1999) also studied the use of chelating agents. They noted that the Pb-EDTA complex was very soluble and therefore a soil migration threat. Furthermore, models suggested that plants might not pick up the Pb-EDTA complex effectively. The study compared uptake of lead by corn using the Pb-EDTA complex and lead complexes with N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED). They found higher lead concentrations in the roots of the plants receiving the HBED treatment. However, EDTA was also found to increase plant transpiration, which is the driving force for metal uptake. To test the impact of HBED and EDTA on lead uptake by corn plants, contaminated soils were spiked with 1.5-mmol/kg soil, 10 days after seed germination. Corn grown in the Pb-contaminated soil that was treated with EDTA had significantly higher lead content than in the soil without EDTA. Apparently, the HBED reacted with other metals in the soil (Cu, Mn, and Fe) and did not solubilize lead as anticipated. Thus, EDTA was proposed to be a superior soil amendment. The only disadvantage with this approach is that EDTA will make the lead mobile and could result in leaching losses of lead from the contaminated zone. The authors suggested further research into this area

is needed to find or synthesize chelating agents that are more lipophilic (for ease of uptake), excellent specificity for lead, and a high affinity for the metal.

Chen et al. (2004) conducted a pot experiment with six dicotyledon and four monocotyledon species of plants. The application of EDTA increased the amount of lead in the shoots of the plants. The lead phytoextraction efficiency varied among the 10 species of plants. Sunflowers extracted the highest concentration of lead. Wheat and barley had the lowest phytoextraction efficiency. In a greenhouse study, Li et al. (2005) compared lead and zinc uptake by corn seedlings in contaminated soil assisted by three forms of chelating agent: a slow release coated EDTA granule (a coated chelating agent (CCA)), uncoated EDTA granules, and EDTA solution. The release of lead and zinc from the soil was examined in a soil column leaching study. The distribution of lead in the sequential extraction procedure showed that the lead concentration in the exchangeable carbonate bound fraction with CCA was significantly lower than that with solid EDTA or EDTA solution. This indicates that slow release of CCA improves the bioavailability of metals from the contaminated soil in the short term and may also reduce the rise of metal leaching from the soil.

Luo et al. (2005) evaluated EDTA and ethylenediamine disuccinic acid (EDDS) to mobilize metals in soil. EDTA can be toxic to plant and soil microorganisms and it can be persistent in the environment due to its low biodegradability (Sýkora et al. 2001). EDDS is a more biodegradable chelating agent and has been proposed to enhance the uptake of heavy metals in soil (Kulli et al. 1999; Kayser et al. 2000; Kos and Lestan 2003). In this experiment EDTA was more effective in extracting Pd, Cd, Cu, and Zn; while EDDS was more effective in extracting Cu and Zn from the soil. The percentage of total Cu that was phytoextracted in one crop cycle was 0.6-1.0 percent in corn and 1.9-5.3 percent in beans. Assuming a constantly high efficiency of copper removal and a constant dissolution of copper, approximately 16 crops of beans would be required to reduce the total copper in the soil from 527 to 100 mg/kg. Meers et al. (2005) evaluated whether EDDS was suitable for enhanced phytoextraction. A laboratory experiment was conducted to examine mobilization of Cd, Cu, Cr, Ni, Pb and Zn into the soil solution upon application of EDTA or EDDS. The stability of the induced mobilization was monitored for a period of 40 days after application. The minimum observed effect half-life of EDTA was 36 days, while for the highest applied dose no decrease was observed throughout

the 40-day period of the mobilization experiment. The performance of EDTA and EDDS for phytoextraction was evaluated by application to *Helianthus annuus*. Uptake of heavy metals was higher in EDDS-treated pots than in EDTA-treated pots. The effects were still too low to be considered efficient phytoremediation. Two biodegradable chelating agents, NTA and citric acid, were also tested in a plant experiment. NTA and citric acid induced no significant effects on heavy metal uptake.

In summary, EDTA is an effective soil amendment to promote the solubilization of metals, lead particularly, and enhance their uptake by plants for phytoremediation. However, EDTA is a potential environmental contaminant itself, which complicates its use. EDTA is non-biodegradable and, though it can be mineralized (Tiedje 1977), the rates are slow and can be greatly affected by environmental factors. EDTA amendments are also expensive (Chaney et al. 1999). Because the Pb-EDTA complex is much more soluble in soil pore water, it can also leach through the soil into groundwater and run off the soil during rainfall events. Consequently, control of the migration of chelated lead is a potential problem with this approach to phytoextraction. Even with these disadvantages, EDTA amendments are, for the time being, the state of the art in phytoremediation. Any soil project would likely require their use. Proponents of EDTA treatments argue that their method can actually reduce food chain exposure, since most of the metal is taken up just after the amendments are added. The plants can then be quickly harvested, reducing ecological exposure. One key criteria missing from the published studies is data on soil concentrations. With the exception of Blaylock (2000), the above-mentioned studies focus on the concentrations of metals taken up by the plants. However, there are no studies that demonstrate that phytoextraction can impact the soil concentrations to the point of meeting cleanup standards.

Pilot-scale studies

Enhancing lead accumulation of high-biomass crops by application of chelating agents to soil has been reported by Blaylock et al. (1997), and Huang et al. (1997). So far, mechanisms of metal-mobilization (Huang et al. 1997; Cooper et al. 1999), plant uptake and transport (Vassil et al. 1998; Wu et al. 1999), and chelator-plant combinations (Huang et al. 1997; Cooper et al. 1999) have been addressed. No data have been published on the possible transfer of the potentially toxic metals to deeper soil layers and groundwaters. Wu et al. (2004) conducted pot and column studies to

evaluate chelator-assisted phytoextraction. Their study found that leachate obtained from all EDTA treatments exceeded drinking water standards. This study showed the risk of pollution to deeper soil layers and groundwater at relatively small rates of EDTA application.

Vetiver grass has been investigated for phytoextraction of lead by Wilde et al. (2005), Chen et al. (2000), and Xia (2003). In a greenhouse study of firing range soil, Wilde et al. (2005) demonstrated that the application of EDTA prior to harvest significantly increased the amount of lead phytoextracted by the Vetiver plants. Significantly more lead was found in the roots of Vetiver grass than in the leaves, suggesting that Vetiver grass would be better used in phytostabilization than phytoextraction.

The study indicated that Vetiver grass coupled with amendments has potential as a remedial strategy for lead-contaminated soils such as those associated with firing ranges. However, Vetiver grass is thought to be an invasive species. Field verification studies need to be conducted to verify the claim of Vetiver grass for phytoremediation of range soils.

Field-scale studies

In the following field case studies, phytoremediation was attempted for heavy metal removal from SAFR soil. In these case studies, extreme methods were employed in order to increase the bioavailability of lead. The case study results indicate some movement of lead into the groundwater.

Field Study I

A field study was conducted by del Rio (2000) to determine the ability of *Brassica juncea* and *B. carinata* to remove lead from a moderately contaminated soil (310 mg/kg total Pb, 1.45 mg/kg soluble Pb at 10-cm depth). Seeds were planted directly in the field and harvested 3 months later. Due to low planting rates and the short growing period, biomass was quite low. This resulted in low Pb concentrations in the plants, despite being higher than plants growing in uncontaminated soils.

Field Study II

Blaylock (2000) presented results from two field studies: one at Bayonne, NJ and the other at Dorchester, MA. Both sites were approximately 92.9-m² (1000-ft²) plots and were contaminated with lead and other met-

als. Within a year, the sites were treated with three harvests using Indian mustard and EDTA amendments. In both cases, most treatment appeared to be in the upper 15 cm of the soil. Treatment goals were not reached, but the decrease in the upper 15 cm at the Bayonne site was, in fact, significantly larger than the authors had estimated based on small-scale pilot test results.

Field Study III: Magic Marker

The U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) program evaluated the process of combining soil amendments (EDTA) and metal accumulating crops to extract and accumulate lead and other metals from shallow soils. The 3-ha Magic Marker site is an urban brownfield. Lead found in the surface soil exceeded the residential regulatory limit of 400 mg/kg of dry soil. The project evaluated multiple crops of Indian mustard (*B. juncea*) grown in a 9.1-by 17-m treatment plot over the spring and summer of 1997. One crop of sunflower plants (*H. annuus*) grew in the summer of 1998. Initial soil samples were collected before planting and final soil samples were collected after harvest of the third planting. The Indian mustard plants contained 830 and 2300 mg/kg of lead on a dry weight basis. Lead in the above-ground plant tissues of the single crop of sunflowers was measured at an average concentration of 400 mg/kg lead on a plant dry weight basis. All of these lead average values exceeded the project objective of achieving a minimum lead uptake of 200 mg/kg lead. Based on estimates of plant biomass from each planting, the total mass of lead removed from the treatment plot by all three crops was approximately 51 grams.

Field Study IV: Fort Dix

A follow-on study to the Magic Marker research was conducted at SAFR #24 located at Fort Dix in New Jersey. The objective of the Fort Dix demonstration was to reduce soil lead concentrations to less than 400 mg/kg lead as mandated by the New Jersey Department of Environmental Protection residential soil standard, or a TCLP concentration of 5 mg/L or less for each sample collected. The Fort Dix study was an ex situ study consisting of a 5,060-m² (0.506-ha) lined treatment cell. Lead fragments were removed from the sandy soil before planting. The cell contained a drainage system to collect excess water from irrigation and a lined precipitation basin was configured to recirculate the system water. As in the Magic Marker study, Fort Dix was planted with three successive crops of

Indian mustard, sunflower, and mixed grasses. The average plant uptakes of lead were 1,400; 1,750; and 4,400 mg/kg lead, respectively. Each crop was subjected to above average rainfall and was also irrigated with cell leachate containing both lead and EDTA. The final post-harvest soil lead concentration was 290 mg/kg, which was below the target soil lead concentration of 400 mg/kg. However, an amount equivalent to 28 mg/kg in the soil was found in the recirculated water from the cell, and 20 mg/kg lead was found in the aboveground plant material. The remaining 177 mg/kg of soil lead was unaccounted for.

Field Study V: Twin Cities

A fourth study was conducted at the Twin Cities Army Ammunition Plant (TCAAP) located in Arden Hills, Minnesota (TCAAP 2001). TCAAP is a federally owned facility, approximately 4 square miles in size. Alliant Techsystems Inc. manufactured ammunition there beginning in 1941. In 1983 it was listed as a federal Superfund site. The Army contracted with the Tennessee Valley Authority (TVA) to oversee a phytoremediation project at the TCAAP. Huang et al. (1997) suggested that after a crop has become well-established and is of sufficient biomass, a selected chelator could be applied to the root zone to facilitate rapid lead accumulation. The plant should be harvested shortly after chelator addition to reduce environmental risk. This approach was applied at TCAAP. Two test plots (C and 129-3) were established in May 1998 and planted with corn and white mustard. The soil at site C was peat, underlain by fine sand and sandy clay. Site 129-3 was composed of fine to medium-grained sand. Both sites contained high volumes of sand, creating an opportunity to observe potential leaching. Amendments containing EDTA and acetic acid were applied to the soil to enhance the mobilization and uptake of lead. A report from the first year indicated that the water balance was too high due to rain and overwatering, and the growing season was shorter than expected. The plants were stressed by insufficient nutrients; therefore, Pb uptake was less than anticipated. The first crop, corn, yielded only 2.1 to 3.6 tons of biomass per acre compared to the anticipated yield of 6 tons per acre, and the dry weight lead concentrations averaged 0.65 and 0.13 percent for sites C and 129-3, respectively. White mustard, the second crop, yielded 1.9 to 2.1 tons of biomass per acre where it was capable of growing. Average dry weight lead concentrations were low, 0.083 and 0.034 percent for sites C and 129-3, respectively. After the application of EDTA, readings from monitors showed increasing amounts of lead and EDTA leaching deeper into the soil column. Beginning in October 2000, contaminated ground-

water from the study areas was extracted and treated to remove the lead and EDTA. At the third year, the project was terminated when lead was found contaminating the groundwater under the site. In June of 2005 the Minnesota Pollution Control Agency (MPCA) fined the U.S. Army Environmental Center (USAEC), Tennessee Valley Authority and Alliant Technologies Inc. for violations stemming from the phytoremediation project, citing failure to obtain a permit for the project and some of the monitoring equipment. They further stated that the project should have been terminated after the first year when it was discovered that lead and EDTA were moving down in the soil column.

Conclusions and recommendations

Metal-contaminated soils are difficult to remediate through phytoremediation. Phytoremediation is most successful at sites with low to moderate concentrations of bioavailable metals at relatively shallow depths, with soil media favorable to plant growth, and in areas where excavation would be detrimental to existing vegetation.

There are at least 400 known metal hyperaccumulators in the world; however, a limited number of these are Pb^{2+} hyperaccumulators. The hyperaccumulation of lead is rare due to the limited free lead (Pb^{2+}) available in soil for absorption. Lead is known to form a precipitate within the soil matrix, has low aqueous solubility, and, in many cases, is not readily bioavailable. In most soils capable of supporting plant growth, the soluble Pb^{2+} levels are relatively low and will not promote substantial uptake by the plant even if it has the genetic capacity to accumulate the metal. In addition, many plants retain Pb^{2+} in their roots via sorption and precipitation with only minimal transport to the aboveground harvestable plant portions.

Therefore, if phytoremediation of lead is to be successful, the bioavailability of Pb^{2+} must be enhanced or specific plants that can better translocate the Pb^{2+} into harvestable portions must be found (Kumar et al. 1995). Synthetic chelators, such as EDTA, have been shown to aid in the accumulation of Pb^{2+} in the plant tissue. EDTA and other chelators have been used in soils and nutrient solutions to increase the solubility of metal cations and the translocation of Pb into shoots (Li et al. 2005, Schmidt 2003). Despite an overall increase of Pb in the shoots, there are differences, however, in the extent of accumulation at equivalent chelator levels among various plant species (Huang et al. 1997). Furthermore, it should

be noted that chelator-induced hyperaccumulation might prove fatal to the plant; however, the dying plant can still be harvested and processed for Pb^{2+} recovery or disposal.

Unfortunately, the disadvantages associated with these amendment strategies include increased bioavailability to other animals and humans, as well as increased mobility in the environment. Increasing Pb solubility increases the chance for it to enter the groundwater. The increased bioavailability to plants also makes it easier for Pb to enter the food chain by being ingested by animals eating the plants. Because of these environmental concerns, if chelators are employed it is necessary to minimize their addition and operate in closed systems.

The costs associated with construction of lined systems, treating surface and leachate water from the site and/or disposal of water containing leachate, reduces or eliminates the cost advantage associated with phytoremediation over traditional “dig and haul” techniques. The high costs associated with extended periods of operation, construction of lined systems, aggressive techniques to increase bioavailability, along with the risks associated with increased lead migration and unwanted bio-uptake make phytoremediation an unattractive technology for small arms range soil remediation.

4 Physical Separation

Overview of separation technologies

Physical separation technologies are the most frequently utilized processes for one-time cleanup of closed SAFRs, as well as for periodic removal of lead as a part of routine maintenance of active SAFRs. Most of the separation technologies and equipment used at ranges have been adapted from the mining industry and are readily available and relatively inexpensive. In some cases, physical separation alone may be sufficient to reach treatment goals. In general, however, physical separation is simply the initial process in which the bulk of the lead is removed. It is followed by additional cleanup technologies that either remove or stabilize the remaining lead fraction. Physical separation can also be an intermediate process for an advanced treatment train. Physical separation processes use particle characteristics such as size, shape, density and/or magnetism for separating particles (Battelle 1997). The two physical characteristics identified as providing the basis for separating particles from ranges are particle size (using sieving) and density (using gravity separation).

Particle size separation

Size separation is a mechanical process in which the soil material is applied to one or more chambers with progressively smaller openings. Material is sorted based on whether it passes through or is retained at each step. The process can be wet or dry, stationary or gyrating. Some common equipment types are screens, sieves and trommels. Particle shape, uniformity, agglomeration and blockage can affect the performance of these systems.

Dry sieving

Dry sieving technologies use different size sieves or screens, often in a nested or sequential configuration, to segregate materials according to particle size. Dry sieving is an effective method for separating different sized particle fractions, is relatively efficient and cost-effective, and requires minimal mobilization effort. Conventional dry sieving is effective for a wide range of particle sizes. However, sieve sizes smaller than 0.25 in. may require very dry soil (depending upon the soil silt and clay content) due to blinding and blockage of the screen, and hard clumps of

soil may not break up and thus may be retained intact on the larger screens. Dry sieving does not differentiate between organic, metallic, and geologic materials, and cannot separate bullets and bullet fragments from soil material of the same size. Most of the fine-grained particulate lead that typically contributes the bulk of leachable metal in the TCLP test of berm material often passes through the finest practical screen size and is not recovered. The metal particles that are recovered may be co-mingled with sufficient non-metal particles to reduce or eliminate the value of the mix for commercial recycling, thus requiring either disposal or additional separation (and cost) using another technology before recycling. There are often health and environmental issues regarding dispersion of dust and distribution of lead adsorbed to the finer-sized soil fractions from dry screening operations. Figure 37 is a sieving unit process at Fort Lewis, Washington.



Figure 37. Vibratory sieving, evergreen remediation (Ft. Lewis, Washington)

Wet sieving

Wet sieving uses water to slurry, de-agglomerate the soil, and aid the passage of the material through screens, often in a nested or sequential configuration, for separation according to particle size. In addition to de-agglomerating soil material, wet sieving is also effective for washing adsorbed contaminants and co-mingled organic matter from sand and gravel, so that they are mixed with the finer size fractions. Similar to the dry process, wet sieving alone does not differentiate between organic, metallic, and geologic materials, and cannot separate bullets and bullet fragments from soil material of the same size.

Some ranges near wetland areas or in naturally wet environments may remain too damp for dry screening, making wet screening the only practical means for particle size separation. Wet separation is most worthwhile if a sizable fraction of the metals is particulate and a substantial proportion of the screened soil can be rendered either non-hazardous or significantly reduce the amount of chemicals needed for further treatment. Some follow-up treatment processes benefit from wetted soils. Wet screening creates some potential problems: wetted soils may be difficult to handle in subsequent treatment steps, water can be recycled within the process but at the end of the process must be handled as a waste product, and some soils such as clays can be difficult to handle in the screening step. Some popular equipment options are drum screens and trommels.

Deagglomeration

Deagglomeration is a mechanical process that separates particles from each other by scrubbing oxide or other coatings from particles. While not specifically a size separation, deagglomeration processes can be used to condition soils prior to size or density separation. At SAFRs, the mixing parameters are selected to aid the breakup of soil agglomerates, separate lead particles from the soil fraction, and remove lead smears from soil particles (Hlousek and Phillips 2000).

Attrition scrubbing consists of two cells each with an aggressive agitator and two opposing turbine blades to mix the soil /water slurry (Hlousek and Phillips 2000). The deagglomeration is a result of soil scrubbing (both particle to particle and equipment to particle abrasion). Studies indicate 60- to 70-percent solids slurry provides optimum deagglomeration of range soils without grinding the particles (Hlousek and Phillips 2000).

A *trommel* is a multi-cell horizontal rotating drum separator. The initial blind section takes the wet feed and acts as a tumble deagglomerator and the rear section(s) contain a wire screen and spray bars to further deagglomerate and screen the particles.

Density/gravity separation

The specific gravity of lead is approximately 11.5, while that of rock/soil/sand can vary, but can be approximated at 2.5. This makes gravity separation techniques effective for range remediation.

Dry gravity separation

Dry gravity separation technologies separate particles based on differential settling (related to particle size, shape, and density) through a horizontal or rising air stream. Dry gravity separation works well for non-plastic soils, such as sand or gravel, that do not contain substantial amounts of silt-and-clay-size particles. Like dry sieving, it works less well for agglomerated clayey or silty soils. Current information indicates that dry gravity separation is most successful for plus-No. 4-sieve size (4.75 mm or 0.187-in.) material. Each fraction consists of various size stones and metal particles that have the same settling velocity through the air stream, so dry gravity separation may be combined with a size classification technology to form a separation system. A major advantage of dry gravity separation is that contaminated aqueous streams are not generated.

Wet gravity separation

Wet gravity separation technologies separate particles based on differential settling (related to particle size, shape, and density) through water. These technologies can be very effective for separating organic, metallic, and geologic particles of the same or similar size, such as segregating spent bullets and bullet fragments from sand and gravel. Wet gravity separation technologies typically have higher mobilization costs (due to fabrication of the different separation modules/circuits) than dry gravity separation technologies, and produce a “waste stream” of process water that must be managed when the separation activities are completed. Each separated fraction consists of various size stones and metal particles that have the same settling velocity in water, so wet gravity separation may be combined with a size classification technology to form a separation system.

The *Mineral jig* (Figure 38) is a wet gravity separation apparatus that uses a pulsating rising and falling flow of water in which the particles of a high specific gravity, such as lead, sink to the bottom and are periodically withdrawn. Lighter particles overflow from the top of the jig.

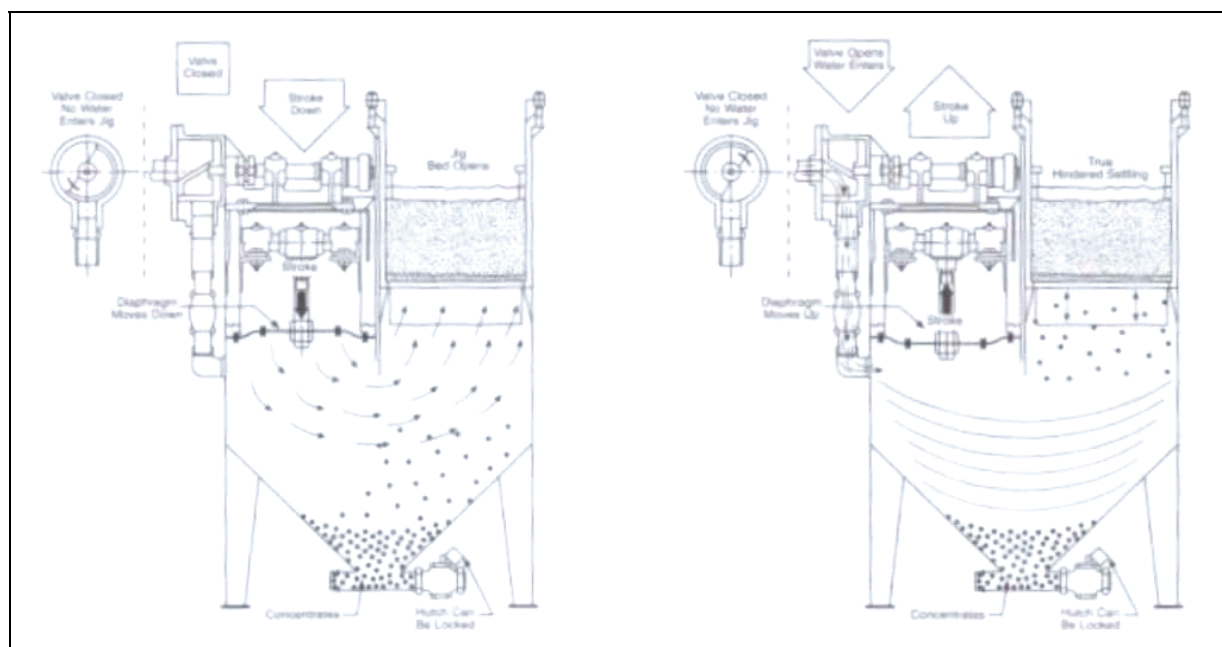


Figure 38. Mineral jig (Hlousek and Phillips 2000).

Spiral concentrators use gravity and centrifugal forces to segregate particles based on specific gravity. Water and solids in a 10 to 40 percent slurry are fed into the top of curved channels in the form of a spiral. Lighter fractions (low specific gravity) are spun by centrifugal forces to the outside, while heavier fractions are held inside by gravity. Ports are strategically located to draw off the different fractions. Figure 39 illustrates a spiral concentrator and a Reichert concentrator.

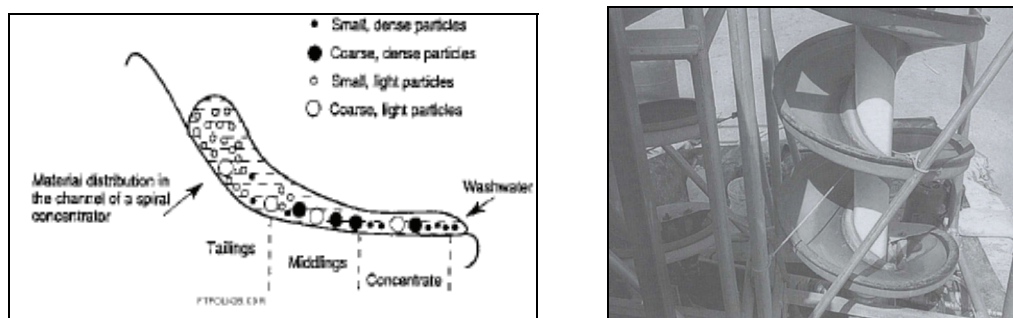


Figure 39. Left: Spiral concentrator (Battelle 1997). Right: Reichert concentrator, Miramar Pilot Plant (Hlousek and Phillips 2000).

Shaking tables utilize water flow, gravity and vibration to separate fractions (Figure 40). A solids slurry (approximately 25 percent) is introduced at the upper corner end of an inclined table with longitudinal riffles (Battelle 1997). The table is vibrated at right angles to the slurry flow with a

slow forward stroke and a quick backstroke. This vibration along with the riffles causes the smaller, denser particles to settle in the riffles near the feed end and the coarser lighter particles to pass over riffles to the opposite side.

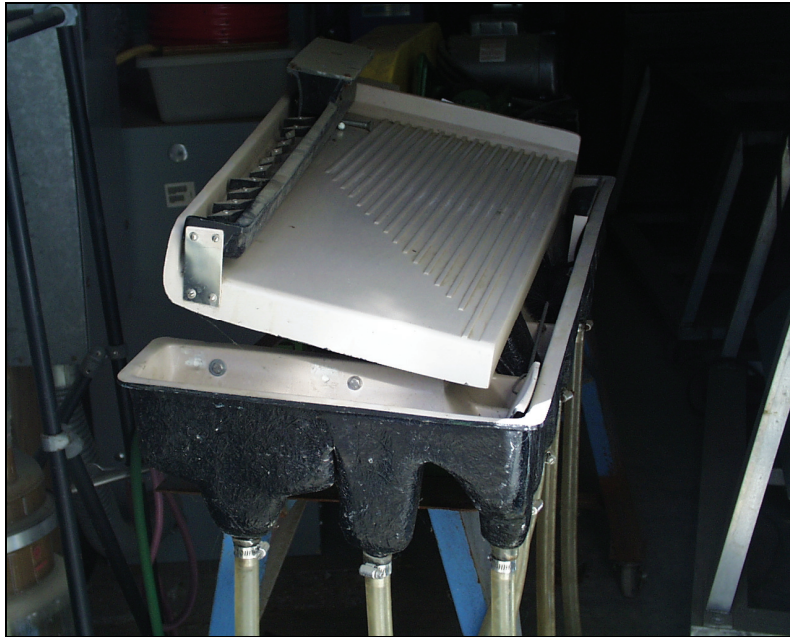


Figure 40. Wet shaking table.

