

Chelant extraction of heavy metals from contaminated soils

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Abstract

The current state of the art regarding the use of chelating agents to extract heavy metal contaminants has been addressed. Results are presented for treatability studies conducted as worst-case and representative soils from Aberdeen Proving Ground's J-Field for extraction of copper (Cu), lead (Pb), and zinc (Zn). The particle size distribution characteristics of the soils determined from hydrometer tests are approximately 60% sand, 30% silt, and 10% clay. Sequential extractions were performed on the 'as-received' soils (worst case and representative) to determine the speciation of the metal forms. The technique speciates the heavy metal distribution into an easily extractable (exchangeable) form, carbonates, reducible oxides, organically-bound, and residual forms. The results indicated that most of the metals are in forms that are amenable to soil washing (i.e. exchangeable + carbonate + reducible oxides). The metals Cu, Pb, Zn, and Cr have greater than 70% of their distribution in forms amenable to soil washing techniques, while Cd, Mn, and Fe are somewhat less amenable to soil washing using chelant extraction. However, the concentrations of Cd and Mn are low in the contaminated soil. From the batch chelant extraction studies, ethylenediaminetetraacetic acid (EDTA), citric acid, and nitrilotriacetic acid (NTA) were all effective in removing copper, lead, and zinc from the J-Field soils. Due to NTA being a Class II carcinogen, it is not recommended for use in remediating contaminated soils. EDTA and citric acid appear to offer the greatest potential as chelating agents to use in soil washing the Aberdeen Proving Ground soils. The other chelating agents studied (gluconate, oxalate, Citranox, ammonium acetate, and phosphoric acid, along with pH-adjusted water) were generally ineffective in mobilizing the heavy metals from the soils. The chelant solution removes the heavy metals (Cd, Cu, Pb, Zn, Fe, Cr, As, and Hg) simultaneously. Using a multiple-stage batch extraction, the soil was successfully treated passing both the Toxicity Characteristics Leaching Procedure (TCLP) and EPA Total Extractable Metal Limit. The final residual Pb concentration was about 300 mg/kg, with a corresponding TCLP of 1.5 mg/l. Removal of the

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exchangeable and carbonate fractions for Cu and Zn was achieved during the first extraction stage, whereas it required two extraction stages for the same fractions for Pb. Removal of Pb, Cu, and Zn present as exchangeable, carbonates, and reducible oxides occurred between the fourth- and fifth-stage extractions. The overall removal of copper, lead, and zinc from the multiple-stage washing were 98.9%, 98.9%, and 97.2%, respectively. The concentration and operating conditions for the soil washing extractions were not necessarily optimized. If the conditions had been optimized and using a more representative Pb concentration (~ 12000 mg/kg), it is likely that the TCLP and residual heavy metal soil concentrations could be achieved within two to three extractions. The results indicate that the J-Field contaminated soils can be successfully treated using a soil washing technique. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Chelant extraction; Soil washing; Soil flushing; Heavy metals; Copper; Lead; Zinc; EDTA

1. Introduction

There are currently many sites that contain soils contaminated with heavy metals and low levels of radionuclides. Heavy metal-contaminated soil is one of the most common problems constraining cleanup at hazardous waste sites across the country. The problem is present at more than 60% of the sites on the U.S. Environmental Protection Agency (U.S. EPA) National Priority List [86]. Leachate and run-off from soils contaminated with heavy metals potentially degrade groundwater and surface water; additionally, wind erosion tends to spread contamination over large areas [41]. Metal most often encountered include lead, chromium, copper, zinc, arsenic, and cadmium. The greatest need for new remediation technologies in the Superfund Program is in the area of heavy metal-contaminated soil [82–85]. The existing remediation technologies are considered expensive and often ineffective.

Many U.S. Department of Energy (DOE) sites are contaminated with radionuclides and heavy metals. Contamination exists in mixed wastes (any media containing hazardous and radioactive components), groundwater, surface soils, and subsurface soils. The volume of soil contaminated with radionuclides and/or heavy metals within the DOE complex is estimated to exceed 200 million m^3 [80]. Over the next five years, DOE will manage over 1 200 000 m^3 of mixed low-level wastes and mixed transuranic wastes at 50 sites within 22 states. DOE sites with radionuclide contamination problems include those found at Oak Ridge, Hanford, Savannah River, and Rocky Flats. The list of most prevalent heavy metals includes mercury, lead, hexavalent chromium, and arsenic. Radionuclides of concern include Pu, U, Am, Th, Tc, Sr, Cs, and tritium. The current baseline technology for remediation of soil contaminated with radionuclides and/or heavy metals is excavation, containerization, transportation, and final disposal at a permitted land disposal facility [80]. The major cost involved with this scenario is for the disposal facility. For example, at the Nevada Test Site, the cost of 'storage' is about US\$10/ ft^3 while storage at a Nuclear Regulatory Commission licensed facility exceeds US\$400/ ft^3 . Development of in situ treatment technologies or effective volume reduction technologies will provide DOE with a significant cost savings in 'storage' fees alone [80].

Typical heavy metals found at DOE facilities include lead, chromium, copper, cadmium, arsenic, and mercury. Sites within the DOE complex are contaminated with radionuclides, among which are uranium ($U^{235/238}$), thorium (Th), radium (Ra^{226}), cesium (Cs^{137}), technetium (Tc^{99}), plutonium ($Pu^{239/240}$), europium ($Eu^{152/154}$), americium (Am^{241}), etc. Existing technology for remediation of heavy soils is dig-and-haul and solidification/stabilization. Neither technology results in the removal and/or concentration of the heavy metals from the contaminated soils nor can either be practically implemented using in situ strategies. Also, both techniques are becoming increasingly costly due to limited landfill space and processing costs. With increasing facility closures and regulatory pressures on operating facilities to improve environmental conditions, innovative heavy metals/radionuclides remediation technologies are needed that can concentrate the metals and radionuclides, return the treated soils back into the environment, possibly recover the metals/radionuclides, and are more cost effective than the either of the two existing techniques.

Currently available technologies that are proven technologies for the remediation of these soils are solidification/stabilization and dig-and-haul. Neither offer attractive options to facilities requiring development of innovative technologies for remediation of these soils. Recent advances in the washing or flushing of heavy metals and radionuclides from contaminated soils using chemical chelators within aqueous solutions have shown much promise for soil flushing as an alternative technology. Unfortunately, the lack of understanding concerning the chemistry of soil metal speciation, interparticle extraction dynamics, extraction fluid transport mechanisms within the aquifer, and spent extractant recycling techniques have limited this promising technology to very small scale applications.

2. Description of the soil washing technology

There are two main types of remediation for metal-contaminated soils: (1) technologies that leave the metal in the soil, and (2) technologies that remove the heavy metal(s) from the soil [71]. Technologies such as solidification/stabilization and vitrification immobilize contaminants, thereby minimizing their migration. Techniques such as soil washing and in situ soil flushing transfer the contaminants to a liquid phase by desorption and solubilization [72]. Soil washing can be a physical and/or chemical process that results in the separation, segregation, and volume reduction of hazardous materials and/or the chemical transformation of contaminants to nonhazardous materials [77]. Generally, in situ technologies are more economical and are safer than ex situ technologies because excavation is not required. However, there are concerns that the mobilized contaminants will not be captured by the recovery well system, leading to an increased public health risk. Cation exchange and specific adsorption are two mechanisms that control metal adsorption [19]. Heavy metals can also be retained by other mechanisms other than sorption (e.g. solid-state diffusion and precipitation reactions) especially when lead exists as $PbCO_3$, $PbSO_4$, or as an organic lead form [19]. Factors affecting heavy metal retention by soils include: pH, soil type and horizon, cation

exchange capacity (CEC), natural organic matter, age of contamination, and the presence of other inorganic contaminants [72]. Metal mobility is also influenced by the organic fraction in the soil and clay and metal oxide content in the subsoils because these soil constituents have significant CECs. Heavy metal contaminants that concentrate in fines include chromium, lead and uranium, while strontium, barium, and cesium appear to be nearly uniformly distributed through the soil size fractions [28]. The initial metal concentration, the presence of inorganic compounds, and the age of contamination also influence metal mobility.

Soils are characterized by a distribution of particle sizes. If the soil is separated according to size, the finest soil fractions (silts and clays) often contain the highest concentrations of contaminants. The finest soil fractions have the highest surface area per unit volume, and thus are favored for adsorption-type phenomena. In addition, the fine soil fraction usually contains the natural organic component of soil, which could serve as a sink for organic contaminants.

Somewhat coarser soil particles (in the range of -10 mesh to $+200$ mesh) are often characterized by surface irregularities enhanced by weathering, inorganic salt precipitation, and oxide formation [88]. This uneven and somewhat porous surface can provide a favorable environment for surface contamination.

Very coarse particles (e.g. pebbles and stones) have a relatively low surface area to volume ratio per unit mass. As long as this material is not porous, contamination is surficial and the effective concentration per unit mass of material tends to be low [86].

Contaminated soils are often composed of coarse and fine grained mineral components and natural organic components. Many unit operations developed in the mineral processing industry can be used to implement soil washing processes. Examples of these unit operations include: trommels 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); and thickeners, filters, and centrifuges (used to dewater solids).

Soil washing involves the separation of contaminants from soil solids by solubilizing them in a washing solution [78]. The technology is generally an *ex situ* method. Soil washing usually employs wash solutions that contain acids, bases, chelating agents, alcohols, or other additives [28]. A chelant is a ligand that contains two or more electron-donor groups so that more than one bond is formed between the metal ion and the ligand [19]. Ethylenediaminetetraacetic acid (EDTA) forms 1:1 molar ratio complexes with several metal ions. Acids and chelating agents are generally used to remove heavy metals from soils, but the particular reagent needed can depend not only on the heavy metal involved but also on the specific metal compound or species involved. Pickering [70] identified four ways in which metals are mobilized in soils: (1) changes in the acidity; (2) changes in solution ionic strength; (3) changes in the REDOX potential; and (4) formation of complexes. In practice, acid washing and chelator soil washing are the two most prevalent removal methods [71]. The most common chelating agent studied in the literature is EDTA [72]. EDTA has been used to remove lead nitrate from artificially contaminated or surrogate wastes with efficiencies ranging typically from 40% to 80%. Because of the strong chelation nature of EDTA, a method for reuse (such

as electrodeposition) must be developed before such a process is economically viable [67,71]. There are also health and safety concerns in the scientific community regarding the use of EDTA [72].

Soil washing is used to treat soils contaminated with semivolatile organic compounds (SVOCs), fuel hydrocarbons, and inorganics (e.g. heavy metals). It is less effective for treating volatile organic compounds (VOCs) and pesticides [8]. Soil washing techniques have been used to treat soils contaminated with soluble metals, halogenated solvents, aromatics, fuel oils, PCBs, chlorinated phenols, and pesticides [82]. Insoluble contaminants such as insoluble heavy metals and pesticides may require acid or chelating agents for successful treatment. The process cannot efficiently treat very fine particles such as silt and clay, low permeability packed materials, or sediments with high humic content [82]. Different minerals and soils behave differently and can affect the binding forces between contaminant and particle [56,82]. A feed mixture of widely ranging contaminant concentrations in the waste feed make selection of suitable reagents necessary. Sequential washing steps may be needed to achieve high removal efficiencies. Residual solvents and surfactants can be difficult to remove after washing.

Contaminants sorbed onto soil particles are separated from soil in an aqueous-based system. The wash water may be augmented with a basic leaching agent, acids, surfactant, pH adjustments, or chelating agents to help remove organics and heavy metals. The concept of reducing sediment contamination through particle size separation rests on the tendency of most organic and inorganic contaminants to bind, either chemically or physically, to clay and silt particles. The clay and silt, in turn, attach to sand and gravel particles by physical processes (primarily compaction and adhesion) [82]. Washing processes that separate fine clay and silt particles from the coarser sand and gravel particles effectively concentrate the contaminants into a smaller volume that can be more efficiently treated or sent for disposal [82]. The larger fraction (now clean) can be returned to the site. These assumptions offer the basis for the volume-reduction concept at the root of most soil washing technologies. It offers potential for recovery of heavy metals and a wide range of organics and inorganics from coarse-grained soils; however, fine-soil particles such as silt and clays are difficult to remove from the washing fluid [8]. Soil washing is being used more frequently in the U.S. in recent years; in Europe, it has been a common technology for many years.

Many of the soil washing studies and field demonstrations conducted to date have been focused on removing volatiles and semivolatile organic materials from contaminated soils. Soil washing has documented 90–99% removal of volatiles and 40–90% removal of semivolatiles [85]. A number of soil washing techniques have been developed and field tested, including the Biotrol (Biological Aqueous Treatment System) [83], the B.E.S.T. solvent extraction technology [83], and the Harmon Environmental Services soil washing technique [87]. Results from soil washing tests involving heavy metal-contaminated soils are summarized in Table 1.

Soil washing can be used as a stand-alone technology or in combination with other treatment technologies. In some cases, the process can deliver the performance needed to reduce contaminant concentrations to an acceptable level. In other cases, soil washing is most successful when combined with other technologies. It is a very cost-effective pretreatment step in reducing the quantity of material to be processed by another

Table 1
Results from soil washing tests involving heavy metal contaminated soils

Contaminant	Total concentration in feed soil (mg/kg)	Total concentration in treated soil (mg/kg)	Total concentration— soluble (mg/l)	Analytical method	Total cleanup objective (mg/kg)	Total cleanup objective—soluble (mg/l)
Lead	4900	250	1.3	TCLP	NS	5
Chromium	1000	NA	NA	TCLP	NS	5
Cadmium	1200	15	< 1.0	STLC	40	1
Lead	130000	80	< 5.0	TCLP	200	5
Lead	5000	32	< 5.0	TCLP	200	5
Copper	7300	180	NA	NS	300	NS
Lead	2900	112	NA	NS	200	NS
Copper	2200	28	NA	NS	250	NS
Mercury	1200	8	0.16	TCLP	20	0.2
Lead	1130	72	0.06	STLC	1000	5
Nickel	1520	88	0.12	STLC	NS	20
Zinc	5100	NA	3.6	STLC	NS	250

technology (such as incineration). It can also transform soil feedstock into a more homogeneous material for subsequent treatment [82].

Soil washing processes generate three waste streams: contaminated solids from the soil washing unit, wastewater, and wastewater treatment residuals. Contaminated clay fines and sludges from the process may receive further treatment by incineration, solidification/stabilization, or thermal desorption. Wastewater may require treatment prior to disposal. As much water as possible should be recovered for reuse in the washing process [82].

Factors affecting soil washing processes include [82]:

- clay content (which makes it difficult to remove contaminants);
- complex waste mixtures (which affects formulations of suitable wash fluids);
- high humic contents (which inhibits contaminant removal);
- metals concentration (the technology does not remove insoluble metals, although some metals can be solubilized);
- mineralogy (which can affect process behavior and contaminant binding);
- particle size distribution/soil texture (which affects removal from the wash fluid—oversize debris requires removal);
- separation coefficient (if the contaminant is tightly bound, excessive leaching is required); and
- wash solution (the solution may be difficult to recover or dispose).

Soil washing is a physical/chemical treatment process in which excavated soil is first treated by physical separation and is then washed with chemical extractants to remove contaminants [89]. Soil washing involves the separation of contaminants from soil fines by solubilizing or suspending the contaminants in a washing solution. Physical separation may include screening followed by density or gravity separation. Mechanical screens and hydrocyclones are often used to separate the soil into various size fractions. The bulk oversize material consists of clean or slightly contaminated cobbles and stones, and may undergo a water rinse before being returned to the site as fill. The silt and clay fraction generally contains the highest concentration of contaminants and is usually treated by solidification/stabilization techniques to immobilize the contaminants prior to landfilling. The remaining fine and coarse sands can be further treated using density/gravity separation processes to isolate high-density aggregates and metal fragments. Extractive soil washing is then performed by mixing these pretreated soils with an extractant solution. The average cost for soil washing typically ranges from US\$120 to US\$200/ton of soil treated, compared to less than US\$100/ton for solidification/stabilization (S/S) techniques [82–85]. However, additional costs for S/S techniques may include transportation and landfill disposal, which may make soil washing a cost competitive process [6]. Additionally, soil washing removes contaminants resulting in a permanent solution to the contamination problem, allows recycling of clean soil, and provides improved future land-use options [89].

The soil washing technology is generally performed as an *ex situ* method, employing acids, bases, chelating agents, surfactants, alcohols, solvents, water, and reducing agents, or other additives as the extracting agent. After chemical treatment, the washed soil is usually rinsed with water to remove residual contaminants and the residual extracting agents from the soil, and the resulting ‘cleaned’ soil is returned to the site. Acid

extraction relies on ion exchange and soil matrix dissolution to solubilize heavy metals. Although acids effectively increase the solubility of metals, strong acids may destroy the basic nature of the soil, thus leaving it unsuitable for revegetation [13]. The mobility of heavy metals in soils is controlled by various physical and chemical phenomena. The finer-sized soil fractions (e.g. clays, silts, metal oxides, organic matter) can bind metals by cation exchange and specific adsorption [18,69]. For cases in which the heavy metal contamination is very high (i.e. thousands of mg/kg), the metal sorption capacity of most soils is exceeded, and the contamination would additionally be present as discrete metal–mineral phases [20]. Such metal ions can be immobilized in soil by the formation of insoluble precipitates, incorporation into the crystalline structure of clays and metal oxides, and/or by physical entrapment in the immobile water surrounding soil micro- and macropores [69]. Metal removal efficiencies during soil washing depend on the soil characteristics (e.g. particle size), metal characteristics (e.g. crystalline, exchangeable, water solubility), extractant chemistry, and processing conditions. pH plays a significant role in the extractability of heavy metals from soils [7]. Well defined clay minerals, free oxides of iron and alumina, and clay fractions separated from soils, all show highly pH-dependent sorption, due to adsorption of hydrolyzed species, such as CuOH^+ , etc. Heavy metals that less soluble in water often require chelating agents or other extractants for successful soil washing. The ability to form stable metal complexes makes chelating agents such as EDTA and NTA effective extractants for heavy metal-contaminated soils [20,23,24,69]. Anionic surfactants have also shown some promise for chromium and lead removal from soils due to their ability to form colloidal micelles that solubilize metals [30]. Several studies have recently addressed the treatment of metal-spiked soils (e.g. metals are added as soluble metal salts) [18,20,25]. Removal efficiencies likely are greater than that observed with washing contaminated soils that have been weathered for long periods of time in situ [69].

In the following sections, previous studies involving chelant extraction and acid extraction for removal of heavy metals from contaminated soils are described, along with a summary of various case histories involving soil washing. Table 2 lists hazardous waste sites where soil washing has been selected in the Records of Decision (RODs) to clean up those sites. Table 2 also provides the site descriptions, the media, and key contaminants involved in order to provide an indication of the situations where soil washing is appropriate.

The mobile soil-washing system (MSWS) was developed in the early 1980s. Scholz and Milanowski [76] describe this system in detail. The drum washer and trommel are a combined unit in which soil is contacted with wash water (which may have chemical additives), and an initial particle-size separation is performed. The drum section contains water knives to promote breakup of soil lumps, and it provides time for the soil to soak in the wash water. The trommel separates particles larger than 2 mm from the rest of the mixture. Ideally, this +2 mm gravel/sand fraction is clean. The –2 mm mixture is fed to a four-stage, counter-current extractor. The soil becomes progressively cleaner as it moves through the extractors, and it contacts progressively cleaner water in each tank. This system relies primarily on chemical extraction to clean the soil of contaminants.