Bowl concentrators use a strong water flow and gravity to separate fractions. The slurry is bottom fed into a ribbed cone, which is rotated, producing about 60 g's of gravitational force. Water is injected into small holes in the cone to fluidize the concentrate bed and keep it from compacting. The lighter fractions overflow the cone into the outer cylindrical shell and are managed as a separate stream. Figure 41 is a photo of a Knelson bowl concentrator.

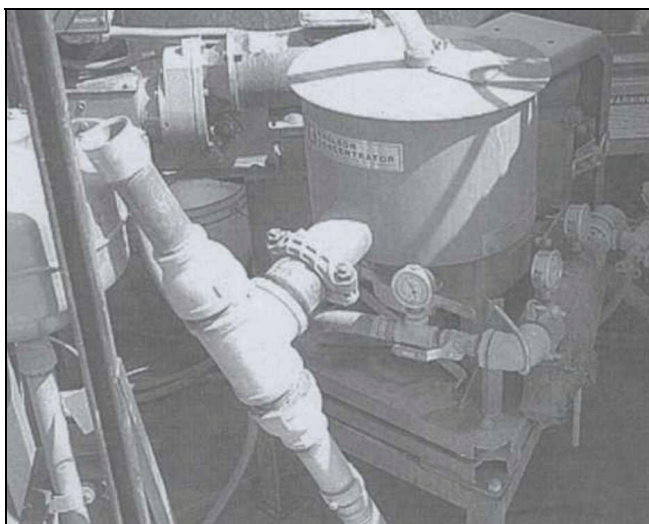


Figure 41. Knelson bowl concentrator, Miramar Pilot Plant (Hlousek and Phillips 2000).

An *elutriator* is a counter-current column in which water is injected into the bottom and particles injected further up the column. Falling particles reach terminal velocity based on the density, shape, and size. The process can be accomplished in a single column where extraction ports at different elevations pull off particles of different terminal velocities, or the particle fractions can be separated in a series of columns with varying water flow rates.

Rake or spiral classifiers separate particles by passing a slurry into a pond, tank, or trough where settling or cross-flow of water carry the lighter fractions over an overflow weir and a rake or screw auger lifts the settled sand fraction. In addition to density separation, rake or spiral classifiers are also effective dewatering processes. Figure 42 is a diagram of a spiral classifier.

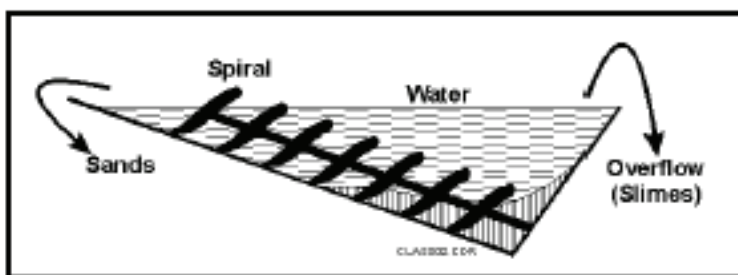


Figure 42. Spiral classifier (Battelle 1997).

Hydrocyclones (Figure 43) are continuous processes that use centrifugal force to separate the larger, denser, particles from the fines. The slurry is

fed into the top of an inverted cone rotating on its axis. The heavier or larger particles move quickly to the outer walls and drift in a spiral motion down the cone walls to the bottom opening. The lighter fractions move to the low pressure zone in the vortex and are pulled off the top.

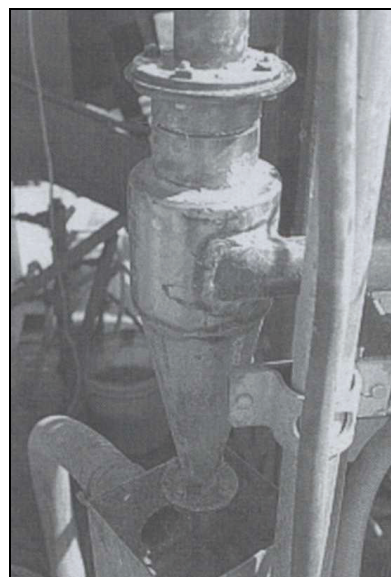
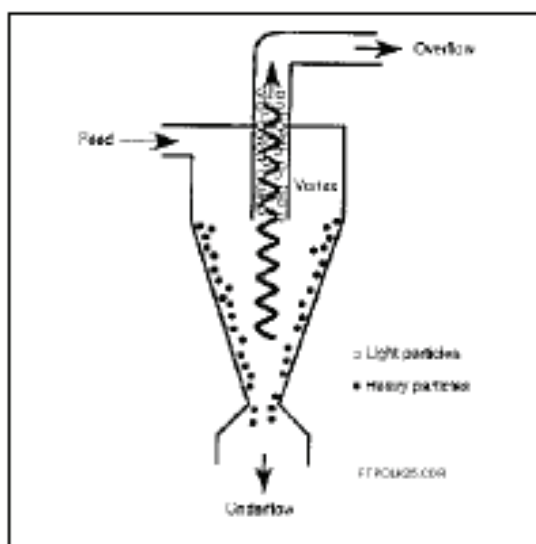


Figure 43a. Hydrocyclone (Battelle 1997), b. Hydrocyclone, Miramar Pilot Plant (Hlousek and Phillips 2000).

Integrated separation systems

Soil separation systems employ combinations of sieving and gravity separation technologies in a system optimized for the properties of the particular soil matrix and metal particles to be processed. In general, a system that combines the two types of technologies provides for recovery of particulate metals and classifies soil fractions by both size and density. Contaminants that are adsorbed to soil fines and organic matter can be partitioned and the concentrated contaminant-bearing material can then be segregated from the clean soil fractions for subsequent treatment or disposal. Particle separation systems that combine dry or wet sieving with water-based gravity separation techniques have proven capable of effectively separating metal particles from selected soil size fractions and producing a recovered product with sufficient purity to be potentially economically recyclable (i.e., 90 percent metals content). Dry (pneumatic) gravity separation techniques are capable of producing coarse metal fractions (i.e., plus-No. 4 sieve size) with a purity of 90 to 95 percent.

Technology conclusions

Size and gravity separation technology offers simple, inexpensive equipment with continuous and high throughput. The equipment is readily available and adaptable from the mining and milling industries. This makes this class of technologies very attractive for range cleanup.

The limitations with these processes include: the screens plug, the finer screens tend to be fragile, the dry processes can produce dust, and the wet processes can be difficult if there are high proportions of clay, silt or humus in the berm material (Battelle 1997). Table 13 presents various equipment types and generalized operating parameters for grain size suitability.

Table 13. Equipment Particle Size Operating Range (adapted from Battelle (1997) and Hlousek and Phillips (2000)).

Separation	Process	Particle Size Range (µm)
Size	Dry Sieving	>3,000
	Wet Seiving	>150
Density	Elutriator	>50
	Hydrocyclone	5 to 150
	Spiral Classifier	5 to 100
	Mineral Jig	>150
	Spiral Concentrator	75 to 3,000
	Shaking Table	75 to 3,000
	Bartles-Mozley Table	5 to 100

For dry and wet gravity separation technologies, as well as for dry and wet size separation technologies, as the size of the metal particles to be segregated gets smaller, the ability of the technology to segregate materials of sufficient purity for cost-effective recycling, as well as the operational efficiency of the equipment, requires more detailed pre-operational testing and evaluation. Performance-based treatability studies are typically required to provide the level of data necessary for selection and design of an optimal site-specific separation process or system, whatever the type of separation technology used. A treatability study may be as simple as determining particle size distribution, distribution of lead in soil fractions, soil density, and percentage of organic material in the soil of interest.

Lab, bench, and field study summaries

Particle separation at Fort Dix Range 25

Concurrent Technologies Corporation (CTC) conducted an evaluation of particle separation technologies for Range 25 at Fort Dix, NJ (CTC 2001). Although the project was specific to this particular range, many of the findings can be extrapolated reliably to SAFRs in general. The evaluation criteria were that the separation technologies effectively separate bullets, bullet fragments, and other metal particles from coarser-grained soil fractions with:

- Efficient separation of the impact berm soil according to predetermined size fraction, based on the sieve sizes in Table 14.

Table 14. Particle (sieve sizes used to characterize soil for CTC (2001) Fort Dix study.

Sieve Sizes
+4.76 mm (+4 mesh)
+2.0 mm (+10 mesh)
+0.425 mm (+40 mesh)
+0.150 mm (+100 mesh)
+0.075 mm (+200 mesh)
-0.075 mm (-200 mesh)

- Separation of metal particles from the largest soil fraction (i.e., above the largest cut point) with a sufficient purity to be recyclable (i.e., 90 percent metal content).
- After particle separation has been completed, the largest soil fraction will have a maximum residual total lead concentration of 400 mg/kg.
- Environmentally hazardous materials will not be used during processing, nor will the separation technology create a secondary waste stream.

The Fort Dix evaluation addressed wet and dry sieving to separate materials into fractions based on passage through various mesh openings, and gravity separation based on settling differences in air or water due to specific gravity, particle size, and particle shape.

The backstop material at Fort Dix Range 25 was of relatively uniform grain size, comprised of 3.52 percent gravel, 89.96 percent sand, and 6.63 percent silt and clay. This made the soil amenable to particle separation technologies. A lead particle size distribution for the Range 25 backstop demonstrated that the majority of lead particles were contained in the plus-No. 4-sieve size material (45.24 percent), while the second highest concentration of lead particles was present in the No. 100 to No. 200 sieve size material (21.17 percent). The minus-No. 200 sieve size fraction represented the third highest lead concentration, which was assumed to be predominantly in the form of ionic lead adsorbed to the silt and clay size particles. The intervening size fractions (minus No. 4 to plus-No. 100 sieve sizes) accounted for 15.30 percent of the lead particles. While the size distribution of lead particles is different in every range backstop (see Chapter 2), this general pattern of the most lead in bullets and large bullet fragments and large amounts in very fine particles is common. The soil and lead particle size distributions were used to estimate the feed soil lead concentrations at Range 25. All soil size fractions had total lead concentrations well in excess of the 400-mg/kg technology evaluation criterion. This indicates that size separation alone would not meet this technology evaluation criteria.

A brief survey of firms that provide particle separation services for SAFR soils identified four nationwide vendors with the capabilities to potentially meet the technology evaluation criteria. One of the four vendors used a dry sieving/dry gravity separation system, while the other three used wet/dry combination systems. The four vendors, their soil-processing systems, and an estimated cost per ton for the site-specific feed soil characteristics of the Ft Dix Range 25 backstop are summarized below.

- **Vendor #1** – Vendor #1 developed a hybrid dry sieving process reportedly capable of size separations as small as the No. 100-sieve size in a totally enclosed and dust-suppressed screen box that can substitute for the more traditional initial wet-screening step of separation systems. The estimated cost for processing large quantities (greater than 10,000 tons) of soil is \$35 to \$40 per ton for a wet sieving and wet gravity separation soil processing system. An estimated potential cost reduction of up to \$10 per ton could be realized by substituting the hybrid dry sieving process for the conventional wet sieving process. This estimate assumes a soil feed rate of approximately 30 tons per hour. With the hybrid approach, Vendor

#1 estimated the total particle separation cost could approach \$25 to \$35 per ton.

- **Vendor #2** - Vendor #2 employed a completely dry separation system operating on pressurized air, and demonstrated the ability to recover 90 – 95 percent pure metal products from sandy soils, which is consistent with economic recycling. Specific information could not be obtained as to the lowest sieve size material that could be processed with this method, nor what residual lead concentrations could be expected in the processed soil. The vendor estimated a cost of \$35 to \$50 per ton of processed feed soil, based on a soil feed rate of approximately 150 to 200 tons per hour.
- **Vendor #3** – Vendor #3 utilized a process that includes dry screening combined with wet gravity separation. The vendor estimates a cost of \$10 to \$15 per ton of processed feed soil, based on a soil feed rate of approximately 50 to 150 tons per hour.
- **Vendor #4** - Vendor #4 also utilizes a process that includes dry screening combined with wet gravity separation. The vendor claims that their particle separation process is capable of size separations as small as the No. 100 sieve size at a soil feed rate of 25 tons per hour. The vendor did not provide an estimated soil processing cost.

The following general conclusions can be drawn from the Fort Dix assessment of particle separation technologies:

- Proven technologies can meet the technology evaluation criteria.
- Four nationwide vendors indicated that their respective particle separation processes could meet the technology evaluation criteria, but estimates of process effectiveness, efficiency, and cost depend on site-specific characteristics of the soil material to be processed.
- Performance-based particle separation and stabilization treatability studies are necessary to determine the site-specific optimum selection of materials for separation and materials to be managed by other methods and/or off-site disposal. In many cases, size separation alone is not likely to reduce the total quantity of material requiring additional treatment to meet site-specific goals for total lead content.

Gravity separation and leaching studies on berm material from three military installations

The Colorado Minerals Research Institute (CMRI) performed bench-scale treatability studies on berm material from NAS Miramar, Twentynine Palms Marine Station, and Fort Dix Army Base in 1996 (Hlousek and Phillips 2000). The intent of the bench studies was to develop data that could be used to select a demonstration site and to optimize pilot plant operations during the field demonstration. The three facilities were selected based on berm lead contents of at least 1,000 mg/kg in large particles, as lead smears on coarse and sand soil fractions, and as lead oxides in the slimes fractions. Two samples from each facility were furnished. There was an initial 3/8-in. wet screening of the samples to deagglomerate. However, no significant agglomeration was noted from any of the samples. The initial step was particle sizing followed by gravity separation. Each sample was sieved into six size fractions and each fraction was analyzed for lead content. The total volume of lead, by weight, in each fraction and in the total sample volume was calculated.

Table 15 lists the six size categories defined in the study by the Sieved Fractions using the U.S. Standard Sieve Series.

Table 15. Sieve size fractions used in CMRI studies.

Sieve Sizes
+9.50 mm (+3/8 in.)
+4.76 mm (+4 mesh)
+1.19 mm (+16 mesh)
+297 μ m (+50 mesh)
+105 μ m (+150 mesh)
-105 μ m (-150 mesh)

The screening fractions were then separated by gravity methods into concentrates, middling, and tailings fractions.

Table 16 presents the original size fractions and the gravity method used for separation and the effluents from those gravity methods.

Table 16. Gravity separation methods used in CMRI studies.

Size Fraction	Gravity Method and Effluents Produced
Humates	Skimmed from +3/8 in. tailings
+3/8 in.	Jig producing a tailings and concentrate
-3/8 in by +4 mesh	Jig producing a tailings and concentrate
-4 mesh by +16 mesh	Jig producing a tailings and concentrate
-16 mesh by 50 mesh	Shaking table producing a tailings, middlings, and concentrate
-50 mesh by +150 mesh	Shaking table producing a tailings, middlings, and concentrate
-150 mesh (First Sample)	Shaking table producing a tailings, middlings, and concentrate
-150 mesh (Second Sample)	Knelson bowl producing a tailings and concentrate

Again, the gravity fractions were analyzed for lead and percent weight to total. It could then be determined what fractions were deemed “clean” (<500- mg/kg) and which required chemical treatment.

NAS Miramar

The NAS Miramar soils contained some gravel particles and a high percentage of sand and fine material. The gravity separation processes (refer to Table A.1, Hlousek and Phillips 2000) indicated two size fractions tailings required additional treatment to meet the 500-mg/kg Pb target; -4 mesh by +16 mesh (Pb concentration 3045-mg/kg) and -150 mesh (3870-mg/kg). These two fractions represented approximately 44 percent of the berm soil by weight. The combined concentrates streams from the gravity separation units averaged 92,500-mg/kg Pb and represented approximately 11 percent of the soil by weight.

Twentynine Palms Marine Corps Base

The Twentynine Palms soil contained coarse gravel and sand particles with a small amount of fine material. The gravity separation processes (refer to Table A.2, Hlousek and Phillips 2000) at the Twentynine Palms Site reported the coarse tailings fraction, representing approximately 25 percent berm soil by weight, was < 500-mg/kg Pb and required no further treatment. The two sand fractions (744-mg/kg and 588- mg/kg Pb, respectively, representing 51 percent soil by weight) and the Fine fraction (19,894-mg/kg Pb representing 9 percent soil by weight) required further treatment. The combined concentrate streams had approximately 65,400-mg/kg Pb and represented about 15 percent soil by weight.

Fort Dix

The Fort Dix material contained sand particles with small amounts of gravel and fine material. The gravity separation processes (refer to Table A.3 (Hlousek and Phillips 2000)) revealed most of the tailings and mid-dlings fractions above size +150 mesh passed the “clean” criteria. The –150 mesh represented about 9 percent of soil by weight (Pb 2590-mg/kg). The total concentrates stream represented 9 percent soil by weight and had an average Pb of 33,400-mg/kg. The Fort Dix samples were eliminated from the leaching studies since there were no coarse size fractions requiring leaching and the weight percentage of the fines fraction was less than 9 percent.

The particle size separation step did not produce a “clean” fraction that could be removed from the treatment stream for all sites and samples. Gravity separation did recover most of the larger metal particles from the coarse and sand fractions and most of the heavy lead-coated soil particles. The particles remaining after gravity separation, that required chemical leaching, were very fine and had a high surface area-to-volume ratio.

The following are general conclusions from the CMRI study sites:

- Size separation alone did not result in lead concentration reduction to 500-mg/kg in all fractions.
- Coupling particle sizing with gravity separation removed most of the lead from +150 mesh particles, yielding a product containing <500 mg/kg.
- The combined concentrates from gravity processes represented about 11 percent of the berm material and had an average concentration of approximately 92,000-mg/kg.
- Attrition scrubbing of the –4 and +16 mesh fraction of Miramar soils demonstrated deagglomeration as indicated by increase of the –16 mesh fraction. Gravity concentration of the scrubbed soil produced a “clean” fraction representing 68 percent of the scrubber feed.
- Hydrocyclone tests were inconclusive.

Equipment recommendations

Based on the range evaluations and field testing at Miramar (Hlousek and Phillips 2000), the equipment recommendations for a full-scale, modular, mobile system for range cleanup include four different processes: deagglomeration, particle sizing, gravity separation, and dewatering.

For deagglomeration, the equipment recommendations were based on soil type (Table 17):

Table 17. Deagglomeration equipment recommendation based on the soil type.

Soil Type	Equipment
Coarse Sand	High Pressure Spray and Vibrating Screen
Clays and High Fines Soil	Trommel Log Washer Combination Unit

Attrition scrubbers were found to be less advantageous for range soils. Antimony in lead bullets reacted over time, making the older bullets brittle and more prone to breaking into smaller fractions with the grinding action of the attrition scrubber agitators. This increased the difficulty of recovering lead fines and possibly would result in more material requiring a chemical treatment. Additionally, it was found that the maintenance requirements increased due to the increase in wear of the scrubber liner from the typical coarse fraction of soil found in range soils.

Particle sizing

Particle sizing was recommended at four stages in the process stream:

- Sizing was recommended for the feed material by using *grizzly screens* (either a two-deck unit or two units in sequence). It was suggested that 2-in. (-50.8-mm) and 1-in. (25.0-mm) screen openings be used.
- The second use of particle sizing was a two- or three-deck *vibrating screen with a high pressure spray* that would immediately follow the *grizzly assembly*. The screen sizes would be determined by treatability testing and based on the operating ranges of the gravity equipment.

- The third particle size operation would use a *spiral classifier* for de-sliming. It would separate the +150 mesh soil from the humates and the -150 mesh soil.
- The final use would be *vibrating screens* to remove water and undersize soil particles from the primary and secondary jig and tailings and water from the spiral concentrate.

Gravity separation

Gravity separation was examined for coarse (+16 mesh, +1.19 mm) and sand (-16 mesh by +150 mesh, -1.19 mm by 105 μ m) fractions.

- *Shaking tables* were considered for both fractions, but lack mobility, required construction of base support and had uniform feed requirements making a mobile field unit impractical.
- *Riffles* were evaluated for the coarse particle range but proved to be labor intensive, produced a concentrate less concentrated than that of the mineral jig, and were inefficient for soils with high clay concentrations.
- *Duplex mineral jigs* were chosen for gravity separation of the coarse fraction. They are easily obtained, effective at removing lead, and use the same amount of water as other processes.
- For the sand fraction, both *Reichert spiral* and *Knelson bowl concentrators* were evaluated and were found effective. The *Reichert spiral concentrator* was recommended for its mobility, ease of installation, and because it is inexpensive to operate.

Dewatering

Dewatering is a critical and costly operation in the soil washing treatment train. The recommended dewatering process includes a *clarifier and small centrifuge*.

Costs

Based on 1997 dollars, the hypothetical mobile treatment train recommended by this study would cost \$119.60 /ton to purchase and operate. This assumes a 3870-yd³ site (5800 tons), a process rate of 15 tons/hr, and 90 percent on-line treatment efficiency.

Picatinny Arsenal, Armaments Technology Facility

Stevens Institute of Technology (SIT 2003) investigated the reuse of lead-contaminated soil from the projectile impact berms as impact media at the Armaments Technology Facility (ATF) at Picatinny Arsenal. The impact media is dredged sand made up of seashells, micas, and weathered products of decomposed granite, all of which are susceptible to pulverization upon repeated bullet impact due to their inherent mineralogy. The grain size distribution and mineralogical and micro-morphological analyses comparison of virgin material to ATF berm material confirmed that the ATF soils had undergone significant pulverization (up to 30-percent increase in fines). Dredged sand was not recommended for firing range berms.

Conclusions and recommendations

Using size and density, relatively uncontaminated fractions can be separated from contaminated ones. As discussed above, removing the bullets alone will generally not meet clean soil requirements for all the size fractions. However, in most cases, substantial fractions can be deemed “clean” based on total lead or TCLP lead analysis. Therefore, physical separation can be an effective approach to minimize treatment or disposal volumes.

Whether it is cost effective to employ separation or separation with secondary treatment depends largely on the size of the range and factors that affect landfilling costs (size of range, distance to landfill, etc.). Physical separation requires certain field mobilization costs that are fixed, regardless of the range size. So, for small ranges, treatment per ton cost is likely to be higher than for larger projects. Similarly, more complex separations are likely to be more cost effective for larger soil volumes. Many of the treatment technologies discussed later in the document (chemical stabilization, soil washing) require intact and large bullet fragments to be removed in order to be effective. To accomplish this, multistage treatment trains are often needed, which further increases costs.

Lead recycling is often cited as a benefit for physical separation. Based on an informal telephone survey of approximately 15 lead reclamation firms, it was not possible to conclude if recovery of lead from firing ranges is profitable. Lead scrap (bullets and fragments) is a low value resource with high transportation costs. Reclaiming firms reported that the price they can get for lead as scrap metal fluctuates widely and unpredictably, mak-

ing it difficult to determine whether the costs of a particular reclamation project will be covered adequately by the price they will be able to obtain for the lead after it is reclaimed. However, Amec, Inc. has reported in several seminars that they have recycled lead from cleanup projects and that the recovered costs have been worthwhile, particularly when compared to disposing the material.

5 Solidification and Stabilization

Introduction

Solidification/Stabilization (S/S) is a group of long-term waste management techniques to control the solubility and mobility of metals in the treated soils and sediments. Historically, S/S described several processes by which organic or metal-bearing wastes could be treated or encapsulated to remove their hazardous characteristic (Cullinane et al. 1986). S/S is an established technology, having been used for almost 20 years to treat a variety of wastes at Superfund remedial sites throughout the country. It is one of the top five source control treatment technologies and has been used at more than 160 sites since FY 1982 (US EPA 2001). Overall, completed S/S projects represent about 30 percent of all completed projects in which treatment technologies have been used for source control. The average operational time for S/S projects was 1.1 months, which is shorter than other technologies such as vapor extraction, land treatment, soil washing, and composting.

The majority (94 percent) of S/S projects at Superfund remedial sites are ex situ applications where inorganic binders and additives were used to treat metal-containing waste. Available performance data for metals for these projects showed that S/S met the established performance goals.

The cost of using S/S to treat wastes at Superfund remedial sites was available for 29 completed projects. The total cost ranged from \$75,000 to \$16 million. The cost per cubic yard for these S/S projects averaged \$264, including two projects with exceptionally high costs (approximately \$1,200/yd³ each). Excluding those two projects, the average cost per cubic yard for S/S was \$194.

An important distinction between the two processes, solidification and stabilization, is generally accepted (ITRC 2003):

“Solidification involves isolating the contaminants from the environment in a solid matrix, resulting in reduced permeability and surface area. The goal is to limit the mobility of the waste constituents to prevent leaching into the groundwater or other losses

to the environment. The end product of solidification is a monolithic block with high structural integrity.”

Solidification. A variety of solidifying agents have been studied including Portland cement, gypsum, modified sulfur cement (consisting of elemental sulfur and hydrocarbon polymers), and grout (consisting of cement and other dry materials such as active fly ash or blast furnace slag) (Cullinane et al. 1986). The process increases the particle size (reduces surface area) and produces a material with a high buffering capacity in the alkaline pH range.

Stabilization. In contrast, stabilization or chemical treatment uses chemical reagents that react with the contaminants and the soil to form product compounds that have very low solubility and high stability (ITRC 2005). Because of the formation of nearly insoluble and very robust mineral compounds, stabilized wastes are often considered more protective of groundwater and the environment than their solidified counterparts. The most promising stabilization process applicable to SAFRs involves the stabilization of lead in soils by the addition of phosphate material, as many lead phosphate minerals have exceedingly low solubility and high stability.

In situ vs. ex situ application

S/S of soils at firing ranges can be performed in situ or ex situ. In situ treatments have advantages in costs because they reduce soil handling. In addition, in situ applications can also reduce or eliminate hazardous waste regulation of the contaminated soil, because, in many cases, soils only become RCRA hazardous wastes when they are excavated. However, in situ applications tend to be more challenging than ex situ approaches, as treatment conditions can be more thoroughly controlled in an ex situ reactor. Factors that limit the applicability and effectiveness of the in situ treatments include:

- Depth of contaminants. This may limit some types of application processes.
- Future usage of the site. Some proposed uses of the site may “weather” the materials and affect their ability to maintain immobilization of the contaminants.
- Possibility of significant volume increases (up to double the original volume).

- Reagent delivery and effective mixing. These are more difficult than for ex situ applications.
- Presence of solidified material. This may hinder future site use.
- Processing contamination below the water table may require dewatering.