The volume reduction unit (VRU) was developed in the late 1980s, and has been described in detail by Masters et al. [47]. This system is a versatile design for

Table 2
Soil washing applications at selected hazardous waste sites

Site name, state	Site description	Media (quantity)	Key contaminants treated
Ewan Property, NJ	Industrial waste dumping	Soil (22 000 cy)	VOCs (BTX), SVOCs (Naphthalene and 2,4-dimethyl-phenol) and Metals (Chromium and Lead)
King of Prussia, NJ	Recycling facility	Soil, sludges, sediments (20 150 cy combined)	Metals (Chromium, Copper, and Silver)
Myers Property, NJ	Pesticide manufacturing	Soil, sediments (50 000 cy combined)	Metals (Aluminum, Cadmium, Chromium, Silver, and Sodium)
Vineland Chemical, NJ	Pesticide manufacturing	Sediments (62 600 cy combined)	Arsenic
Cape Fear Wood Preserving, NC	Wood preserving	Soil (20 000 cy)	Creosote, PAHs, Copper, Chromium, Arsenic, and Benzene
American Creosote Works, FL	Wood preserving	Soil (21 000 cy)	Creosote, PAHs, SVOCs (PCP), and dioxins
Coleman-Evans Wood Preserving, FL	Wood preserving	Soil (27 000 cy)	PCP, dioxin
Southeastern Wood Preserving, MS	Wood preserving	Solids (8000 cy)	SVOCs (PCP), PAHs, and creosote
Moss American, WI	Wood preserving	Soil (80 000 cy)	PAHs
United Scrap Lead/SIA, OH	Lead battery recycling	Soil (45 000 cy), sediments, (45 550 cy)	Lead and arsenic
Arkwood, AR	Wood preserving	Soil (20 400 cy)	PCP, PNA, and dioxins
Koppers/Texarkana, TX	Wood preserving	Soil (19 400 cy)	PAHs and SVOCs (PCP)
South Cavalcade Street, TX	Wood preserving and coal tar distillation	Soil (19 500 cy)	PAHs
Sand Creek Industrial, CO	Refinery, pesticide manufacturing, and landfill	Soil (14 000 cy)	Chlordane, dieldrin, 4,4-DDT, 2-4 D, heptachlor, and metals (arsenic and chromium)
Koppers (Oroville Plant), CA	Wood preserving	Soil, sediments (200 000 cy combined)	PAHs, SVOCs (PCP), and dioxin

performing experiments to learn more about soil washing. The heated screw is a jacketed screw feeder capable of warming soil to approximately 200°F for low temperature desorption tests. The miniwasher is a small trough-bottom hopper fitted with a ribbon blender. Soil is blended with a small quantity of water and concentrated surfactant, caustic, or other washing additive(s). High attrition is achieved in this mixture. A small feed screw on the axle of the ribbon blender pushes the washed mixture from the miniwasher into an adjacent trommel. Soil in the trommel is sprayed with additional wash water, and a particle-size cut is made at 2 mm. Coarse soil overflow from the trommel is usually collected in a drum. Ideally, this fraction is clean. Underflow from the trommel falls to a series of two vibrating screens that have replaceable inserts. Typically, a particle-size cut is made at 40 or 60 mesh (420–250 μm) in the first screen and 100 to 200 mesh (149 to 74 μm) in the second screen. The overflows from these two screens are also collected in drums. Ideally, they are both clean. Some of the remaining suspended fines are removed in a conventional lamella-type parallel-plate separator, which is capable of removing any floatables that make it to this point. More thorough removal of fines is achieved by addition of flocculation agents such as alum and a polyelectrolyte. The dosed wash water is passed through two static mixers and a small tank that allows time for the flocculation reactions to begin. The growing floc is then allowed to settle out in the larger floc/clarifier tank.

The GHEA Associates process applies surfactants and additives to soil washing and wastewater treatment to make organic and metal contaminants soluble [81]. The process components include a 25-gal extractor, solid/liquid separation, rinse, mixer/settler, and ultrafiltration systems. The technology is claimed that it can be applied to soils, sludges, sediments, slurries, groundwater, surface water, end-of-the-pipe effluents, and in situ soil flushing. The process yields clean soil, clean water, and a highly concentrated fraction of contaminants. The process is claimed to be able to meet all National Pollutant Discharge Elimination System groundwater discharge criteria allowing it to be discharged without further treatment or reused in the process itself or reused as a source of high purity water for other users. Process costs for the treatment range from US\$50 to US\$80/ton. Contaminants that can be treated include both organics and heavy metals, nonvolatile and volatile compounds, and highly toxic refractory compounds. Pilot testing reduced chromium in a contaminated soil from 21 000 ppm to 640 ppm, corresponding to a 96.8% removal. In another test, iron(III) was reduced from 30.8 mg/l to 0.3 mg/l in a water, corresponding to a 99.0% removal.

3. Background on chelant extraction

One of the primary focuses of this effort is to select appropriate chelators that are compatible with microbubble formulations, yet have appreciable removal capabilities for adsorbed metal species. Chelators have been used for removal of heavy metal species from soil matrices using hydraulically-based introduction techniques. It is postulated that the scouring effects of extraction foams on the soil matrix plus the increased area of impact associated with the swept-fronts afforded by foams in porous media will greatly

eliminate some of the shortcomings observed with the aqueous-based (hydraulic) technology proposed for application by many groups for chelator introduction. A brief background on removal mechanisms are presented below.

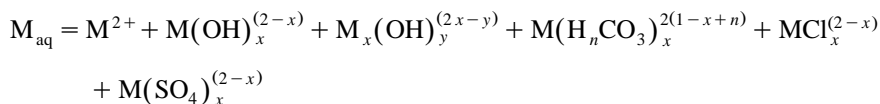
3.1. Chelant extraction technology description / background

Contaminants sorbed to soil particles are separated from soil in an aqueous-based soil washing system. The wash water may be augmented with a basic leaching agent, acids, surfactants, pH adjustments, or chelating agents to help remove organics and heavy metals. Factors affecting soil washing/soil flushing processes include clay content, complex waste mixtures, high humic content, metals concentrations, mineralogy, particle size distribution/soil texture, separation coefficient, and wash solution. DOE has investigated a number of chelator approaches for removing radionuclides from soil, including microbial iron chelators, Tiron, carbonate/bicarbonate, citrate, and citrate/dithionite. These techniques have focused primarily on removing uranium from contaminated soils (DOE, Landfill Stabilization Focus Area, 1995).

Given that metals are not like organics and can not be destroyed or degraded away, the metals and radionuclides can merely be transformed or transferred. This particular proposal addresses the removal of radionuclides and heavy metals from soils using chelant extraction and REDOX manipulation techniques. Previous studies involving chelant and acid extraction for removal of heavy metals from soils are described below.

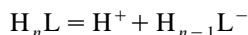
3.1.1. Chemistry of metals extraction using chelating agents

3.1.1.1. *Metal speciation in natural waters.* In the presence of ambient ligands such as HCO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} , an aqueous divalent contaminant metal ($\text{M}_{\text{aq}}^{\text{II}}$) can speciate in various free and complex forms:



In contaminated soils, the total amount of metals in the aqueous and solid phases is at levels much higher than those found in the solution phase. The solubilities of metals are typically too small to effect satisfactory results by washing with water alone. The solubilities of contaminant metals are controlled by predominant mineral phases depending upon the pH and/or ambient ligands available. Commonly observed metal mineral phases include those of oxide, hydroxide, carbonate, and hydroxy-carbonate, such as $\text{MO}(\text{s})$, $\text{M}(\text{OH})_2(\text{s})$, $\text{MCO}_3(\text{s})$, and $\text{M}_x(\text{OH})_y(\text{CO}_3)_z$.

3.1.1.2. *Acid–base equilibrium of chelating agents.* Effective chelating agents typically have multiple coordination sites (i.e. ligand atoms) available for complexation with a metal center. They are often multi-protic acids (H_nL) capable of undergoing acid–base equilibrium reactions in the aqueous phase, e.g.:



and subsequently,

$$H_{n-m}L^{m-} = H^+ + H_{n-(m+1)}L^{-(m+1)}.$$

3.1.1.3. Metals complexation with chelating agents. Each conjugate acid/base of the chelating agent may form a strong complex with the metal, resulting in the formation of various complexes $M_x(H_{n-m}L)_y^{2x-my}$:

$$xM^{2+} + yH_{n-m}L^{m-} = M_x(H_{n-m}L)_y^{2x-my}$$

with the total complexes concentration (ML_{Tot}) given by ML_{Tot} :

$$ML_{Tot} = \sum M_x(H_{n-m}L)_y^{2x-my}.$$

Thus, the total metal solubility, M_{Tot} , is computed by:

$$M_{Tot} = M_{aq} + ML_{Tot}.$$

3.1.1.4. Interaction of soil with metals and complexes. When the amounts of heavy metals of interest (e.g. Pb, Cd, Cu, Zn, Ni) exceed the solubilities of their corresponding hydroxides, carbonates, and/or hydroxy-carbonate mineral phases at a given pH value, the metals will be precipitated as solids. Hence these solid minerals will be entrapped in the soil or sediment matrix. In addition, soils contain mineral and humic constituents which carry hydroxyl and carboxylic groups. The acid–base characteristics of these functional groups contribute to the formation, at the soil surface, of electrically charged groups important for the retention of metal ions and complexes. Thus, solution pH can influence the acid–base equilibrium reactions of the surface groups; this in turn can influence the soil's retention of metals by adsorption and complexation with metal ions and complexes to different degrees depending on the pH_{zpc} (pH of the zero point of charge) of the soil. Hence, in addition to physical entrapment of metal hydroxide or carbonate solids, the soil can accommodate metals through more direct interactions, including surface complexation and surface precipitation mechanisms.

The complexation power of chelating agents toward heavy metals will be evaluated on the basis of the equilibrium computation procedures formulated above. The strong chelators will demonstrate a total solubility M_{Tot} (with chelators) that is much higher than the M_{aq} (without chelators). In addition, chelating agents will be evaluated for their interaction with and partition potential to soil surfaces according to clay content, metal and waste characteristics, humic contents, mineralogy, particle size distribution, soil texture, and pH_{zpc} .

3.1.1.5. Chelating agents' selectivity toward target heavy metals. For target heavy metals extraction application, the chelating agents should satisfy the following criteria.

(a) The chelating agents (with and without the chelated metal) will be compatible with the foam and will display no adverse effects on the stability of the foam.

(b) The ligands possess high metal complexing abilities toward heavy and transition metals as opposed to hard sphere cations such as Ca or Mg. The relative magnitudes of

the equilibrium complexation constants toward heavy metals and toward alkali metals are an indicator.

(c) The ligands containing sulfur and nitrogen as donor atoms are generally preferred for higher selectivity toward metals of interest, which are transition metals (e.g. Cu^{II} , Ni^{II}) and B-type (soft sphere) cations (e.g. Zn^{II} , Cd^{II} , Pb^{II} , Hg^{II}). Ligands containing sulfur or nitrogen as donor atoms generally form more stable complexes with soft sphere metals, whereas ligands containing oxygen as the donor atom prefer hard sphere cations.

(d) Multidentate ligands are preferable because they contain multiple coordinating sites capable of forming more stable complexes with metals.

The selectivity of chelating agents toward heavy metals can be quantitatively computed on the basis of a 'selectivity ratio (SR)' which is defined as $\text{ML}_{\text{Tot}}/\text{FeL}_{\text{Tot}}$ or $\text{ML}_{\text{Tot}}/\text{CaL}_{\text{Tot}}$, i.e. the ratio of the solubility of heavy metal (e.g. Pb, Cd) to that of ambient cations (e.g. Fe, Ca, Al) for a given set of metal and chelator concentrations in the system. A high selectivity ratio (SR) for the heavy metals indicates a strong preference of the heavy metals by the chelator. The selectivity ratios will be computed for DOE contaminant metals and for a large number of chelating agents (several hundreds) before a list of choice chelators will be decided.

3.2. Previous literature studies involving chelant extraction of heavy metals from contaminated soils

For more than 20 years, environmental reclamation research involving heavy metal chelation has centered on the following areas [35]: (1) the detrimental effects of chelants on the release of heavy metals from soil, sediment, and solid waste into the adjacent water phase; (2) chelants as scavenging agents for removal of heavy metals from sludge at wastewater treatment plants; and (3) use of chelants for in situ flushing of heavy metal-contaminated soils and sediments. Additionally, chelating agents may also be useful in electrokinetic extraction of metal contaminants from soils, where the application of an in situ direct current produces an electroosmotic water flow and an acid front which moves through the soil from the anode to the cathode and dissolves adsorbed metals. The use of chelants can help buffer the system to prevent heavy metal precipitation in the high pH zone near the cathode [35].

Hong and Pintauro [35] investigated the desorption/complexation/dissolution behavior of cadmium from kaolin (as a representative soil component) using four different chelating agents: NTA, EDTA, ethylene glycol-(*-*aminoethyl ether)-*N,N,N',N'*-tetraacetic acid (EGTA), and 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (DcyTA), in which the pH-dependence of cadmium adsorption/desorption was studied. The ability of the four chelants to dissolve cadmium from kaolin over the pH range of 2.5 to 12.0 differed significantly. For NTA, incomplete Cd desorption/dissolution was observed for solution pH in the range of 4.0–7.5 and 9.0–12.0. Only 45% of the original kaolin-bound Cd was detected in solution at pH ~ 6, while at pH 12.0, only 44% of the absorbed Cd was detected. For EDTA, 15% of the Cd remained on the kaolin at pH in the range of 5 to 6, but all of the Cd dissolved when the pH of the kaolin suspension was greater than 8. Complete dissolution was found over the entire pH range for the chelant DcyTA. For the EGTA/cadmium/kaolin system, Cd dissolution was complete except near pH ~ 4

(where $\sim 2\%$ of the Cd remained undissolved). Hong and Pintauro [35] noted that when either EGTA or DcyTA was present in solution, there was no observable change on the pH of zero point of charge (pH_{zpc}), indicating no readsorption of negatively charged Cd–chelator complex. However, for the case of EDTA and NTA, there was an acidic displacement in pH_{zpc} (as compared to the clay system without chelant or cadmium being present), indicating that a positive to negative surface charge shift occurs in the pH range of 2.4–4.4 and 3.6–4.4 for NTA or EDTA being present in solution, respectively. In the pH range of 2.4–4.4 for NTA, readsorption of a CdNTA^- complex causes a sign reversal (positive to negative) in the surface charge of kaolin. A similar effect was observed for the Cd–EDTA–kaolin system for solution pH in the range of 3.6 to 4.4. As compared to the EDTA and NTA systems, DcyTA and EGTA complexed strongly with Cd ($\sim 100\%$ dissolution) over a wide pH range (2.5–12.0). The capacity of the four chelators for removing Cd from kaolin was found to be in the order $\text{DcyTA} > \text{EGTA} > \text{EDTA} > \text{NTA}$.

Hong and Pintauro [36] further studied the competitive desorption/dissolution of kaolin-adsorbed heavy metal mixtures and mixtures of adsorbed Cd with magnesium and/or calcium using the same four chelants: NTA, EDTA, EGTA, and DcyTA. EGTA was the best chelant for removing cadmium from kaolin when calcium was present on the clay particles and when Ca^{2+} was present in solution. When $50 \mu\text{M}$ each of Cd^{2+} , Pb^{2+} , and Cu^{2+} were adsorbed on the kaolin clay, for a chelant concentration of $150 \mu\text{M}$ (the concentration required to ligand-bind all the adsorbed metals assuming one metal ion combined with one chelant molecule), none of the chelating agents removed all of the adsorbed metals and the order (selectivity) of metal removal differed for each chelant type. For the multimetal/kaolin/NTA system (with NTA $150 \mu\text{M}$), Cu was preferentially dissolved over Cd and Pb. EDTA and DcyTA showed the same sequence for metal removal with Cd removed first when the chelant concentration was less than $150 \mu\text{M}$, followed by lead and then copper. For EGTA, the dissolved/chelated Pb concentration in solution increased dramatically after nearly of the Cd and Cu had been removed from the kaolin. DcyTA and EDTA removed Cd first, although they exhibited a stronger chelating affinity for Pb as compared to Cu. Among the four chelants, NTA had the poorest removal selectivity between Cd and the alkaline-earth metals (e.g. Ca and Mg). When the chelant concentration in solution was insufficient to combine all the metals adsorbed on the kaolin, the metal removal was in the order listed below [36]:

Chelating Agent	Metal Selectivity
EGTA	$\text{Cd} > \text{Cd} > \text{Pb}$
EDTA	$\text{Cd} > \text{Pb} > \text{Cu}$
DCyTA	$\text{Cd} > \text{Pb} > \text{Cu}$
NTA	$\text{Cu} > \text{Cd} > \text{Pb}$

Ellis et al. [24] demonstrated the sequential treatment of soil contaminated with cadmium, chromium, copper, lead, and nickel, using EDTA, hydroxylamine hydrochloride, and citrate buffer. The EDTA chelated and solubilized all of the metals to some degree; the hydroxylamine hydrochloride reduced the soil iron oxide–manganese oxide matrix, releasing bound metals, and also reduced insoluble chromates to chromium(II) and chromium(III) forms; and the citrate removed the reduced insoluble chromium and additional acid-labile metals. Using single shaker extractions, using a 0.1 M solution of

EDTA was much more effective in metal removal than using a 0.01 M solution. A pH of 6.0 was chosen as optimum because it afforded slightly better chromium removal than that obtained at pH 7 or 8. EDTA was the best single extracting agent for all metals; however, hydroxylamine hydrochloride was more effective for removal of chromium. Results of the two-agent sequential extractions indicated that EDTA was much more effective in removing metals than the weaker agents. The results of the three-agent sequential extraction showed that, compared to bulk untreated soil, this extraction removed nearly 100% of the lead and cadmium, 73% of the copper, 52% of the chromium, and 23% of the nickel. Overall, this technique was shown to be better than three separate EDTA washes, better than switching the order of EDTA and hydroxylamine hydrochloride treatment, and much better than simple water washes. The EDTA washing alone can be effectively used, however, resulting in only a slight decrease in overall removal efficiency. Lead was easily removed by the EDTA and was also effectively removed by citrate, cadmium was easily removed by EDTA and was also effectively removed by the hydroxylamine hydrochloride, while copper was only removed by the EDTA. Although nickel removal was poor with EDTA alone, the treatment with all three agents showed no better removal.

Several chemical washing procedures were applied to a Zn-contaminated (artificially) soil column in an effort to determine metal extraction efficiencies [20]. Extracting agents investigated included EDTA, diethylenetriamino-pentaacetic acid (DTPA), acid solution, and sodium hypochlorite (NaOCl), all at various concentrations. The effect of extraction solution flow rate, ionic strength, and temperature were investigated. Flow rates in the range of 0.5 to 15 ml/min were employed using EDTA at a concentration of 3×10^{-3} M at pH 6. At the lowest flow rate (0.5 ml/min), removal continued through the entire period; and nearly 100% removal of the zinc was recovered after 33 h. As the flow rate increased to 3 ml/min, total Zn removal decreased to 85%. Zinc removal was primarily related to the delivery of the washing solution and was not dependent on a chemical reaction rate. Reaction with the washing solution caused the Zn to dissolve, thus producing a volume dependency. Little was gained in washing efficiency by employing the lower flow rates. The fastest flow rate produced Zn removal efficiencies near that of the slower rates, but required a much shorter wash time. The removal of Zn was observed for pH in the range of 2 to 6. At pH 4 and 6, a maximum zinc removal of only 38–42% was observed. Most of the zinc was removed by the first 15 pore volumes; an insignificant amount of zinc was removed in the remaining 235 pore volumes of washing solution. At pH 2, 81% of the total zinc was removed from the soil column; most of the zinc was once again removed during the initial portion of the washing. At pH 2, even in the presence of chelating agents, most of the zinc removal was due to dissolution by the acid (because the effluent zinc concentrations were significantly higher than the influent complexing agent concentration). There was only a slight enhancement in zinc removal by EDTA at a concentration of 3×10^{-4} M as compared to that in the absence of EDTA at pH 6. Total zinc removal efficiency increased to 79% with the 10^{-3} M EDTA extractant solution. Further increasing the EDTA concentration to 3×10^{-3} M increased the zinc extraction; most of the zinc was removed during the first 75 pore volumes, after which little subsequent zinc removal was observed. Increasing the ionic strength from 10^{-3} to 10^{-1} M slightly increased Zn removal (from

34% to 43%). In all cases, more than 90% of the zinc removal occurred during the first 8 pore volumes. The Zn removal efficiencies at 12°C, 25°C, and 32°C were 76%, 85%, and 88%, respectively. However, there is little effect of temperature and ionic strength on Zn removal efficiency. Metal removal efficiency depended in the metal compound associated with the contamination due to variations in solubilities. Washing of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ from the soil was much easier than for ZnO. Thus, speciation of the heavy metal contamination is very important in determining the success of a soil washing process.