In addition, firing ranges have special properties that tend to favor ex situ applications:

- Ranges can have substantial chunks of metallic lead, which act as reservoirs for further contamination (Chapter 2). Physical separation (Chapter 4) can effectively remove these, but this requires excavation of the affected soils.
- In most ranges, the most highly contaminated areas are berms and backstops. These are artificial mounds that would likely be removed or leveled upon the closure of the range, making ex situ treatment a logical approach.

Ex situ solidification methods differ from in situ methods in that the soil is usually stockpiled prior to treatment, then mixed with reagents with the use of pug mills or other specialized mixing equipment, and transported to its final resting site (Cullinane et al. 1986). Ex situ solidification usually supports higher rates of treatment in terms of tons/day, and provides much better mixing, creating a more homogeneous mix of the contaminated soils and the stabilizing agent. Consequently, ex situ solidification produces a more uniform final product that can easily be tested for uniformity and effectiveness throughout the processing. Ex situ treatment also allows for coupling with physical separation technologies (Chapter 4). Removing large bullet fragments improves long-term performance and separates out uncontaminated soil fractions, reducing treatment costs.

Some in situ approaches have been developed for ranges, particularly for treating large areas with low levels of contamination, such as the floor areas of a range. Nevertheless, ex situ treatment is likely to be best for most situations. Figure 44 is a schematic demonstrating how ex situ treatment could be used in the field. A firing berm is excavated, and physical separation methods (Chapter 4) are used to remove larger bullets and fragments. The resulting fine material undergoes stabilization treatment. This allows the soil to be disposed off-site as a non-hazardous waste, or even disposed on-site as a clean fill material. Better yet, the soil could be recycled either

as a construction material or as a new firing berm. This avoids many regulatory hurdles.

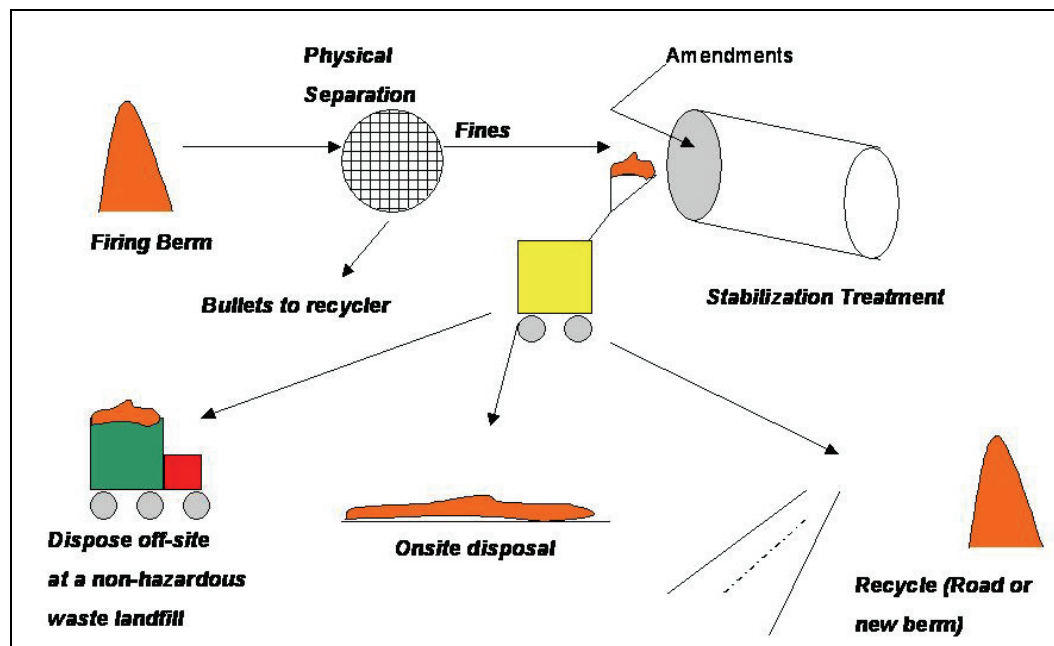


Figure 44. Schematic of ex situ chemical treatment of soil.

Solidification methodologies

Pozzolanic solidification methodology

These processes are based on silicates from pozzolanic-based materials like fly ash, kiln dust, pumice or blast furnace slag, and cement-based materials like Portland cement. These materials chemically react with water to form a solid cementitious matrix that improves the handling and physical characteristics of the waste (Jones 1990). Verification testing of the product depends upon the regulatory program, but generally includes analyzing for TCLP lead and any other metals present. Testing frequencies vary from one TCLP every 250 yd³ of soil treated, to every 500 yd³, based on the throughput of the operation. In addition, follow-up SPLP testing is often required. Total metals analysis of the final product should be performed to verify the site-specific remediation goals are met. The final product may be disposed of on-site, transported to a municipal landfill, or put to beneficial reuse.

Evaluation of pozzolanic solidification

TCLP alone is an inappropriate tool to evaluate the effectiveness of pozzolanic solidification. Losses of contaminants associated with particulates are not measured by the TCLP (Larson et al. 2004). In addition, the highly basic agents used in pozzolanic solidification processes introduce a significant future risk of large losses of soluble lead from the solidified wastes. The majority of solidification schemes currently used for treating heavy metals, especially lead, involve mixing a lime-based agent, such as Portland cement, or cement or lime kiln dust into the soil. During the TCLP, the lime added to the waste neutralizes the TCLPs' acidic leaching solution. This limits the leaching of the lead in the test resulting in "successful" waste solidification. However, when the waste is exposed to groundwater, precipitation, or surface water, this added lime will produce leachate having high pH (11-12). Under these conditions, due to the amphoteric nature of lead (and several other metals), lead levels may reach unacceptably high concentrations in the leachate and runoff. Therefore, lime-based treatments may enable wastes to pass the regulatory TCLP requirement, but can create severe environmental problems under actual future leaching conditions.

Table 18 illustrates this problem. It shows the results of an experiment in which a treated waste was submitted to a TCLP test followed by a single SPLP test (ITRC 2003). As seen, TCLP of the untreated soil contained high levels of lead, approximately 600-mg/L; however, the following SPLP resulted in <0.003 mg/L lead due to the low acid level of the SPLP leaching solution and the naturally low solubility of lead at natural soil pH values. The addition of 10 percent lime, or Portland cement at 10 or 15 percent, were successful in lowering the lead TCLP concentration to less than the 5.0-mg/L toxic characteristic cutoff, indicating successful lead isolation. However, neither were successful in passing a follow-up SPLP (i.e., Pb <5 mg/L) due to the very basic pH of the resulting SPLP leachate. The long-term effectiveness of solidification using alkaline pozzolanic materials or Portland cement in sequestering lead in contaminated media is questionable.

Table 18. Treatment of a TCLP-hazardous metal processing waste.

Treatment Media	Treatment (percent by weight)	TCLP result (mg/L Pb)	Final pH TCLP	SPLP result (mg/L Pb)	Final pH SPLP
Untreated	0	600	6.0	<0.003	8.2
Lime (Calcium hydroxide)	5	76	6.5	290	12.2
	10	0.2	8.6	540	12.5
	15	6.2	10.4	510	12.5
Portland cement	5	450	5.3	19	11.5
	15	<0.2	10.4	11	11.9
	25	1.2	11.6	12	11.9
Adapted from ITRC (2003).					

Vitrification

Vitrification is a solidification process that uses an electric current to melt the soil at extremely high temperatures. It immobilizes most inorganic contaminants and destroys organic pollutants by pyrolysis (Brice Environmental Services Corporation 1998, Brookhaven National Laboratory 2001, US Department of Energy 1998). This technology could conceivably be applied to SAFR soil pockets or excavated soil (ITRC 2003). However, because of its high cost and because the treatment area is converted to a glass with little reuse potential, vitrification is not a viable, cost-effective SAFR treatment approach.

Asphalt emulsion batching – Encapsulation

Asphalt-based emulsions and tall oil pitch have been used for many years to stabilize soils for dust control and to minimize wind or water erosion. The same emulsions have been modified to encapsulate soils containing heavy metals and some organics (Conca and Testa 1994). Asphalt stabilization is fundamentally different from cement or pozzolanic-based stabilization processes in that pozzolanic materials are very high pH inorganic materials. In contrast, emulsified asphalt is an organic material with a more neutral pH (Asphalt Institute 1997).

Cold-mix asphalt batching incorporates low-level contaminated soils into paving material with the addition of a heated asphalt emulsion at 100 to 120 °F. This treatment produces a finished material that reduces infiltra-

tion and is resistant to wind and water erosion. The emulsions can be mixed into the soil and/or applied topically.

The principal advantages of cold mix asphalt batching are:

- The final product is a beneficially useful material, keeping it out of landfills.
- The process is fast (up to 650 yd³/day).
- The price is cost competitive.
- It minimizes transportation of contaminated soils, and associated VOCs and particulate emissions by on-site treatment.

Major disadvantages are:

- Stockpiled material awaiting treatment must be covered.
- Extensive testing is required to determine the exact percentage of emulsion in the mix.

Once a site-specific emulsion design has been developed and tested in the laboratory, the technology can be implemented in the field with normal construction equipment and crews (ITRC 2003). In a typical application, the asphalt emulsion is delivered from a tanker truck and mixed with the soil in a pug mill. Gravel is sometimes added to further stabilize the asphalt product. The product is cured for 48 to 72 hr to bind the contaminants to the asphalt and to prevent contaminant evaporation and leaching.

Asphalt treatment is a more “permanent” treatment than the pozzolanic approaches, as asphalts have been demonstrated to maintain integrity for indefinite periods of time. Because of this, asphalt encapsulation technologies have been determined by US EPA to qualify as recycling for RCRA characteristic wastes in that permanent chemical bonding is achieved in a commercially useable endproduct. The treated soils have increased soil strength and can be used as an asphalt base material. This technology is especially applicable for military ranges and military reuse sites where treated soils can be used in new road construction. It has also been shown to be an effective technology for the stabilization of depleted uranium and other radioactive wastes.

In order to be used for a paving material, asphalt-treated bases must be strong enough to not shove, flow, or rut under traffic loading, but be resilient enough not to crack, chip, or break apart under the same loads. They

must be resilient through weather extremes of heat, cold, water, snow, and ice. Guidelines have been developed for the use of cold-mix asphalt emulsions to create road-base materials (Asphalt Institute 1997). In a field project at the Massachusetts Military Reservation, over 650,000 yd³ of contaminated soils have been cold-asphalt batched with no contaminant leaching detected in 8 years of leachability testing (U.S. Air Force Center for Environmental Excellence (AFCEE) 1999).

Encapco Technologies, LLC has patented a physical-chemical treatment technology for the cleanup of contaminated soil involving mixing the soil with asphalt or tall oil pitch emulsion that is chemically enhanced to bind and stabilize the target contaminants (Naval Facilities Engineering Command (NAVFAC) 2004). During the process, chelating and/or precipitating agents are added into the asphalt emulsion to promote chemical bonding of the target contaminants. A typical emulsion formulation is shown in Table 19. A feed hopper is used for storage of the excavated soil and a tanker truck is used to hold the asphalt or tall oil emulsion. A pug mill mixer then blends and thoroughly mixes the soil and emulsion before it is placed in a dump truck for transportation to the construction site. After treatment, the final product can be used for road base, covers, berms, fill, or other purposes. Total cost of treating 500 tons of soil, including the treatability study and site preparation, was \$79,491 or \$158.98 per ton. The total price to treat 100 tons of contaminated soil is estimated to drop to around \$100 per ton.

Table 19. Typical emulsion formulation.

Material	Volume (percent)
Tall oil pitch or asphalt	50
Non-ionic surfactant	2
Water	42
Proprietary acid	6
Taken from NAVFAC (2004)	

Testing

Preliminary laboratory testing is necessary to select the optimum reagent mixes and to determine the presence of interfering materials (Jones 1990). Inorganic salts affect the set rate, through either acceleration or retardation, and can affect the long-term integrity of the final product. Other

types of wastes, such as organic chemicals or inorganic acids that also may interfere with the solidified product, pose special concerns. Chlorinated organics may increase set time and decrease durability of cement if present in too high a concentration. The presence of oil and/or grease decreases the ultimate compressive strength. In all cases, solidification will result in an increase in the volume of the material, in some cases up to double the original volume. The amount of reagent necessary to attain an adequately solidified product also is site and soil dependent (Bricka and Jones 1993).

Process design and reagent composition must be tailored to each site and pollutant. Data needs include particle size distribution, Atterberg limits, moisture content, metal content, sulfate and organic material content (interfere with setting), density, permeability, unconfined compressive strength, leachability and pH.

Lead stabilization methodology

The bioavailability and environmental risk of a contaminant are directly related to its accessibility to the biota in the soil medium, which is generally controlled by its solubility and mobility (Traina and Laperche 1999, Brown et al. 2004). Linking lead bioavailability to its solubility rather than to its total concentration makes possible the consideration of remediation strategies based on in situ reduction of contaminant solubility, rather than its complete removal or physical isolation (solidification). For this reason, a chemical reaction between lead and reagents, such as phosphate, to form insoluble minerals has been demonstrated to be an efficient and cost-effective method of lead stabilization (Nriagu 1984, Ma et al. 1993).

Solubility and mobility of lead minerals

The speciation of metals in a soil is a major factor affecting pore water concentration of the metals. For example, the orthophosphate ion forms sparingly soluble solids with several metals, including lead and other metals associated with SAFRs. Metal speciation in the soil is influenced by hydrogen-ion concentration (pH) and redox potential (Eh) within the soil. Lead is an amphoteric metal, increasing in solubility in environments that are more acid as well as in environments that are more alkaline. Figure 45 illustrates the pH dependence and amphoteric nature of common lead salt compounds. Table 20 lists the formulas and the logarithm of the solubility

products of several common lead salts and minerals. Most of these lead salts are relatively insoluble or only slightly soluble, with the notable exceptions of lead nitrate and lead acetate. Lead phosphate minerals are some of the most insoluble solids known to form under typical geochemical conditions, making lead especially amenable to remediation by stabilization.

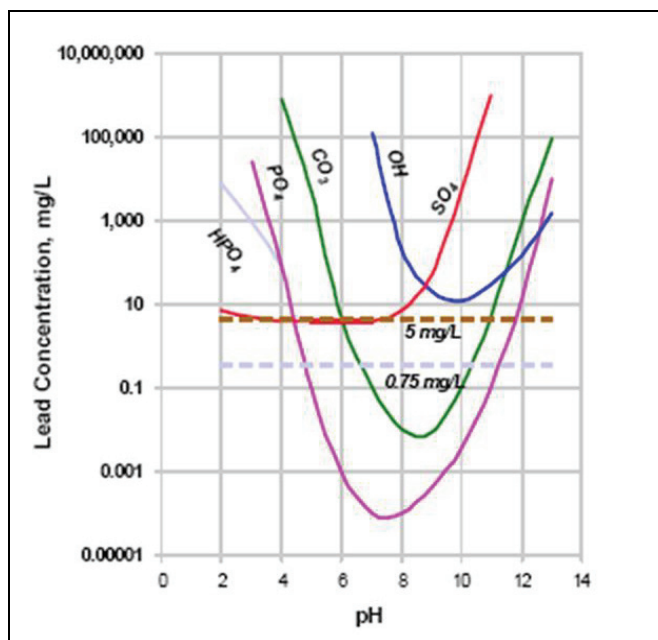


Figure 45. Lead solubility of common lead compounds by pH.

Soil organic matter and clays can also affect exchange capacity of a soil and significantly influence pore water lead solubility. The decay of soil organic matter, such as straw or pine litter, may produce organic acids. These acids will lower soil pH and increase the solubility of lead. Total concentration of other dissolved cations and anions also have significant effects on lead solubility.

Various studies have explored the utility of using phosphates to reduce the mobility and bioavailability of lead and other metals in contaminated environments such as SAFRs as well as in a number of other waste types (Ma et al. 1993, 1995; Laperche et al. 1996, 1997; Berti and Cunningham 1997, Yang et al. 2001, Hettiarachichi and Pierzynski 2002, Tardy et al. 2003). Effective remediation may not require complete conversion of soil lead to insoluble ore-like forms, but rather, only transformation of the most chemically and/or biologically reactive or labile forms for lead (Laperche et al. 1996).

Table 20. Solubility products of selected Pb minerals.

Mineral	Formula	Log K_{sp} ¹
Lead acetate	Pb(C ₂ H ₃ O ₂)	1.0
Lead nitrate	Pb(NO ₃)	0.8
Lead chloride	PbCl ₂	-4.8
Litharge (lead oxide)	PbO	-14.9
Anglesite (lead sulfate)	PbSO ₄	-7.7
Cerussite (lead carbonate)	PbCO ₃	-12.8
Lead orthophosphate	Pb(PO ₄) ₂	-43.5
Pyromorphite	Pb ₅ (PO ₄) ₃ Cl	-84.4
Hydroxypyromorphite	Pb ₅ (PO ₄) ₃ OH	-76.8
Fluoropyromorphite	Pb ₅ (PO ₄) ₃ F	-71.6
Bromopyromorphite	Pb ₅ (PO ₄) ₃ Br	-78.1
Corkite	PbFe ₃ (PO ₄)(SO ₄)(OH) ₆	-112.6
Hindsalite	PbAl ₃ (PO ₄)(SO ₄)(OH) ₆	-99.1
Plumbogummite	PbAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O	-99.3
¹ From Traina and Laperche (1999).		

Laboratory studies with phosphate reagents

Many different phosphate reagents have been studied for their effect on lead solubility in several types of contaminated soils and sediments: phosphoric acid (Yang et al. 2001), calcium hydrogen phosphate and calcium carbonate (Wang et al. (2001), potassium dihydrogen phosphate (Berti and Cunningham 1997), limestone, mineral rock phosphate and diammonium phosphate (Basta and McGowen 2004), and powdered hydroxyapatite, and calcium, sodium, potassium and ammonium phosphates (Tardy et al. 2003). Several recent studies have also reported that phosphate addition lowered the toxicity of the lead in the contaminated soils, primarily by making it less bioavailable (Yang et al. 2001, Davies et al. 2002, Hettiarachchi et al. 2002, Maenpaa et al. 2002).

Yang et al. (2001) added phosphoric acid at 1.25 to 10 g/kg phosphorous to smelter-contaminated urban soils. They reported a reduction in lead bioavailability by 60 percent. Wang et al. (2001) used calcium hydrogen phosphate and calcium carbonate to treat a multi-metal contaminated soil. This reduced lead concentration in the TCLP test by 99.8 percent and cadmium, copper, and zinc concentrations by more than 87 percent.

Berti and Cunningham (1997) reported significant reduction in “leachable” lead to below 5 mg/L when potassium dihydrogen phosphate was added to soils at concentrations as low as 0.1 percent phosphate and potassium phosphate at 0.5 percent. They also reported similar success with an iron-rich mineral byproduct formed in the commercial production of titanium dioxide. Other additives tried by the authors, which were not suitably effective in reducing lead leaching in the TCLP, were agricultural limestone, gypsum, sulfur, and various sources of organic carbon, including ground alfalfa, sphagnum peat moss, biosolids from industrial and mining processes, and composted leaves.

In a study using limestone, mineral rock phosphate and diammonium phosphate (Basta and McGowen 2004), the diammonium phosphate was found to be the most effective, reducing cadmium, lead, and zinc by 94.6 percent, 98.9 percent, and 95.8 percent, respectively, in 60 pore volumes of leachate. The rock phosphate was also tried as a reactive barrier under the soil layer (180 g/kg soil) where it reduced lead transport from the soils by 99.9 percent.

Tardy et al. (2003) compared seven potential reagents (five phosphate and two iron-based) on their ability to reduce lead leaching from six soils, four soils from SAFRs, and two test soils (quartz sand and WES Loess) contaminated with four levels of lead. The reagents, added at 0, 1, 3 and 5 percent w/w, were granular and colloidal zero-valent powdered iron, powdered hydroxyapatite, and calcium, sodium, potassium and ammonium phosphates. The powdered iron additions were much less effective than any of the phosphate additives. The treatment of lead-contaminated SAFR soils with these five phosphate reagents was found to reduce losses of lead to leaching even when the leachant was maintained at pH 3. Although all reagents were effective in lowering the lead concentrations, the less soluble forms, hydroxyapatite and calcium phosphate, typically produced the lowest lead concentrations at pH 3. On average, a 3-percent (w/w) application was sufficient to reduce leachate lead concentrations to near 1 percent of the control. The more soluble forms of phosphate salts were also effective but to a lesser degree. The use of the highly soluble forms of phosphates may increase the risk of offsite phosphate migration. Tardy et al. (2003) also concluded that, as the concentration of the additive relative to the lead content of the soil increases, its effectiveness decreases and larger amounts of additive are required to achieve the same stabilization ef-

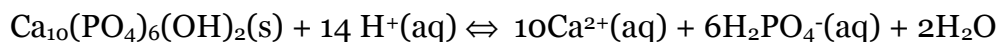
fectiveness. Soils with low lead levels require relatively less reagent per unit of lead than soils with higher lead content.

Apatite and pyromorphite chemistry

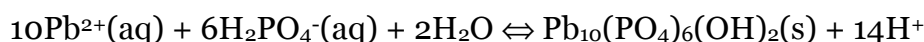
Members of the apatite family of minerals have been selected for use in the majority of recent studies on lead stabilization (for example: Ma et al. 1995; Laperche et al. 1996, 1997; Chen et al. 1997; Manecki et al. 2000; Ryan et al. 2001; Larson et al. 2004, 2005). The apatite mineral family has the general formula, $\text{Ca}_5(\text{PO}_4)_3(\text{X})$, where the three dominant end members, X, are: OH (hydroxyapatite), F (fluorapatite), or Cl (chlorapatite). The log of the solubility product constants of the most commonly used forms, hydroxyl- and fluoro- end members are -3.1 and -25 , respectively. Fluorapatite and chlorapatite are the most common forms found in nature. Hydroxyapatite is a rare mineral in abiotic systems although it is the principal inorganic constituent of bones and teeth. Natural apatite minerals exhibit extensive substitution with the incorporation of cations such as K, Na, Mn, Ni, Cu, and Zn in the Ca crystal sites (Traina and Laperche 1999). Some heavy metal ion species, such as antimony (found in shotgun pellets), will not combine into an apatite mineral form. For these heavy metal species, mineral forms such as sulfides and sulfates would be preferred for the purpose of reducing leachability.

Ma et al. (1993) reacted synthetic hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$], calcium biphosphate [CaHPO_4], and fluoroapatite (a naturally occurring apatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) with aqueous lead, resin exchangeable lead, and lead-contaminated soil. All three sources of calcium phosphate were effective in immobilizing the lead in all three systems. They hypothesized that the resulting solids were formed by the conversion of lead to insoluble hydroxypyromorphite [$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$] by a two-step reaction sequence: first via apatite mineral dissolution followed by subsequent precipitation of pyromorphite minerals. Two reactions were proposed (Ma et al. 1993):

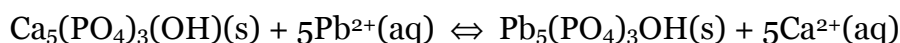
The dissolution of hydroxyapatite:



Followed by the precipitation of hydroxypyromorphite:



These reactions occur to completion in the absence of competing metals or ligands. The overall reaction between lead and hydroxyapatite to form hydroxypyromorphite can be written as:



The reaction is exothermic with a standard state Gibbs energy change of -137 KJ/mol (Traina and Laperche 1999).

The pyromorphite group, in addition to hydroxypyromorphite, includes the mineral pyromorphite $[\text{Pb}_5(\text{PO}_4)_3\text{Cl}]$, fluoropyromorphite $[\text{Pb}_5(\text{PO}_4)_3\text{F}]$, bromopyromorphite $[\text{Pb}_5(\text{PO}_4)_3\text{Br}]$ and various other analogs. The pyromorphites are isostructural with the apatites forming hexagonal crystals. The exact composition of the products formed by the reaction of aqueous lead with apatite depends upon the solution pH (Chen et al. 1997). At a solution pH between 3.1 and 6.2, mixtures of dissolved lead and carbonate-containing fluorapatite react to form fluoropyromorphite; at pH values near neutral, hydrocerrusite $[\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2]$ and carbonated hydroxylfluoropyromorphite $[\text{Pb}_5(\text{PO}_4, \text{CO}_3)_2\text{3}(\text{F}, \text{OH})]$ were formed; and at very basic pHs between 10.7 to 11.9, the reaction products consisted of hydrocerrusite, hydroxypyromorphite and lead oxide fluoride $[\text{Pb}_2\text{OF}_2]$.

The solubility of the pyromorphites decreases (Table 20) fluoropyromorphite > hydroxypyromorphite > bromopyromorphite > pyromorphite, with log of the solubility products (log Ksp) of -72 , -77 , -78 and -84 , respectively. At standard state, the common lead pyromorphites are at least 44 orders of magnitude less soluble than galena (PbS), anglesite, cerussite, litharge and crocoite (PbCrO_4), which are lead solids common to soils contaminated by mining and smelting activities and by lead-based paint (Ruby et al. 1994a, 1994b; Laperche et al. 1996; Ryan et al. 2001). At low lead concentrations, only pure pyromorphite and not (Pb, Ca)-apatite was formed when aqueous lead reacted with apatite (Laperche et al. 1996).

Lead must be in ionic form (dissolved) in order to react with the added phosphate materials during remediation. For this reason, the rate of formation of pyromorphite from phosphate materials such as hydroxyapatite can be limited by the dissolution rates of the lead contaminants. Under neutral pH conditions, the observed solubility of lead and phosphate remain low, causing a major limitation for an efficient lead/phosphate reaction (Zhang and Ryan 1998). Dissolution of the initial lead phase has been reported to be the limiting factor in the formation of hydroxypyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$) at pH values between 5 and 8 (Laperche et al. 1996). The conversion of Litharge (PbO) to hydroxypyromorphite was most rapid at pH 5. Zhang et al. (1997) also found that the rate of dissolution of anglesite (PbSO_4) and cerussite (PbCO_3) limited the rate of the formation of hydroxypyromorphite. Effective lead immobilization by phosphate amendments was enhanced by increased lead solubility in an acid environment (Cao et al. 2003).

The effects of aging and pH on the dissolution kinetics and stability of chloropyromorphite were studied by Scheckel and Ryan (2002). They found that the formation of chloropyromorphite was kinetically rapid and that it was thermodynamically stable to dissolution in acid. In terms of aging prior to dissolution, X-ray absorption fine structure and X-ray diffraction analyses were unable to distinguish fundamental differences in progressively aged samples. Stirred-flow and batch dissolution studies suggested that the aging process ceased within 24 hr and that the dissolution rate of the 1-day aged sample was not significantly different than the 1-year aged specimen.

Lower et al. (1998a, 1998b) studied the aqueous lead (0.5 to 500 mg/L) sorption by hydroxyapatite at pH 6 using a combination of atomic force microscopy, scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy, electron diffraction and X-ray diffraction. After a 2-hr reaction time, concentrations of aqueous lead decreased from 500 mg/L to <100 mg/L, and from 0.5 to 100 mg/L to <15 $\mu\text{g/L}$. The loss of aqueous lead resulted from the simultaneous dissolution of hydroxyapatite and the precipitation of hydroxypyromorphite. They found that the initial saturation state strongly influenced the precipitation process and resulting crystal formation. At a high degree of saturation (defined as the ratio of the ion activity product to equilibrium solubility product) with initial aqueous lead concentrations of >100 mg/L, small nuclei or aggregates of poorly crystalline hydroxypyromorphite precipi-

tated homogeneously in solution. However, at a low degree of saturation (initial aqueous lead concentrations <10 mg/L) a needle-like lead containing phase grew heterogeneously on the HAP crystals. At intermediate aqueous lead concentrations (between 10 and 100 mg/L), large, euhedral crystals of hydroxypyromorphite precipitated homogeneously in solution. Their results agreed well with concepts derived from nucleation theories and demonstrated that the initial saturation state strongly influences the sorption process.

Lower et al. (1998a, 1998b) also showed that transport-controlled hydroxyapatite dissolution provided the phosphate for precipitation of the hydroxypyromorphite, which in turn sequestered the aqueous lead. At 100 mg/L aqueous lead at pH 6, hydroxypyromorphite needles were found in close association with the hydroxyapatite surfaces, most probably due to diffusional controls on phosphate concentrations. Diffusion of phosphate away from the dissolving hydroxyapatite appeared to be the rate-limiting step in the overall reaction sequence. Both studies visualized the formation of small hydroxypyromorphite crystals either homogeneously in the solution or heterogeneously on the hydroxyapatite surface.

Competing reactions by other anions and cations

Several studies have evaluated the influence of competing cations and anions on the effectiveness of the reaction of lead with hydroxyapatite to immobilize lead. Ma et al. (1994a) have made an extensive study of the effects of common multivalent metals (Al, Cd, Cu, Fe(II), Ni and Zn) on hydroxyapatite immobilization of lead. At initial lead solution concentrations of less than 20-mg/L, hydroxyapatite was effective not only in removing lead in the presence of Al, Cd, Cu, Fe(II), Ni or Zn, but also in reducing the concentrations of these metals themselves. In general, the effectiveness of hydroxyapatite in removing these metals was in the order Al>Zn>Fe(II)>Cd>Cu>Ni (Ma et al 1994a). The reduction varied from metal to metal and with the initial metal ion concentrations. As was observed for lead, final dissolved Al, Cd, Cu, Fe(II), Ni or Zn increased with increasing initial metal concentrations (increase in either initial lead concentrations or metal/lead molar ratios).

The order of the effectiveness of the metal ions at high concentrations in inhibiting lead immobilization by hydroxyapatite was Al>Cu>Fe(II)>Cd>Zn>Ni. Thus, the amount of metal removed was not related to its effectiveness in inhibiting lead immobilization by hydroxyapatite. In addition,

the amount of Zn and Fe(II) removed from solutions increased with an increase in their final concentrations; those of Cd, Ni and Cr decreased and those of Al removed reached a plateau. Even in the presence of the other metal ions, the primary reaction of lead with hydroxyapatite was in accordance with the two-step equations given above.

Ma et al. (1994b) also studied the effect of the common anions, Cl, F, CO₃, NO₃, and SO₄, on the effectiveness of hydroxyapatite to immobilization of lead. Lead concentrations were reduced from initial levels of 24.1 to 482 µmol/L to below the EPA action level of 72.4 nmol/L for all anion concentrations, except for high concentrations of lead and carbonate.

The presence of nitrate did not have an appreciable effect on the reaction of lead with hydroxyapatite and did not seem to take any part in the process. Its concentration was unchanged during all experiments. Sulfate and carbonate also did not appear to alter the mechanism by which lead was removed by hydroxyapatite although both sulfate and carbonate could possibly substitute for the phosphate in the hydroxyapatite or hydroxypyromorphite structures. The fact that hydroxypyromorphite was the only mineral detected by X-ray diffraction suggested that hydroxyapatite dissolution and hydroxypyromorphite precipitation were the dominant mechanisms during lead immobilization by hydroxyapatite and that substitution of sulfate or carbonate for phosphate was limited.

In the presence of Cl and F, the reaction products were changed to chloropyromorphite and fluoropyromorphite, respectively. The same two-step dissolution/precipitation reactions were suspected in both cases with the substitution of Cl or F. Formation of fluorite (CaF₂) may have contributed to lower Ca ion concentrations and increased phosphate concentrations at high F ion concentrations. However, fluorite was not detected by X-ray diffraction.

Chen et al. (1997) studied the effects of pH on Pb, Zn and Cd reactions with mineral apatite. The heavy metals were applied as single or multiple species. Lead was removed from solution at all pHs from pH 3 to 12. The sorption of aqueous lead was primarily through the dissolution of apatite followed by the precipitation of variable pyromorphite-type minerals under acidic conditions, or of hydrocerussite [Pb₃(CO₃)₂(OH)₂] and lead oxide fluoride (Pb₂OF₂) under alkaline conditions.

Reduction in soil toxicity by phosphate stabilized lead

Bioavailable lead is the fraction of lead that is taken up by living organisms. This is commonly determined by in vivo tests on live organisms such as earthworms, weanling pigs, and rats, and by in vitro tests such as sequential extraction or physiological based extraction tests for “bioaccessible” lead (ITRC 2003). Several recent in vivo studies have compared the effect of phosphate treatment of lead-contaminated soils to a corresponding reduction in earthworm lead uptake and toxicity (Maenpaa et al. 2002, Davies et al. 2002, Nahmani et al. 2007). In all cases, phosphate addition lowered the toxicity of the lead in the contaminated soils or increased the LC₅₀ and/or survival time of the earthworms exposed to the soil. The physiologically based extraction test (PBET) assesses bioavailability based on extraction acids that mimic the human digestive system. The concept is that if the lead is not released during digestion, it will pass through the human body with minimal impact. Several authors have reported that phosphate treatment reduced lead extracted by the PBET, leading to the (controversial) conclusion that phosphate treatment could lead to disposal of the treated soils with unrestricted exposure to oral uptake (Ruby et al. 1996, Berti and Cunningham 1997, Hettiarachichi et al. 2002, Yang et al. 2001).

Laboratory studies

Based on the literature studies presented above, the SAFR program targeted S/S approaches for soil treatment. Laboratory studies were conducted to evaluate the use of chemical treatments for SAFR soils. Two approaches were evaluated:

- The use of asphalt emulsions produced through a patented process by Encapco Technologies, LLC. These emulsions include chelating additives and stabilizing agents (such as phosphoric acid), meaning that they combine both solidification and stabilization.
- The use of phosphate-based additives.

Batch experiments

In regard to the experiments discussed in the asphalt solidification and phosphate stabilization sections, soils were collected from the field and brought back to ERDC, where they were characterized and used for laboratory testing (Figure 46). The additives (emulsions or phosphate treat-

ments) were mixed into the soils. The treated soil was then packed into columns and allowed to set. The testing included extraction or column leaching. Both the leachate and the soils were analyzed to determine the effectiveness of the treatment.

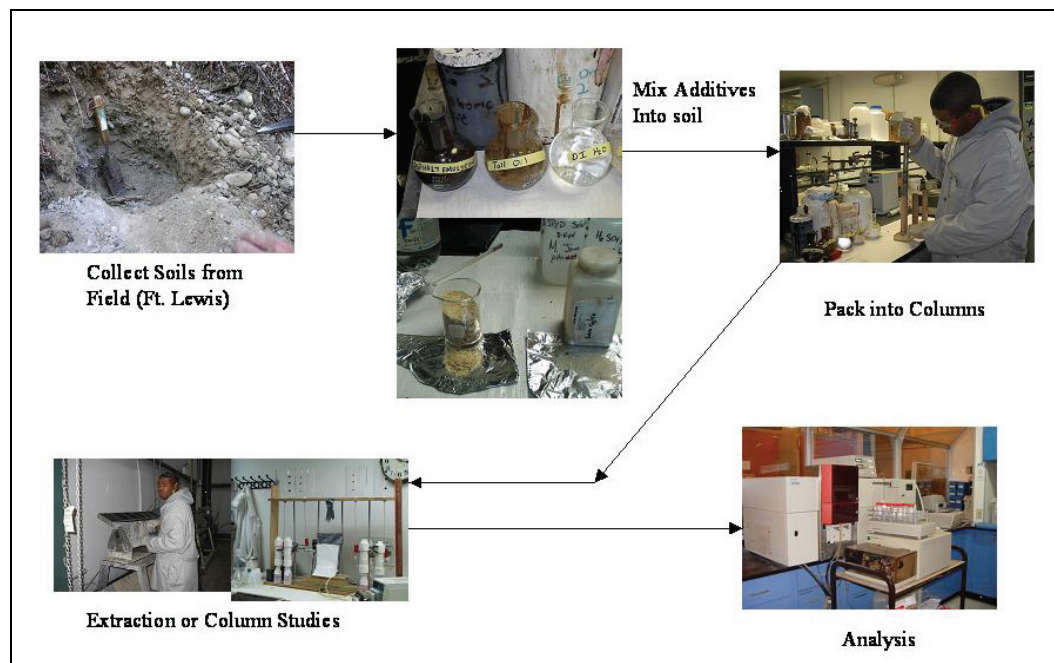


Figure 46. Experimental approach for asphalt and phosphate studies.

Asphalt solidification studies

Reduction of TCLP. The TCLP of the Ft. Lewis soil fraction greatly exceeded criteria for non-hazardous disposal (Table 21). However, with a treatment of 3-percent lime and 10-percent asphalt emulsion, the TCLP was reduced 600-fold, and easily met the 5-mg/L criteria.

Table 21. TCLP of untreated Fort Lewis soil compared to that of the same fraction treated with 3-percent lime and 10-percent asphalt emulsion.

Soil	TCLP (mg/L)	
	Average	Standard Deviation
Untreated Fort Lewis Soil	608.8	23.9
Treated with 3-percent lime and 10-percent asphalt emulsion	1.1	0.2

Factors affecting treatment effectiveness. The factors determined to be most important when evaluating treatment performance were lime concentration and emulsion concentration. As seen in Figure 47, increasing the lime concentration from 0 to 3 percent resulted in noticeably better treatment. Increasing the lime concentration again, to 5-percent lime, did not appreciably improve performance. Similarly, increasing emulsion concentration from 6 to 10 percent improved performance, although in this case, even the 6-percent application met the 5-mg/L TCLP goal.

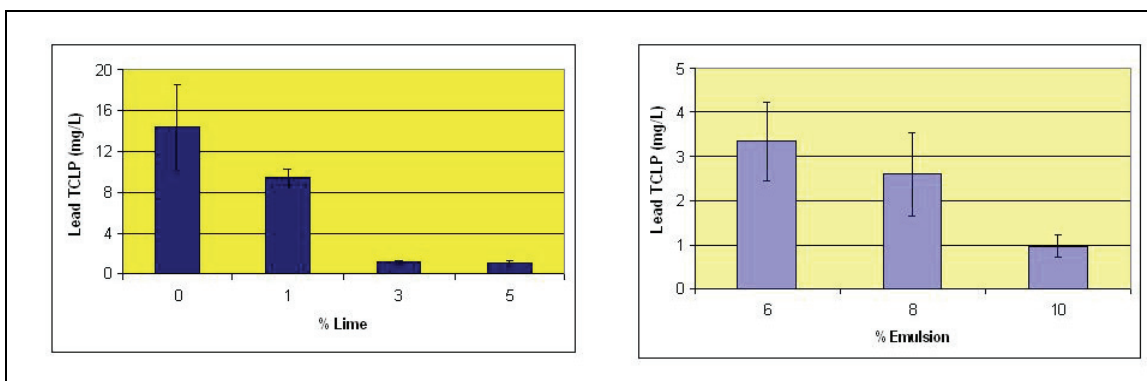


Figure 47. Effect of lime and emulsion for treatment of Ft. Lewis soils as measured by TCLP extraction.

Comparison of TLCP/DI Extraction/CA WET. California has a more stringent definition for hazardous wastes. Waste streams must, in addition to passing the Federal TCLP, pass the Waste Extraction Test, or WET test. This test uses a more aggressive, citric acid instead of acetic acid. Citric acid has chelating properties, which make it a far more effective extractant at a given pH. The authors have worked with facilities such as Fort Ord and McClellan AFB (see “Laboratory Study of Combined Soil Washing and Stabilization” in Chapter 6 for a discussion of treatment at McClellan AFB) to meet the higher standards of the CA WET test. As seen in Table 22 regarding emulsion treatment of Fort Ord soils, a treatment that easily met TCLP and DI extractions, failed the WET extraction. More aggressive soil treatments did allow attainment of the CA WET test goals. In general, these treatments required much larger quantities of treatment additives, which must be taken into account in cost-effectiveness calculations.

Table 22. Comparison of DI extraction and WET test results to TCLP for and untreated soil and for a successful TCLP treatment.

Treatment	Extraction	Concentration (mg/L)	
		Average	Standard Deviation
Untreated	DI Extraction	BDL ¹	n.a.
	TCLP	146.0	188.0
	WET	251.6	111.1
1 percent Lime, 10 percent Tall Oil	DI Extraction	BDL	n.a.
	TCLP	0.8	0.1
	WET	9.7	0.3
¹ BDL = Below Detection Limit			

Inconsistency in formulation. One issue, discovered throughout testing, was the inconsistency in the emulsion products, which could influence performance. Identical products tended to differ between batches in parameters such as thickness, consistency, and viscosity. In some cases, this actually affected performance, as illustrated in Table 23, which compares treatments of two separation batches of the same tall oil pitch emulsion.

Table 23. Comparison of TCLP from treatment of Fort Ord with 5-percent tall oil pitch and 1-percent lime.

Formulation	TCLP (mg/L)	
	Average	Standard Deviation
1	6.95	2.86
2	1.50	0.27

Geotechnical results. Geotechnical measurements were conducted on emulsion-treated soils because treated soils can be used as road construction material or fill. These tests included compressive strength and Marshall Strength (Tables 24 and 25). Each soil had a compaction of 33.8 lb/in². Each case resulted in substantial improvements compared to untreated soils. Compressive strength was improved from essentially zero to 3.51 TSF. The treated soils had a Marshall Strength of nearly 800 lb, adequate for most road construction. Both compressive strength and

Marshall Strength could be substantially increased by greater compaction and by the addition of aggregate.

Table 24. Compressive strength of treated Fort Lewis samples.

Parameter	Chamber Pressure (TSF)			Average
	0.50	1.00	2.00	
Compressive Strength (TSF ¹)	2.36	3.17	5.00	3.51
¹ TSF = Tons per Square Foot.				

Table 25. Marshall Test results of asphalt-treated Fort Lewis samples.

Condition	Marshall Results (lbs)	Flow
Standard Test Temperature (140 °F)	793	11
Ambient Temperature	2130	12

Another use for treated soils could be as a cover material. The treated and compacted (33.8 lb/in.²) material had conductivity of 9×10^{-6} cm/sec (Table 26). This is slightly higher than that required for a RCRA landfill cover, but still useful for many semi-impermeable cap applications. High levels of compaction would likely result in still lower permeability.

Table 26. Hydraulic conductivities of multiple Fort Lewis samples treated.

Sample	Hydraulic Conductivity (cm/sec)
1	1.78×10^{-5}
2	6.77×10^{-5}
3	3.67×10^{-5}
Average	9.40×10^{-5}
Standard Deviation	7.41×10^{-5}

Phosphate stabilization studies

A study evaluating the effectiveness of phosphate minerals for stabilization was conducted using soils from firing ranges at United States Coast Guard Station Cape May (Cape May). The study focused on two phosphate sources. The first was a material marketed under the name of Enviroblend,

which is a calcium phosphate rock produced by Premier Chemicals, LLC. The second was processed fishbone, commonly called PIMS, which served as a source of apatite II.

Effectiveness in meeting TCLP requirements. Table 27 summarizes treatment by apatite II, applied as processed fish bones, and a mineral product known as Enviro 50:50. These were applied to Cape May firing berm soils. As seen in all cases, the treatments reduced the lead concentrations extracted by the TCLP. In addition, all the treatments, except for the 1-percent Enviro 50:50, also met the TCLP standard of 5-mg/L.

Table 27. Phosphate treatments of Cape May soils.

Sample ID	Total Pb (mg/kg)	
	Average	Standard Deviation
Background	2698.33	83.94
Treatment Set I TCLP (mg/L)		
Background	104.88	52.53
Control	52.29	24.69
3 percent Apatite II	1.82	0.22
5 percent Apatite II	0.57	0.33
8 percent Apatite II	0.32	0.04
1 percent Enviro 50:50	64.69	16.02
3 percent Enviro 50:50	0.07	0.07
5 percent Enviro 50:50	0	0
Treatment Set II TCLP (mg/L)		
1 percent Enviro 50:50	122.03	41.73
3 percent Enviro 50:50	0.40	0.10
5 percent Enviro 50:50	0.31	0.04

Column study to evaluate effectiveness against rainwater leaching. Column studies were conducted using 3- and 5-percent apatite treatments, a 3-percent Enviro 50:50 treatment, and a mix (3-percent Enviro and 3-percent apatite). In each case, these treatments dramatically reduced the lead concentrations in the leachate compared to the control

(Figure 48). The release of phosphate was also studied. The control did not have any measurable phosphate. Levels up to 20 -mg/L were detected for the 3-percent apatite and 3-percent Enviro treatments. The 5-percent apatite treatment had large concentrations, over 100 mg/L. Interestingly, the blend treatment had only a single phosphate detection of 6 mg/L. This is an important parameter to consider when field-scale studies are initiated because phosphate increases of just 1-mg/L can affect eutrophication.

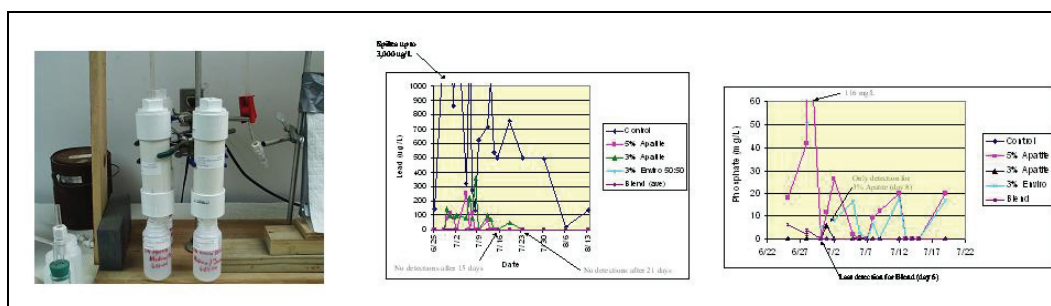


Figure 48. Column study, lead leaching, and phosphate leaching.

Multiple extraction procedure to evaluate long-term effectiveness. The multiple extraction procedure (MEP) was also used to assess long-term effectiveness of treatment. The MEP is an aggressive series of 9- and 24-hr extractions using a strong mixture of sulfuric and nitric acids. The pH is adjusted over the first 4 hr of the extraction. In this case, 3-percent Enviro 50:50 and 3-percent Apatite were tested and compared to the untreated control. Over the first four extractions, the treatments did reduce the extracted lead compared to the control (Figure 49). After that point, the concentrations of each of the treatments were about equal.

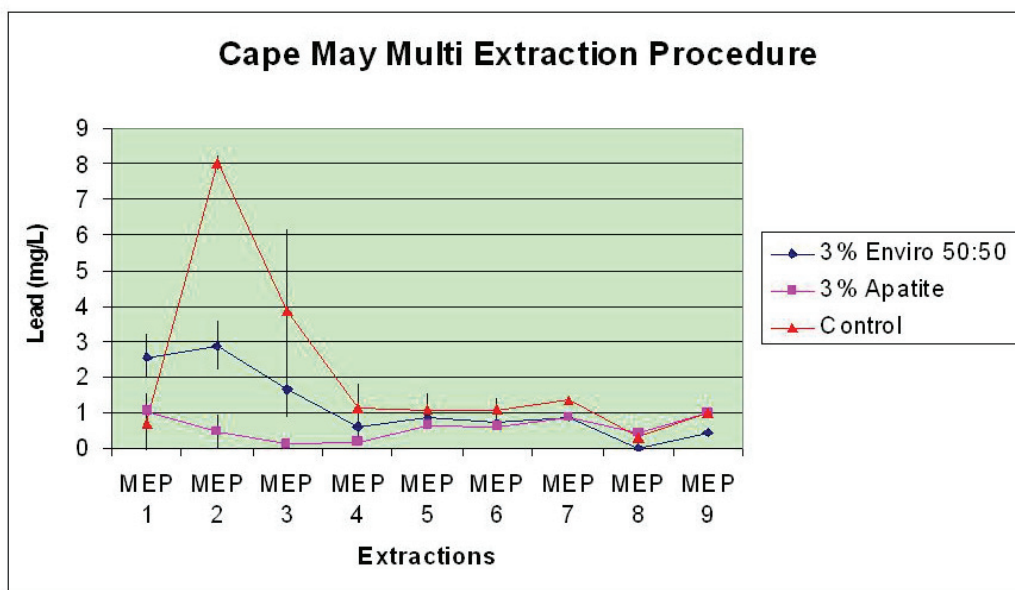


Figure 49. Multiple extraction procedure results.

Larger scale treatments

Lysimeter study of hydroxyapatite treatment

A 1- by 1-m lysimeter was designed and built to allow the application of simulated rain to 100-kg soil samples (Figure 50). The design allowed for the collection both of leachates through the soil as well as runoff from the surface. The lysimeter was tilted at a 1° to 3° slope toward the runoff collection well.

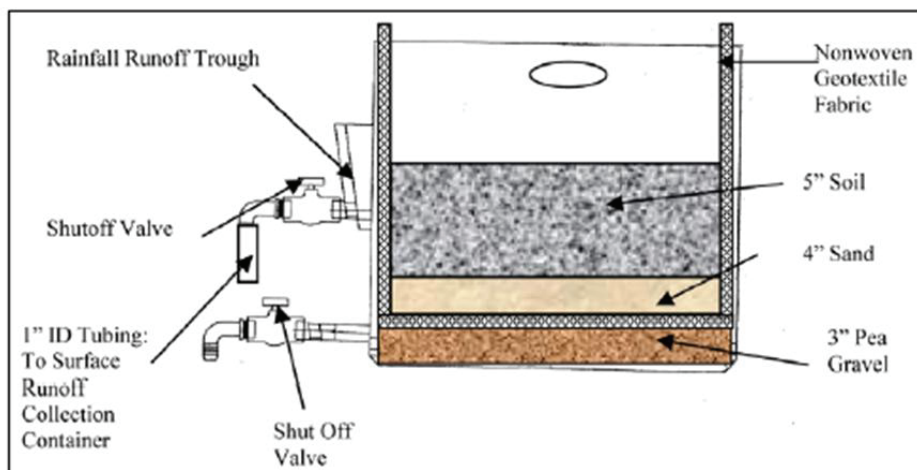


Figure 50. Cross-section of simulated rain lysimeter (Larson et al. 2004).

The simulated rain lysimeters were used to test hydroxyapatite (HAP) stabilization of lead in lead-contaminated soils collected at different SAFRs. Six soils having great variability in structure, clay and organic carbon content, and chemical composition were selected for the study: clay, sandy clay, glacial till, sand, loess and muck soils (see Chapter 2). The large-scale simulated rainfall lysimeters were filled with untreated soil (controls) and soils treated with 5-percent w/w hydroxyapatite, which was well mixed into the soils.

The hydroxyapatite treatment was successful in reducing the amount of lead in filtered and unfiltered leachates and runoff samples (Table 28). Lead losses, as determined in digested leachate and runoff samples, exceeded those measured in filtered samples in all cases. Values varied from less than 1 percent for the soils with the highest percent of fines (clay, sandy clay glacial till and loess) to considerably higher for the sand and organic muck.

Table 28. Comparison of lead average concentrations in effluents.

Soil and treatment	Filtered as percent of digested Pb conc.		Percent reduction in lead conc. by treatment			
	Leachate	Runoff	Leachate		Runoff	
			Filtered	Digested	Filtered	Digested
Clay	bdl ¹	1.05	n.c. ²	90	>97	84
Clay + 5 percent HAP	bdl	bdl				
Sandy Clay	3.76	1.97	>92 ³	91	69	62
Sandy Clay + 5 percent HAP	bdl	1.65				
Glacial till	0.35	0.90	>90	80	71	37
Glacial till + 5 percent HAP	bdl	0.41				
Sand	22.70	17.18	96	69	94	77
Sand + 5 percent HAP	3.29	4.41				
Muck	bdl	39.33	n.c.	61	82	55
Muck + 5 percent HAP	bdl	15.83				
Loess	bdl	1.02	n.c.	11	65	6
Loess + 5 percent HAP	bdl	0.30				
¹ bdl = below detection limits.						
² n.c. = negligible change.						
³ Treated effluent concentration below detection limits (0.2 µg/L) in all samples.						

Also included in Table 28 is the percent reduction in average lead concentrations as a result of hydroxyapatite treatment. The apparent effectiveness of the hydroxyapatite treatment is much greater when measured by

the filtered effluents than by the digested effluents. Hydroxyapatite treatment had less effect on the lead in particulates, presumably because particulate lead could not react with the hydroxyapatite.

Sequential extraction procedures were performed on the treated and untreated soils. The highest percentage of the lead was found in the carbonate fraction for the sand, sandy clay, and glacial till soils. These soils also had the lowest percentages of lead in the residual fraction. In contrast, the clay, muck, and loess all had over 50 percent of the lead found in the organic/sulfide and residual fractions with very little in the exchangeable and carbonate fractions. These differences between the two soil groups were statistically significant (95-percent confidence level). The average lead concentrations in the effluents follow the same patterns: the three soils with the majority of lead in the more available fractions also had much higher effluent lead concentrations. Conversely, the soils with the majority of lead in the residual fraction have very low average lead effluent concentrations.

Full-Scale Field Application at Evergreen Firing Range, Fort Lewis, Washington

A project was undertaken to evaluate the use of phosphate amendments to treat soils at the Evergreen Firing Range, in Fort Lewis, Washington. The project was a joint effort by ERDC, the Seattle District, the Department of Public Works at Fort Lewis, and TPA-CKY, a MARC contractor for the Seattle District. The Evergreen Range is an abandoned infiltration range in which 0.30-caliber machine guns had been fired. The range is dominated by a berm approximately 20 ft high by 100 yd long. Due to base expansion, the space was needed for construction. It was necessary to remove the contaminated soil, which was concentrated in the impact berm, from the range.