Mcardell et al. [48] studied the removal of $\text{Co}^{\text{III}}\text{OOH}$ and $\text{Mn}^{\text{III}}\text{OOH}$ using EDTA, NTA, and related aminocarboxylate chelating agents. One site at Oak Ridge, TN, contains a cobalt- and EDTA-containing plume that has migrated several kilometers away from the disposal site. $\text{Co}^{\text{III}}\text{EDTA}^-$, tentatively identified in the plume, sorbs poorly onto aquifer solids and resists chemical and biological degradation. NTA and other aminocarboxylate chelating agents (e.g. breakdown products of EDTA) may also be capable of solubilizing cobalt, facilitating its movement in the hydrologic cycle. Mcardell et al. [48] noted that adsorption is the basis for all surface chemical reactions. Free EDTA, free oxidation products, free metal ions, metal ion–EDTA complexes, and metal ion–oxidation product complexes may all adsorb to some degree; adsorption affects all other reactions and interferes efforts to monitor reaction progress. Their results indicate that EDTA, NTA, and IDA can solubilize mineral surface-bound Co^{III} .

Nivas et al. [54] compared removal of subsurface chromium (VI) by deionized (DI) water, and water containing surfactants with and without complexing agents. The researchers found that surfactants were able to enhance the extraction of chromate 2.0–2.5 times greater than water. In the presence of a complexing agent the system was able to enhance the chromate elution by 9.3–12.0 times greater than water alone (3.7–5.7 times greater than surfactant without the complexing agent). The influence of chelating agents on extraction of metals with foam has not been found in the technical literature [29].

Hsieh et al. [37,38] studied soil washing for removal of chromium from soil. Chromium was selected for their study due to its prevalence in contaminated sites in north New Jersey. In the first portion of their study, they investigated the effect of chromium concentration, the type of soil, and pH on chromium adsorption [37]. Sand did not adsorb Cr(III); pH and the quantity of sand had no effect on Cr(III) adsorption. Both Cr(III) and Cr(VI) adsorb onto kaolinite and bentonite clay, with Cr(III) being more prone to adsorption. The amount of chromium adsorbed was proportional to the concentration of chromium added to the soil. After reaching the maximum adsorption, the soil did not adsorb any more chromium. Kaolinite had less adsorption capacity for chromium compared with bentonite. Cr(VI) had a higher adsorption at low pH. Cr(III) precipitates above pH 5.5. Results from preliminary soil washing experiments indicated that the amount of chromium washed out from the soil was proportional to the number of washings performed and the amount of extracting agents used (sodium hypochlorite and EDTA were used as the extracting agents).

Pichtel and Pichtel [69] investigated the ability of EDTA, NTA, sodium dodecyl sulfate (SDS), and hydrochloric acid (HCl) to solubilize chromium (Cr) and lead (Pb) from a contaminated soil ($\text{Cr}_{\text{tot}} \sim 4940 \text{ mg/kg}$; $\text{Pb}_{\text{tot}} \sim 1300 \text{ mg/kg}$; $\text{pH} \sim 10.3$) from an abandoned industrial facility. EDTA, NTA, and SDS were contacted with the soil

over a wide pH range (~ 2 to 11). The extent of Cr and Pb solubilization was strongly influenced by both solution pH and the chelant–metal chemistry. Increasing the chelant concentration generally resulted in enhanced recovery of Cr from the soil. Cr and Pb recovery increased with higher EDTA concentrations, with maximum recoveries occurring at greater than 1:1 molar ratios of chelant:metal. The 0.1 M EDTA solution removed $\sim 100\%$ of the lead up to pH ~ 4.3 , and 54% of the chromium and 96% of the lead were recovered at pH ~ 12 . The NTA was less effective: ~ 33 –48% removal of Cr (pH 8.9–11.0) and a maximum of 38% lead removal was achieved at pH 4.5. The SDS removed 30–40.5% of the lead for pH in the range of 4.4 to 10.9, and 29–35% of the chromium for pH in the range of 2.2 to 3.2. SDS was not effective at removing soil Cr and Pb, even at molar ratios of greater than 1:1. The authors speculated that the anionic surfactant may be precipitated with soil Ca and Mg, as well as bound to positively charged metal oxides and hydroxides. The acid wash using HCl concentrations ranging from 2% to 8% removed 100% of the Cr and Pb; however, 49–51% of the matrix solids were also dissolved, which creates a potential loading problem in wastewater treatment plant operations. High acid strengths destroyed the soil structure and dissolved much of the soil solids. A 1% acid solution was much less effective in metal removal (15.7% and 3.8% removal of Cr and Pb, respectively).

Steele and Pichtel [78] investigated the ability of various chemical extractants to remove lead and cadmium from a Superfund soil. The initial heavy metal concentrations were $Pb_{tot} = 65\ 200$ mg/kg soil and $Cd_{tot} = 52$ mg/kg soil. The extractants investigated included: EDTA, *N*-2(acetamido)iminodiacetic acid (ADA), pyridine-2,6-dicarboxylic acid (PDA), and HCl. Specific objectives of their study were to (1) investigate the effectiveness of EDTA, ADA, PDA, and HCl to remove Pb and Cd from soil, and (2) evaluate the ability of Ca^{2+} to displace Pb from the metal–ligand complex and recover the extracted lead. The extractants were evaluated over a range of concentrations and reaction times in batch studies. Soil extraction experiments were performed batchwise using EDTA (pH ~ 4.5), ADA (pH ~ 6.5), PDA (pH ~ 4.5), and HCl. The extractant concentrations used in the study were 0.0225 M, 0.0375 M, and 0.075 M corresponding to 1.5:1, 2.5:1, and 5:1 ligand:Pb molar ratios, respectively. The HCl concentrations used were 0.01 N and 0.10 N. The lead extraction was observed to be independent of EDTA concentration for the first hour of extraction, but the removal was significantly affected by concentration as reaction time increased. EDTA was capable of removing all the nondetrimental metals when present at least stoichiometrically. Increasing the EDTA concentration to $> 1.5:1$ EDTA:Pb molar ratio resulted in greater Pb removal; however, the extraction efficiency was small as the EDTA concentration was progressively increased. Initially, extraction of lead was rapid, but then slowed, indicating a rapid desorption within the first hour, followed by a subsequent gradual release. Extraction with 0.075 M ADA in 2.5 h removed nearly all the nondetrimental Pb. The investigators noted that differences in soil chemistry (e.g. presence of competing ions, pH, and metal ion speciation) affect the extractability of the heavy metals present [78]. ADA did not remove the lead as effectively as EDTA; ADA is tridentate and 1:1 complexation with lead (six coordination sites) theoretically leaves three sites available for interaction with the soil surface. Lead removal by 0.075 M PDA was significantly greater than at the lower PDA concentrations at all extraction times studied. Hydrochloric acid extractions

were independent of concentration and reaction time; lead extraction efficiencies averaged 29%, 35%, and 32% at 1 h, 2.5 h, and 5 h, respectively.

Steele and Pichtel [78] also performed three extractions performed sequentially. Lead extraction efficiency was independent of EDTA concentration, and greater than 82% of the lead was removed. The majority was extracted within the first hour (58%), with significantly smaller amounts removed in the second and third extractions. The second 1-h extraction removed 48% of the remaining Pb contained in the soil. Lead extraction efficiency was significantly dependent on ADA concentration; extraction efficiency increased from 66% to 84% with increasing concentration. Extraction efficiency with PDA was 59%, 64%, and 70% with 0.0225 M, 0.0375 M, and 0.075 M, respectively. Hydrochloric acid removed 54% of the lead; extraction efficiency was independent of the acid concentration. All extractants followed the same general pattern; the majority of the lead was removed in the first hour, with smaller increments being removed in the second and third extractions. The three repeated extractions did not reduce the total lead concentration in the soil below the site-designated limit of 1000 mg/kg. The number of extractions was increased to five 1-h extractions using 0.075 M EDTA or ADA. Extraction efficiencies ranged from 89% to 97% using 0.075 M EDTA; the treated soil had an average Pb content of 4,200 mg/kg soil. Using ADA, extraction efficiencies ranged from 79% to 90%, with a residual Pb content of about 11 500 mg/kg. The order of Pb extraction efficiency was EDTA > ADA > PDA > HCl for all reaction times.

For extraction of cadmium, all extractants reduced the soil Cd content below the proposed regulatory limit of 40 mg/kg soil, regardless of concentration and extraction time [78]. Cadmium extraction efficiency with EDTA was concentration dependent; the 0.075 M EDTA removed significantly greater amounts of lead than the two lower concentrations used. The 0.0375 M and 0.075 M EDTA concentrations removed all the nondetrital Cd. Extraction efficiency of Cd with ADA was concentration dependent for only the first 0.5 h, and changed minimally after 1 h. Cadmium removal with PDA was dependent on concentration for all reaction times. Extraction efficiency was highest at 2.5 h for all concentrations, and removed all the nondetrital Cd. Hydrochloric acid was the most effectively extractant for removal of Cd; removal was concentration-dependent at 1 and 5 h. At 5.0 h, removal of Cd was 68% and 98% using 0.1 N and 1.0 N HCl, respectively. The HCl removed all nondetrital Cd, and in some cases nearly all the Cd contained in the soil. Additional Cd removal was obtained with three repeated extractions. At 0.075 M, all the chelants extracted 85% to ~ 100% of the Cd contained in the soil. Repeated extractions with 0.1 N and 1.0 N HCl removed 79% and ~ 100% of the Cd, respectively. The removal behavior for Cd followed the same trends as that experienced for lead; the majority of the Cd was removed with the first hour, and smaller amounts released during the second and third extractions. Cadmium removals ranged from 71% to ~ 100% with three repeated 1-h extractions.

Li and Shuman [44] investigated the extractability of zinc, cadmium, and nickel in soils amended with EDTA. Extractability was determined using Mehlich-1 (0.05 M HCl + 0.0125 M H₂SO₄) and DTPA extraction procedures to estimate the plant-available form of micronutrients in soil. These solution extract the relatively mobile forms of metals in soil; as such, they can be used to estimate metal mobility in soil. Additionally, 1 M Mg(NO₃)₂ (pH ~ 7.0) was used to determine the exchangeable fraction of metals in

the soil. EDTA significantly elevated the extractability of Zn and Ni in both natural and metal-amended soils in the Mehlich-1 and DPTA extractions, but it did not affect the extractability of Cd in the metal-amended soils. The order of mobility based on extractability was $Cd > Zn > Ni$ for metals added to soils. When EDTA was present, added nickel was more extractable than Zn or Cd.

Hessling et al. [30] investigated soil washing techniques for remediation of lead-contaminated soils at battery recycling facilities. Three wash solutions were studied for their efficacy in removing lead from these soils: (1) tap water alone at pH 7, (2) tap water plus anionic surfactant (0.5% solution), and (3) tap water plus 3:1 molar ratio of EDTA to toxic metals at pH 7–8. Tap water alone did not appreciably dissolve the lead in the soil. Surfactants and chelating agents such as EDTA offer good potential as soil washing additives for enhancing the removal of lead from soils. There was no apparent trend in soil or contaminant behavior related to Pb contamination (predominant Pb species), type of predominant clay in the soil, or particle size distribution. The authors concluded that the applicability of soil washing to soils at these types of sites must be determined on a case-by-case basis.

Elliot et al. [21] performed a series of batch experiments to evaluate extractive decontamination of Pb-polluted soil using EDTA. Their study studied the effect of EDTA concentration, solution pH, and electrolyte addition on Pb solubilization from a battery reclamation site soil containing 21% Pb. The heavy metals concentrations in the soil were determined to be: 211 300 mg Pb/kg (dry weight); 66 900 mg Fe/kg; 1383 mg Cu/kg; 332 mg Cd/kg; and 655 mg Zn/kg. A nine-step chemical fractionation scheme was used to speciate the soil Pb and Fe. Results from their study indicated that increasing EDTA concentration resulted in greater Pb release. Recovery of Pb was generally greatest under acidic conditions and decreased modestly as the pH became more alkaline. Even in the absence of EDTA, a substantial increase in Pb recovery was observed below pH 5. As the pH became more alkaline, the ability of EDTA to enhance Pb solubility decreased because hydrolysis was favored over complexation by EDTA. The researchers observed that EDTA can extract virtually all of the non-detrital Pb if at least a stoichiometric amount of EDTA is employed. When increased above the stoichiometric requirement, the EDTA was capable of effecting even greater Pb recoveries. However, the Pb released with each incremental increase in EDTA concentration diminished as complete recovery was approached. The researchers also investigated the release of Fe from the soil by EDTA. The Fe release increased markedly with decreasing pH. Despite the fact that the total iron was nearly 1.2 times the amount of lead in the soil, only 12% of the Fe was dissolved at pH 6 using 0.04 M EDTA, compared with nearly 86% dissolution of the Pb [22]. Little of the Fe was brought into solution during the relatively short contact time of the experiments (5 h). The iron oxides retained less than 1% of the total soil Pb [22].

Elliot et al. [21] observed that Pb recovery increased by nearly 10% in the presence of $LiClO_4$, $NaClO_4$, and NH_4ClO_4 . They attributed this increase to an enhanced displacement of Pb^{2+} ions by the univalent cations and the greater solubility of Pb-containing phases with increased ionic strength. Below pH 6, calcium and magnesium salts also enhanced Pb recovery. Above pH 6, however, Pb recovery decreased due to a competition between Ca or Mg and Pb for the EDTA coordination sites. Their research [21,22]

did not provide any evidence that the suspension pH must be raised to at least 12 to prevent Fe interference in soil washing with EDTA to effectively remove Pb.

The U.S. EPA conducted a series of laboratory bench-scale soil washing studies using water, EDTA, or a surfactant to treat soils from metal recycling sites [57,74]. Soil washing did not remove significant quantities of lead from any of the soil fractions. The lead was not concentrated in any particular soil fraction, but rather was distributed among the fractions. EDTA was more effective in removing lead than either the surfactant or water washes. Data from the U.S. Bureau of Mines indicates that the effectiveness of EDTA in removing lead varies with the species of lead present [75].

Studies involving extraction of lead from soil containing approximately 70% silt and clay, Peters and Shem [67] removed 58 to 64% of the lead using EDTA over the entire pH range ($4.9 \leq \text{pH} \leq 11.3$). In their study, the soil was spiked with lead nitrate solutions resulting in lead concentrations on 500 to 10000 mg/kg soil. The chelants studied included EDTA and NTA. The removal of lead using water and NTA as extractants were both pH-dependent, whereas the removal of lead using EDTA was pH-insensitive over the pH range investigated ($3 \leq \text{pH} \leq 12$). Extraction of water alone removed a maximum of 7.55% for $\text{pH} \sim 4$. The initial lead concentration had little effect on the metal removal efficiency for the EDTA system (for initial lead concentrations in the range of 500 to 10000 mg/kg soil). The applied EDTA concentration over the range of 0.01 to 0.10 M also had little effect on the removal efficiency of lead from the soil. Soils containing a greater fraction of sand (sand > 78%), the removal efficiency of lead from the soil typically exceeded 85%. Peters and Shem [66] noted that the adsorptive behavior between the soil containing a high silt and clay fraction differed significantly from the sandy soil. Previous studies have indicated that heavy metals are preferentially bound to clays and humic materials [91].

Peters and Shem [66] observed that extraction of lead with EDTA was rapid, reaching equilibrium within a contact time of 1.0 hr; extraction of lead with NTA was slower requiring a contact of approximately 3.0 hrs to reach equilibrium. The order of lead removal efficiency for the various extractive agents was as follows: EDTA \gg NTA \gg water [66] The maximum lead removals observed for this high clay and silt soil were 68.7, 19.1, and 7.3, respectively, for the cases of EDTA, NTA, and water used as the extractive agents on the lead-contaminated soil [68].

Abumaizar and Khan [1] investigated the influence of organic matter in soils while removing heavy metals by soil washing techniques employing sodium metabisulfite and EDTA solutions. Both low and high organic matter content soils were used in the study. The organic phase of the soils may be humus or nonhumus. The high molecular weight humus organic substances have a high affinity for metals and form water-insoluble metal complexes, while nonhumus substances of low molecular weight (such as organic acids and bases) are relatively soluble when complexed with metals. The metal-organic matter bond within the soil pores can be broken and the metal extracted by the action of a sequestering ligand (such as EDTA). The first soil had a negligible organic matter content, and was spiked with lead sulfate (PbSO_4) and zinc chloride (ZnCl_2) and aged for 14 days. The Pb and Zn concentrations of this soil after spiking were 204 mg/kg and 79 mg/kg for Pb and Zn, respectively. The second soil was a mixture of millpond sludge and sand, containing 1535 mg/kg Pb and 15600 mg/kg Zn. The hydraulic

conductivities of these two soils were 2×10^{-5} and 3.5×10^{-5} cm/s, respectively. Their results indicated that washing the contaminated samples with tap water had little or no effect on the heavy metal contaminants; removal of lead was nondetectable, and removal of zinc was only 1.3%. The researchers performed four stages of soil washing, with the first stage employing tap water, and the subsequent stages employing either sodium metabisulfite or EDTA. Sodium metabisulfite removed 48% and 75% of the lead and zinc, respectively; EDTA removed 70.4% and 92.7% of the lead and zinc from an identical sample. They also observed that the type of permeant had a profound effect on the rate of flow through the soil column. The flow rates of tap water, sodium metabisulfite, and EDTA were 5.3×10^{-2} L/h, 2.7×10^{-2} L/h, and 1.5×10^{-2} L/h, respectively. Their results indicated that sodium metabisulfite and EDTA were effective extraction agents for removal of Pb and Zn from both a silty clay soil and from the millpond sludge. For the millpond sludge, better removal efficiencies were achieved using a 0.05 M EDTA solution than using a 0.2 M sodium metabisulfite solution. Zinc was more readily extracted than lead, and the flow rates of the sodium metabisulfite and EDTA solutions were significantly slower than that of tap water [1].

Cline and Reed [19] investigated the removal of lead from eight study soils collected from the eastern United States. The efficiencies of five different washing solutions was investigated via batch washing experiments. Each study soil was artificially contaminated with lead nitrate [$\text{Pb}(\text{NO}_3)_2$] at three different concentrations (10, 100, and 1000 mg Pb/l). Seven samples were prepared for each soil type and extractant concentration, enabling a sample to be removed at each of the following time periods: 15 min, 30 min, 1 h, 4 h, 8 h, 1 day, and 7 days. The slurry pH of each sample was measured. The washing solutions investigated included: tap water (H_2O), HCl, EDTA, acetic acid (CH_3COOH), and calcium chloride (CaCl_2). The concentration of the acids used in the study were 0.1 N and 1.0 N, and the concentration of EDTA was 0.01 M and 0.1 M, and the CaCl_2 concentration was 0.1 M and 1.0 M. Washing with tap water removed less than 3% of the lead, indicating that the sorbed lead could not be readily removed by rinsing with water alone even though the soils were artificially contaminated. EDTA and HCl achieved the highest removal efficiencies (92% and 89%, respectively), followed by CH_3COOH (45%) and CaCl_2 (36%). EDTA was highly effective in removing lead from the contaminated study samples. Only small differences were observed in removal efficiencies of the 0.01 M and 0.10 M EDTA washes. The removal efficiencies for the 0.01 M and 0.10 M EDTA washes were not significantly different for the 100 and 1000 mg Pb/l contaminated samples. The final slurry pH of the EDTA washes were in the range of 4.0 to 5.4 for the 0.01 M washes and between pH 4.3 and 4.8 for the 0.10 M washes. The removals were generally independent of soil type and washing solution concentration. The authors [19] speculated that dissolution of some of the soil components controlled lead removal in the HCl washes and that chelation was the dominant lead-release mechanism for the EDTA washes, while lead removal by CaCl_2 was by ion exchange with Ca^{2+} and/or complexation with the chloride species.

In another application involving application of chelating agents to contaminated soils, Huang et al. [39] observed that addition of chelants to a Pb-contaminated soil ($\text{Pb}_{\text{tot}} \sim 2500$ mg/kg) increased shoot Pb concentrations of corn (*Zea mays* L. cv. Fiesta) and pea (*Pisum sativum* L. cv. Sparkle) from less than 500 mg/kg to greater than

10 000 mg/kg). The order of effectiveness in increasing Pb desorption from the soil was EDTA > HEDTA (hydroxyethylethylenediaminetriacetic acid) > DTPA > EGTA > EDDHA. EDTA significantly increased Pb translocation from the root to the shoots. Within 24 h after applying EDTA solution (1.0 g EDTA/kg soil) to the contaminated soil, Pb concentration in the corn xylem sap increased 140-fold, and net Pb translocation from the roots to the shoots increased 120-fold as compared to the control. Their results indicated that chelants enhanced Pb desorption from the soil to the soil solution, facilitated Pb transport into the xylem, and increased Pb translocation from the roots to the shoots. Their results suggest that with careful management, chelant-assisted phytoremediation may provide a cost-effective soil decontamination strategy.