Negotiations were undertaken with the Washington State Department of Ecology. They agreed that soils with total lead concentrations of less than 250 mg/kg (a State of Washington Model Toxics Control Act Method A goal) could be abandoned on site. For the soil fractions exceeding this concentration (mostly fine soils), chemical treatment could be used in order to pass TCLP criteria, and the treated soil reused as new berm material in ranges at other locations on the base. This procedure avoids categorizing the soil as a hazardous waste. Based on the characterization work performed by the Seattle District, only the contaminated portion of the berm

was excavated and treated. This resulted in the treatment of 5000 yd³ of berm soil.

Bench Scale Study. A bench scale study was conducted on berm soils from the Evergreen Range. The total lead and untreated TCLP of these soils was higher than those of Cape May (Table 29). Consequently, the three apatite treatments (3 to 8 percent) reduced the lead in the TCLP substantially, but did not meet the RCRA standard of 5 mg/kg. The 1-percent Enviroblend treatment did not meet treatment goals, either. However, the 3- and 5-percent Enviroblend treatments were very effective at reducing the leachable lead. Because of the testing, a 4-percent Enviroblend treatment was implemented in the field application.

Table 29. Laboratory phosphate treatments of Evergreen Range (Fort Lewis, Washington) soils.

Sample ID	Total Lead (mg/kg)	
	Average	Standard Deviation
Evergreen	12,790.00	788.86
Sample ID	TCLP (mg/L)	
Untreated	3,157.00	379.00
3 percent Apatite II	12.16	6.79
5 percent Apatite II	7.55	0.65
8 percent Apatite II	11.95	5.69
1 percent Enviro 50:50	1,141.00	78.89
3 percent Enviro 50:50	1.22	0.52
5 percent Enviro 50:50	0.39	0.04
10 percent Enviro 50:50	0.44	0.12

Field Application. Full-scale treatment of the berm included physical screening, which divided the waste stream into three fractions: greater than 1.5 in., 1.5-0.44 in., and less than 0.44 in. The “greater than 1.5 in. fraction” was demonstrated to be clean and no further treatment was required. The 1.5- to 0.44-in. fraction contained bullet fragments. The fragments were removed magnetically, sent to a lead recycler, and the remaining soil was then disposed of on site. The finer soil fraction, less than 0.44-in., was treated using the 4-percent Enviroblend addition. Effective-

ness of the treatment was demonstrated by 3 TCLP measurements per ton of treated soil. The soil passed the TCLP in all cases. It was therefore re-used (non-regulated by RCRA), as new berm material. The cost of the project was \$800,000, which was approximately half the estimated cost for excavation and landfill disposal of the soil (\$1.5 million). Figures 51, 52, and 53 illustrate the treatment process.



Figure 51. Partially excavated Evergreen Range Berm.

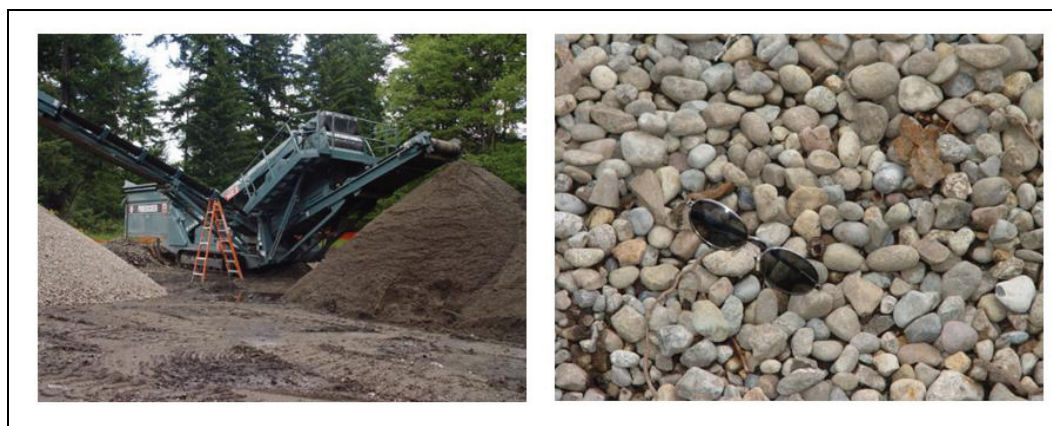


Figure 52. Size separation and the >1.5-in. fraction.



Figure 53. Rotary mixer used for addition of the Enviroblend amendment into soils.

Surface Application

The studies discussed in previous sections involved ex situ chemical additives, which allow for complete mixing of the additives in the soils. Alternatively, additives could be surface applied. Vendors have marketed this approach as a cost-savings method for treating SAFR soils. ERDC conducted experiments to assess the effectiveness of surface application.

The lysimeters were used to study the effects of surface treatment using 1 percent and 5 percent (w/w) dihydrogen phosphate [$\text{KH}_2(\text{PO}_4)$] and hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] on the losses of lead from a contaminated SAFR soil (a clay loam with 80 percent fines and 8,100-mg/kg lead). The soils were fired upon using actual M855 rounds to produce soil contamination of 10,000 mg/kg lead and 6,000 mg/kg copper. The soils were sieved through an 8-mesh sieve before being loaded into the lysimeters. The sieved soil was used in all tests.

Approximately 275 L of artificial rainwater (reverse osmosis [RO] water) with an unadjusted pH of 6 - 7, or artificial rainwater adjusted to pH 3 with nitric acid, was added in 16 weekly applications. Approximately half of the rainwater was collected as leachate and half as runoff from the surface. An important feature of the study was the analysis of the leachates and runoff before and after filtration. This permitted a measure of the soluble lead (lead that passes through a 0.45- μm syringe filter) and total lead, including lead sorbed onto particulates. Most studies, including the regulatory TCLP, use only the analysis of filtered leachates as a measure of effectiveness. As expected, both phosphate additives effectively reduced the levels of lead in both the filtered leachates and filtered runoff at either

pH 7 or pH 3. TCLP testing of the soils released over 600-mg/L of lead. The TCLP was lowered to below 1 mg/L by both phosphate additives added at 5 percent.

The greatest reduction in total mass of lead released (14 percent lower than the control) was observed for the 5 percent (by weight) dihydrogen phosphate amendment system. None of the treatments resulted in significant reductions of lead release. Nor were reductions sufficient to expect these reagents to be useful in one-time cleanup of SAFRs with these types of soils. In comparison to dihydrogen phosphate, the hydroxyapatite-amended systems more than doubled the total amount of particulate lead released in the pH 7 runoffs. This result may indicate that addition of this amendment aggravated soil erosion.

A similar pattern was observed for the total lead leaving the system in the unfiltered samples when acidic artificial rainwater was used. The total mass of lead leaving the model environment was not reduced sufficiently by any of the four treatments using the pH 3 rainwater as the water source. The 1 percent dihydrogen phosphate treatment reduced lead losses by less than 25 percent. The greatest reduction in total lead (46 percent lower than the control) was again observed for the 5 percent (by weight) dihydrogen phosphate amended system. A nearly 50 percent reduction in lead release is not expected to be adequately effective for even slightly contaminated sites. In contrast, the 1 percent and 5 percent hydroxyapatite amendment systems showed no reduction in lead release and again increased the total lead leaving the system by 1.42 and 2.45 times the control, respectively, both representing a negative instead of a positive reduction in lead releases.

Before rain simulation testing, phosphate amendment of the soil reduced the initial TCLP lead results significantly in all four of the phosphate amendment systems, compared with the unamended control soil. After the soil had gone through 16 rain cycles over 4 months, the soil was re-tested using the TCLP. With pH 7 rain as the water source, the unamended control soil showed a four-fold reduction in the TCLP leachate lead concentration; however, the treated soils all showed approximately a two- to ten-fold increase in the TCLP leachate lead concentrations. With pH 3 rain as the water source, the unamended control soil showed a two-fold reduction in the TCLP leachate lead concentration as compared with the treated soils, which showed an increase in the TCLP leachate lead

concentrations between approximately three- and twelve-fold. The reduction of TCLP leachate lead in the control soil suggests a removal of the most available lead during the rainfall simulation series. The increase in TCLP leachate lead in the amended soil suggests a possible impermanence of the stabilization from phosphate treatment over time. The addition of phosphate to lead-containing soils to immobilize the lead may increase the total amount of lead lost, particularly if lead is leaving the site in leachate or runoff in the form of small, mobile, lead-containing particles.

Although the more soluble potassium salts of phosphate were the most successful at reducing the lead leaving the lysimeters, this treatment also produced very large amounts of phosphate in the leachate waters. These data indicate that similar results of lead and phosphate leaving SAFR sites would be expected. Soluble phosphate concentrations in runoff water from dihydrogen phosphate-amended soils were observed at levels above 100-mg/L, with concentrations reaching over 20,000-mg/L in runoff waters from initial rainfall events. Since phosphorous is an essential macro-nutrient needed for cell growth in such organisms as algae and cyanobacteria, and it typically comprises about 2 percent of the mass algae and bacteria, the additional release of phosphorous from leachate and runoff could become a source of eutrophication in lakes and streams. Batch testing using site soils should be undertaken to optimize treatment levels and determine whether phosphate could become a problem at the site.

Conclusions

No single S/S treatment system is suitable for the remediation of all SAFRs. Ranges are highly variable with respect to soil, climate, contaminant characteristics and quantities of soil requiring treatment. In addition, treatment goals vary between different political regions and with intended future land uses of the site. Selection of the best management solution requires complete understanding of the site characteristics and bench-scale trials of potential treatments. With these caveats, it does appear that S/S treatment with excavated SAFR material is technically feasible and cost-effective. This is an acceptable approach for dealing with range soils in most states that follow Federal standards; however, an effective approach to meet the California standard still needs to be developed.

S/S will likely need to be combined with physical separation to achieve effective treatment. In addition, it can be combined with soil washing.

On-site disposal, recycling, or reuse of the soils greatly increases the economic advantages of stabilization.

Although these studies support the use of S/S in a well-mixed, excavated system, they do not support the surface application of treatment chemicals. These are quickly eroded off, and the lead becomes as available as before treatment.

6 Soil Washing of SAFR Soils

The soil washing process

Soil washing is an ex situ process that includes both physical separation methods (such as sieving or density or gravity separation) followed by a water-based process for scrubbing the soils, or soil components, to extract the contaminants from soils (Battelle 1997, US EPA 1997a, ITRC 2003). As generally practiced, the overall process of soil washing first separates the soil into two or more fractions by particle size separation, gravity separation, and/or attrition scrubbing similar to techniques used in sand and gravel operations (Mann 1999) and discussed in detail in Chapter 4 of this report. The soil fractions with the highest contaminant levels are then treated to dissolve or suspend the contaminants in an aqueous wash solution. The wash solution often incorporates acid or chelating agents to solubilize the metal contaminants and must be further treated to remove the metal contaminant. The cleaned solution is typically reused in the process to reduce the release of wastewater (Battelle 1997, Mann 1999).

Soil washing is potentially applicable to lead-contaminated SAFR soils. However, SAFR soils differ from most lead-contaminated industrial or mining waste soils in that they typically contain a large proportion of zero-valent lead from spent bullets and pellets. This makes physical separation critical for the success of the process. The remaining soil fractions can then be treated by aqueous extraction techniques to remove the residual lead compounds and the smaller lead particles.

Ex situ soil washing

Ex situ soil washing systems and treatment trains are quite flexible in terms of number, type, and order of processes involved, depending upon the lead-soil matrix characteristics, cleanup goals, and specific process employed. Many unit operations were developed in the metal ore and mineral processing industries, and include:

- Trammels and log washers (used to slurry solids).
- Attrition machines (used to scour mineral surfaces).
- Flotation machines (used to remove hydrophobic material from aqueous slurries).

- Screens, hydrocyclones and spiral classifiers (used to separate coarse minerals from fine minerals).
- Thickeners, filters and centrifuges (used to dewater solids).

These are primarily physical separation techniques and equipment described in detail in Chapter 4. In summary, these processes and equipment exploit physical differences such as size, density, shape, and wettability between contaminated particles and soil particles in order to produce a clean (or acceptably clean) coarse fraction and one or more lead-concentrated streams. Physical separation processes that involve the use of water as a transport medium will result in transfer of a portion of the metals to the aqueous phase.

Site and soil applicability. Three specific fractions are important to soil washing: an oversize fraction (>5 mm), a sand fraction (<5 mm and >0.063 mm), and the fines (< 0.063 mm). In most cases, the majority of the contaminant will reside and be concentrated in the fines (Mann 1999). Lower concentrations often exist in the sand and oversize fractions. To determine if a given soil is amenable to ex situ soil washing, representative samples from the site are classified by simple wet sieving to produce a particle-size distribution curve. The materials retained on each of the sieves are analyzed chemically for the contaminants of concern, usually lead, in the case of SAFR soils. This information, coupled with existing site background information, provides significant insight into the possible treatment scenarios and soil washing system configurations.

The finest soil fractions (silts and clays) typically contain the highest concentration of lead as these fractions have the highest surface area per unit volume and thus greatest potential for adsorption of the lead (Martin and Ruby 2004). In addition, these fractions often contain the natural organic component of the soil, which also tightly adsorbs the metals. The higher the proportion of fines in the contaminated soil, the more difficult and expensive is the soil washing process (Battelle 1997, Van Benschoten et al. 1997). An ideal soil for soil washing has a high proportion (>80 percent) of soil particles greater than 2 mm.

The treatment of the fine-grained fractions has much lower production rates and higher unit costs and extended time frames (Mann 1999, Martin and Ruby 2004). The reduced production rates result from the tendency of clay to agglomerate, which requires additional time, energy and high

water-clay ratios to produce a leachable slurry. In addition, the finer particles have slow settling velocities that require additional time and/or capital equipment to produce acceptable soil/water separation for multi-batch or countercurrent processing, or at the end of treatment. The additional difficulty and expense of handling the fine-grained fraction(s) at any given site brings up the question of whether the fines should be treated to produce clean fines, or be handled as a residual waste stream and disposed of directly.

The use of the sequential extraction procedure to determine the speciation of the lead in the soil has been used by several authors to estimate the applicability of soil washing for remediation of SAFR soils (Van Benschoten et al. 1997, Grasso et al. 1997, Peters 1999). The sequential extraction procedure has been discussed in detail in Chapter 2. This technique separates the lead into five fractions: easily extractable (exchangeable), carbonate, reducible oxide, organically bound, and residual fractions. Soils with the bulk of the lead in the exchangeable, carbonate and reducible oxide forms were found to be most amenable to soil washing techniques.

Several site conditions that do not favor soil washing are:

- Soils with a high proportion (>40 percent) of silt and clay.
- Soils that vary widely and frequently in significant characteristics such as soil type, contaminant type and concentration where blending for homogeneity is not feasible.
- Soils with high cation exchange capacity or humic acid content which interfere with lead desorption.
- Carbonate-based soils as they can neutralize acid leachates, which reduces the effectiveness of the acid wash due to pH change.
- Lead compounds having a very low solubility and a stable form (such as PbS or pyromorphites), which would require long contact times and excessive amounts of reagents.

Solid/liquid separation (dewatering). An important function of soil washing involves developing methods to separate soil and metal particulates from the leaching fluid, often termed “dewatering.” This occurs first in the separation of the soil particles from the leaching fluid after the soil has been exposed to the leachant. This can be a significant problem in soils with a large proportion of fines. In the second, if the leachant is to be regenerated and reused, the usual situation, the extracted metal in the so-

lution is generally precipitated from the leachate. This metal precipitate must then be separated from the leachant. The ability to accomplish these separations is so important that it is often the determining factor in calculating the efficacy of soil washing for a specific soil.

The solid/liquid separation techniques used in soil washing are those commonly used in many industries for this purpose. Four of these techniques, sedimentation, filtration, expression and centrifugation, are listed in Table 30 along with some of their advantages and limitations. Of these, sedimentation with added flocculants is generally the least expensive and simplest, but also the slowest of the processes. A combination of these methods is often used to obtain successively drier solids. Some of these techniques are discussed in detail in Chapter 4.

Table 30. Some basic solid/liquid separation (dewatering) techniques used in soil washing.

Technique	Filtration	Expression	Centrifugation	Sedimentation
Basic Principle	Passage through porous medium: particle size	Compression with fluid escape through porous medium: particle size	Artificial gravity settling: particle size, shape density and fluid density	Gravity settling: particle size, shape, density, and fluid density; aided by flocculants
Advantages	Simple operation, more selective separation	Handles slurry materials that are difficult to pump. Produces solid with low water content	Fast with large capacity	Simple, less expensive equipment; large capacity
Limitations	Batch nature of operations, washing may be poor	High pressures required, high resistance to flow in some cases	Expensive, more complicated equipment	Slow
Example types of equipment	Drum, disk, horizontal (belt) filters	Batch and continuous pressure	Solid bowl sedimentation and centrifugal, perforated basket	Cylindrical continuous clarifiers, rakes, overflow, lamella, deep cone thickeners
Typical bench test equipment	Vacuum filters, filter press	Filter press, pressure equipment	Bench or floor centrifuge	Cylindrical tubes, beaker, flocculants

Adapted from Battelle (1997).

Generation and management of waste streams. An important aspect in determining the applicability and cost of treating a contaminated soil is management of the generated waste streams (Mann 1999, Bricka et

al. 1999, ITRC 2003). Of the waste streams, handling of the lead-enriched leachant is the most important consideration in the overall process, especially if the leachant is to be recycled through the system. Leachant recycling reduces logistical requirements and costs associated with makeup water, storage, permitting, compliance, analysis, and leaching agents. It also reduces external coordination requirements and eliminates the dependence of the remediation on the ability to meet POTW discharge requirements.

The leachant first must have adequate lead solubility so that the lead reduction goals can be met without using excessive volumes of leaching solution. Second, the leachant must be readily, economically and repeatedly adjustable to a form in which the metal contaminant has very low solubility. This is necessary so that the recycled aqueous phase retains a favorable concentration gradient compared to the contaminated soil. In addition, efficient soil-water separation is important prior to recovering the metal from the loaded leachant in order to minimize contamination of the metal concentrate.

Other residual streams that may be generated and require proper handling include the untreatable, un-crushable oversize materials. These are the recyclable metal-bearing particulates, concentrates, soils, sludges or organic debris that fail TCLP thresholds for RCRA hazardous wastes. They also include soils or sludges that are not RCRA hazardous wastes but are also not sufficiently clean to permit return to the site, and rinse water from treated soil. Additional site requirements depend upon the treatment system selected, the amount of soil storage space and the number of ponds or tanks needed for wash water preparation and wastewater storage and treatment. Several commercial vendors have developed transportable, self-contained units.

In situ soil flushing

Soil flushing shares many of the characteristics of soil washing but is accomplished in situ by extracting contaminants from the soil by use of an appropriate washing solution. Soil flushing is usually not applicable to SAFR soils as the bulk of the lead in these soils is in a zero-valent form and difficult to dissolve. Therefore, it is usually necessary to use physical separation to first remove the intact lead bullets and lead fragments.

Metal extraction leachants

The solubilities of lead minerals are typically too small to effect satisfactory results by leaching with water alone. The solubilities of contaminant metals are controlled by predominant mineral phases that depend upon the pH and/or ambient ligands available. Studies have shown that the primary result of weathering of lead from bullets and pellets is the formation of hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and, to a lesser extent, cerussite (PbCO_3) (Lin 1996, Hardison et al. 2003). Vantelon et al. (2005) proposed that the transition of lead species after oxidation of Pb to Pb^{2+} follows the sequence: litharge [PbO] to hydrocerussite to cerussite. Consequently, the solubility of cerussite would limit the activity of Pb^{2+} in the soil solution in contact with weathering bullets to $\leq 1.28 \times 10^{-6}$ at pH 7, assuming that the CO_2 concentration is equal to or greater than that of the atmosphere.

In general, solubilization rates are dependent upon pH, liquid-to-solid ratio, type of metal species, and the contact time. The pH determines the equilibrium solubility (concentration) achievable, and the liquid-to-solid ratio determines the total mass of metal removed. The contact time required is usually relatively short unless coarse metal particulates are present. Metallic lead dissolves very slowly, so that the maximum physical removal of particulate lead is necessary before leaching the soil. Contact times between 10 and 60 minutes are commonly used for typical SAFR soils (Peters and Shem 1992, Battelle 1997).

Acid leaching

Acid leaching helps mobilize much of the fine particulates and soil-bound lead into solution by lowering the pH of the wash solution. Most of the common lead salts such as PbCO_3 , PbHPO_4 , $\text{Pb}(\text{OH})_2$ (except PbSO_4) greatly increase their solubility as the pH becomes more acidic (Figure 54). Acetic acid and hydrochloric acid have been commonly used to remove lead because both acids produce water-soluble lead salts. Acetic acid is a weak acid and may be effective at sites where lead is mostly in the form of carbonate minerals (cerussite, hydrocerussite, etc). At SAFR sites, lead carbonates may be formed from the weathering of elemental lead in the presence of native soil alkalinity.

Other forms of lead, such as lead dioxide and lead sulfates, are more recalcitrant to solubilization by acetic acid (Neilson et al. 2003). Lead sulfates are more common at lead acid battery sites, but could occur on firing

ranges in anaerobic swampy areas where sulfate reduction occurs. When lead sulfates or phosphates are present, the pH must be lowered to well below 3 to solubilize the lead. A stronger acid, such as hydrochloric or nitric acid, is more economical when the lead species requires a much lower pH. A 0.1-M solution of HCl has a pH of 1 and is more aggressive than acetic acid. A disadvantage of the nitric acid is that it may generate toxic oxides of nitrogen and is difficult to handle. These strong acids are more corrosive on equipment and more aggressive on the native soil matrix and biota, so if a weaker acid (acetic acid) is effective, it is best to use the weaker one.

A typical acid leaching treatment train consists of a continuous process involving at least four vessels (Figure 54). The acid solution is first mixed with the soil in the leaching tank to leach the metals from the soil. The contact time is set by designing the volume of the tank to achieve the required throughput rate. Small arms berms tend to be highly variable in terms of soil texture and the level of lead accumulation, so that some degree of over-design is advisable.

The soil slurry is pumped from the leach tank to a clarifier in which the solids settle out and are discharged from the bottom. The addition of a flocculent may be necessary to give adequate clarification. The overflow from the clarifier is the metal-rich leachant, which is pumped to a metal recovery (precipitation) tank. The lead is then precipitated out of the leachant by the addition of a hydroxide, phosphate, carbonate or sulfide salt. The precipitated lead sludge may be separated from the leachant by centrifugation or the use of a filter press and the leachant reconstituted and recycled.

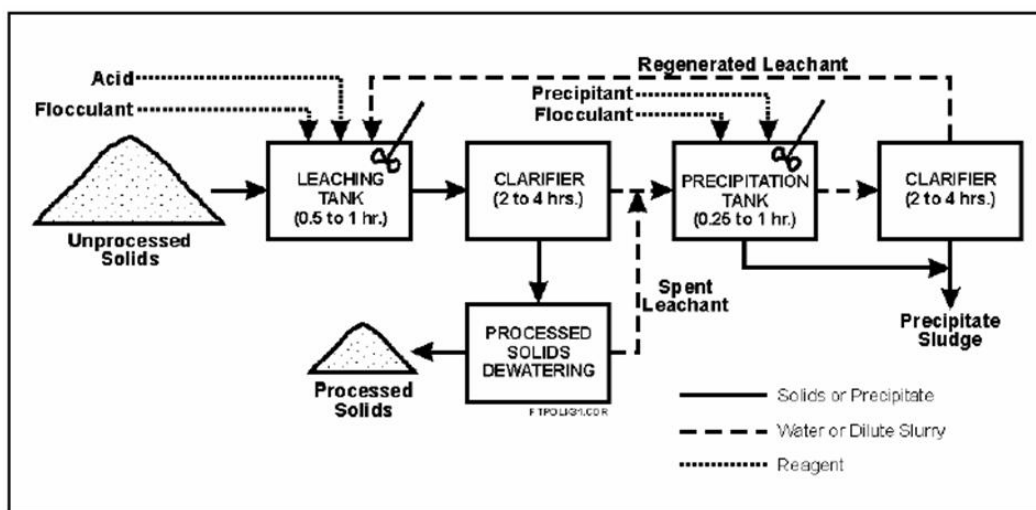


Figure 54. Schematic of basic soil washing process train (from ITRC 2003).

Metal chelators and surfactants as leachants

Extensive studies have been concluded using synthetic metal chelators with high metal stability constants to extract lead from contaminated soils. Effective chelators studied include EDTA, NTA, N-2(acetamido) iminodiacetic acid (ADA), pyridine-2,6-dicarboxylic acid (PDA), DTPA, and [S,S]-ethylenediaminedisuccinic acid (EDDS) (Neale et al. 1997, Davis and Hotha 1998, Steele and Pichtel 1998, Abumaizar and Smith 1999, Bricka et al. 1999, Peters 1999, Kim et al. 2003, Tandy et al. 2004). Environmental and health risks are associated with the majority of these environmentally persistent chelators and are suspected carcinogens (Peters 1999, Neilson et al. 2003, Nowack 2002, Tandy et al. 2004). Residual chelators in the soil also have the potential to mobilize metals in the future. Most studies of chelator-assisted soil washing have found that a ratio >1 between chelator and metal contaminant is required to achieve toxic metal extraction (Steele and Pichtel 1998, Tandy et al. 2004). When the ratio is increased, the extraction efficiency increases until the extraction efficiency levels off (Kim et al. 2003). Higher ratios are necessary for efficient extraction of the toxic metal due to the presence of the major cations in the soil such as Mn, Mg, Fe and Ca, which react with the active chelator, depleting the soil of major cations.

The extraction of lead with EDTA was found to be rapid, reaching equilibrium within a contact time of 1 hr (Peters and Shem 1992). Extraction of lead with NTA was slower, requiring a contact of about 3 hr to reach equilibrium. The maximum lead removal from the highly clay soil

(70 percent silt and clay) was 69, 19 and 7 percent for EDTA, NTA and water, respectively. They noted that the adsorptive behavior between the soil containing a high silt and clay fraction differed significantly from that of a sandy soil.

The removal of lead from eight study soils by extraction with five different washing solutions was investigated by batch washing experiments (Cline et al. 1993, Cline and Reed 1995). The soils were contaminated with lead nitrate [$\text{Pb}(\text{NO}_3)_2$] at 10, 100, and 1000 mg/kg. The washing solutions used included: tap water, HCl, EDTA, acetic acid, and CaCl_2 at 0.1 M and 1.0 M (except EDTA: 0.01 M and 0.1 M). Washing with water removed less than 3 percent of the lead, indicating that the sorbed lead was not readily removed by rinsing alone even though the soils were artificially contaminated. EDTA and HCl had the highest removal efficiencies of 92 percent and 89 percent, respectively, followed by acetic acid (45 percent) and CaCl_2 (36 percent). The removal efficiencies were generally independent of soil type and washing solution concentrations. The authors speculated that the dissolution of some of the soil components controlled lead removal in the HCl washes; chelation was the dominant lead-release mechanism for the EDTA washes; and lead removal by the CaCl_2 was by ion exchange with Ca^{2+} and/or complexation with the chloride species. Reed et al. (1996) reached similar results and conclusions using the same three extractants for flushing a lead-contaminated soil. While EDTA removed nearly all of the lead (both background and supplemental), its potential adverse health effects and persistence in the environment make its use in the field problematic (Tandy et al. 2004). The final soil pH for the HCl treatment was near 1.0, raising concern of increased contaminant mobility, decreased soil productivity and adverse changes in the soil's chemical and physical structure due to mineral dissolution. Final soil pH for the extractants EDTA and CaCl_2 ranged between 4.85 and 5.2.

Tampouris et al. (2001) also used HCl- CaCl_2 mixtures (0.44 mol HCl/kg soil and 4-M total chloride concentration) to remove lead from a fine-grained, clay loam soil. They first agglomerated the fine soil particles with sodium carboxymethyl cellulose, to increase the permeability of the soil, and leached the soil in laboratory columns. The lead was removed from the leachant by the addition of $\text{Ca}(\text{OH})_2$ at pH 9.0. The leachant was regenerated and recycled. Over 90 percent of the lead was removed from the soil. The soil was washed with tap water to remove the retained chloride solution and residual metal contaminants. The treatment had very limited

effect on the soil matrix (final pH 5.15) with a loss of only 3.5 percent dry weight. Fe and Al dissolution was limited to 11.5 and 16.7 percent, respectively. They suggested that heap leaching with this solution was a cost-effective soil washing technique with fine-grained soils that will not permit leachant percolation. Heap leaching is a process used in mining precious metals where a solution is allowed to percolate through a pile of soil and thus extract the metals.

A few studies have been made on the potential for surfactants to remediate heavy metals from soils. For example, Kornecki et al. (1998) investigated 10 cationic surfactants for their ability to remove lead from a contaminated soil. The most effective surfactant, isostearamidopropyl morpholine lactate (at 0.1 M), desorbed 82 percent of the lead from a sandy loam soil, but only 36 percent from a loamy soil. They also compared the lead extraction efficiency to that using EDTA, which desorbed 94 to 97 percent of the lead from the same soils over a broad range of pH. The use of a solution of sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), an inexpensive reducing reagent, either alone or with Na_2EDTA , did not enhance lead removal from a spiked silty sand soil (Abumaizar and Smith 1999).

Extractant regeneration

As discussed above, the commercial success of soil washing depends upon the ability to re-extract the lead from the leachant so the leachant can be reused or disposed of as a non-hazardous material. For acid leachants, the lead is typically precipitated out of the leaching solution by raising the pH and adding phosphate or sulfide salts. After the precipitated lead is removed by filtration, centrifugation or settling (usually with added flocculants), the leachant can be regenerated by the addition of concentrated acid to lower the pH back to the desired level.

Regeneration of EDTA-based leachants is more difficult. Three different methods have been investigated: 1) electrolysis with cation exchange membrane, 2) reacting chelated metal with zero valent metals, and 3) water soluble polymer.

One of the recycling methods investigated was the application of electrolysis in conjunction with a cation-exchange membrane for the recovery of metals in a solution of metal-EDTA complexes (Allen and Chen 1993, Juang and Wang 2000, Arévalo et al. 2002). The process involved electrochemical reduction of the metal-EDTA complexes in which metal cations

were reduced/deposited onto the cathode surface while EDTA is released into solution and isolated from the anode using a cation exchange membrane. The authors did not reuse the EDTA to verify that it was regenerated in an active state. This method is reported to be cost prohibitive due to several operational problems such as membrane fouling or degradation and EDTA precipitation (Kim and Ong 1999).

A second method of regenerating the metal-laden chelators involves reacting the metal-EDTA complex with zero-valent metals, which can result in precipitation of the metallic contaminants while liberating the EDTA (Lee and Marshall 2002). The metal-laden aqueous extract was treated with zero-valent magnesium or bimetallic mixtures to precipitate the heavy metals from solution while liberating the chelating reagent. The regenerated EDTA was readjusted to pH 5 and successfully reused to extract more heavy metals.

Steele and Pichtel (1998) recovered the lead from spent EDTA, ADA, and PDA solutions by hydroxide precipitation in the presence of excess calcium. Recovery was 70, 98, and 97 percent, respectively. Kim and Ong (1999) used a different strategy to recover the loaded EDTA by substituting the lead complexed with EDTA with Fe(III) ions at low pH, followed by precipitation of the lead ions with phosphate or sulfate ions. Fe(III) ions complexed with EDTA were then precipitated at high pH using sodium hydroxide. The resulting solution (Fe-precipitated solution) was tested on three lead-contaminated soil-sands and was found to have similar extraction capabilities as fresh EDTA solution. Experimental results showed that the regenerated EDTA solution could be recycled several times without losing its extractive power.

Lim et al. (2005) proposed the regeneration of EDTA after metal extraction by first destabilizing the EDTA-Fe(III) complex to liberate the lead, cadmium and nickel. This was followed by precipitation of the liberated metals in their phosphate forms and precipitation of the excess Fe(III) to produce free EDTA for reuse. Two hours of reaction time each for the complex destabilization reaction and the metal phosphate precipitation reaction was sufficient to achieve equilibrium. With the optimized process conditions identified, a total of 95, 89, and 90 percent of the lead, cadmium and nickel, respectively, could be precipitated from the spent EDTA solution with 84-percent EDTA recovery. The reused EDTA maintained more than 90 percent of its preceding extraction power in each cycle of reuse.

In the second method, Sauer et al. (2004) studied the use of a water-soluble polymer (polyethylenimine [PEI]) to clean a lead-contaminated Superfund soil. The polymer was treated with varying amounts of bromo- or chloroacetic acid to yield an aminocarboxylate chelating group, which effectively binds lead. The resulting polymer had extraction properties similar to EDTA and removed over 97 percent of the lead from the soil in batch tests. The polymer could be concentrated and regenerated using ultrafiltration. The lead was released by acidification to pH 1 with HCl, followed by a second ultrafiltration, which concentrated the soluble lead in the filtrate.

Lead extraction from SAFR soils in batch and counter-current extraction processes

The Environmental Laboratory at the U.S. Army Engineer Research and Development Center undertook an extensive research project to test the applicability of soil washing to lead-contaminated SAFR soils (Bricka et al. 1999). The study included a preliminary batch extraction study followed by a pilot-scale chemical extraction using a specially designed, four-stage, counter-current extraction apparatus (Neale et al. 1997).

Batch extraction test

Two grams of each soil sample (800 mg/kg Pb) were weighed (± 0.02 g) and placed in a 50-mL polypropylene centrifuge tube. A solid-to-liquid ratio of 0.05 was used; 40 ml of the extracting agent was added to the 50-ml centrifuge tube containing the soil. Each of the samples was placed in an end-over-end tumbling apparatus operating at 18 ± 2 rpm for 30 hr to ensure that chemical equilibrium was established. After tumbling, the samples were centrifuged for 30 min at approximately 15,000 rpm, after which the liquid portion of the sample was decanted. The concentrations of dissolved lead in each sample were determined and the percent of lead extracted calculated. The batch extraction tests used a variety of leachant solutions: HCl, HNO₃, H₃PO₄, citric acid, gluconic acid, EDTA, DTPA, NTA and NaOH. All reagents were run at three different reagent concentrations: 0.01, 0.05, and 0.1 M.

The results of the batch extraction tests are illustrated (Figure 55) for one of the SAFR soils (Cape May). The most successful of the leachants extracted nearly 75 percent of the lead in the soil. Of the acids used, HCl and HNO₃ were the most effective, extracting between 60 and 70 percent of the

lead from the soil. Phosphoric and citric acids were about half as effective (~30 to 50 percent of lead extracted) and H_2SO_4 and gluconic acids were least effective, extracting only between 10 and 15 percent of the lead from the soil. All three of the chelating agents were equally effective as the HCl and HNO_3 acids, extracting between 55 and 65 percent of the lead from the soil.

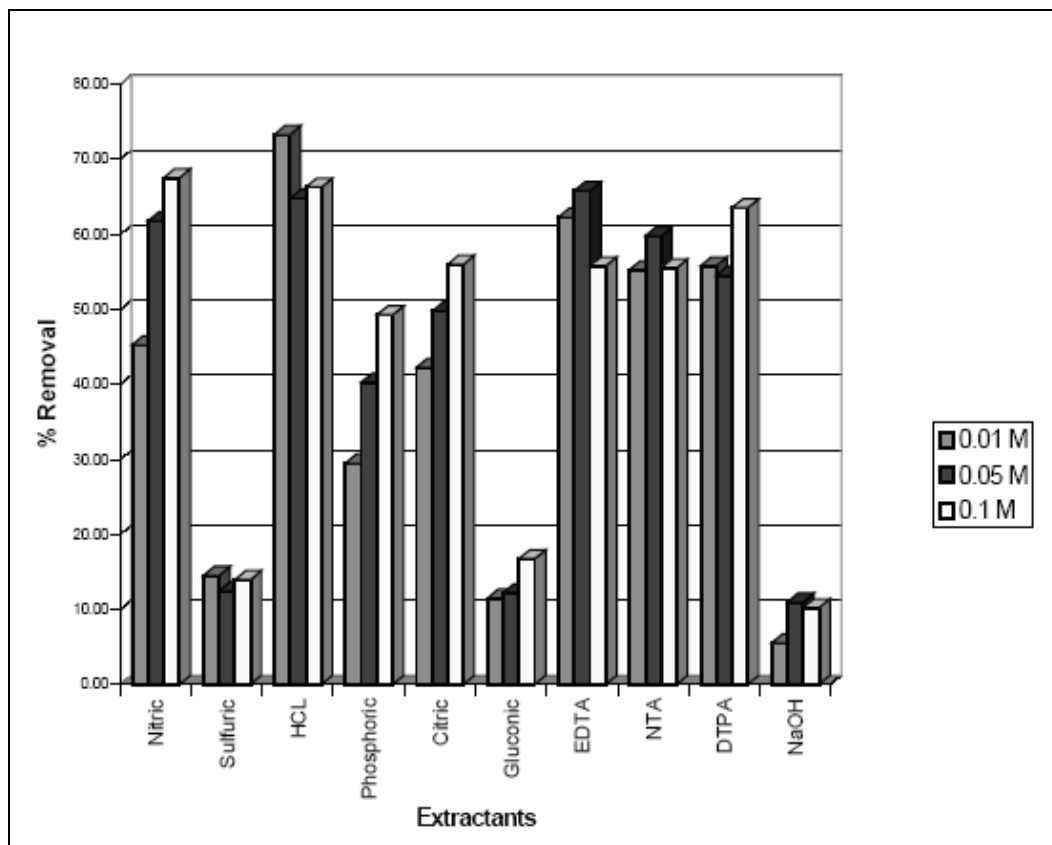


Figure 55. Batch extraction of lead from Cape May SAFR soil by different reagents. (Bricka et al. 1999).

Similar tests on three other SAFR soils showed very similar patterns between the different leachants, but great variability in their effectiveness. In one highly lead-contaminated soil (Kodiak soil, 20,000 mg/kg Pb), the three acids (HCl , HNO_3 and citric acid) and the three chelating agents extracted nearly 100 percent of the lead from the soil. However, in a third soil (New Orleans soil, 1,000 mg/kg Pb), none of the extractants were deemed to be effective. The very large variation between the soils shows the requirement for testing each soil at each site for the applicability of metal extraction. The results of the batch extraction tests were used to design the counter-current test procedures.

Counter-current extraction pilot tests at ERDC

Design and construction of the chemical extraction system. A pilot-scale counter-current metal extraction (CCME) system was designed and constructed at ERDC, to simulate large-scale chemical extraction systems (Neale et al. 1997). Figure 56 is a detailed schematic of the pilot-scale system. The system consisted of four identical sets of reactors and clarifiers. System flow was regulated by using two identical, digitalized, console pump drives. Each had a maximum flow rate of 380 mL/min. One drive was used to control the flow of the initial, fresh (contaminated) soil slurry and fresh (uncontaminated) extracting agent solution, while the other drive pumped the underflow slurries from clarifiers in each of the four stages to reactors in the previous stages.

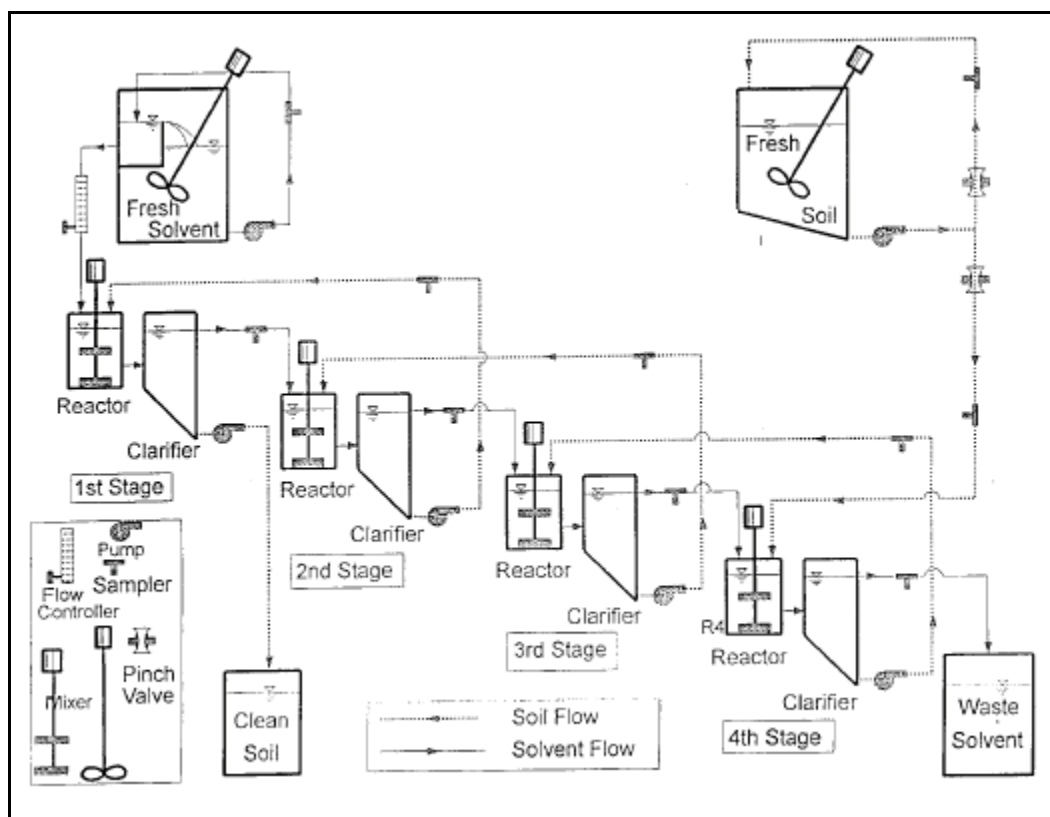


Figure 56. Schematic of the continuous-flow, pilot-scale counter-current metal extraction system (from Neale et al. 1997).

During operation, the fresh slurry was introduced into the fourth stage reactor and was eventually pumped up to the first stage reactor while fresh extracting solution was introduced into the first stage reactor, and the spent extraction fluid eventually exited the system via the fourth stage clarifier. In this way, true counter-current flow was achieved. Each reac-

tor held approximately 2 L of slurry and contained four baffles that were designed to ensure complete mixing of the soil slurry. Each clarifier held approximately 2 L of slurry and was equipped with two $\frac{3}{4}$ -in. inlets and two $\frac{3}{4}$ -in. outlets. The two inlets were connected to the reactor outlets using $\frac{3}{4}$ -in. tubing. The clarifier bottoms were angled to allow solids to move more easily to the bottom outlet of the vessel while the less turbid extracting fluid remained near the top of the clarifier. Each of the four reactors was equipped with a variable speed mixer with 30-in. shaft that delivered a maximum mixing speed of 1800 rpm. The mixers ensured adequate contact between the soil slurry and extracting agent. A 200-L tank was used to store the fresh soil slurry.

Operation of counter-current metal extraction system. A schematic of the counter-current metal extraction system can be seen in Figure 56. The extracting agent (100-L) was prepared in a 50-gal Nalgene® tank located adjacent to the first stage reactor and clarifier. The concentrated acid or chelating agent was added to 100 L of tap water and the solution was thoroughly mixed using the single speed mixer. The experimental run was initiated by starting the extraction solution influent pump at a rate of 277-mL/min. In approximately 1 hr, all of the reaction and clarification vessels of Stages 1-4 in the system were filled with fresh extracting agent. For each pilot-scale run, the system was operated for 12 hr.

The feed soil slurry was prepared by slurring 10.8 kg of soil, and 63 L of tap water, added to a tank to produce a 15-percent soil slurry. A mixer (~220 rpm) was used to prepare the soil and water slurry. Once the reactors and clarifiers were filled with reagent and the slurry was well mixed, all console pump drives (underflow, reagent influent, slurry influent) were set at 100-mL/min to maximize retention time without causing serious plugging problems in the system. All of the variable speed mixers were set at 600 rpm. Total retention time of soil in the counter-current system was approximately 3 hr. Samples consisting of 100 ml of slurry and overflow were taken at 4, 8, 10, and 12 hr from each of the sampling ports, with the exception of the reagent or solvent samples, which were only collected at the beginning of the test.

EDTA and HNO_3 at 0.05-M concentration were selected for CCME testing of the Cape May soil. EDTA approached steady state in 4 to 8 hr of operation. More lead was removed in the liquid as it exited the system in stage 4

than was removed in stage 1, indicating extraction was occurring in each stage. In contrast, steady state was not approached until after 10 to 12 hr for the HNO_3 extract. The lead removal from the soil in all four stages was calculated to be only 15 to 18 percent for both extractants.

For the Kodiak soil, where batch extraction removed almost 100 percent of the lead, steady state was again reached for both the HNO_3 and citric acid leachants after about 8 to 10 hr. Steady state concentrations were 600 to 1000 mg/L for EDTA. The percent of lead removed by EDTA was higher, about 30 percent. The steady-state concentration for citric acid was 400 to 500 mg/L and removal efficiency was only about 15 percent.

Field experience of SAFR soil washing

Soil washing has been used most extensively in Europe and is gaining popularity in Canada. The bulk of this activity is done at fixed facilities with the contaminated soils being transported from the site to the facility (ITRC 2003). A fixed facility for soil washing is a centralized facility that accepts wastes from a number of sites, which enables operators to adjust their systems to meet the needs of a variety of waste streams. For soil washing, a technology that relies on variable process flows, this is extremely beneficial. The permitting process to gain approval typically takes over a year and is extremely expensive. As a result, it is nearly impossible for a mobile plant to be profitable with throughput less than about 25,000 tons per year. Mobile plants are used almost exclusively for feasibility testing or at sites where there are no other alternatives.

One model fixed facility in the United States is currently under development in Boss, MO. The Doe Run Company has mined and smelted lead in Missouri for over 100 years. In 1997, the Doe Run Company purchased the TerraMet™ process to leach lead and other heavy metals from contaminated soils. They use the extracted lead in existing operations and the clean fractions of the recycled soils are returned to a site as fill. The facility operates under a revised RCRA part B permit. Under RCRA exemptions for reclamation of “useful products” from hazardous wastes, some metal-bearing soils can be shipped as non-hazardous to a recycling facility. Although the soil washing plant operates as a fixed facility, they also have the capacity to transport the soil washing technology off-site for mobile treatment or testing as needed.

Several factors made the siting of the fixed facility feasible. The company had an existing facility operating under an RCRA part B permit. They had the ability to reuse most of the end products in their primary operation; the separated metals are used as a feedstock for their smelting process. Because it is recycling metals from contaminated media, the facility is eligible for exemptions in operational and transportation regulations under RCRA. These regulatory exemptions are vital to the success of fixed facilities.

Several vendors have developed and commercialized acid leaching processes to recover lead from soils (Battelle 1997). These processes use an acid leachant to remove metals from the soil and are reported to treat most types of lead including metallic lead, soluble ions and insoluble lead oxide and salts. Physical separation is the first step in the commercial processes. Simple dry screening removes oversize materials. The lead-laden fines are processed by at least two contacts with fresh acid. The treated solids are separated from the leaching solution, which is treated by ion exchange or reduction to recover the lead and regenerate the leaching solution for reuse.

Brice Environmental Services Corporation (1998) has developed a portable, above-ground, soil-washing process that reduces the overall volume of contaminated soil requiring treatment. The soil washing process involves site-specific unit operations depending upon the soil and contaminant characteristics, cleanup standards, cost, and client specifications. The process includes a volume reduction operation, in which intensive scrubbing, followed by density, magnetic, and size separations, cleans oversized soil. The fines are acid-leached by at least two contacts with fresh acid. The treated solids are then separated from the leaching solution. The spent leaching solution is treated by ion exchange or reduction to recover the lead and regenerate the leaching solution for reuse. A small-scale, volume reduction plant used for demonstration and pilot testing, is contained on a single trailer and can process between 4 and 20 tons per hour depending upon the soil and contaminant characteristics.

The BESCOP/COGNIS system (TerraMet™) was used for full-scale remediation of about 20,000 tons of lead-bearing soil at the Twin Cities Army Ammunition Plant, New Brighton, MN (Fix and Fristad 1993). The average total lead concentration in the untreated soil, 17,000 mg/kg, was reduced to less than 300 mg/kg by the treatment process. The treated

residual passed the TCLP test. The lead was recovered as part of solvent regeneration.

Pilot scale acid leaching of SAFR soils at Fort Polk, LA

Physical separation and acid leaching technology was demonstrated on SAFR berm soils from an M-16 range (Range 5) at Fort Polk, LA (Battelle 1997). The demonstration was a joint effort between the Naval Facilities Engineering Service Center (NFESC) and USAEC. During this period, two vendors demonstrated their variations of the technology. At the request of USAEC and NFESC, Vendor 1 used acetic acid leaching and Vendor 2 used hydrochloric acid leaching. The goal of the demonstration was to evaluate physical separation and acid leaching for SAFR soil processing. The demonstration had the following objectives:

- Design and mobilize the vendors' respective plants at Fort Polk and process up to 1,000 tons of Range 5 soil at an average continuous rate of 5 tons/hr.
- Evaluate the efficiencies of two potentially effective acids for leaching.
- Vendor 1 was asked to use acetic acid and Vendor 2 was asked to use an acid other than acetic acid.
- Make a good faith effort to process the range soil to meet the TCLP criterion of 5 mg/L or less of lead.
- No criteria were set for other metals, but the removal of copper, zinc, and antimony by the process was also tracked.
- Achieve the TCLP criterion through metals removal, without the use of stabilization agents.
- Achieve total metals targets for the processed soil.
- Vendor 1's target was 1,000 mg/kg. Vendor 2's target was reduced to 500 mg/kg to better meet the TCLP criterion.
- Ensure that the processed soil would be physically and chemically suitable for reuse in an active berm.

The raw soil from the berm (feed) had a lead assay of 4,880 mg/kg. The +10-mesh coarse fraction constituted 2.3 percent of the berm material, but contained almost 80 percent of the original lead. Therefore, the majority

of the lead in the range soil is recoverable by relatively simple size or gravity separation equipment, such as screens or jigs.

The <10-mesh fraction constituted 98 percent of the berm material, but contained only 20 percent of the lead. The <10-mesh fraction did not contain lead amenable to gravity separation. Physical separation alone was not sufficient to meet target criteria. The <10-mesh material contained sufficient fine particulate and/or ionic lead to require removal by leaching.

Results of Vendor 1

Vendor 1 assembled a plant on-site and processed 263 tons of soil by acetic acid leaching. On the first day of processing, the processed soil met the total and TCLP lead targets. Approximately 93 percent of the total lead, 93 percent of the total copper, 77 percent of the total zinc, and 70 percent of the total antimony were removed during this initial effort, indicating that acetic acid has the potential to remove heavy metals to target levels. Subsequently, however, both total and leachable lead levels rose incrementally. This decline was due to increasing lead levels in the raw soil and a buildup of lead in the regenerated leachant caused by inadequate precipitation.

Organic matter collected in the process contained high levels of lead, but this stream was very small in volume. Both coarse and fine processed fractions individually failed the TCLP test. This was because inadequate precipitation caused dissolved lead to build up in the regenerated leachant, at times reaching levels as high as 627 mg/L. The pH levels of the regenerated leachant and precipitate indicate that the precipitation step was being implemented at a very low pH, at which most precipitants may be expected to be inefficient.

Lessons learned. The low plant reliability and an inability to meet processing targets were caused by:

- Inadequate bench-scale testing - precipitation efficiency was not optimized during the bench-scale tests and key operating parameters, such as precipitant dosage and effective pH range, were inadequate.
- Inadequate process control - the problem with the buildup of lead in the leachant was not identified and corrected in time during the demonstration because the vendor's atomic absorption (AA) ana-

lyzer was not functional, and there was no other means to provide reliable on-site verification. Vendor 1 also appeared to be inadequately staffed. Additional operators (including an on-site process chemist) would have provided better process control.

- Inadequate attention to material handling and equipment sizing during plant design. Various material handling problems were encountered in the feed hopper, plate feeder, soil deagglomerator, sand screw, vacuum belt filter, and plate-and-frame filter press. These difficulties caused frequent bottlenecks and downtime.

Results of Vendor 2

Vendor 2 assembled an on-site plant and processed 835 tons of Range 5 soil by hydrochloric acid leaching. The processed soil from Vendor 2's plant consistently met total and TCLP lead targets. Total lead was reduced from an average of 4,117 mg/kg in the raw soil to an average of 165 mg/kg in the processed soil. Leachable lead levels as measured by TCLP were reduced to an average of 2 mg/L. Processing removed an average of 96 percent total lead, 97 percent total copper, 89 percent total zinc, and 60 percent total antimony from the range soil. Most of the metals that were removed by the process were collected in the jig bed and in the precipitate sludge. The organic matter separated from the classifier overflow showed high concentrations of lead. This organic matter was blended with the final processed soil.

The metals collected in the jig bed were not expected and were due to the process stream that resulted from on-site modifications made to the plant by the vendor. Because of difficulties encountered in screening the raw soil, Vendor 2 eliminated the screening unit and the coarse material jig from the planned plant configuration. Instead, the raw soil was sent directly to the attrition scrubber and classifier. The coarse fraction from the classifier was sent to the fine material jig. In this jig, the metal fragments, instead of sinking into the jig concentrate, were retained on top of the jig sieve along with the other coarser materials. These metal fragments were hand-sorted and removed by an operator.