Semer and Reddy [77] investigated the development of a soil washing process to treat a number of contaminants (both organic and inorganic) simultaneously. The soil used in their study was a sandy loam material containing 66% sand and 34% silt and clay. This soil was spiked with a number of contaminants including various pesticides (Lindane, Methoxychlor, and Endrin), heavy metals (cadmium, copper, and silver), organics (ethyl benzene and methyl isobutyl ketone), and halogenated compounds (chloroethene and tetrachloroethylene). The soil contamination levels are indicated in Table 3.

The wash solution investigated included HCl, nitric acid (HNO₃), sulfuric acid (H₂SO₄), and a combination of sulfuric acid and isopropyl alcohol. Results from batch extractions are summarized in Table 4. Hydrochloric acid was the most efficient wash solution for removal of the heavy metals; generally, the stronger the acid, the greater the heavy metal removal. Sulfuric acid was more effective than HCl in removing pesticides from the soil. Isopropyl alcohol enhanced the effectiveness of H₂SO₄ in the removal of pesticides. Treatment time was found to be significantly longer for pesticide removal than for removal of volatiles and metals. In a pilot-scale test, the removal efficiencies of copper, silver, and cadmium were 95%, 71%, and 97%, respectively. Lindane and methoxychlor removals were 96%, and 97%, respectively. The contaminant removal

Table 3

Soil contamination levels and desired remediation levels (adapted from Semer and Reddy [77])

Contaminant	Concentration in soil (mg/kg)	Remediation criteria (mg/kg)	Desired removal efficiency (%)
Pesticides, herbicides, insecticides:			
Lindane	150	10	93.3
Methoxychlor	150	10	93.3
Endrin	150	10	93.3
Heavy metals:			
Cadmium	350	15	95.7
Silver	100	15	85.0
Copper	100	15	85.0
Organic compounds:			
Ethylbenzene	75	10	86.7
Methyl isobutyl ketone	100	10	90.0
Halogenated compounds:			
Chloroethene	75	14	81.3
Tetrachloroethylene	100	14	86.0

Table 4

Evaluation of different extractant solutions (tumbling time ~ 1 h)—adapted from Semer and Reddy [77]

Chemical contaminant	HCl (% removed)			H ₂ SO ₄ (% removed)			HNO ₃ (% removed)			Required (% removal)
	4.0 N	1.0 N	0.5 N	5.0 N	1.0 N	0.5 N	5.0 N	1.0 N	0.5 N	
Methyl isobutyl ketone	92.0	98.1	95.2	98.5	98.0	97.8	97.6	98.3	ND	90.0
Tetrachloro-ethylene	49.3	90.4	75.6	92.0	86.8	87.7	83.0	89.0	ND	86.0
Ethylbenzene	76.9	94.8	89.5	94.7	93.0	93.2	91.4	93.8	ND	86.7
Chloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	81.3
Lindane	58.0	26.0	63.0	63.0	72.0	55.0	51.0	57.0	69.0	93.3
Methoxychlor	58.0	7.0	60.0	60.0	65.0	45.0	40.0	53.0	66.0	93.3
Endrin	99.0	38.0	76.0	76.0	83.0	56.0	84.0	79.0	84.0	93.3
Cadmium	97.2	96.9	95.7	95.7	85.4	81.3	97.3	21.5	88.0	95.7
Silver	99.0	98.0	62.1	62.1	78.8	84.3	86.6	86.6	79.8	85.0
Copper	87.5	78.9	73.2	73.2	39.6	24.0	59.4	49.9	44.6	85.0

efficiencies exceeded the desired remedial levels for all the contaminants except silver. The authors concluded that the combination of sulfuric acid and isopropyl alcohol was an appropriate wash solution capable of treating a variety of mixed contaminants simultaneously [77].

Reed et al. [72] investigated the removal of Pb(II) from a synthetically contaminated sandy loam soil using 0.1 N HCl, 0.01 M EDTA, and 1.0 M calcium chloride (CaCl₂) in a continuous flow mode. Initial Pb concentrations ranged from 500 to 600 mg/kg. Pb removal efficiencies (and final soil Pb concentrations for HCl, EDTA, and CaCl₂ were 85% (77 mg Pb/kg soil), ~ 100% (~ 0 mg Pb/kg soil), and 78% (135 mg Pb/kg soil), respectively. For all flushing solutions, there was significant Pb removal after 1 pore volume of flushing solution while there was little additional lead removal after 4 pore volumes. The width of the Pb effluent curve was highest for HCl, followed by EDTA and CaCl₂. The width of the Pb effluent curve was about 1 pore volume for HCl and CaCl₂ and about 2 pore volumes for EDTA, indicating that removal kinetics were slower for EDTA. Using HCl, lead was removed by low pH enhanced desorption and ion exchange (H⁺ for Pb²⁺). Using EDTA, lead was removed due to chelation, and for CaCl₂, Pb removal was by a combination of ion exchange (Ca²⁺ for Pb²⁺) and complexation with Cl⁻. For HCl and CaCl₂, 78% to 85% of the lead was removed, indicating that a portion of the lead was strongly sorbed to the soil. The extractants of HCl and CaCl₂ were not able to reduce the soil lead concentration to background levels (25 mg Pb/kg soil) for a synthetically contaminated soil. While EDTA removed nearly all the lead (indigenous and artificial), its treatment and reuse and potential adverse health effects makes its use difficult [72]. The final soil pH was near 1.0 for HCl, raising concern of increased contaminant mobility, decreased soil productivity, and adverse changes in the soil's chemical and physical structure due to mineral dissolution [72]. Final soil pH for the extractants EDTA and CaCl₂ ranged between 4.85 and 5.2.

Rampléy and Ogden [71] investigated the use of a newly developed water soluble chelator, Metaset-Z, which exhibits a high selectivity for lead. Parameters of interest include the amount of adsorption and desorption of polymer under varying conditions such as ionic strength and the presence of other ions (e.g. lead and calcium), the rate of

lead removal from artificially contaminated soil, and pertinent equilibrium considerations. Metaset-Z rapidly chelates soluble lead and does not have a high affinity for quartz. The investigators observed two removal rates, corresponding to the presence of a two discrete binding sites for lead, one from which lead is easily removed, and the other for which removal is more difficult. They observed that 48% of the lead was removed by the fast reaction, and 52% was removed by the slower reaction; the overall removal efficiency of lead was about 85%. The rate constants indicated that lead removal occurs on the time scale of hours, and is therefore a feasible method for site remediation [71]. The investigators noted that the chelation process appeared to be insensitive to ionic strength over ranges typically encountered in groundwater. In addition, the process was not affected by the presence of calcium.

Surfactants have shown some potential for environmental remediation of heavy metals from soil, although research in this area has been limited. Cationic surfactants can be used to modify soil surfaces to promote displacement of metal cations from the solid to the liquid phase. Surfactants cause the transfer of the soil-bound metal to the liquid phase through ion exchange processes. This desorption and mobilization process of previously adsorbed metal cations on negatively charged soil surfaces can be applied to in situ soil remediation. Results from batch equilibrium tests on clay suspensions indicated that cationic surfactants were effective in desorption of lead, cadmium, copper, and zinc from montmorillonite clays [9]. One of the more promising aspects of their study involved the very low solution concentrations (0.005% by weight) required to cause desorption. Kornecki et al. [41] investigated the feasibility of using cationic surfactants to desorb lead (Pb) from contaminated soil using a two-phase test program. In Phase I, Pb desorption from a sandy loam was measured as a function of the surfactant concentration for ten cationic surfactants. In Phase II, a sandy loam and a loam soil were used to determine the impact of pH (pH in the range of 4 to 9) on surfactant desorption of Pb for an initial surfactant concentration of 0.025 mol/l. For nearly all the surfactants, increasing the surfactant solution concentration results in decreased pH and increased Pb desorption. Deionized water alone desorbed only 1% of the lead. The Phase I work indicated that three surfactants: isosteamamidopropyl morpholine lactate (ISML), lapyrium chloride (LC), and dodecyl pyridinium chloride (DPC) were the best surfactants for desorbing lead from the soils. The highest surfactant adsorption and highest lead desorption occurred with ISML. At a solution concentration of 0.1 M, ISML, LC, and DPC desorbed 82%, 59%, and 50% of the lead from the sandy loam soil. Lead desorption using a 0.025 M surfactant solution was pH dependent. As the pH decreased, desorption of Pb increased. At pH 4, removal of Pb was 83%, 78%, and 68% using ISML, DC, and DPC, respectively. Similarly, for the loamy soil, removal of Pb was 36%, 32%, and 29% using these same three surfactants. The researchers [41] also compared the Pb extraction efficiency to that using EDTA; EDTA desorbed 94% to 97% of the lead and was not influenced by either solution pH or soil type.

3.3. *Chelant extraction modeling activities*

A mathematical model has been developed for metal leaching from contaminated soils subjected to acid extractions in batch reactors [26]. The model considers transport

by pore diffusion and film transfer, leaching of metal bound to reversible and irreversible phases, and metal complexation by ions in solution. Contaminant metal is considered to be partitioned into two fractions: irreversibly and reversibly bound metal phases. Irreversible and reversible kinetic reactions describe the release of metal from these two fractions. The model incorporates intraparticle transport of chemical species by molecular diffusion. Simulation results and sensitivity analyses indicated that leaching kinetics vary according to the metal binding mechanism and location within a soil particle. Depending on leaching conditions, diffusion, reaction, or a combination of both may control metal leaching for time scales of interest in soil washing operations. The rate and extent of lead leaching were pH-dependent and lower pH results in faster release of Pb. The fast release of Pb at low pH is caused by the H^+ dependence of the reversible and irreversible reactions. Slow rate of leaching at $pH \sim 3$ is due to both diffusion and reaction limitations.

Kedziorek et al. [40] investigated the solubilization of lead and cadmium using EDTA both in pulse and step modes in contaminated soil columns. They developed a numerical model that linked solute transport of EDTA and EDTA–metal chelates to the metal solubilization process. The transport of metal complexes was not calculated directly from a single advection–dispersion equation, but rather it was simulated after having calculated the transport of uncomplexed EDTA. The leaching reaction was expressed as a second-order irreversible kinetic term that included not only the concentration of metal in solution, but also the fraction of metal still extractable. The model was developed to simulate the following phenomena: (a) EDTA transport (advection/dispersion equation); (b) solubilization with EDTA of heavy metals bound to the soil, and (c) transport of EDTA–metal complexes in solution. No significant adsorption of EDTA was observed in the soil. As EDTA percolates through the soil, it extracts metals, and therefore becomes complexed. Experimental break-through curves for the pulse and step addition modes were used to validate the model. Neither EDTA or Cd or Pb (migrating as EDTA complexes) were retarded with respect to the tracer (bromine), further demonstrating the absence of any significant adsorption of EDTA species on the soil. The model accounted for the diminishing metal extraction efficiency as the metal solid was depleted or as the available EDTA concentration decreased. The authors concluded that dispersive properties had little effect on the heavy metal extractions, whereas, the larger the porosity, the more efficient the extraction process becomes [40].

3.4. Previous ANL studies involving chelant extraction

Argonne National Laboratory's Energy Systems Division has performed chelant extraction studies for the past 6+ years, addressing the removal of heavy metals (arsenic, cadmium, copper, chromium, lead, zinc, and mercury) from a variety of heavy-metal-contaminated soils [10–12,43,58–64,66–68]. Chelating agents used in these studies have included: EDTA, NTA, ammonium acetate, citric acid, oxalic acid, phosphoric acid, hydrochloric acid, Citranox, gluconic acid, and pH-adjusted water. Generally, EDTA, NTA, and citric acid performed reasonably well in removing the heavy metals from the soils. Using a sequential batch washing approach, the lead concentration was reduced from $\sim 21\,000$ mg/kg to < 300 mg/kg when using EDTA as the extractant.

3.4.1. Arsenic contaminated soils and groundwaters

Soils and groundwaters were contaminated through the use of arsenic trioxide as an herbicide at electric power substations. Treatability studies were performed to identify effective chelating agents for removing arsenic from soils [60,62]. Extractants studies included citric acid, oxalic acid, gluconic acid, phosphoric acid, sodium carbonate, triethylamine, three commercially available surfactants, and pH-adjusted water. Oxalic acid, citric acid, phosphoric acid, and polysodium vinyl sulfonate were all fairly effective at removing arsenic from the soil.

3.4.2. Grafenwöhr training area, Germany

Peters [65] and Peters et al. [63] performed feasibility/treatability study to investigate the leaching potential of heavy metals (with attention focused on lead) from soils obtained from the Grafenwöhr Training Area in Germany and to determine the effectiveness and potential of using chelant extraction as a remediation technique to clean-up the heavy metal-laden soils at the site. The results from batch shaker flask studies indicated that EDTA was more effective at removing cadmium, copper, lead, and zinc, as compared to citric acid (both present at 0.01 M). EDTA and citric acid were equally effective for their ability to mobilize chromium and barium from the soil. The batch shaker experiments showed that chelant extraction offers promise as a remediation technique for on-site clean-up of the contaminated soil. Heavy metals removal was slightly more effective at pH in the range of 5–6 (compared to pH > 7).

Dynamic column experiments indicated that deionized water was the least effective leaching solution used in terms of mobilization of the heavy metals; the maximum solubilization involved was 3.72% for cadmium. Extraction with deionized water indicated that all of the heavy metals are very tightly bound to the soil; the quantity of heavy metals leached into solution generally was less than 1.7% of the total heavy metals contained in the soil sample. The deionized water extraction results indicated that the heavy metals were very stable in the soils at Grafenwöhr Training Area and did not represent a serious threat to the groundwater system. EDTA (0.05 M) had the greatest removal of lead with a maximum removal of 50.6% and an average removal of 17.6%. EDTA (0.05 M) was more effective at removing cadmium, chromium, and iron than 0.05 M citric acid or distilled water; the average removal was 13.0, 2.8, and 0.5%, respectively for these three heavy metals. Citric acid (0.05 M) was more effective at mobilizing copper and zinc than either EDTA (0.05 M) or deionized water; the average percent copper and zinc mobilized using citric acid was 8.96 and 10.59%, respectively. The amount of heavy metals mobilized from these soils constituted a relatively low percentage (typically < 20%). Due to the relatively small percentage of heavy metals mobilized in these columnar flow studies, in situ heavy metal mobilization employing chelant extraction probably does not represent a viable remediation technique to clean-up the soils at Grafenwöhr Training Area, although chelant extraction employing batch treatment offers some promise.

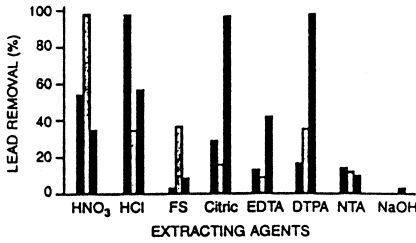
3.5. Previous WES studies involving metal extraction and chelant agents

Results for the metal extraction studies conducted by the Waterways Experiment Station (WES) [14,46,49–53] are briefly summarized below.

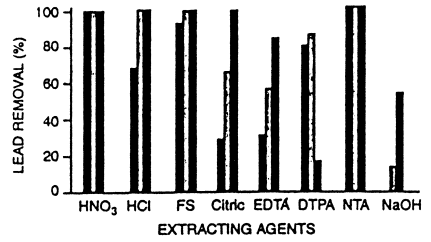
Marino et al. [46] investigated the use of attrition scrubbing on a gravity concentration process (wet tabling). Attrition scrubbing employs a high energy mixer to impart a mechanical scrubbing action on a slurried soil. The mixing results in vigorous particle to particle scrubbing in a high solids environment. The major effects of this particle scrubbing include scouring, and dispersion and disintegration. Scouring removes coatings or films from individual soil grains and produces clean soil surfaces. Dispersion/disintegration form a 'slime' (ultrafine particles) or a dispersed slurry resulting from the breakup of agglomerated particles. Attrition scrubbing of a heavy metal-contaminated soil can either concentrate the contaminants into a particular soil fraction, or separate the soil particle from the metal surface, and increase the effectiveness of a particle density separation. Attrition scrubbing enhanced the physical separation process on the wet shaker table by liberating the lead contamination from the bulk soil, resulting in a large volume of clean soil while simultaneously producing a small volume of Pb-concentrated soil. Laboratory tests indicated that over 96% of the contamination was concentrated on 20% of the original soil mass. Attrition scrubbing increased the Pb concentration in the concentrates and decreased the concentration in the middlings and tailings. Although the actual mass percentage of lead was relatively unchanged in the pre- and post-attrition for all fractions, attrition scrubbing prior to tabling produced a smaller, more concentrated fraction, and a larger, less contaminated middling fraction. The Pb concentration increased from $\sim 81\,900$ mg/kg in the original soil to $\sim 202\,300$ mg/kg following attrition scrubbing. The majority of the Pb contamination was concentrated onto a small volume of finer sized soil particles (0.063–2.0 mm in size). The wet shaker successfully produced a larger fraction of soil that was relatively free of Pb contamination.

A variety of acids and chelating agents were investigated for their ability to extract heavy metals from eight soils collected from various Military Installation Restoration (IR) and Base Realignment and Closure (BRAC) sites. Neale et al. [52] studied the ability of various chelating agents and acids to extract heavy metals from three soil types (i.e. clay, silt, and sand) collected from eight U.S. Army facilities. The soils were contaminated with varying concentration of lead (4000–30 000 mg/kg), cadmium (40–1000 mg/kg), and chromium (500–2000 mg/kg). Strong acids investigated included: HNO_3 , HCl, fluorosilicic acid, and citric acid; chelating agents investigated included: EDTA, DTPA, and NTA, plus sodium hydroxide (NaOH). Each agent was evaluated at three different concentrations: 0.01 M, 0.05 M, and 0.1 M. For each test, the extracting agent was added to the contaminated soil and mixed for 30 h. Results obtained indicated the following order in the ability to remove heavy metals: $\text{Cd} > \text{Pb} > \text{Cr}$. Results are summarized in Fig. 1. Their results indicated that contrary to metal solubility predictions, NTA outperforms EDTA and DTPA. NTA averaged 20% greater Pb removal than EDTA, and also achieved greater Cd and Cr removal than both EDTA and DTPA.

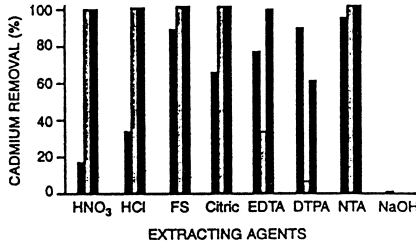
Results from their study [50–53] indicated that cadmium was the easiest of the three metals to remove, followed by lead, and then chromium. When initial concentrations of the heavy metals are higher, the resulting extraction efficiency is also higher. Extractant efficiency was generally unaffected by a change in concentration in DTPA and NTA. Lower system pH generally leads to the protonation on the ionized chelant species,



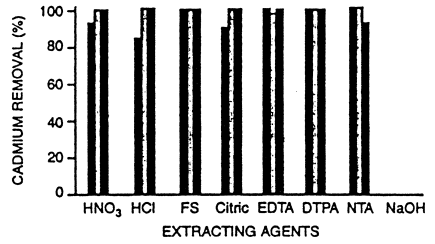
a) Lead Removal From Clayey Soil Sample Number 1



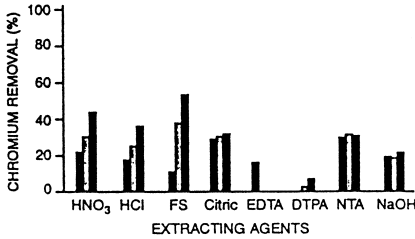
b) Lead Removal From Sandy Soil Sample Number 2



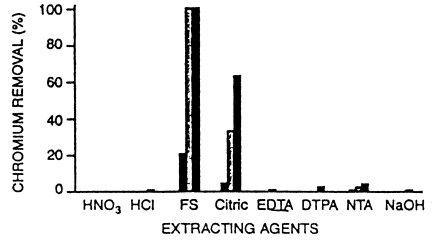
c) Cadmium Removal From Clayey/Silty Soil Sample Number 3



d) Cadmium Removal From Clayey/Silty Soil Sample Number 4



e) Chromium Removal From Clayey/Silty Soil Sample Number 5



f) Chromium Removal From Clayey/Silty Soil Sample Number 4

HNO₃ = nitric acid; EDTA = ethylene diamine tetraacetic acid; 0.01 Molar
 HCl = hydrochloric acid; DTPA = diethylene triamine pentaacetic acid; 0.05 Molar
 FS = fluorosilicic acid; NTA = nitrilotriacetic acid; 0.1 Molar
 Citric = citric acid; NaOH = sodium hydroxide.

Note: Soil sample numbers correspond with those listed in Table 1.

Source: Adapted from C.N. Neale et al.

Fig. 1. Heavy metal removal efficiencies of extracting agents in various soils (adapted from Neale [53]).

resulting in competition for binding sites between the hydrogen and metal ions, which causes a net decrease in metal solubilization. Increasing the extracting agent concentration does not always correspond to increased extraction efficiency. Contrary to theoretical predictions, NTA was generally more effective than EDTA and DTPA in removing all three metals (Cd, Pb, and Cr). Fluorosilicic acid and HCl were the most effective extracting agents for removal of Pb from soils, followed closely by HNO₃, NTA, and

DTPA. Fluorosilicic acid and citric acid were the most effective extracting agents for removal of Cr from soils. HNO_3 , NTA, and citric acid were the most effective extracting agents for removal of Cd from soils. The extraction of metals from a contaminated soil using an extracting agent was significantly affected by decreasing the solid:liquid ratio from 0.5 to 0.005. Rapid extraction of all three metals was generally observed in the initial 3 h contact time between the contaminated soil and extractant.

The three acids (HNO_3 , HCl, and citric acid) were consistently effective in removing lead, while EDTA and NaOH were consistently less effective. All of the extractants removed lead more effectively from sandy soil than from clayey soil. All of the acids and the chelating agents were effective in removing cadmium from the soils; only NaOH was ineffective. Acids were generally more effective than chelating agents in removing chromium from soils; fluorosilicic acid was the most effective followed by citric acid. The results indicate that both strong acids at low pH and chelating agents with near neutral to alkaline pH were effective extracting agents for removal of heavy metals. Strong bases with high pH were not effective metal extractants.

Studies were also conducted using a four-stage counter-current pilot extraction unit. Thus unit was calibrated to the full-scale soil washing facility utilized at Twin Cities Army Ammunition Plant (TCAAP). Four soils were processed through the counter-current extraction unit to determine the kinetics of extraction. These studies indicated that generally a 30-min hydraulic retention time (HRT) was required for optimal extraction. Over 90% of the metal extraction occurred in the first reactor. The conclusion from this study indicated that a series of reactors were of little benefit and resulted in higher capital costs for the process.

3.6. Reusability of chelating agents

For a system having the ligand to metal at a specified concentration ratio, a degree of complexation (DOC) parameter can be taken as the ratio of the total metal solubility with chelation to the aqueous solubility without chelation, i.e. $M_{\text{Tot}}/M_{\text{aq}}$. A large DOC ($\gg 1$) indicates a high degree of complexation by the chelating agent and thus great enhancement of solubilization by chelation, whereas a small DOC (≤ 1) indicates little enhancement by chelation or occurrence of precipitation as metal mineral at the specified pH condition.

The DOC ratio was found to be a function of pH [33]. For strong chelating agents, the DOCs were found to remain high over a broad pH range (e.g. 1 to 14); however, for chelating agents of moderate strength, the DOCs were typically found to be high at low or moderate pH value but low at high pH. This means that a chelator of moderate strength can enhance metal solubilization by complexation at lower pH but release the complexed metal as precipitate at a higher pH value. This feature can be exploited to recover extracted heavy metals and the chelator for further reuse. Chen et al. [16] evaluated about 200 chelating agents for their complexation and recovery potential and reported the effective pH ranges for chelating extraction of heavy metals including Pb, Cu, Cd, Zn, Ni, and Hg. They also predicted for each chelator the pH at which the extracted metals and chelator are to be recovered. They demonstrated the extraction, recovery, and reuse of several selected chelators for limited kinds of metals (Pb, Cu, Cd,

and Zn) [16,17,31,33,34,45]. The recoverabilities of heavy metals and chelating agents will be predicted on the basis of this equilibrium modeling approach. This determination will be extended to other heavy metals and radionuclides, including cesium, strontium, and cobalt, that are of interest to the DOE.

Hong et al. [32] investigated metal extraction and recovery for the following treatment conditions: varying soil type and contamination level (sandy loam soil with 15 500 mg Pb/kg soil and loamy sand with 2370 mg Pb/kg soil); EDTA concentration (3 to 50 mM), soil content (5% to 40% slurry), washing cycles (Nos. 1 through 6), precipitant concentration (3 to 50 mM Na_2S with and without $\text{Ca}(\text{OH})_2$), and pH (recovery at 6.5–11). Two separate soils were used in the study, a sandy loam soil having an initial Pb concentration of 15 500 mg/kg, and a loamy sand having an initial Pb concentration of 2,370 mg/kg. In batch studies on the more contaminated soil, extraction of Pb, Zn, and Cu after one cycle were as high as 91%, 60%, and 56%, respectively, for EDTA concentrations in the range of 3 to 20 mM. Batch results on the lower concentration soil indicated removals after one cycle of washing with 50 mM EDTA were 88%, 13%, and 36%, for Pb, Zn, and Cu, respectively. Over six cycles of operation, removal of Pb, Zn, and Cu were 100%, 14% and 48%, respectively. Their results indicated that: (1) better extraction performance was achieved with the higher EDTA concentration and with more washing cycles; (2) metal extraction could be performed with a wide soil slurry content ranging from 5% to 40%; and (3) EDTA could be reclaimed using a slight excess (on a molar basis) of sodium sulfide precipitant at moderately alkaline conditions (e.g. pH \sim 10), and reused over several cycles of operation.

3.6.1. Recovery and reuse of the spent chelating agents

Allen and Chen [2] investigated the electrochemical recovery of heavy metals and EDTA for remediation of lead-contaminated soil. Their study involved extraction of lead from the soil using EDTA and subsequent recovery and reuse of the EDTA. The lead deposited on the electrode in a form that was easily reclaimed for subsequent recycling and reuse. Allen and Chen [2] demonstrated that under diffusion limited conditions of polarography and voltammetry, the free ion protonated metal complexes, M^{2+} and MHY^- , are reused at the electrode surface. Allen and Chen constructed a two-chamber electrolysis cell in which the anode compartment was separated from the cathode compartment by a cation exchange membrane, which prevented the EDTA from being oxidized at the anode during the electrolysis. High recoveries of copper, lead, and EDTA were achieved by electrolysis of Cu–EDTA or Pb–EDTA complexes. The recoveries typically exceeded 95%. As the current density increased, the current efficiency decreased. The current efficiency was greater for free metal ion than for the metal–EDTA complexes. Allen and Chen [2] noted that it will be necessary to have a low current density in order to minimize side reactions and to use an electrolysis cell having a high efficiency.

3.7. Biodegradation of chelating agents

Chelating agents are organic compounds that could be subject to biodegradation under field conditions. The premature biodegradation of these compounds during metal

extraction from soil would be undesirable. In chelant extraction and recovery processes, naturally occurring microorganisms in the soil might metabolize chelating agents, thereby reducing the amount present in solution and the complexing capacity of the chelators. Therefore, the degree of biodegradability of a chelator is an important factor in the selection of chelating agents for soil extraction and in determining the frequency of their reuse. It also enables assessment of the amount required to be added to the extraction solution in each extraction cycle.

Regmi et al. [73] studied the biodegradation of EDTA, *S*-carboxymethyl-L-cysteine (SCMC), and pyridine-2,6-dicarboxylic acid (PDA) under simulated soil remediation conditions. They found that unacclimated microorganisms did not degrade EDTA, but acclimated microorganisms were able to degrade EDTA slowly. Degradation measurements for SCMC and PDA showed similar, but faster, kinetics, with EDTA being the most biostable chelant, followed by SCMC, and by PDA. The measurements also demonstrated that SCMC was metabolized by mixed microbial culture as a carbon source for cellular buildup as indicated by biomass increase and chemical oxygen demand (COD) decrease in solution. PDA was shown to be utilized by microorganisms without lag for their cellular buildup and growth even at the concentration of 1000 mg/l with no dependence upon concentration [73].

3.8. Previous studies involving acid extraction of heavy metals from contaminated soils

Strong acids with concentrations of up to 2 N were used to extract heavy metals from contaminated sandy soils [90]. Commercial pilot-scale systems utilizing HCl have been used to recover lead from contaminated soils; the extraction pH was in the range of 1.8 to 2.2 [55]. Paff [56] has indicated that the results for lead removal from contaminated soil are very soil dependent; removals of lead range anywhere from 50 to 97%, depending on the type of soil and lead present. Legiec [42] performed a series of equilibrium batch extractions using hydrochloric, acetic, and citric acid for removal of lead from contaminated soil. Maximum lead removal occurred with aqueous acidic solutions and ranged from 70 to 89%. Sequential batch extractions performed with dilute HCl solution indicated that most of the lead was removed in the first stage. Results from various soils treated with acidic solutions are summarized below from a study by Burson and Elston [15].

In addition to studying the ability of EDTA, NTA, and pH-adjusted water to extract lead (Pb) from soil, Peters and Shem [66] also investigated the ability of HCl to extract Pb from soil. The lead extracted from the soil is shown in Fig. 2 for the cases involving EDTA, NTA, and HCl. HCl required less time (30 min) to reach pseudo-equilibrium conditions versus the 1.5 and 3.0 h required for EDTA and NTA, respectively. However, HCl was very inefficient in extracting lead from the soil (extracts were typically less than 2 mg/l Pb from that particular soil), which contained a high silt and clay fraction (~ 35%). The Pb extraction ability of HCl was comparable to that of pH-adjusted water [66].

Cline et al. [18] studied the retention and release of lead from various soils using the following extractants: HCl, HNO₃, EDTA, acetic acid, calcium chloride (CaCl₂), in

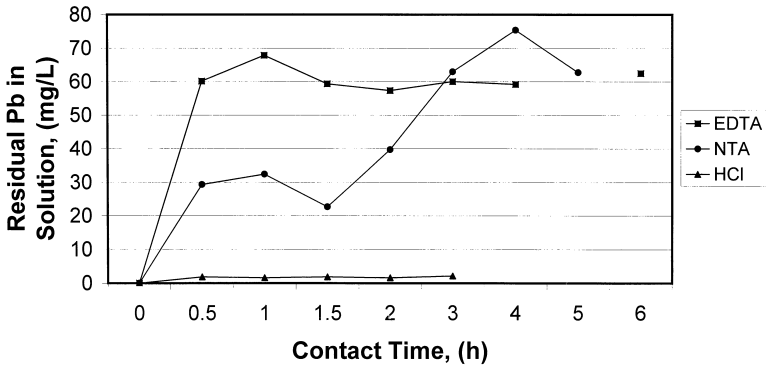


Fig. 2. Lead concentration in solution following extraction of lead from contaminated soil using various extractive agents [66]. Initial Pb concentration = 100 mg/kg soil; initial extractant concentration = 0.2 M.

addition to tap water. EDTA and HCl achieved the highest lead removals (92% and 89%, respectively), followed by HNO_3 (87%), acetic acid (45%), and CaCl_2 (36%). Tap water washes removed only 4.1% of the lead. The average lead removal at the 1000 mg/l contamination level was 14% greater than that of the 10 mg/l contaminations due to the metal binding tightly to a soil's high energy surface sites at low adsorption densities, making Pb removal difficult [18]. HCl and EDTA obtained the best Pb removals in their study. The removals tended to be independent of soil type and washing solution concentration. The researchers speculated that some of the soil components controlled Pb in the HCl washes, and that chelation was the predominant Pb release mechanism for the EDTA washes. The acetic acid and CaCl_2 washes yielded removals that were much lower than those obtained by HCl, EDTA, or HNO_3 . The researchers noted, that although removals by CaCl_2 were the lowest of all the washing solutions investigated, the use of CaCl_2 to remediate heavy metal contaminated soils will not destroy the soil structure, as often occurs with acid treatment [18].

A bench-scale study of seven Pb-contaminated soils from industrial sites was undertaken by Van Benschoten et al. [89] to determine the feasibility of soil washing using hydrochloric acid treatment to meet cleanup goals. In addition, soil characteristics and operation factors affecting washing performance were identified. The soils were characterized using sequential extraction procedures and using scanning electron microscopy. Hydrochloric acid (HCl) was used as the extractant at pH ~ 1, 25°C, a liquid:solid (L/S) ratio of 20:1, and 24 h contact time. Using standard wash conditions, the washed-soil Pb concentrations met the site specific goals of five of the seven soils tested, with the cleanup goal of one other soil almost being met. The density separation methods effectively reduced both total Pb (up to ~ 84% reduction) and Toxicity Characteristics Leaching Procedure (TCLP) concentrations (up to 69% reduction) from the test soils. The lead removals ranged from 22% to 93%, suggesting that lead was bound more strongly in some soils than others. Aging may play a role in Pb binding; real waste-site soils are not expected to have lead in loosely bound forms. The carbonate fraction plus the sum of the oxide fractions (easily reducible, amorphous and crystalline

iron oxides) contained the majority of lead in most cases. All of the treated soils met the TCLP limit of 5.0 mg/l. Soil washing using HCl was effective in treating the Pb-contaminated soils, although low pH was required in most cases. Both leaching kinetics and partitioning of Pb between the solid and aqueous phases was found to be pH dependent. pH and the use of complexing agents were the most important factors in reducing Pb levels in the contaminated soils. Solid/liquid-phase partitioning was influenced more strongly by pH. Operational factors such as EDTA addition significantly improved soil washing performance, and temperature and the L/S ratio had lesser effects for the range of conditions studied. The soil washing performance, interpreted using sequential extraction data, indicated that Pb not removed during soil washing was associated primarily with four sequential extraction fractions: noncrystalline Fe oxides, crystalline Fe oxides, sulfide, and residual.

Atanassova and Okazaki [7] studied copper adsorption/desorption under acid conditions by clay fractions in 0.01 M $\text{Ca}(\text{NO}_3)_2$. The clay soils studied showed pH-dependent adsorption and desorption. The desorption ranged from 2% to 88%, depending on pH and clay type. A considerable amount of sorbed Cu could be solubilized by decreasing the pH to ~ 4 , where desorption ranged from 39% to 45%.

4. Soil washing case histories

4.1. *King of Prussia Technical Corporation site*

The King of Prussia Technical Corporation Site is located in a rural area approximately 30 miles southeast of Philadelphia. The 10-acre site was operated for about 3 years with the intention of converting industrial sludges into materials that could be marketed as construction grade materials. That plan did not materialize, and over the operational period, approximately 15 trillion gallons of sludges were transported and treated at the site. The Remedial Investigation identified soil and groundwater contamination, a Feasibility Study was completed, and the Potentially Responsible Parties (PRPs) Group chose to take the lead responsibility in remediating the site. The Record of Decision (ROD) specified soil washing as the remedial technology to be used to treat the source materials. Five key contaminants (including copper, chromium, and nickel) were identified in the soils and treatment standards were established.

The PRP Group took a strong proactive approach to working with the U.S. Environmental Protection Agency Region II and the New Jersey Department of Environmental Protection (NJDEP) to implement the requirements of the ROD. Substantial time and money could be saved by taking action and completing the requirements. Additionally, because an aggressive approach could move the cleanup forward at a faster pace than the consent order required, the regulators, were interested in being a part of an effort that posted a possible early construction completion. With that goal, several contractors performed initial soil evaluations, and it was clear that several subsources existed at the site: lagoons with pure sludge, lagoons with sludge and soil-like material, and an area of

natural soils with sludge intermittently disposed. Further, the soil matrix, due to its particle size distribution, was a good candidate for volume reduction activities, with about 10–15% fines.

Alternative Remediation Technologies was selected to perform a detailed treatability study in accordance with the Comprehensive Environmental Response Compensation Liability Act (CERCLA). guidance document. The treatability study defined the particle size and contaminant relationships for each source area, examined the nature of the particle and soil relationships using scanning electron microscopy/electron probe microanalysis. In this first phase, the contaminants were found to be primarily bound in the fine-grained fraction of the soils, but in some cases, the coarse-grained fractions also exceeded the treatment standards. Bench-scale tests were conducted to specifically evaluate screening, separation, and treatment steps that could be used in the configured full-scale treatment system. As a result of the treatability study, soil washing was concluded as being very promising and was configured in the report as being able to meet the requirements of the ROD.

During the process equipment and configuration phase of the study, mechanical screening to 30 mesh (500 μm), hydrocycloning, gravity separation, flotation, dewatering, sludge handling, and process testing were performed and documented. After the unit operations were selected, the combined treatment train was operated on a sequential batch basis in the laboratory in a process simulation run. The results of that study provided the basis for development of a system mass balance and design/operational parameters.

To confirm the findings of the treatability study and to provide additional assurance to all parties, a demonstration run was performed using actual King of Prussia site materials at the full-scale Heidemij plant located in Moerdijk, The Netherlands. Approvals were obtained from the U.S. EPA and the Dutch equivalent organization (VROM). The project team (PRPs, U.S. EPA, the soil washing contractor, and the consultant) developed a detailed plan, excavated representative soils totalling 200 tons, packaged the material in 'Super Sacks', loaded the material into transportation containers, and shipped the material to the Port of Rotterdam. The material was then downloaded to the plant and prepared for the demonstration.

The Heidemij plant is a treatment, storage, and disposal (TSD) facility with an annual treatment capacity of about 80 000 tons. The plant consists of all the unit operations to be used at the King of Prussia site and was configured in exactly the same manner as proposed in the King of Prussia treatability study. The treatment included feed preparation, loading, wet screening, hydrocyclone separation, surfactant addition, flotation, and dewatering of the fines. Three process residuals (oversize material, sand, and a dense sludge cake) were produced, staged, examined, sampled, and analyzed. The oversize sand products were intended for placement back on-site and were analyzed for the target contaminants. The sludge cake was disposed at a hazardous waste landfill and was analyzed to confirm compliance with applicable land disposal restrictions. At the time of the documentation [6], the process plant is now in the design phase. Full-scale operations were expected to begin in early 1993. The demonstration run was extremely successful in meeting the stated objectives of confirming that soil washing can effectively treat the King of Prussia soils in compliance with the ROD requirements.

Prior to full-scale operations, a pilot-plant run was performed on 1000 tons of composited site soils. The pilot-plant run was successful and cleanup levels below the ROD-specified standards were reached. The ROD standards are listed below:

- Chromium—483 mg/kg
- Copper—3571 mg/kg
- Nickel—1935 mg/kg

Full-scale operations were begun on June 28, 1993 and ran until mid-October, 1993. During the operation of the soil washing facility, clean soils were returned to the site as backfill. The contaminated fraction was disposed of at an appropriate disposal facility. The site was then revegetated and returned to its natural condition.

4.2. MacGillis and Gibbs site

A Superfund Innovative Technology Evaluation (SITE) program evaluation demonstration was performed using the soil washing technique developed by Biotrol. The site is located in New Brighton, MN. Key contaminants included polyaromatic hydrocarbons (PAHs), pentachlorophenol (PCP), copper, chromium, and arsenic.

The Biotrol soil washing process is a patented, water-based, volume reduction process used to treat excavated soil. The system can be applied to contaminants concentrated in the fine-size fraction of soil (silt, clay, and soil organic matter), or to contamination associated with the coarse (sand and gravel) soil fraction. As a part of the process, debris is removed from the soil, and the soil is mixed with water and subjected to various unit operations common in the mineral processing industry, such as mixing trommels, pug mills, vibrating screens, froth flotation cells, attrition scrubbing, hydrocyclones, screw classifiers, and various dewatering techniques. The core of the process is a multi-stage, countercurrent, intensive scrubbing circuit with interstage classification. The scrubbing action disintegrates soil aggregates, freeing contaminated fine particles from the coarser material. In addition, surficial contamination is removed from the coarse fraction by the abrasive scouring action of the particles themselves. Contaminants can also be solubilized. Residual products that are contaminated can then be treated by other methods. Process water is normally recycled after biological or physical treatment. Options for the contaminated fines include off-site disposal, incineration, stabilization, and biological treatment.

The technology was initially developed to clean soils contaminated with wood preserving wastes such as polynuclear aromatic hydrocarbon (PAHs) and pentachlorophenol (PCP). The technology should also be applicable to soils contaminated with petroleum hydrocarbons, pesticides, polychlorinated biphenyls (PCBs), various industrial chemicals, and heavy metals.