Both coarse and fine processed fractions contained low levels of lead. These two fractions were combined to form the final processed soil that was neutralized and returned to the range. The processed soil had a loose texture and appeared to be suitable for reuse in the active berm at Range 5.

10,000 tons of contaminated soil. The projected cost per ton for remediation of 10,000 tons of berm soil is around \$170/ton.

An additional cost consideration when using HCl for leaching is its corrosive effect on equipment. Analysis of the precipitate sludge showed that it contained over 4 percent iron, much of which was from corrosion of the carbon steel equipment itself. The use of HCl at the required pH would be expected to reduce the life of the equipment.

Laboratory study of combined soil washing and stabilization at McClellan AFB

A study was conducted on SAFR soils from ranges at the former McClellan Air Force Base, near Sacramento, CA. Treatment of lead-contaminated SAFR soils at the site focused on two technologies: soil washing using methods developed by Brice Environmental, and stabilization using treatments of tall oil pitch (TOPEIN S manufactured by Encapco Technologies, LLC.) and lime. Two treatment goals, both based on extraction tests, were established. The first was to pass the Federal standard TCLP for lead (5 mg/L). Passing this goal would allow the facility to dispose of the soil in a non-hazardous waste landfill outside the state of California. The second goal was to pass the California Waste Extraction Test (WET), also 5 mg/L. The WET test is significantly more challenging than the TCLP in that it is a longer extraction (40 hr), has a less favorable solid to solution ratio (1:10 instead of 1:20), and it uses a more aggressive acid system (citric acid, which is a strong metal chelating agent). Passing the WET extraction would allow for disposal in a non-hazardous landfill in California, and more importantly, could allow for on-site disposal. In addition, the soils underwent a 40-hr extraction in deionized water (DI extraction) to test for possible amphoteric effects resulting from treatment (i.e. raising the pH to defeat acid extraction, but as a result, shifting the stability of the lead so that it is more soluble in neutral water).

Soil washing results

Soil washing was applied to untreated soil. This removed 98 percent of the total lead in the soil (Figure 58). The TCLP was reduced by 99 percent, but the resultant level (15 mg/L) did not meet the treatment goal. Similarly, the WET extraction was reduced by nearly 90 percent, but also did not meet the 5 mg/L level. The DI extraction was reduced by more than 90 percent. All of these reductions were statistically significant at the 90-

percent confidence interval. Soil washing was effective at removing most of the total lead, and in substantially reducing lead in TCLP extractions, but did not fully meet the treatment goal.

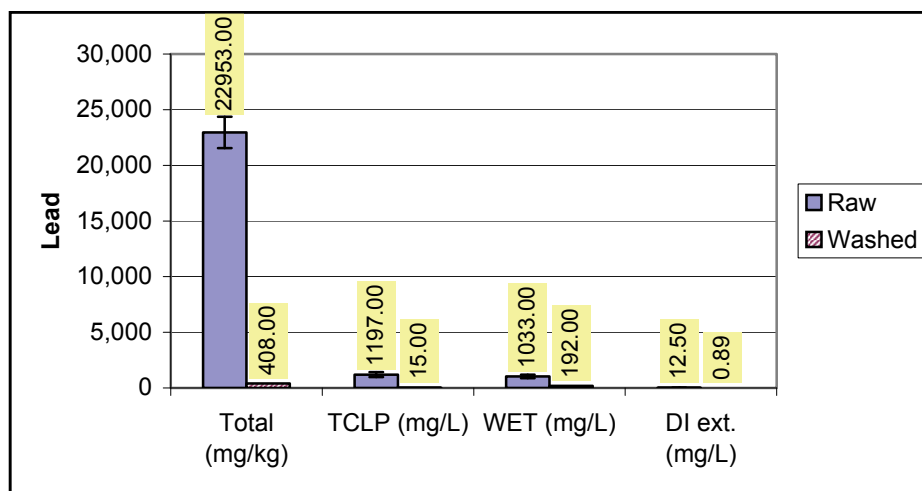


Figure 58. Treatment of lead contaminated soils using soil washing.

Stabilization

Similar results occurred from stabilization treatment (3 percent lime and 8 percent tall oil pitch) of the base soil (Figure 59). Both the TCLP and the WET extractions were reduced by more than 90 percent. However, both exceeded 5 mg/L Pb. In addition, the DI extraction decreased Pb slightly, but significantly (90 percent CI), indicating an amphoteric effect from the treatment.

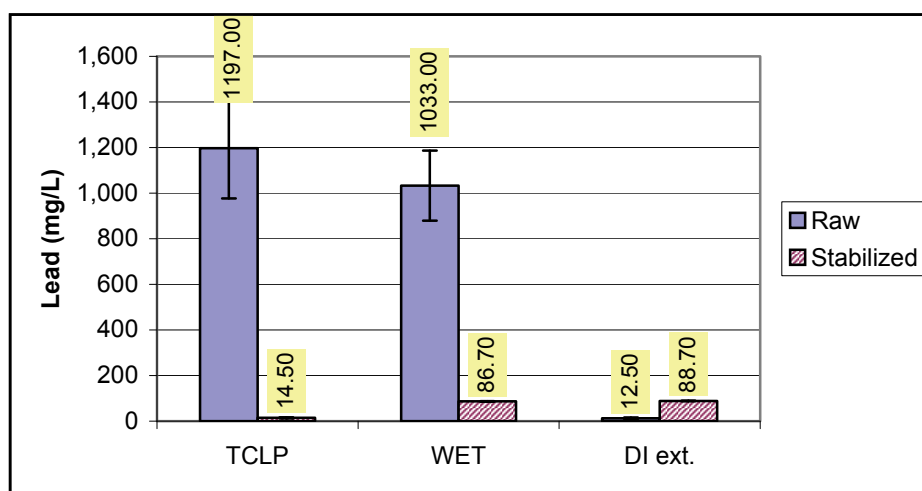


Figure 59. Treatment of raw lead contaminated soils stabilized by treatment with 8-percent asphalt emulsion and 5-percent lime.

Combining soil washing with emulsion treatment

Figure 60 summarizes results when the washed soil was stabilized with tall oil pitch. The treatment was effective at lowering the TCLP extraction to below 5 mg/L. The WET extraction, however, only had a modest decrease in concentration, and was still well above the 5 mg/L goal. DI extraction increased slightly, but the increase was not statistically significant (90-percent CI).

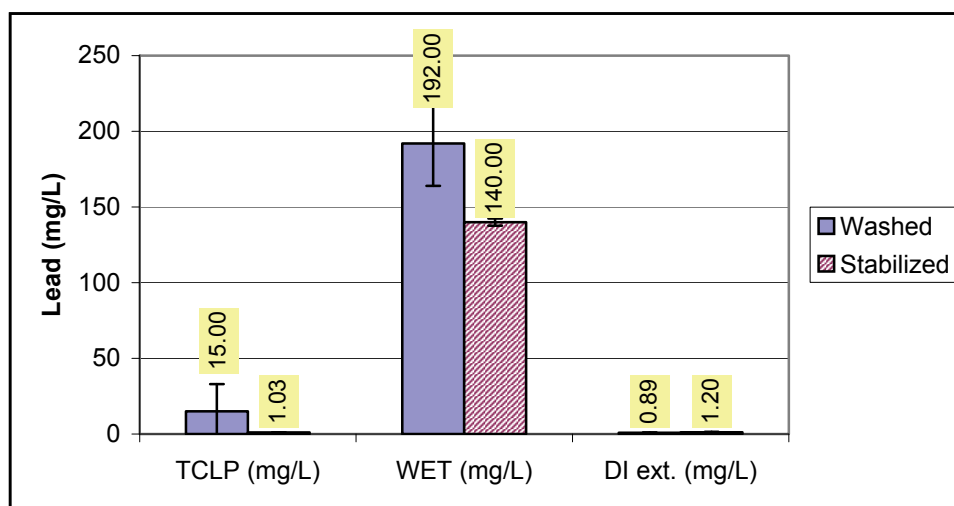


Figure 60. Treatment of soil wash treated soils by asphalt/chemical fixation.

Combining soil washing and tall oil pitch stabilization met the goal of disposing of the waste off-site for TCLP and DE extraction procedures. Additional treatments were conducted to determine if it would be possible to meet the CA WET test to allow on-site disposal. Treatments included higher lime doses and addition of carbonate (Figure 61). The combination of 10 percent lime and 10 percent carbonate, both with and without tall oil pitch, was effective at meeting the on-site disposal treatment goal.

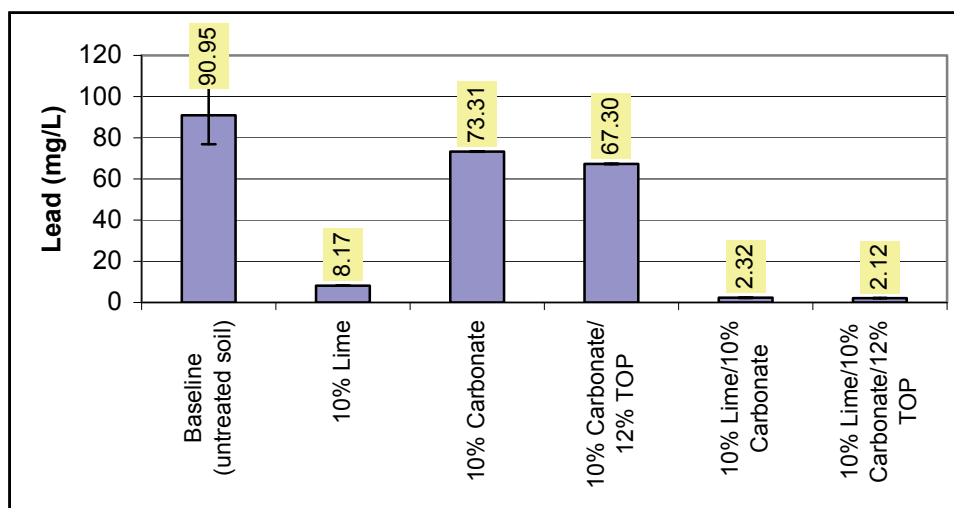


Figure 61. WET extraction results for various aggressive treatments of lead.

Conclusions

Soil washing technologies have been developed and used widely in Europe for the last decade. Most of the soils in Europe were processed in fixed facilities due to the high land values, high landfill costs, small size of the countries (short haul distances) and ease of permitting. In the United States, due to the usually greater haul distances, most activity has been in development of mobile units that are set up on-site even though the permitting process must be completed at each site.

SAFR sites that have soils with low levels of fines, carbonate, and humic content are candidates for soil washing. The most common reagents used in the leachant are aqueous mixtures of acids (hydrochloric, nitric or acetic acid) or organic chelators and surfactants. The regeneration and reuse of the leachant is important to the cost-effectiveness of the soils washing process. It also relieves the regulatory process of disposing of a hazardous waste stream.

However, at this time, soil washing combined with physical separation (\$1,400 – 1997 \$) is generally more expensive than landfill disposal (\$50 to \$100 per ton). Therefore, the authors expect its use to be limited, unless stricter landfill regulations are implemented.

7 Range Remediation Strategy

Purpose and objectives

This document is primarily intended for SAFRs on property owned or controlled by the U.S. Army; however, it may be useful for parties evaluating restoration of non-Army small arms training ranges, law enforcement (military police, Federal law enforcement, etc.) training ranges, and recreational rifle, pistol, trap, skeet, and sporting clays ranges. This chapter is meant to assist decision makers faced with the remediation of small arms firing ranges once it has been determined that a former range property requires restoration. This chapter is expected to be useful for parties involved in the process of selecting the most cost-effective restoration approach that reduces long-term liability associated with the property and materials removed from the property. Because of the wide array of range characteristics found at SAFRs such as soil type, firing distance, range age, weapons used, and climate, no single low-cost strategy is dictated for all ranges.

To this end, a flow chart approach with a number of decision points is presented through which alternative technologies can either be eliminated or considered as potential remediation approaches. The starting point for this decision process is the determination that a SAFR requires restoration. For the purposes of this chapter, it is assumed that a decision has been made, and that remediation of a SAFR will be performed.

Remediation technology selection process: Cost basis

Traditional remediation approaches involve complete excavation and disposal of soils as hazardous waste. Cost savings achievable by using alternative restoration approaches can be significant. For ranges where more than 10,000 yd³ of soil are to be remediated, savings of greater than \$1,000,000 can be achieved through application of an alternative approach, if the approach is effective for those specific range characteristics. The Evergreen Range remediation at Ft. Lewis, Washington will be used as an example to illustrate the decision-making process. In the case of the Evergreen Range, the site was restored and 5,000 yd³ of range soil was processed for \$700,000. This is a cost savings of \$800,000 as compared to an estimated cost of \$1,500,000 for traditional excavation and disposal.

The flow diagram presented in Figure 62 moves through the first actions that need to be taken once the decision has been made to remediate a closed SAFR. These are:

- Determine soil volume requiring separation/removal/treatment.
- Determine the degree and extent of contamination.
- Evaluate physical separation approaches.
- Evaluate stabilization approaches.

Each of these four process boxes will be expanded in separate sections to assist decision makers performing the process.

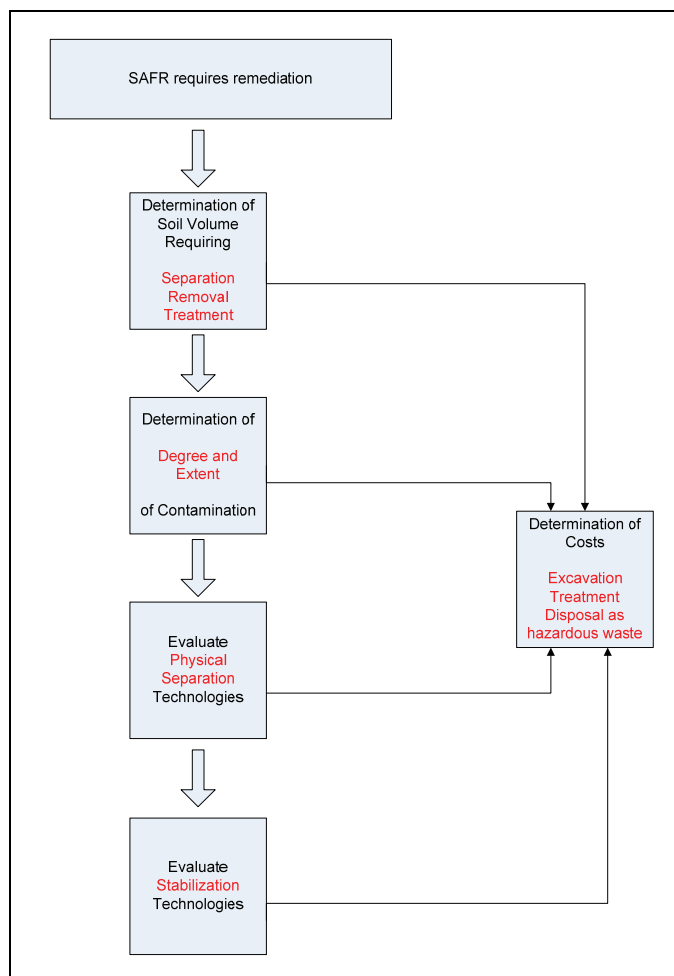


Figure 62. Decision areas for determination of remediation costs.

Determine soil volume requiring separation/removal/treatment

Knowledge of the volume of soil that requires handling at a SAFR designated for restoration is a critical piece of information for technology selection. Because of the economics associated with on-site processes, the cost per cubic yard varies considerably with the total volume for many remediation approaches. In order to make informed comparisons between remediation options, a good estimation of the total volume of soil is required.

In general, the process of performing a remedial investigation for a SAFR site includes much more than determining the volume of soil that requires action. The RI/FS process identified under CERCLA (Interim Final Guidance Conducting Remedial Investigations and Feasibility Studies under CERCLA, OSWER Directive No. 9355.3-01, 1988) will be followed in the decision-tree for SAFR soil remediation presented here. There are a number of unique issues associated with SAFR remedial investigations that can affect the calculation of total soil volume requiring treatment. These issues are important because miscalculation of the soil volume can result in selection of less than optimal remediation technologies. Chapter 1 details the preliminary steps to a range cleanup, discusses regulatory issues, and provides an overview of cleanup options.

Figure 63 provides a chart for determining the approximate volume of soil that will require handling for a SAFR. Three major steps are involved:

- A historical investigation.
- A site survey.
- A determination of contaminant concentration in site samples.

Historical investigation. A historical investigation involves thorough research and collection of historical information in determining areas that may contain significant quantities of lead due to SAFR activities. This historical information can include range design diagrams, range maintenance logs, aerial photographs, training logs, personal interviews with past and present range personnel, and any other documentation pertaining to use, modification, and maintenance of the SAFR. Using this information, a map of the area can be prepared and subdivided into areas where heavy metal contamination may exist (Document- Maps, Boundaries, Landmarks, Usage Levels).

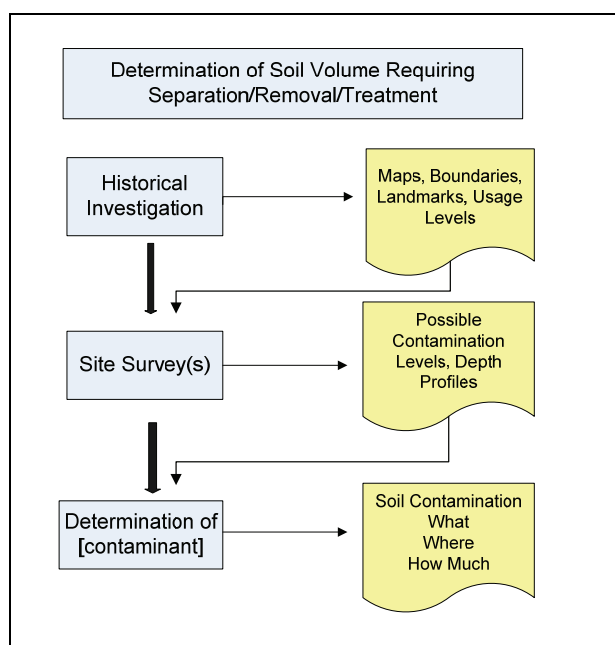


Figure 63. SAFR flow diagram to determine the approximate volume of soil that requires remediation.

As discussed in Chapter 1, the type of range and the ammunition used will govern the areas in which bullets or shot may be deposited. Changes in range usage over the lifetime of the SAFR may result in numerous areas of contamination by dissimilar projectiles. Firing practices that involve bullet impact with an earthen backstop will produce discrete volumes of soil with high metals content. Firing ranges without backstops result in bullets traveling long distances prior to impacting soil, producing contamination by relatively larger metallic particles at shallower depths.

The bullet impact areas are not the only soils on SAFRS that may contain significant quantities of heavy metals. The impact of bullets creates dust, which may contain various metals and can be carried away from the primary impact area by either wind or water erosion. The heat of firing bullets can also atomize metals into a vapor, which can condense on soil particles at the firing line. The spatial distribution of lead (for example) in soil at SAFRs varies based upon range use, size and impact velocity of the round, and range management practices. The information on the historical use of the range is helpful in identifying possible sites of contaminated soil.

Site survey. Site surveys are conducted to determine, first, whether ranges are, in fact, contaminated and, then, which metals are involved and at what concentration. To accomplish this, representative soil samples are

taken for analysis. Several factors affect the depth of contamination and the depth profile of metals over the range area: past range activities of maintenance and construction, weathering on the ranges, and sample heterogeneity.

A challenge for SAFRs is trying to determine the depth of the soil that requires excavation (Figure 64) in order to reach the minimum heavy metal concentration permitted to remain in place. On many ranges using earthen berms, berm locations have changed over time through either natural (migrating sand dunes) or range design operations (re-placement of impact berm to accommodate a variation in training). The depth of metal contamination within a berm can also vary greatly. Rounds fired from M-16s at a distance of 25 m generally penetrate into soil a distance from 6 to 18 in. depending on soil type. Berms that quickly erode may contain predominantly shallow lead as the poorly vegetated front berm surface erodes. Berms that have received regular re-surfacing with clean soil may have bullet residues at a greater depth. The heterogeneous nature of metal concentrations at SAFRs can require extensive site and soil characterization. Sufficient soil mass should be collected at different depths and sample locations in order to obtain a representative soil particle and metals distribution in a specific location.



Figure 64. Using a front-end loader for sample collection at depth.

Contaminant concentration. The third major point in the decision tree (Figure 63), is determining the concentration of the contaminant in the soil samples taken during the site survey. Unlike many heavy metal-contaminated sites (such as mines), the heavy metal contamination at SAFRs was initially deposited in the soil in a particulate, zero-valent form (as ammunition). As noted in Chapter 2 (section titled Soil and Associated Lead Particle Size Distribution), these particulates are closely associated with the largest size fraction of soil particles. Over time, weathering of the metallic particulates occurs, producing metal oxides, mobile metal ions, metal ions exchanged onto charged soil surfaces, and metal ions exchanged onto organic matter. All of these forms of weathered metals have varying solubilities. In addition to the metallic species, metal sulfides, phosphates or other heavy metal containing minerals may form. These compounds also have differing solubilities. The rate of oxidation of metallic particles varies with a number of environmental factors. These include:

- Moisture content of the soil.
- Salinity.
- Soil pH.
- Particle size distribution (metallic surface area).
- Soil buffering capacity.
- Precipitation pH.

Few systems show the type of rapid corrosion of bullet residues that would be required in order for lead particles to disappear from SAFR impact area soil over the lifetime of a range. For this reason, individual metal particles have a large effect on soil metal concentrations when measured using traditional sampling and analysis techniques.

From the historical data and site survey, a sampling and analysis plan (SAP) can be prepared for the range. SAPs for SAFRs are not significantly different from any other remedial investigation. The particulate nature of the contamination and its heterogeneity can make it challenging to ensure samples are representative of the site contamination. It is advised that soil samples are of large enough mass that the particulate distribution in the sample represents that in the entire soil volume. The large sample can then be ground and homogenized. Take replicate soil samples from this ground mass and use them for digestion and heavy metal analysis. This method will ensure a representative soil analysis without spending inordinate amounts of funding for replicate analysis. For example, grinding one

5-kg representative sample and performing triplicate analysis will give a comparable average metal concentration to collecting and analyzing 2,500 2-gm samples from the same area.

Soil analysis for the contaminant of concern has the potential to produce significant cost savings. A treatability study may be as simple as determining particle size distribution, distribution of lead in soil fractions, soil density, and percentage of organic material in the soil of interest. Three basic analytical procedures should be performed on each soil sample from each site:

- Separate each soil sample into its size fractions. There are several choices for this, including sieve analysis. Details are provided in Chapter 4, Physical Separation.
- Determine total metals concentration for each size fraction.
- Analyze each size fraction for its TCLP performance. The leaching test is outlined in Figure 65 and detailed in Chapter 2 (sections titled Soil and Associated Lead Particle Size Distribution and Metals Leachability) of this report. There are three possible outcomes, as illustrated in Figure 65 and detailed in Figure 66.
 - The metals concentration at a site, or in a specific area of a site, or in a size fraction of a site soil, may fall **below** the remedial action limits (set by State and Federal requirements) that require treatment. If this is the case, the soil can remain in place. Disposal as hazardous waste, or stabilization or other treatment will result in unnecessary cost increases.
 - The metals concentration at a site, or in a specific area of a site, or in a size fraction of a site soil, falls **above** the remedial action limits (set by State and Federal requirements) that require treatment, but the soil **passes** the TCLP (i.e., <5 mg/L of the regulated metal) analysis. These soils or size fractions of soils, can be placed into a non-regulated waste landfill, either on-site (less expensive) or off-site (more expensive).
 - The metals concentration at a particular site falls **above** the regulatory limits and **fails** the TCLP test (i.e., >5 mg/L of the regulated metal). In accordance with RCRA land disposal restrictions, soil that fails the lead toxicity characteristic procedure cannot be placed in a typical solid waste landfill or used for an-

other purpose. Soils characterized as hazardous waste must be treated, either in situ or ex situ, before being placed in a hazardous waste landfill and/or reused on-site.

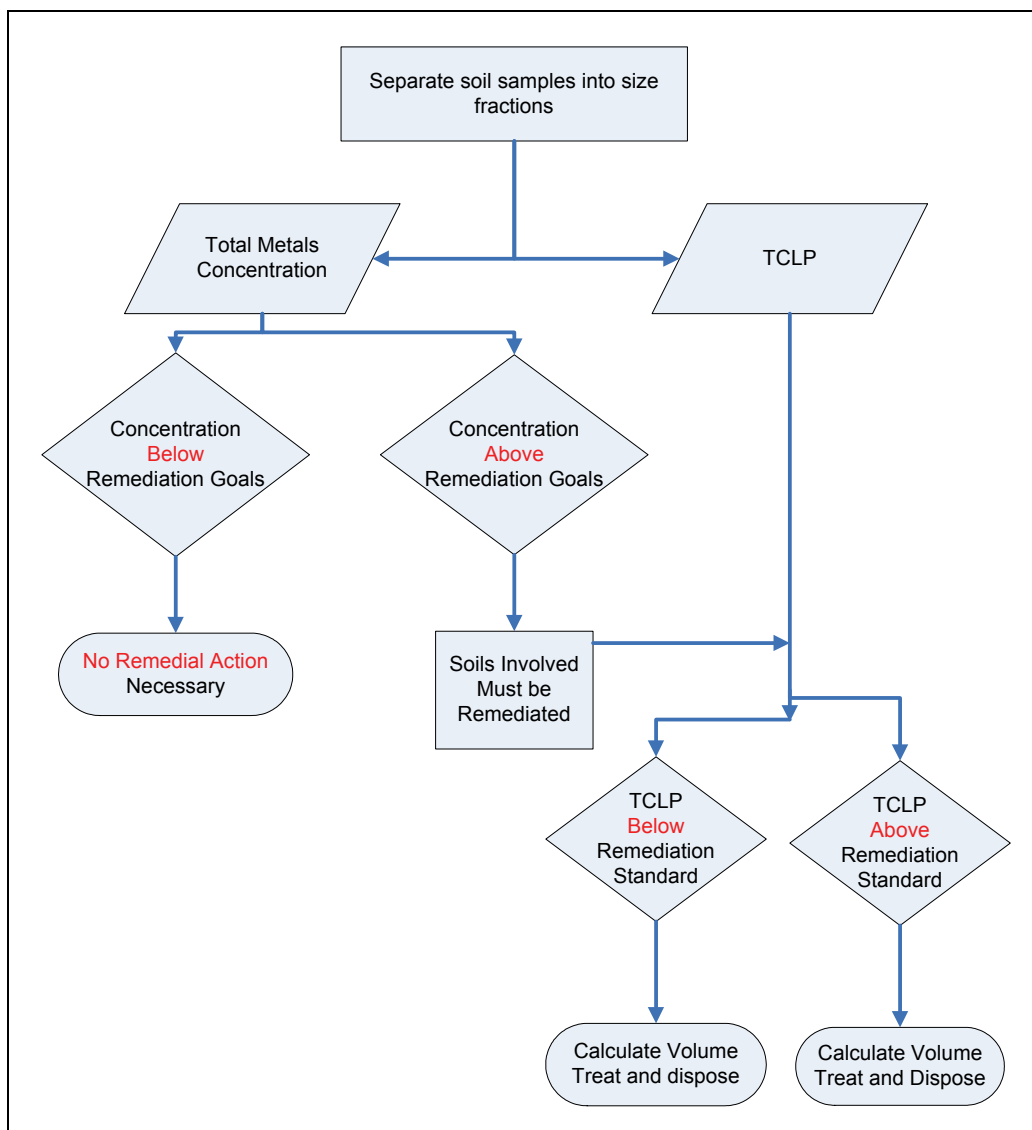


Figure 65. Possible remediation outcomes following soil analysis by size fractions.