The demonstration took place from September 25 to October 30, 1989. A pilot-scale unit with a treatment capacity of 500 lbs/h was operated 24 h/day during the demonstration. Feed for the first phase of the demonstration (2 days duration) consisted of soil contaminated with 130 ppm PCP and 247 ppm PAHs. During the second phase of the demonstration (7 days duration), soil containing 680 ppm PCP and 404 ppm PAHs was fed to the system.

Contaminated process water from soil washing was treated biologically in a fixed-film reactor and was recycled. A portion of the contaminated fines generated during the soil washing was treated biologically in a three-stage, pilot-scale EIMCO Biolift™ reactor system supplied by the EIMCO Process Equipment.

Key findings from the demonstration are summarized below:

- Feed soil (dry weight basis) was successfully separated into 83% washed soil, 10% woody residues, and 7% fines. The washed soil retained about 10% of the feed soil contamination, while 90% of the feed soil contamination was contained in the woody residue, fines, and process wastes.
- The soil washer removed up to 89% of the PCP and 88% of the total PAHs, based upon the difference between the contaminated (wet) feed soil and the washed soil.
- The system degraded up to 94% of the PCP in the process water during soil washing.
- Cost of a commercial-scale soil washing system (assuming use of all three technologies) was estimated at US\$168/ton. Incineration of the woody material accounted for 76% of that cost.

Because this was a demonstration, there were no treatment standards. Removal of the PCP during soil washing ranged from 87% to 89%. For the PAHs, the removal ranged from 83% to 88%. The bioreactor removed 91% to 94% of the PCP in the influent washwater. Removal efficiencies in the slurry bioreactor increased 90%.

The demonstration showed that the contamination in the bulk of the soil can be greatly reduced. The contaminants were concentrated in a much smaller volume of soil fines than could be successfully treated biologically. The overall operation consisted of three units: the soil washing process, a fixed-film bioreactor to treat process wastewater prior to recycled, and a slurry bioreactor to treat the residuals from the soil washing process.

4.3. U.S. army corps of engineers, Saginaw, MI

Bergmann USA was contracted by the U.S. Army Corps of Engineers to conduct a Pilot Sediment Washing Demonstration on the Saginaw River Project. The site contained 500 tons of contaminated soil, with the key contaminant being PCBs. In this technology, after contaminated soil is screened to remove coarse rock and debris, water and chemical additives (such as surfactants, acids, bases, or chelating agents) are added to the soil to produce a slurry feed. The slurry feed flows to an attrition scrubbing machine. Rotary trommel screens, dense media separators, cyclone separators, and other equipment create mechanical and fluid shear stress, removing contaminated silts and clays from granular soil particles. Different separation processes then create output streams consisting of granular soil particles, silts and clays, and wash water. Upflow classification and separation (also called elutriation) are used to separate light contaminated specific gravity materials (such as contaminated leaves, twigs, roots, or wood chips).

The technology is suitable for treating soils and sediment contaminated with PCBs. It has also been used to treat soils and sediments contaminated with organics and heavy metals (including cadmium, chromium, lead, copper, lead, nickel, zinc, mercury, and radionuclides, in addition to creosote, cyanides, fuel residues, and heavy petroleum.

In-house, bench-scale treatability evaluations were performed, followed by the design and fabrication of a 5–10 ton/h pilot-scale demonstration to effectively separate fines from coarse fractions of river dredge sediments. The pilot-plant was placed in operation in October 1991 a mile and a half aboard a 120 ft × 33 ft U.S. Army Corps of Engineers dredge support barge for the processing of about 500 tons of PCB-contaminated soil.

Preliminary results indicated a reduction of 91% of the initial PCB concentration, with only 0.2 mg/kg of PCBs remaining in the 'clean' coarse (> 74 μm corresponding to > 200 mesh) fraction. The < 74 μm (< 200 mesh) fines were enriched to a level of 14 mg/kg PCBs, and the humic fraction (e.g. leaves, twigs, roots, grasses, etc.) contained 24 mg/kg PCBs. The materials were scheduled for biodegradation during the spring and summer of 1992.

The system was evaluated by the SITE program in May and June 1992. Preliminary analytical tests were available in July 1992, followed by the Applications Analysis Report in August 1992, and the Technology Evaluation Report in February 1993. This 10 ton/h plant processed approximately 200 tons of PCB-contaminated dredge sediments prior to winter. An additional 300 tons of material was washed during the May through June 1992 evaluation period.

4.4. *Toronto Harbor Commission (THC)*

The Toronto Harbor site contained 4400 tons of contaminated sediment; key contaminants included cadmium, arsenic, copper, lead, mercury, zinc, nickel, oil and grease, and polyaromatic hydrocarbons (PAHs).

The demonstration project integrated soil washing, metal extraction by chelation, and organics reduction by upflow air reactors. Two soil washing processes were evaluated, the first using the Bergmann USA chemicals attrition scrubbing system (See the above case history) treating 5–10 tons/h, and the Bodensaneling Nederland (BSN) high pressure wash system operating at 50 tons/h at a wash plant in Holland. The objective was to treat contaminated soil, so that the cleaned soil could be reused on industrial land and the metals removed could be recycled.

The BSN wash system was tested by shipping three 350-ton bagged samples to Holland for washing. Residual soil was returned in bags; the residual slurry with the concentrated contaminants was returned in 2600 forty-five-gallon drums for metal removal and bioremediation. The process studied involved soil washing for volume reduction, then metals reduction, followed by organics reduction by bioremediation. The objective was to meet Ontario Ministry of the Environment standards for cleaning soil for industrial use.

The soil washing systems effectively cleaned the coarse (> 6 mm) and intermediate streams (0.63 to 6 mm) size fractions to meet industrial standards. The metals extraction process was shown to remove heavy metals to meet residential and agricultural standards. The bioremediation process reduced the oil and grease to industrial levels. The estimated cost of a commercial-scale treatment system (50 ton/h) was about US\$25 000 000. The treatment cost was estimated at about US\$175/ton to clean the soil.

4.5. *Poly-Carb site, Wells, NV*

This site is located in Wells, NV; key contaminants include phenol and creosote. The demonstration was performed during 1987–1988. Soils contaminated with phenol and creosote were placed in a double-lined, half-acre leach field. The leach field extraction system contained a water supply, an irrigation system, to distribute water onto the soil, a leachate collection system above the top liner, a holding tank, disposable granular activated carbon cartridges, and pumps. The contaminated soils were treated in a passive soil washing system. Clean water was spray irrigated onto the waste, collected as leachate, and reused. Soil leaching reduced the phenol concentration in the soil by 99.9% and lowered creosols by 99.7%. The influent phenol concentration averaged 980 mg/kg, and after treatment, the concentration was less than 1 mg/kg.

4.6. *Center for hazardous materials research*

The Center for Hazardous Materials Research has been studying the acid extraction treatment system that uses hydrochloric acid to extract contaminants from soils. Following treatment, the soil may be disposed of or used as fill material. The first step involves separation of large particles and gravel from the soil. After coarse particle removal, the remaining soil is scrubbed with an attrition scrubber to break up agglomerates and cleanse surfaces. The sand and silt/clay fractions (< 4 mm) are retained for treatment. HCl is slowly added to the water and soil slurry to achieve and maintain pH < 2. Precautions are taken to avoid lowering the pH significantly below pH 2 and disrupting the soil matrix. The residence time in the unit varies depending on the soil type, contaminants, and contaminant concentrations, but generally ranges between 10 and 40 min. The soil–extractant mixture is continuously pumped out of the mixing tank, and the soil and extractant are separated using hydrocyclones. The extraction solution and rinsewater are regenerated. The regeneration process remove entrained soil, organics, and heavy metals from the extraction fluid. Heavy metals are concentrated in a form potentially suitable for recovery. Recovered acid is recycled to the extraction unit.

This process can extract organic contaminants from soil, but its primary application is the removal of heavy metals such as arsenic, cadmium, chromium, copper, lead, nickel, and zinc from contaminated soil. The process technology can treat all fractions of soils including fines. The major residuals expected from the treatment include the cleaned soil (which is suitable for fill or return to the site, and the heavy metal concentrate. Depending on the concentration of heavy metals found at the site, the mixtures of heavy metals present, and the presence of other compounds (e.g. calcium and sodium) with the heavy metals, heavy metals may be reclaimed from the concentrate. The projected treatment capacity is 30 tons/h. This technology has been tested in the laboratory on a limited, bench-scale basis. The developer has constructed a pilot-scale plant to test the technology on heavy metal-contaminated soils, capable of treating between 20 and 100 kg of soil per hour. Five soils were tested including the EPA synthetic soil matrix, and soils from four Superfund sites (Pedricktown, NJ; King of Prussia, NJ; Butte, MT; and Palmerton, PA). These sites contained elevated concentrations of arsenic, cadmium,

chromium, copper, lead, nickel, and zinc [83]. Preliminary results showed that the process could treat a wide range of soils. Conversations with the technology developer [56] indicated that the process was very good for removal of copper and zinc from soils; the results for lead were variable. Removal of lead ranged from 50% to 97%, depending on the soil and contaminants (i.e. the heavy metal speciation) involved. The treated soil generally passed TCLP tests.

Results from the SITE demonstration are summarized below [83].

- The technology can treat a wide range of soils containing a wide range of heavy metals to reduce the TCLP below the RCRA limit and can reduce the total metals concentrations below the California mandated total metals limitations.

- In most cases, the technology can treat the entire bulk soil, without separate stabilization and disposal of fines and clay particles, to the required TCLP and total limits. The only exception noted [83] among the soils tested was the synthetic soil matrix, which may require separate stabilization and disposal of 20% of the soil to reduce the total TCLP lead concentration appropriately. The technology, however, treated all the other soils successfully for arsenic, cadmium, chromium, copper, nickel, and zinc.

- Costs of treatment under the expected process conditions, range between US\$100 and US\$180/yd³, depending on the site size, soil types and contaminant concentrations. Operating costs ranged from US\$50 to US\$80/yd³.

5. Soil remediation costs

While accurate cost estimates must be done on a site specific basis, there are general cost ranges that can be used to characterize the different soil remediation technologies. Table 5 summarizes the comparative costs of some of the on-site soil waste treatment technologies [8,84]. The soil washing technique can treat both organic- and inorganic-contaminated soils and is one of the lower cost treatment techniques.

Table 5
On-site waste treatment technologies

Technology	Cost (US\$)/yd ³	Waste types treated	
		Organic	Inorganic
Incineration	600–1500	Yes	No
Vitrification	350–450	Yes	Yes
Low-temperature thermal treatment	50–150	Yes	No
High-temperature thermal treatment	100–300	Yes	No
Chemical treatment	250–300	Yes	No
Soil washing	75–200	Yes	Yes
Bioremediation	25–100	Limited	No
Solidification/stabilization	20–100	Limited	Limited

6. field site description

J-Field on the Gunpowder Neck Peninsula at the Aberdeen Proving Ground has contamination resulting from past field activities at the facility. Disposal operations conducted in this region include: toxic burning pits, white phosphorus burning pits, riot control burning pits, South Beach Demolition Ground, South Beach trench, Robins Point Demolition Ground, Robins Point Tower Site, and the Ruins Site. J-Field is relatively flat, with a maximum relief of about 10 ft. The ground surface slopes gently toward marshy areas or toward Chesapeake Bay and on-site surface water. The Toxic Burning Pits (TBP) area is bounded to the northeast by marsh and to the south and southeast by woods and marsh. Because the ground surface elevation is highest in the northwestern portion of the TBP area, surface water drainage probably flows toward the south–southeast into the marsh area. The direction of groundwater flow in the surficial aquifer is also probably toward the marsh. Sieve analyses indicated that the surface soil (the upper 6 in. in the TBP area is mainly silty sand (with a silt/clay fraction of up to 47.1%) and sandy silt (with a silt/clay fraction of up to 64.4%) with an organic content ranging from 1.4% to 10.5%.

The Toxic Burning Pits were used to dispose of munitions, explosives, nerve and chemical agents, mustard gas, liquid smoke, chlorinated solvents, and radioactive chemicals. Three of the burning pits were used to dispose of methylphosphonothioic acid (VX), dichlorodiethyl sulfide (mustard gas), and the primary components of liquid smoke—titanium tetrachloride (FM) and sulfur trioxide/chlorosulfonic acid (FS). In addition, fuel was used to ignite materials placed in the pits. From soil gas measurements collected between 1987 and 1992 by the U.S. Geological Survey, contaminants identified included trichloroethylene, tetrachloroethylene, dichloroethylene, trichloroethane, phthalates, combined hydrocarbons, simple aromatics, and heavy aromatic hydrocarbons. The surface soil contain elevated levels of metals, especially lead (up to 2.6% in places), mercury (up to 10 mg/kg), and cadmium (up to 16.6 mg/kg). Other contaminants include PCBs (up to 143 000 $\mu\text{g}/\text{kg}$), 1,1,2,2-tetrachloroethane (up to 3 270 000 $\mu\text{g}/\text{kg}$), 1,1,2-trichloroethane (up to 8500 $\mu\text{g}/\text{kg}$), tetrachloroethylene (up to 25 700 $\mu\text{g}/\text{kg}$), and trichloroethene (up to 263 000 $\mu\text{g}/\text{kg}$). The highest level of organic compounds were found at a depth of 6 ft.

Soil samples collected in 1983 indicated the presence of lead, zinc, nitrate, and petroleum hydrocarbons in each of the samples, and mercury and cadmium in one of the samples. Lead has been detected both by X-ray fluorescence (XRF) data and atomic absorption data, ranging from non-detectable to 8% lead. The whole area is probably above the 500 mg/kg Pb preliminary clean-up level.

7. Procedures and equipment

Research relating to the soil washing task performed in this study are described below.

Table 6
Analytical procedures or methods for determining physical/chemical characteristics of fill samples

Soil parameter	Method
Total extractable metals	EPA 3050A—methods of soil analysis
TCLP analyses (metals only)	EPA, 40 CFR, Part 261
Cation exchange capacity	EPA 9081—methods of soil analysis (Part 8)
Moisture content (total residue)	Standard methods 209A
Color	Munsell soil color charts
Oxidation reduction potential (ORP)	Standard methods 2580
<i>Particle size characterization</i>	
Size gradation—sieving	ASTM D2487-85 [4]
Particle size analysis—hydrometer	ASTM D422-63 [5]
Particle size analysis	U.S.C.S. ^a
Soil pH	EPA 9045—methods of soil analysis (Part 9)
Organic carbon	Methods of soil analysis (Part 29)

^aParticle size classification are in accordance with the Unified Soil Classification System.

7.1. Physical and chemical soil characterization

Soil samples (background, representative, and worst-case) used in the study were composited over a depth interval of 4 ft. Before being shipped to Argonne, all samples were screened and found to be free of agent materials. Physical and chemical analyses were performed to characterize the soil (see Table 6). Characterization analyses included total extractable metals, TCLP for metals only, cation exchange capacity, soil pH, metal speciation via sequential extraction, moisture content, color, bulk density, soil texture, and particle size analysis.

The soils were analyzed for total extractable metals, TCLP metals, and metal speciation. The sequential extraction procedure (developed by the U.S. Army Corps of Engineers [27] and adapted from Tessier et al. [79]) used to identify the metal speciations is described in Table 7.

7.2. Soil washing

7.2.1. Batch shaker tests

Soils contaminated with heavy metals, primarily lead, were subjected to a series of batch-shaker flask experiments to identify the chelating agents and surfactants that show

Table 7
Heavy metal speciation procedure by sequential extraction

Classification	Extraction reagent and conditions
Exchangeable	1 M MgCl ₂ , 60 min
Carbonate	1 M acetate buffer, pH ~ 5, 5 h
Reducible oxides	0.04 M hydroxylamine hydrochloride in 25% acetic acid, 96°C for 6 h
Organically bound	30% H ₂ O ₂ and 0.02 M HNO ₃ , 85°C for 2 h, followed by extraction with 3.2 M ammonium acetate in 20% HNO ₃
Residual	Concentrated HNO ₃ , 95°C for 8 h

promise in mobilizing lead and other metals from the TBP soils. Chelating and mobilizing agents evaluated included EDTA, citric acid, Citranox, gluconic acid, phosphoric acid, oxalic acid, NTA, and ammonium acetate, in addition to pH-adjusted water. Soil washing experiments were performed by first placing nominal 5-g portions of TBP soils in plastic shaker containers. To these containers, 45 ml of extractant solution (0.01 M, 0.05 M, or 0.1 M) were added. Contact time was maintained at 3 h. This time requirement was determined from a previous study to be adequate for equilibrium conditions to be achieved [66–68]. Following this agitation, the samples were centrifuged in plastic Nalgene centrifuge tubes equipped with snap-on caps, filtered using No. 42 Whatman filter paper, and stored in glass vials maintained at $\text{pH} < 2$ (prepped using ultrapure HNO_3) to await atomic absorption spectrophotometry (AAS) analysis. At least 10 ml of sample was collected for the AAS analysis. The filtrates collected were analyzed for copper, lead, and zinc by AAS. The analyses were performed in accordance with the procedures described in *Standard Methods* [3].

Data collected in these studies included the following: operating temperature, extractant type and concentration, heavy metals concentration on the soil before treatment (and after treatment as determined by calculation), heavy metals concentration in the extract solution after treatment, pH of the solution before and after treatment, and batch shaking time.

7.3. Enhancements to soil washing / soil flushing

These sets of experiments were aimed at improving the performance of soil washing/soil flushing by pretreating the soils before performing soil washing/soil flushing operations. The use of sonication and REDOX manipulation to increase the removal of heavy metals from the Toxic Burning Pits was investigated. Sonication involves the application of high-energy sound waves to degrade organic pollutants and enhance the removal of heavy metals from the soils. A laboratory scale apparatus (Sonics and Materials, VC 600) was used for the sonication treatment. Variables investigated included input power, operation temperature, pH, and addition of chemical enhancements.

The sonication-enhanced soil washing experiments were performed by first placing nominal 5-g portions of TBP soils in 50-ml plastic centrifuge tubes. After 25 ml of deionized water was added to each centrifuge tube, the samples were subjected to sonication for 10 min. Then, the lids to the centrifuge tubes were replaced, and the tubes were centrifuged to separate the solid and liquid phases. Aliquots (5 ml) were collected and analyzed for metals by atomic absorption spectrophotometry. To the solutions remaining in the centrifuge tubes, 25 ml of the 0.05 M chelants (citric acid or EDTA) was added. The extractant solutions were pH-adjusted ($\text{pH} \sim 5$ or $\text{pH} \sim 9$) before being added to the sonication-treated TBP soils. Standard batch-shaker soil washing tests were then performed on the samples to determine the effect of sonication on heavy metal extraction by soil washing.

REDOX manipulation can provide conditions that maximize the solubilities of contaminants and promote their removal. Reducing agents studied included sodium borohydride, sodium metabisulfite, and thiourea dioxide. For some soils, oxidizing agents may enhance metals removal by degrading organometallic complexes and

releasing the metals that have an affinity for natural organic matter. Hydrogen peroxide, sodium percarbonate, sodium hypochlorite, and potassium permanganate were the oxidants evaluated for REDOX manipulation. The oxidizing and reducing agents used were chosen on the basis of their REDOX characteristics, operating conditions (e.g. pH, concentration, etc.), ionic content, and availability.

The oxidizing and reducing agents used for REDOX modification were screened by adding 45-ml aliquots of 1000-ppm solutions of each reagent to nominal 5-g portions of the representative TBP soils. The soil samples were then processed in a manner similar to the batch shaker flask soil washing method. Variables monitored to determine the effect of REDOX manipulation included pH, ORP, and metals removal efficiencies. As the result of the screening tests, sodium borohydride (highest change in ORP), sodium metabisulfite (most common and versatile of the reducing agents studies), and sodium percarbonate (highest lead removal of the oxidants studied) were used to further study the enhanced heavy metal extraction by treating the TBP soils with the REDOX modifiers before performing the chelant extraction procedures.

REDOX modification was combined with chelant extraction to extract copper, lead, and zinc from the representative TBP soil sample. Aliquots (45 ml) of the 1000-ppm solutions of the oxidizing and reducing agents were combined with nominal 5-g portions of the TBP soils. After the required contact time, solid/liquid separation was performed by vacuum filtration. To the residual soils, 45 ml of the 0.05 M chelant (EDTA or citric acid) solutions were added. The chelant extraction step was done according to the soil washing procedure described earlier. Variables measured in the intermediate (following REDOX manipulation) and final (after chelant extraction) samples to quantify and explain the combined REDOX modification/chelant extraction approach included pH, oxidation/reduction potential (ORP), and copper, lead and zinc concentrations.

8. Results and discussion

The soils from a DoD site (Aberdeen Proving Ground) all were generally brownish in color, had a low cation exchange capacity (1.2–4.0 meq/100 g), were slightly alkaline in nature (soil pH in the range of 7.5 to 8.4), had a moderate volatile solids content (2.5–8.8%), and had a sandy loam soil texture. The particle size distributions determined from hydrometer tests were approximately 60% sand, 30% silt, and 10% clay. The total extractable metal characteristics for the three soils from Aberdeen Proving Ground are summarized below in Table 8 for the metals Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn, and As.

These soils contained appreciable copper, lead, zinc, and iron concentrations, and moderate concentrations of chromium and manganese, with minor concentrations of cadmium, mercury, nickel, and arsenic. The results from the TCLP test are summarized below in Table 9 for the 10 metals. The results indicate that both the worst case and representative soils had appreciable leachable Cu, Pb, and Zn concentrations.

Sequential extractions were performed on the 'as-received' soils (worst case and representative) to determine the speciation of the metal forms. This technique speciates the heavy metal distribution into an easily extractable (exchangeable) form, carbonates,

Table 8
Soil characterization results for the Aberdeen Proving Ground J-field soils

Heavy metal	Total extractable metals, (mg/kg)		
	Worst case	Representative	Background
Cd	7.4	6.6	2.2
Cr	238.7	311.7	38.7
Cu	1241.3	1533.2	88.4
Fe	39858.0	48312.3	10913.3
Hg	1.52	1.52	1.39
Mn	203.5	286.3	92.7
Ni	27.7	35.7	4.0
Pb	21560.4	15294.1	56.9
Zn	3729.0	3677.0	64.7
As	17.8	21.8	9.5

reducible oxides, organically bound, and residual forms. Sequential extractions were performed on the worst case and representative bulk soil samples; in addition, sequential extractions were performed on the sand and silt/clay fractions of the worst case soil. The heavy metals analyzed were: Cd, Cu, Cr, Pb, Zn, Mn, Fe, and Ca. The data indicated that most of the metals were amenable to a soil washing technique (i.e. Exchangeable + Carbonate + Reducible Oxides). The metals Cu, Pb, Zn, and Cr had greater than 70% of their distribution in forms amenable to soil washing techniques, while Cd, Mn, and Fe were somewhat less amenable to soil washing using chelant extraction.

The bulk, sand, and silt/clay soil fraction were very similar in their heavy metal distribution. This behavior also indicated that the heavy metals were distributed throughout the soil matrix and were not concentrated in a single soil fraction (such as the clay fraction). As a consequence, pretreatments such as hydrocycloning would not be

Table 9
Toxicity characteristics leaching procedure (TCLP) results for heavy metals at Aberdeen Proving Ground's J-field

Heavy metal	TCLP results (mg/l)			Regulatory level (mg/l)
	Worst case	Representative	Background	
Cd	0.09	0.085	0.02	1.0
Cr	< 0.01	< 0.01	< 0.1	5.0
Cu	5.57	6.86	0.22	–
Fe	0.01	0.18	0.13	–
Hg	0.002	0.002	0.002	0.2
Mn	1.31	3.96	0.52	–
Ni	< 0.1	< 0.1	< 0.1	–
Pb	230.6	113.2	0.48	5.0
Zn	58.0	46.2	0.31	–
As	0.023	0.025	0.038	5.0

effective in an effort of reducing the amount of soil to be treated, since the heavy metals are found in all three soil fractions. The soils were predominantly sand and silt in content; therefore, soil washing and soil flushing techniques should be effective in treating these soils, particularly given that greater than 70% of the metals of concern were present in forms that are conducive to soil washing techniques.

8.1. Batch soil washing experiments

The Aberdeen Proving Ground soils contaminated with heavy metals (primarily lead) were subjected to a series of batch-shaker flask experiments to identify the chelating agents and surfactants that showed promise in mobilizing lead and other heavy metals from the TBP soils. The chelating and mobilizing agents investigated included EDTA, citric acid, Citranox, gluconic acid, phosphoric acid, oxalic acid, NTA, and ammonium acetate, in addition to pH-adjusted water. These chelating agents have been used in other studies as means to solubilize, sequester, and extract heavy metals into solution. The contact time in all the batch shaker flask experiments was maintained at 3 h; preliminary experiments indicated that this time was sufficient to achieve pseudo-equilibrium conditions.

It is important to realize that all eight heavy metals are being extracted simultaneously. Further, some of the concentrations of heavy metals appear to plateau out (i.e. become saturated). It should also be pointed out that the soil contains an appreciable amount of iron; iron is not a serious contaminant of concern, due to its common presence in many soils and groundwaters. Therefore, an important property of the optimum chelating agent is one that minimizes the extraction of iron into solution, while maximizing the extraction of the other heavy metals of concern.

Table 10 summarizes the range and mean extraction efficiencies for the worst-case and representative TBP soils for the eight heavy metals and nine extracting agents used. Note that the data contained in this table neglects the chelating agent concentration used and pH-effects associated with the extractions. As examples, for the representative soil, the overall removal efficiency of zinc was 11.450% for gluconate; at pH ~ 4, the overall removal efficiency was ~ 36.798%, as compared to 3.001% for pH in the range of 7 to 9. Similarly, for the representative soil, the overall removal efficiency of zinc was 14.616% for ammonium acetate; at pH ~ 4, the overall removal efficiency was ~ 30.928%, as compared to 1.977% for pH in the range of 7 to 9.

The removal efficiencies of the various heavy metals from the worst-case and representative soils were generally not statistically different (level of significance (α) > 0.05), indicating that the two soils behaved similarly for their efficacy for extracting heavy metals from them using chelating agents.

Several general trends were observed and are summarized below. In terms of heavy metal removals from the soil employing the various chelating agents, the performance by each chelating agent for the worst-case and representative soil are summarized below.

- Comparison of heavy metal removals from soil using various chelants:

WC soil

EDTA	Cu > Zn > Pb ~ Hg > Cd ≫ Cr > As ~ Fe
Oxalate	Cu ~ Hg > Cd > Zn ~ As > Cr ~ Fe > Pb

Table 10
Comparison of heavy metal removal efficiencies using different chelating agents

Soil sample	Heavy metal	Statistic	% Heavy metal removal											pH-Adjusted H ₂ O		
			EDTA	Oxalate	Citrate	Citrinox	Glucuronate	H ₃ PO ₄	NH ₄ -Ac	NTA						
WC	Cd	Range	8.262–89.252	6.044–18.137	7.743–~ 100	3.687–20.502	2.418–26.114	2.439–9.869	2.322–29.917	2.431–42.717	5.912–7.342					
		Mean	25.811	8.843	40.007	10.402	9.352	5.235	23.189	23.189	6.361					
		Range	24.124–62.996	1.477–32.114	11.394–35.929	2.668–22.545	0.438–22.867	0.265–2.186	0.142–16.487	13.503–45.466	0.077–0.225					
Cu	Cu	Mean	40.574	15.339	23.717	10.351	7.169	1.306	29.375	29.375	0.119					
		Range	23.494–46.123	0.051–0.967	1.599–11.734	0.847–3.701	0.385–14.704	0.008–0.099	0.042–17.297	11.469–92.988	0.008–0.054					
		Mean	31.910	0.390	5.261	1.866	5.319	0.029	2.379	35.530	0.022					
Pb	Pb	Range	16.270–57.692	0.740–11.454	3.163–64.460	1.588–35.137	0.904–41.412	0.472–21.005	0.919–49.586	15.666–53.134	0.272–4.879					
		Mean	36.133	4.963	21.660	14.683	10.867	5.350	11.634	30.543	1.562					
		Range	0.329–3.296	0.020–7.337	0.177–2.184	0.052–1.188	0.042–0.969	0.005–0.069	0.001–0.015	0.193–3.622	0.006–0.013					
Zn	Zn	Mean	1.619	1.511	0.784	0.455	0.214	0.018	1.076	1.076	0.0085					
		Range	0.375–7.661	0.270–9.201	0.319–6.161	0.189–1.964	0.366–6.763	0.371–0.526	0.110–0.846	0.111–5.735	0.183–0.189					
		Mean	3.437	2.061	2.182	0.727	1.523	0.433	0.180	2.186	0.187					
As	As	Range	1.152–2.875	2.322–9.802	1.976–9.549	0.165–2.249	0.392–1.306	0.539–1.492	0.064–0.257	0.129–0.880	0.245–2.273					
		Mean	1.684	4.837	4.892	0.706	0.587	0.889	0.120	0.391	1.212					
		Range	2.322–~ 100	2.080–42.922	1.191–90.906	1.170–31.422	0.704–18.691	1.723–42.059	1.127–26.577	1.330–25.423	1.187–5.912					
Hg	Hg	Mean	31.611	14.245	18.245	8.364	5.134	7.631	3.360	7.716	2.649					
		Range	6.796–41.603	6.855–14.012	8.471–~ 100	2.703–35.426	2.701–33.546	2.701–11.018	2.628–25.530	4.090–40.284	6.596–7.192					
		Mean	23.605	8.859	40.735	10.959	12.071	5.926	9.466	24.729	6.796					
REP	Cu	Range	26.463–61.847	1.645–26.342	11.553–68.623	2.169–17.181	0.385–25.484	0.244–1.594	0.114–9.974	13.417–41.286	0.099–0.176					
		Mean	45.546	12.001	23.949	7.020	7.448	0.915	2.071	27.431	0.136					
		Range	20.421–~ 100	0.104–1.633	1.058–12.426	0.333–2.181	0.066–12.547	0.011–0.922	0.025–8.868	12.569–77.988	0.025–0.048					
Pb	Pb	Mean	37.804	0.496	3.828	0.969	2.452	1.05	1.354	34.545	0.033					
		Range	20.489–92.893	0.793–12.789	1.386–42.015	1.486–45.481	1.360–44.006	0.273–9.202	0.611–48.240	2.375–50.386	0.420–1.327					
		Mean	36.752	4.832	16.535	14.194	11.450	3.731	9.215	24.570	0.668					
Zn	Zn	Range	0.616–6.156	0.040–8.674	0.349–3.260	0.030–1.480	0.093–0.928	0.003–0.053	0.001–0.078	0.001–0.079	0.001–0.013					
		Mean	1.743	1.288	0.494	0.279	0.0136	0.0207	0.0207	0.0065	0.0165					
		Range	0.729–8.888	0.232–6.338	0.382–4.678	0.143–1.500	0.281–6.866	0.266–2.625	0.064–0.574	0.322–3.621	0.139–0.223					
Fe	Fe	Mean	3.565	1.620	1.718	0.587	1.423	0.515	1.333	2.100	0.165					
		Range	0.292–4.113	1.186–9.057	1.719–5.585	0.220–1.541	0.080–3.043	0.368–0.714	0.057–0.159	0.145–0.650	0.159–1.653					
		Mean	1.204	3.500	3.414	0.616	0.757	0.569	0.087	0.385	0.5645					
As	As	Range	1.150–90.334	1.689–~ 100	1.226–36.717	1.188–31.068	0.878–10.333	1.912–16.559	1.141–12.471	1.142–1.249						
		Mean	20.488	32.614	13.351	11.294	1.874	5.249	3.942	23.280	1.1805					
		Range	6.796–41.603	6.855–14.012	8.471–~ 100	2.703–35.426	2.701–33.546	2.701–11.018	2.628–25.530	4.090–40.284	6.596–7.192					

Citrate	Cd > Cu > Zn > Hg ≫ Pb ~ As > Cr ~ Fe
Citranox	Zn > Cd ~ Cu > Hg ≫ Pb > Cr ~ As > Fe
Gluconate	Zn ~ Cd > Cu > Pb ~ Hg > Cr > As ~ Fe
H ₃ PO ₄	Hg > Zn ~ Cd > Cu > As > Cr ≫ Pb ~ Fe
NH ₄ -Ac	Cd ≫ Zn ≫ Hg ~ Cu ~ Pb > Cr ~ As > Fe
NTA	Pb > Zn ~ Cu > Cd ≫ Hg > Cr ~ Fe > As
pH-adjusted H ₂ O	Cd > Hg > Zn ~ As ≫ Cr ~ Cu > Pb ~ Fe

REP soil

EDTA	Cu > Pb ~ Zn > Cd ~ Hg ≫ Cr ~ Fe ~ As
Oxalate	Hg ≫ Cu > Cd > Zn ~ As > Cr ~ Fe > Pb
Citrate	Cd ≫ Cu ≫ Zn ~ Hg ≫ Pb ~ As ~ Cr > Fe
Citranox	Zn > Hg ~ Cd > Cu ≫ Pb ~ As ~ Cr > Fe
Gluconate	Cd ~ Zn > Cu ≫ Pb ~ Hg ~ Cr > As > Fe
H ₃ PO ₄	Cd ~ Hg > Zn ≫ Cu > As ~ Cr > Pb ~ Fe
NH ₄ -Ac	Cd ~ Zn ≫ Hg > Cu ~ Pb > Cr ~ As ~ Fe
NTA	Pb > Cu > Cd ~ Zn ~ Hg ≫ Cr > As ~ Fe
pH-adjusted H ₂ O	Cd > Hg > Zn ~ As > Fe ~ Cr ~ Cu > Pb

Conversely, the effectiveness of the various chelating agents for removal of specific metals from the soil is summarized below (in terms of heavy metal concentrations contained in the extracts).

- Chelating agent comparison for heavy metal concentrations in chelant extract:

WC soil

Cd	Citrate ≫ EDTA ~ NTA > Citranox ~ Gluconate ~ Oxalate > pH-adjusted H ₂ O ~ H ₃ PO ₄ ~ NH ₄ -Ac
Cu	EDTA > NTA > Citrate > Oxalate > Citranox > Gluconate ≫ NH ₄ -Ac ~ H ₃ PO ₄ > pH-adjusted H ₂ O
Pb	NTA > EDTA ≫ Citrate ~ Gluconate > NH ₄ -Ac ~ Citranox > Oxalate ≫ H ₃ PO ₄ ~ pH-adjusted H ₂ O
Zn	EDTA > NTA > Citrate > Citranox > NH ₄ -Ac ~ Gluconate ≫ H ₃ PO ₄ ~ Oxalate > pH-adjusted H ₂ O
Fe	EDTA ~ Oxalate ~ NTA > Citrate ~ Citranox > Gluconate > H ₃ PO ₄ ~ NH ₄ -Ac ~ pH-adjusted H ₂ O
Cr	NTA > EDTA ~ Citrate ~ Oxalate > pH-adjusted H ₂ O > Gluconate > Citranox ≫ H ₃ PO ₄ ~ NH ₄ -Ac
As	Citrate ~ Oxalate > EDTA > pH-adjusted H ₂ O > H ₃ PO ₄ > Citranox ~ Gluconate > NTA > NH ₄ -Ac
Hg	EDTA > Citrate > Oxalate ~ Citranox ~ NTA > H ₃ PO ₄ ~ Gluconate > pH-adjusted H ₂ O ~ NH ₄ -Ac

REP soil

Cd	Citrate ≫ NTA ~ EDTA > Gluconate ~ Citranox ~ NH ₄ -Ac ~ Oxalate ~ pH-adjusted H ₂ O > H ₃ PO ₄
Cu	EDTA ≫ NTA > Citrate > Oxalate > Citranox ~ Gluconate > NH ₄ -Ac ~ H ₃ PO ₄ > pH-adjusted H ₂ O

Pb	EDTA ~ NTA ≫ Citrate > Gluconate > Oxalate ~ NH ₄ -Ac ~ Citranox > H ₃ PO ₄ ~ pH-adjusted H ₂ O
Zn	EDTA > NTA > Citrate ~ Citranox > Gluconate ~ Oxalate ~ NH ₄ -Ac ~ H ₃ PO ₄ > pH-adjusted H ₂ O
Fe	EDTA ~ Oxalate ~ Citrate > Citranox ~ Gluconate > H ₃ PO ₄ ~ NH ₄ -Ac ~ NTA ~ pH-adjusted H ₂ O
Cr	EDTA > NTA > Citrate ~ Oxalate > Gluconate ~ Citranox > H ₃ PO ₄ > pH-adjusted H ₂ O ~ NH ₄ -Ac
As	Citrate > Oxalate > EDTA > Gluconate > Citranox ~ pH-adjusted H ₂ O ~ H ₃ PO ₄ > NTA > NH ₄ -Ac
Hg	Oxalate ~ NTA ~ Citrate > Citranox > EDTA ~ NH ₄ -Ac > H ₃ PO ₄ ~ Gluconate ~ pH-adjusted H ₂ O

The effectiveness of the various chelating agents (in terms of overall heavy metal removal) are listed for each heavy metal below:

- Chelating agent comparison for heavy metal removal:

WC soil

Cd	Citrate ≫ EDTA ~ NTA ~ NH ₄ -Ac ≫ Citranox ~ Gluconate ~ Oxalate > pH-adjusted H ₂ O ~ H ₃ PO ₄
Cu	EDTA ≫ NTA > Citrate > Oxalate > Citranox > Gluconate ≫ NH ₄ -Ac ~ H ₃ PO ₄ > pH-adjusted H ₂ O
Pb	NTA > EDTA ≫ Gluconate ~ Citrate > NH ₄ -Ac ~ Citranox > Oxalate > H ₃ PO ₄ ~ pH-adjusted H ₂ O
Zn	EDTA > NTA > Citrate > Citranox > NH ₄ -Ac ~ Gluconate > H ₃ PO ₄ ~ Oxalate > pH-adjusted H ₂ O
Fe	EDTA ~ Oxalate > NTA ~ Citrate > Citranox > Gluconate > H ₃ PO ₄ ~ NH ₄ -Ac ~ pH-adjusted H ₂ O
Cr	EDTA > NTA ~ Citrate ~ Oxalate > Gluconate > Citranox > H ₃ PO ₄ ~ NH ₄ -Ac ~ pH-adjusted H ₂ O
As	Citrate ~ Oxalate > EDTA ~ pH-adjusted H ₂ O > H ₃ PO ₄ ~ Citranox ~ Gluconate ~ NTA > NH ₄ -Ac
Hg	EDTA > Citrate > Oxalate > Citranox ~ NTA ~ H ₃ PO ₄ > Gluconate > NH ₄ -Ac ~ pH-adjusted H ₂ O

REP soil

Cd	Citrate ≫ NTA ~ EDTA > Gluconate ~ Citranox ~ NH ₄ -Ac ~ Oxalate > pH-adjusted H ₂ O ~ H ₃ PO ₄
Cu	EDTA ≫ NTA > Citrate > Oxalate > Gluconate ~ Citranox > NH ₄ -Ac > H ₃ PO ₄ > pH-adjusted H ₂ O
Pb	EDTA > NTA ≫ Citrate ~ Gluconate ~ NH ₄ -Ac ~ Citranox > Oxalate > H ₃ PO ₄ ~ pH-adjusted H ₂ O
Zn	EDTA > NTA > Citrate ~ Citranox ≫ Gluconate ~ NH ₄ -Ac > Oxalate ~ H ₃ PO ₄ > pH-adjusted H ₂ O
Fe	EDTA ~ Oxalate > Citrate > Citranox ~ H ₃ PO ₄ ~ NH ₄ -Ac ~ pH-adjusted H ₂ O > Gluconate ~ NTA

Cr	EDTA > NTA ~ Citrate ~ Oxalate ~ Gluconate > Citranox ~ H ₃ PO ₄ > pH-adjusted H ₂ O ~ NH ₄ -Ac
As	Oxalate ~ Citrate > EDTA > Gluconate > Citranox ~ pH-adjusted H ₂ O ~ H ₃ PO ₄ > NTA > NH ₄ -Ac
Hg	Oxalate > NTA > EDTA > Citrate ~ Citranox > H ₃ PO ₄ ~ NH ₄ -Ac > Gluconate ~ pH-adjusted H ₂ O

To summarize the trends observed, of the chelating agents investigated, EDTA and citric acid appeared to offer the greatest potential as chelating agents to use in soil washing Aberdeen Proving Ground soils. NTA was also a very effective chelant; however, it is a Class II carcinogen, and as such would probably not be used in remediating the site. The other chelating agents studied (gluconate, oxalate, Citranox, ammonium acetate, and phosphoric acid, along with pH-adjusted water) were generally ineffective in mobilizing the heavy metals from the soils. It is particularly interesting to note that phosphoric acid was generally one of the least effective extractants used in this study, despite being a strong acid.