The historical investigation and the site survey(s) should result in a good approximation of the volume of soil that will require handling and treatment. This volume requiring excavation can be used with the next three sections to develop a basis for comparison of remedial options for the site.

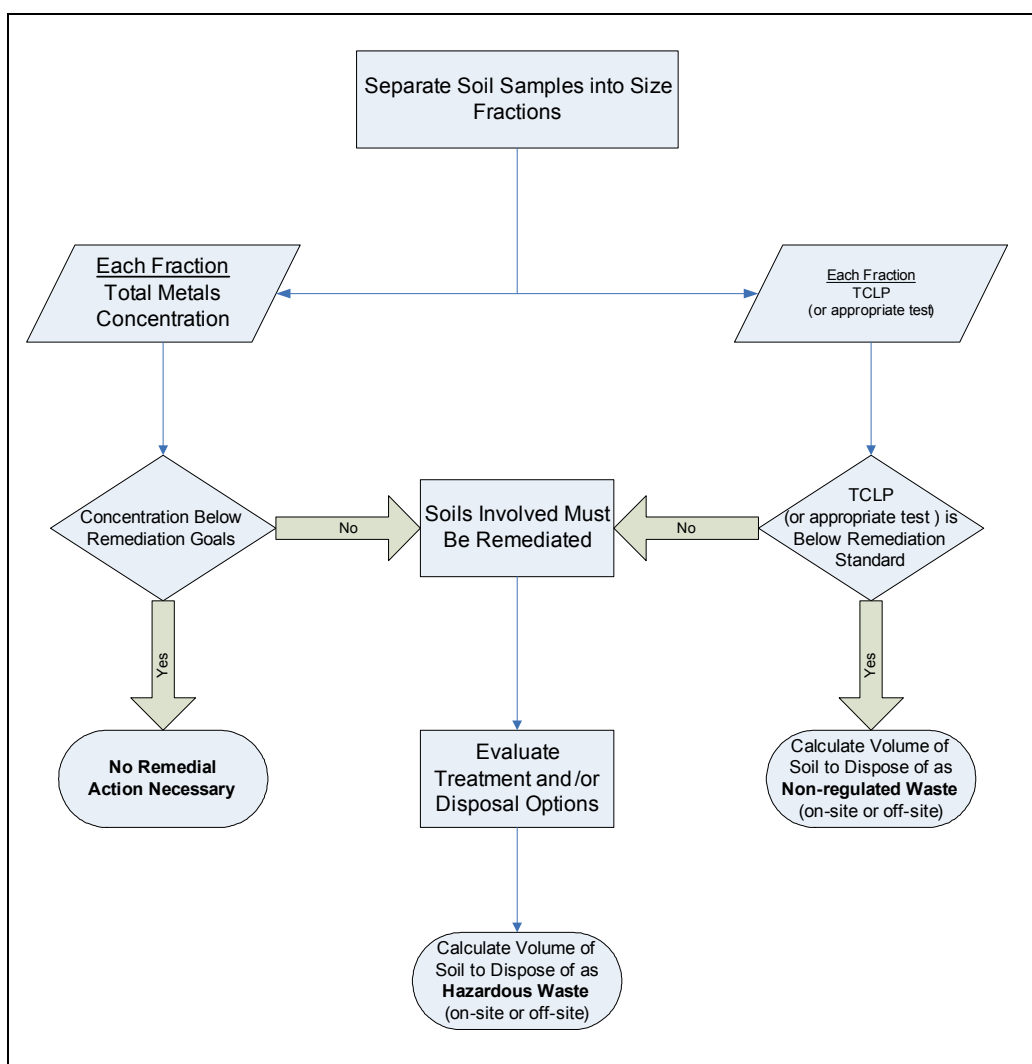


Figure 66. Possible outcomes from determination of metals concentration in size fractions of site soil samples.

Determine cost associated with excavation and disposal as hazardous waste

For nearly all SAFRs, soil volumes will be identified that will require one of these three options discussed above; no action, disposal, treatment/disposal. The first outcome from soil sample contaminant analysis (i.e., the metals concentration falls below the remedial action limits), requires no cost calculation as no action is required. The second and third outcomes require a cost calculation to compare treatment alternatives; stabilization and replacement of the soil on-site or stabilization and land-fill disposal. Costs associated with hazardous waste vary greatly across the country, and disposal as hazardous waste can exceed ordinary landfill costs by 10 to 100 times. In some cases, the costs are scaled to the amount

of contaminant present in the soil so it is important to know the metal concentration as well as the soil volume in order to obtain good price estimates. The baseline (conventional) approach to remediation of soils from closed SAFRs is excavation and off-site disposal at an approved facility. Because the impact berm soils routinely qualify as a characteristic hazardous waste, the requirements of RCRA apply for the excavation, transportation, and disposal of these soils. A comparison cost estimate for excavation and off-site disposal at a secure RCRA disposal facility was prepared by the NDCEE (Table 31) during a cost analysis of the physical separation process performed at Ft. Dix. The unit cost is approximately \$231 per ton.

Table 31. Impact berm soil estimated disposal costs.

Description	Cost per Ton	Total Cost
Disposal Charges: 3,500 tons New York State Hazardous Waste Fee	\$125.00 \$26.50	\$437,500 \$92,750
Freight Charges (roll-off containers, liners, surcharges)	\$79.94	\$279,773
Labor/Mobilization	Lump	\$13,062
Equipment	Lump	\$28,519
Total	\$231.44	\$851,604

It is important to include all applicable costs when determining the cost per ton associated with excavation and disposal as a hazardous waste. As can be seen in Table 31, the cost of transporting the excavated material represents a significant portion of the cost. SAFR sites located near hazardous waste landfills that can accept SAFR soil will have a significantly lower cost associated with excavation and disposal compared to SAFRs requiring long transportation distances. Note that the Labor/Mobilization and Equipment costs do not scale with the soil volume but can be evaluated as a lump cost. An economy of scale is present (i.e., the cost per ton decreases as the number of tons increases) when calculating transportation and disposal charges.

Evaluate physical separation approaches

The goal of size separation is to reduce the volume of soil that needs to be either treated or disposed off-site, both of which increase the remediation cost. The decision matrix illustrated in Figures 65 and 66 indicated that

there are treatment options available when a soil/size fraction of a soil has a contaminant concentration higher than the guidelines set in the remediation goals and also fails the TCLP analysis (i.e., the leachate contains a higher concentration of the contaminant than allowable by law, >5 mg/L). Physical separation approaches can be used as a first cleanup step. Physical separation will reduce the volume of soil to be treated and/or disposed of, thus reducing costs. If necessary, separation can be followed by chemical treatments to further clean or stabilize the soil. Figure 67 provides more detail of the relationship between sieve particle size separation and the treatment options commonly used in range remediation.

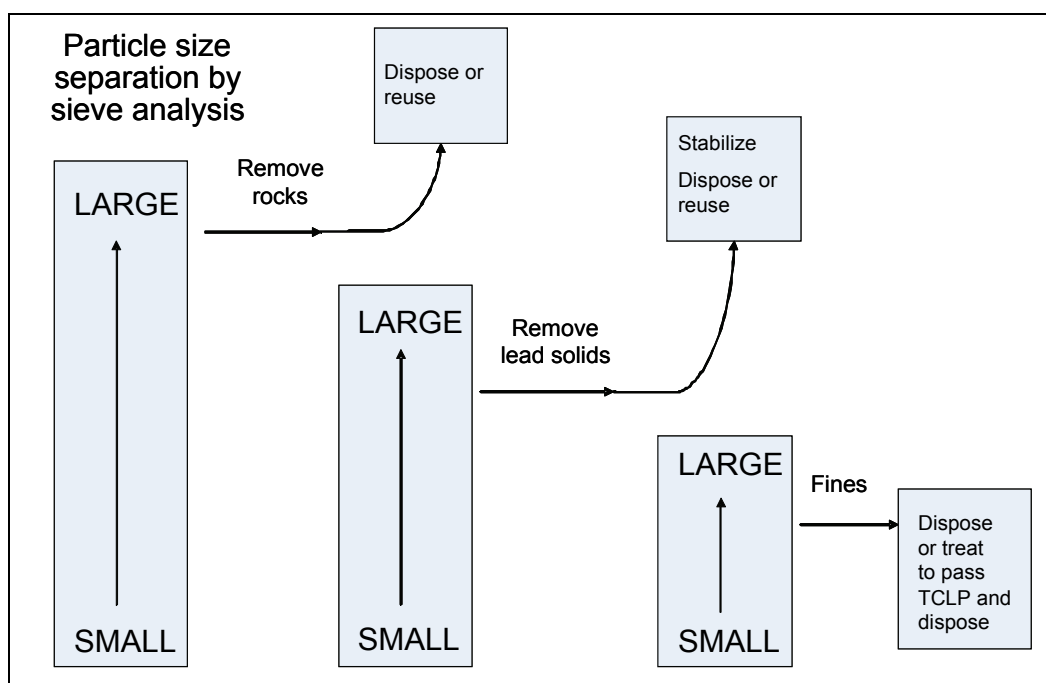


Figure 67. Particle size separation and physical separation/stabilization.

As illustrated in Figure 67, to accomplish this, the soil samples must first be graded into size fractions ranging from silt to rocks. The rocks can be returned to the site, reducing the total volume of material to be treated, and therefore, the total cost. Then, the larger size fractions are treated by physical separation methods, as discussed in Chapter 4 of this report. In general, physical separation processes use particle characteristics such as size, shape, density and/or magnetism for separating particles. On ranges specifically, two physical characteristics are identified as providing the basis for separating particles: particle size using sieving and density using gravity separation.

Size separation is a mechanical process based on particle size whereby material is applied to one or more chambers with progressively smaller apertures allowing material to be sorted based on whether it passes through or is retained at each step. The process can be wet or dry, stationary or gyrating. Some common equipment types are screens, sieves, and trommels. Particle shape, uniformity, agglomeration and blockage can affect the performance of these systems. Density separation is based on the difference in specific gravity between lead (11.5) and that of rock/soil/sand (approximately 2.5). This makes gravity separation techniques effective for range remediation. Size and gravity separation technology offers simple, inexpensive equipment with continuous and high throughput. The equipment is readily available and adaptable from the mining and milling industries. This makes this class of technologies very attractive for range cleanup.

Soil separation systems can be designed that employ a combination of sieving and gravity separation technologies. These systems are optimized for the properties of the particular soil matrix and metal particles to be processed. In general, a system that combines sieving and gravity separation technologies provides for recovery of particulate metals and classifies soil fractions by both size and density. As discussed in Chapter 4, removing the bullets alone will generally not meet clean soil requirements for all the size fractions. However, in most cases, substantial fractions can be deemed “clean” based on total lead or TCLP lead analysis. Therefore, physical separation can be an effective approach to minimize treatment or disposal volumes and, therefore, cost.

Soil washing is an ex situ process that includes both physical separation methods (such as sieving, density, or gravity separation) followed by a water-based process for scrubbing the soils, or soil components, to extract the contaminants. As summarized in Chapter 6, soil washing technologies have been developed and used widely in Europe for the last decade. Most of the soils in Europe were processed in fixed facilities due to the high land values, high landfill costs, small size of the countries (short haul distances) and ease of permitting. In the United States, due to the greater haul distances, mobile units have been developed that are set up on-site. SAFR sites that have soils with low levels of fines, carbonate, and humic content are candidates for soil washing. The most common reagents used in the leachant are aqueous mixtures of acids (hydrochloric, nitric or acetic acid) or organic chelating agents and surfactants. A wet stripping process such

as soil washing for the removal of heavy metals will produce substantial volumes of contaminated leaching/washing solution. The regeneration/reuse and final disposal of the leachant is an important cost consideration when evaluating the soils washing process. Also, the leachant must be accounted for under the regulatory process as a hazardous waste stream.

As illustration of the benefits of this process, the majority of lead in about one third of the soil from a SAFR at Ft. Lewis was retained on a 1-1/2-in. sieve; this portion contained only background lead levels and was capable of reuse on site. The soil that passed through a 1-1/2-in. sieve and was retained on a 7/16-in. sieve contained bullet fragments that were large enough to be separated with a magnet. This portion of the soil was also left on site after the physical separation of the bullets from the soil. The remaining soil that passed through the 7/16-in. sieve was chemically stabilized with an amendment and was reused in SAFR berm construction projects. Understanding the particle size characteristics of the berm soil and the type of rounds present can influence the scope of cleanup at a SAFR.

Whether it is cost-effective to employ separation or separation with secondary chemical removal for heavy metals depends largely on the size of the range and factors that affect landfilling costs (size of range, distance to landfill, etc). Physical separation requires certain field mobilization costs that are fixed, regardless of the range size. For small ranges, treatment per ton costs are likely to be higher than for larger projects. Similarly, more complex separations are likely to be more cost-effective for larger soil volumes. Many of the treatment technologies discussed in this document (chemical stabilization, soil washing) require intact and large bullet fragments to be removed in order to be effective. To accomplish this, multi-stage treatment trains are often needed, which further increase costs.

A physical separation system with secondary treatment consists of several components integrated into one continuous process. The components might include a wash plant, a gravity separation unit, a soil dewatering unit, a clarification and fines dewatering unit, a water storage and management unit, and a recovered metal management unit.

Evaluation of stabilization approaches

The technology options currently available under solidification/stabilization (S/S) are summarized in Table 32. They are discussed in detail in Chapter 5, Solidification and Stabilization. No single S/S treatment system is

suitable for the remediation of all SAFRs. Ranges are highly variable with respect to soil, climate, contaminant characteristics and quantities of soil requiring treatment. In addition, treatment goals vary between different political regions and with intended future land uses of the site. Selection of the best management solution requires complete understanding of the site characteristics and bench-scale trials of potential treatments.

Table 32. Summary of solidification/stabilization technologies.

Treatment		Qualifying characteristic	Reference (in this report)
Solidification	Pozzolanic addition	Not reliable for lead contamination	Chapter 5, p. 83
	Vitrification	Not cost-effective for SAFR remediation	Chapter 5, p. 84
	Asphalt emulsion - encapsulation	Interfering co-contaminants include oil and grease, chlorinated organics, inorganic salts	Chapter 5, p.84
Stabilization	Phosphate additions	Interfering co-contaminants include soil organic matter, organic acids and high clay content	Chapter 5, p. 89
	Apatite additions	Some heavy metals do not form apatite minerals.	Chapter 5, p. 91

All S/S approaches act on the surface of the metal and/or metal-soil complex. Because of this, loose lead particles/fragments cannot be adequately stabilized. Therefore, S/S will most likely need to be combined with physical separation to achieve effective treatment. On-site disposal, recycling, or reuse of the soils greatly increases the economic advantages of stabilization. With these caveats, it does appear that S/S treatment with excavated SAFR material is technically feasible and cost-effective at many closed SAFR sites. Also, it does appear that S/S is an acceptable approach for dealing with range soils in most states that follow Federal standards. We have yet to find an effective approach to meet the California standard.

Remediation technology selection process: long-term liability basis

Active SAFRs generally do not fall under Federal solid or hazardous waste regulations, such as RCRA or CERCLA. For example, according to the U.S. Environmental Protection Agency Region 2 manual (US EPA 2001),

“Lead is not considered a hazardous waste subject to RCRA at the time it is discharged from a firearm because it is used for its intended purpose. As such, shooting lead shot (or bullets) may not be regulated nor is a RCRA permit required to operate a shooting range.”

However, once a range is closed, the impact areas could fall under these regulations, particularly RCRA. Lead bullets and shot, if abandoned, may be a solid and/or hazardous waste and may present an actual or potential imminent and substantial endangerment. In a precedent-setting legal case, the United States Court of Appeals in 1993 reached its decision with respect to RCRA and SAFRs, stating that firing ranges and gun clubs are not subject to RCRA’s regulatory (as opposed to statutory) requirements. That is, active firing ranges are not viewed as facilities that manage hazardous wastes subject to RCRA regulations and, as such, do not require RCRA permits. However, the court concluded further that lead shot and bullets meet the statutory definition of solid waste because these materials were “discarded (i.e. abandoned)” and “left to accumulate long after they have served their intended purpose.” If the range is closed and lead munitions are discarded, these materials are considered a solid waste, or even a hazardous waste. However, if the discharged lead is recovered or reclaimed on a regular basis, the berm would not be a statutory solid waste (or hazardous waste). The recovered lead could be recycled. However, if disposed, the recovered material would be a solid waste and a potential hazardous waste.

Several major reports suggest that the best management practice for an operating range is periodic removal of the lead (USAEC 1998, USEPA 2001, ITRC 2005), and that the soil, if then placed back on the range, is exempt from RCRA. However, if the soil were transported off-site, then it would require testing to determine if it is RCRA hazardous waste. The metals recovered during the removal process, if recycled or reused, may be considered a scrap metal and excluded from RCRA. This is a critical factor when a SAFR under remediation is part of a larger complex of ranges. For SAFRs where no other active ranges are present, then the options of disposal and/or treatment with disposal, or reuse must be evaluated.

A major decision point in range remediation rests on the results of the TCLP test of soil samples. The USEPA developed the TCLP to support the Resource Conservation and Recovery Act (RCRA) Toxicity Characteristic (40 CFR 261.24). The aggressive solvent system of the TCLP test mimics the effects of accelerated aging of an MSW landfill. It was to be used as a tool to predict the mobility of a toxic compound in the landfill over time. The USEPA is reexamining the TCLP for a number of reasons, but primarily because of the relative inability of the method results to reflect the wide variety of conditions under which some wastes are stored (Kimmel et al. 2001). This is particularly evident when assessing heavy metal leaching and is partially due to problems with the pH and redox potential of the metal waste and particulates in the waste stream, among others (Al-Abed et al. 2006). Chapter 2 of this report (Metals Leachability-TCLP) discusses many of these problems as they affect SAFRs. Dermatas et al. (2006) examined the effect of firing range soil geochemistry on lead speciation and leaching. They found that soil pH and the concentration of available lead and carbonate were the most important parameters for predicting TCLP lead leachability.

Larson et al. (2004, 2005) reported difficulties when TCLP alone is used to evaluate the effectiveness of the stabilization of metals in SAFR soil. Losses of contaminants associated with particulates are not measured by the TCLP (also Chapter 5, Solidification and Stabilization, this report). In addition, the highly basic agents used in pozzolanic solidification processes introduce a significant future risk of large losses of soluble lead from solidified wastes. The majority of solidification schemes currently used for treating heavy metals, especially lead, involve mixing a lime-based agent, such as Portland cement, or cement or lime kiln dust into the soil. During the TCLP, the lime added to the waste neutralizes the TCLPs' acidic leaching solution and limits the leaching of the lead in the test resulting in "successful" waste solidification. However, when the waste contacts groundwater, precipitation, or surface water, this added lime will produce leachate having high pH (11-12). Under these conditions, due to the amphoteric nature of lead (and several other metals), lead levels may reach unacceptably high concentrations in the leachates and runoff. Therefore, lime-based treatments may enable wastes to pass the regulatory TCLP requirement, but can create severe environmental problems under actual future leaching conditions. McKinley et al. (2001) have also reported this possibility. They hypothesize that the increased release of heavy metals

from aged, stabilized (lime) sediment is due to degradation of the metal-organic matter complex.

While the USEPA has recognized the shortcomings of the TCLP (Kimmell et al. 2001), replacement of the test will be difficult considering the variety of situations in which it is used and the many remediation decisions that have been made based on TCLP leaching results. The range remediation manager should recognize that even when initial stabilization of SAFR soils results in a material that passes TCLP, there might be future liability if material disposed of as non-hazardous waste is later determined by TCLP to be hazardous due to non-permanent stabilization. However, despite the limitations imposed by the broad scope of the TCLP test, the procedure is the legal means of defining a solid material as non-hazardous for disposal purposes. Therefore, because individual range conditions differ, and some State laws may supersede RCRA, it is advisable in most cases to seek the advice of a regulatory specialist.

8 Conclusions

This document may be useful for parties evaluating restoration of DoD and non-military SAFRs such as law enforcement (military police, Federal law enforcement, etc.) training ranges, and recreational rifle, pistol, trap, skeet, and sporting clays ranges. This document is meant to assist with SAFR remediation strategies and the understanding of the science and application of those strategies. It incorporates case studies that have proven successful and, with use of the flow diagrams, is meant to assist range managers with remediation strategy development. Due to the variability of range characteristics found at SAFRs such as soil type, firing distance, range age, weapons used and climate, no single low-cost strategy is dictated for all ranges.

To this end, a flowchart approach with a number of decision points was presented through which alternative technologies can either be eliminated or considered as potential remediation approaches. The decision chart in its entirety is illustrated in Figure 68. The starting point for this decision process was the determination that a SAFR requires restoration and that remediation of a SAFR will be performed.

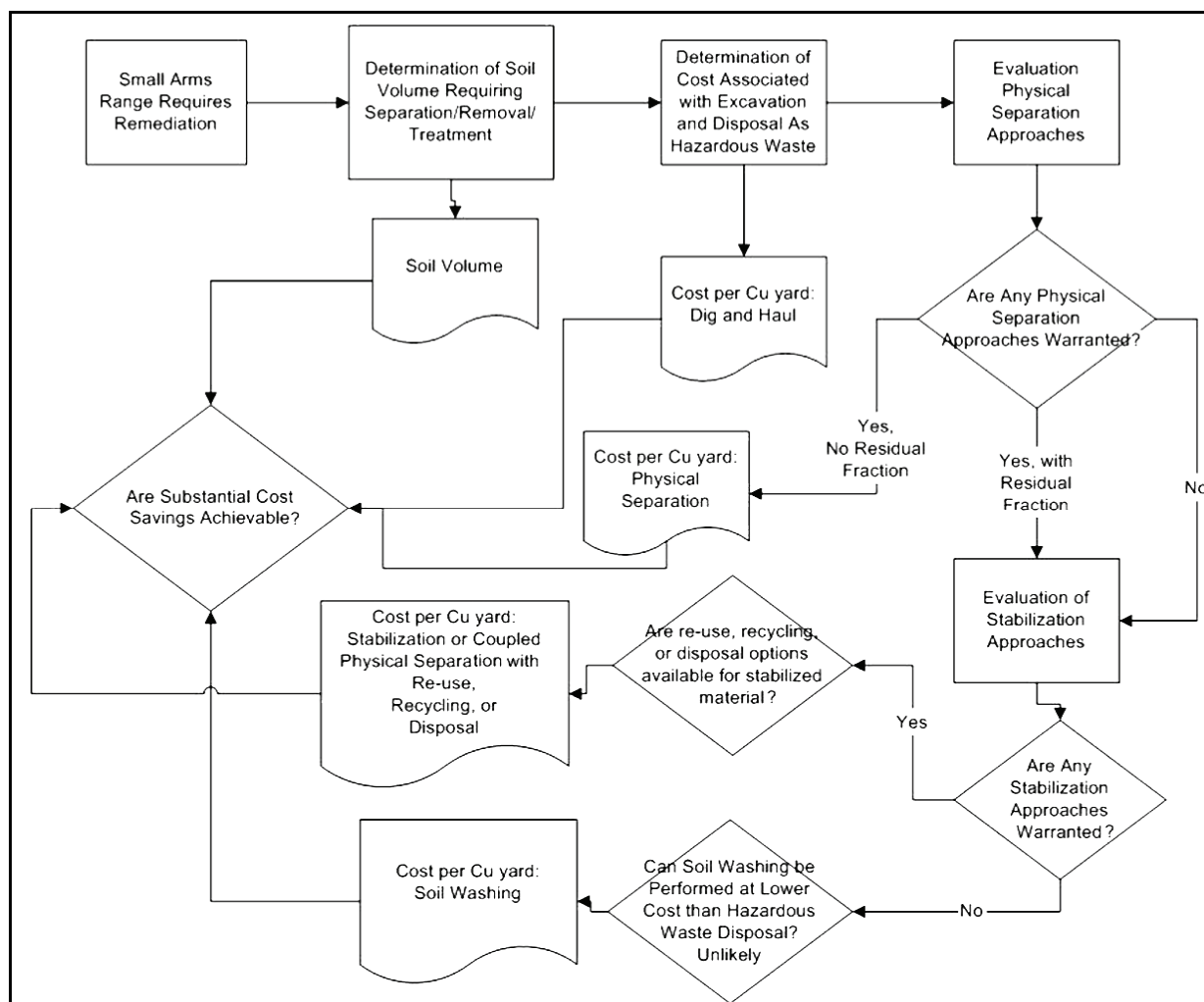


Figure 68. Flow chart with decision points through which alternative technologies can either be eliminated or considered as potential remediation approaches.

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14. ABSTRACT The objective of this document is to provide environmental professionals and project managers with the information required to understand the effect of range type and soil type on technology selection for one-time cleanup of closed Small Arms Firing Ranges (SAFRs). The one-time cleanup of closed SAFRs typically differs in purpose, environmental context, and applicable regulations from environmental operation and maintenance (O&M) of active SAFRs. This report summarizes and evaluates available technical information relevant to cleanup of lead and other metals when a SAFR is closed. SAFRs include military small arms training ranges, law enforcement (military police, Federal law enforcement, etc.) training ranges, and recreational rifle, pistol, trap, skeet, and sporting clay ranges. Each type of SAFR uses different types of ammunition with different physical distributions, chemical compositions, and environmental behaviors. In the context of this document, the definition of SAFRs does not include indoor ranges and is limited to outdoor ranges on which no explosives or rounds more powerful than .50-caliber armor-piercing ammunition are used. Although this document only considers cleanup of closed SAFRs, the technologies considered here might be useful under some circumstances in environmental O&M of active SAFRs.					
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