8.2. Columnar chelant extraction studies

Soil flushing/column flooding experiments were performed using contaminated soil that had been hand-packed in the soil columns. EDTA and citric acid were employed as the chelating agents during these studies. The experimental procedure for conducting these experiments has been previously summarized. Enhanced removal of copper, lead, and zinc was observed in these soil column flooding experiments for the EDTA extraction system; however, chelant column flooding extraction by citric acid alone resulted in better heavy metal removal over the case where contaminated soil was first pretreated with sodium borohydride.

Experiments were performed using EDTA and citric acid columnar extraction of copper, lead, and zinc with and without REDOX manipulation (using sodium borohydride) as a function of pore volume throughput. In both cases, EDTA resulted in better heavy metal removal as compared against citric acid.

8.3. Sequential batch chelant extraction studies

Due to the observation from both the batch shaker test study and the columnar chelant soil washing study that the solutions became nearly saturated, several batch experiments were performed in which the soil was repeated subjected to chelant extraction, followed by washing with deionized water. A total of six cycles of operation were performed to monitor the extraction of the three primary heavy metals of concern (copper, lead, and zinc) as a function of the number of extractions performed.

In order to compare the results of the metal speciations via sequential extractions, six stage batch extractions were performed using the worst-case soil. In addition, TCLP tests were performed on the untreated soil and on the soils after the first-, third-, and fifth-stage extractions, respectively. The results, describing the concentrations of heavy

metals remaining in the soil, removal efficiency of the heavy metals, and TCLP vs. number of stage extractions for lead, copper, and zinc, are presented in Table 11 and Figs. 3–5.

The results show that the heavy metals, Cu and Zn, present as exchangeable and carbonate fractions, are completely extracted in the first extraction stage (see Figs. 4 and 5), whereas these same fraction for Pb were not extracted until after the second stage of extraction (see Fig. 3). Removal of Pb, Cu, and Zn present are exchangeable, carbonates, and reducible oxides occurred between the fourth- and fifth-stage extractions. Also between these two extraction stages, the Pb TCLP passed the EPA limit for lead of 5.0 mg/l (Fig. 3). The corresponding Pb removal at this point was 86.1%, and the residual

Table 11
Multi-stage batch extractions with EDTA for Pb, Cu, and Zn on the TBP worst-case soil

Contaminant concentration	Pb	Cu	Zn
Untreated soil—total extractable metals (mg/kg)	21560.4	1241.3	3729.0
Exchangeable + carbonates (%)	57.80	44.93	54.92
Exchangeable + carbonates + Reducible oxides (%)	81.71	87.91	89.18
Organic + residual (%)	18.28	12.09	10.82
TCLP (0) (mg/l)	340.91	5.71	56.07
<i>After 1st washing</i>			
Metal concentration remaining in soil (mg/kg)	13000.0	668.89	1365.15
Heavy metal removal (%)	49.94	54.63	63.39
TCLP (1) (mg/l)	30.39	2.95	6.38
<i>After 2nd washing</i>			
Metal concentration remaining in soil (mg/kg)	10137.4	390.45	737.50
Heavy metal removal (%)	60.96	73.52	79.33
TCLP (2) (mg/l)	NA	NA	NA
<i>After 3rd washing</i>			
Metal concentration remaining in soil (mg/kg)	8063.2	264.37	489.04
Heavy metal removal (%)	68.95	82.07	86.46
TCLP (3) (mg/l)	29.31	0.32	1.31
<i>After 4th washing</i>			
Metal concentration remaining in soil (mg/kg)	7327.5	209.11	386.77
Heavy metal removal (%)	71.78	85.82	89.41
TCLP (4) (mg/l)	NA	NA	NA
<i>After 5th washing</i>			
Metal concentration remaining in soil (mg/kg)	3383.5	112.68	208.36
Heavy metal removal (%)	86.97	92.36	93.95
TCLP (5) (mg/l)	1.56	0.14	0.49
<i>After 6th washing</i>			
Metal concentration remaining in soil (mg/kg)	297.18	15.85	74.02
Heavy metal removal (%)	98.86	98.92	97.20
TCLP (6) (mg/l)	NA	NA	NA

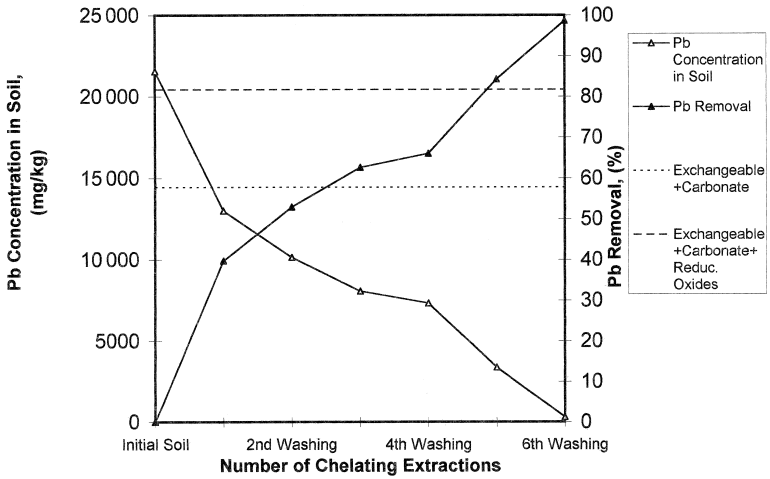


Fig. 3. Multi-stage batch extraction of TBP worst-case soil using EDTA–Pb extraction.

concentration of Pb remaining in the soil was about 3400 mg/kg, well above the EPA Total Extractable Metal Limit for Pb of 500 mg/kg. However, by treating with a sixth EDTA extraction stage (operated at pH ~ 9), the residual lead concentration was reduced to about 300 mg/kg (thereby passing the EPA Total Extractable Metal Limit). After the sixth stage of treatment, the residual concentrations of Pb, Cu, and Zn in the soil were approximately 300, 16, and 75 mg/kg, respectively. The overall removals of copper, lead, and zinc from the multiple-stage soil washing were 98.9%, 98.9%, and 97.2%, respectively, using EDTA as the chelant. Note during the conduct of these

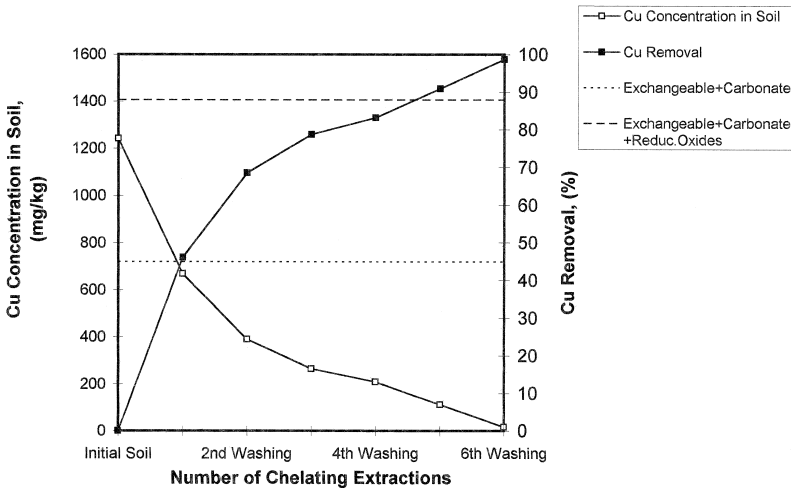


Fig. 4. Multi-stage batch extraction of TBP worst-case soil using EDTA–Cu extraction.

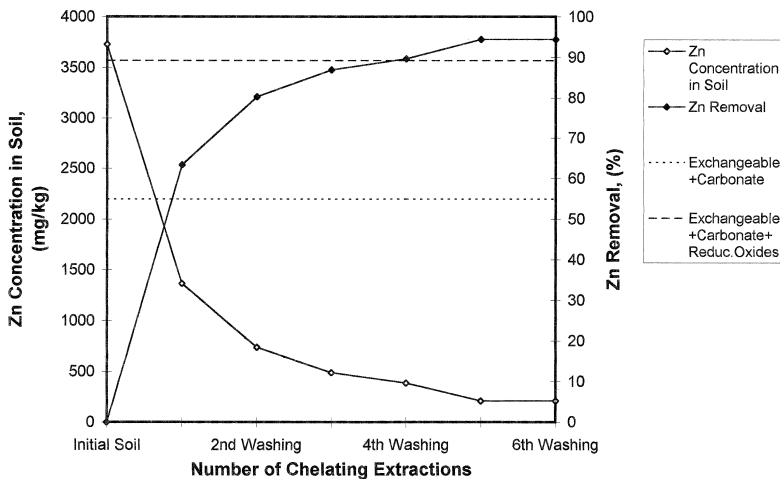


Fig. 5. Multi-stage batch extraction of TBP worst-case soil using EDTA–Zn extraction.

experiments, the concentration and operating conditions for the extractions were not necessarily optimized. If the conditions had been optimized, it is the belief of this researcher that the TCLP and residual heavy metal concentrations could probably be met

Table 12
Effect of REDOX manipulation

REDOX agent	Chelant	Removal increase (%)		
		Copper	Lead	Zinc
Sodium borohydride	EDTA	0	1.4	5.7
Sodium metabisulfite	EDTA	6.3	0	13.7
Sodium percarbonate	EDTA	2.7	0	4.0
Sodium borohydride	Citric Acid	0	3.5	27.0
Sodium metabisulfite	Citric Acid	0.6	0	20.5
Sodium percarbonate	Citric Acid	0	2.6	24.8

The results from the REDOX manipulation followed by chelant extraction are summarized as follows:

Copper	EDTA: metabisulfite > percarbonate > borohydride Citrate: metabisulfite > percarbonate ~ borohydride
Lead	EDTA: borohydride > metabisulfite ~ percarbonate Citrate: borohydride > percarbonate > metabisulfite
Zinc	EDTA: metabisulfite ≫ borohydride > percarbonate Citrate: metabisulfite > borohydride ≫ percarbonate
Overall	EDTA: metabisulfite ≫ borohydride ~ percarbonate Citrate: metabisulfite ~ borohydride ~ percarbonate

within three or four extractions. The above results, however, show that it is very possible to treat the J-Field contaminated soils using a soil washing technique; the treated soil can meet EPA's TCLP and Total Extractable Metal Limits.

8.4. REDOX manipulation

Initial screening experiments were performed investigating sodium borohydride, sodium metabisulfite, thiourea dioxide, hydrogen peroxide, sodium percarbonate, sodium hypochlorite, and potassium permanganate, for their effectiveness in solubilizing contaminants from the soil matrix. The results of these screening tests identified the following REDOX agents to pursue in further studies: sodium borohydride (highest change in ORP), sodium metabisulfite (most common and versatile of the reducing agents studied), and sodium percarbonate (highest lead removal of the oxidants studied).

Results presented in Table 12 indicate that lead and copper removal by chelant extraction with EDTA and citric acid was minimally affected by pretreatment with sodium borohydride, sodium metabisulfite, and sodium percarbonate. Zinc removal by the stronger chelant (EDTA) was slightly increased by each REDOX agent studied. The reagents used for REDOX manipulation significantly improved the performance of citric acid for removing zinc from the worst-case TBP soils.

Figs. 6–8 summarize the results of soil washing/soil flushing (i.e. EDTA and citric acid) and enhancement to soil washing/soil flushing portions of this study. The results indicated that EDTA was much more effective than citric acid for removing copper, lead, and zinc from the worst-case TBP soils. For chelant extraction with EDTA, the removal efficiencies of copper, lead and zinc tended to plateau at values comparable to

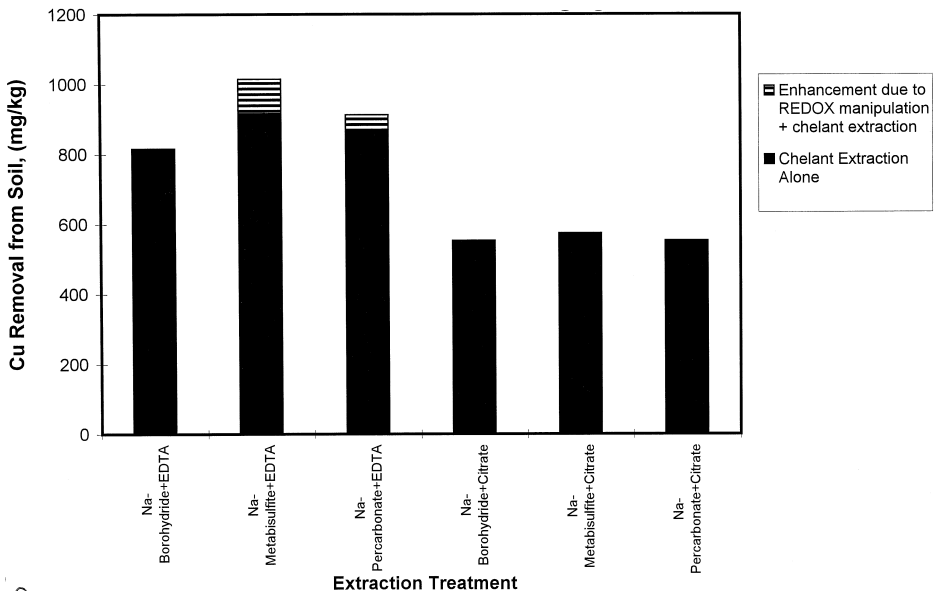


Fig. 6. Copper removal by REDOX manipulation and chelant extraction.

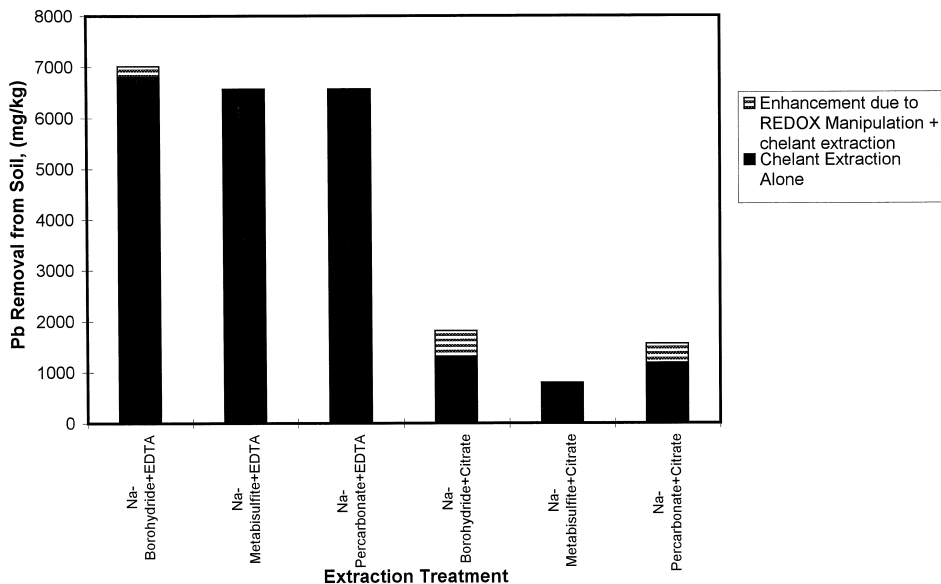


Fig. 7. Lead removal by REDOX Manipulation and chelant extraction.

the forms present as exchangeable and carbonate species. The results in Fig. 8 indicated that REDOX manipulation combined with chelant extraction with citric acid can be used to achieve zinc removal efficiencies comparable to those of EDTA. Depending on the

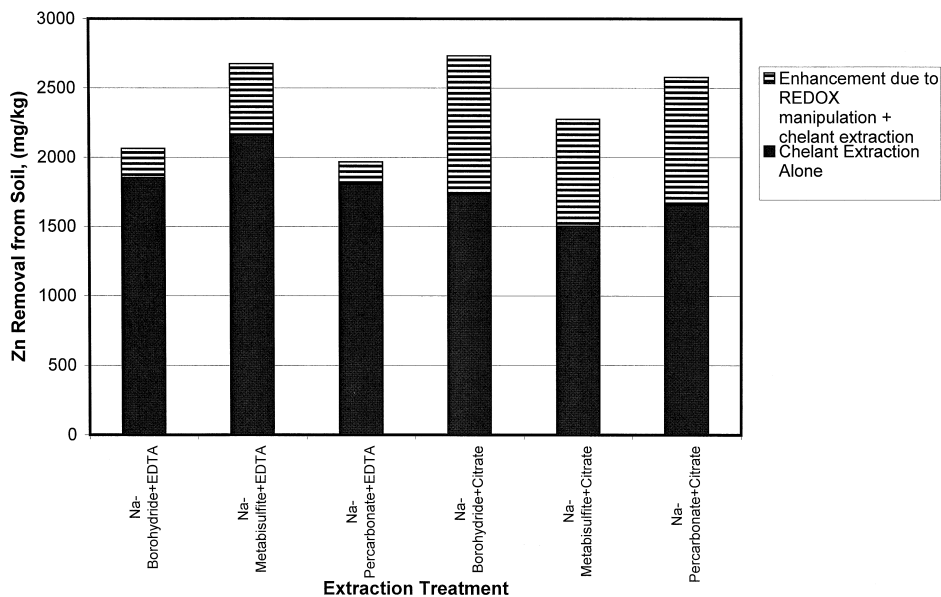


Fig. 8. Zinc removal by REDOX manipulation and chelant extraction.

method used to treat the heavy metal-containing extraction solutions, it may be desirable to use REDOX manipulation and mild chelation in place of EDTA. Because it is more difficult to remove heavy metals from extraction solution containing EDTA, the citrate-containing effluent will be easier to treat by conventional wastewater treatment technologies. Treatment of the citrate-containing effluent may result in citrate recovery and reuse.

9. Summary and conclusions

Characterization of the worst-case and representative soils from Aberdeen Proving Ground's J-Field indicated that the soils were generally brownish in color, have a low cation exchange capacity (1.4–4.0 meq/100 g), are slightly alkaline in nature (soil pH in the range of 7.5 to 8.4), have a moderate volatile solids content (2.5% to 8.8%), and have a sandy loam soil texture. The particle size distribution characteristics of the soils determined from hydrometer tests are approximately 60% sand, 30% silt, and 10% clay.

Sequential extractions were performed on the 'as-received' soils (worst case and representative) to determine the speciation of the metal forms. The technique speciates the heavy metal distribution into an easily extractable (exchangeable) form, carbonates, reducible oxides, organically-bound, and residual forms. The results indicated that most of the metals are in forms that are amenable to soil washing (i.e. exchangeable + carbonate + reducible oxides). The metals Cu, Pb, Zn, and Cr have greater than 70% of their distribution in forms amenable to soil washing techniques, while Cd, Mn, and Fe are somewhat less amenable to soil washing using chelant extraction. However, the concentrations of Cd and Mn are low in the contaminated soil.

From the batch chelant extraction studies, EDTA, citric acid, and NTA were all effective in removing copper, lead, and zinc from the J-Field soils. Due to NTA being a Class II carcinogen, it is not recommended for use in remediating contaminated soils. EDTA and citric acid appear to offer the greatest potential as chelating agents to use in soil washing the Aberdeen Proving Ground soils. The other chelating agents studied (gluconate, oxalate, Citranox, ammonium acetate, and phosphoric acid, along with pH-adjusted water) were generally ineffective in mobilizing the heavy metals from the soils. The chelant solution remove the heavy metals (Cd, Cu, Pb, Zn, Fe, Cr, As, and Hg) simultaneously.

Sonication was ineffective in enhancing the heavy metal extraction efficiencies associated with chelant extraction. Although sonication may have mobilized the heavy metals from the soil matrix, it is likely that the metals re-adsorbed back onto the soil matrix during the solid/liquid separation phase for analysis.

REDOX manipulation offers potential to enhance the removal of heavy metals associated with chelant extraction. Of the oxidizing and reducing agents studied, sodium borohydride, sodium metabisulfite, and sodium percarbonate enhanced removal of copper, lead, and zinc during screening experiments. Due to the ability to enhance the oxidation/reduction potential (ORP), sodium borohydride was selected for further study and was used in conjunction with the soil flooding experiments. Enhanced removal of copper, lead, and zinc was observed in these soil column flooding experiments for the EDTA extraction system.

Using a multiple-stage batch extraction, the soil was successfully treated passing both the TCLP and EPA Total Extractable Metal Limit. The final residual Pb concentration was about 300 mg/kg, with a corresponding TCLP of 1.5 mg/l. Removal of the exchangeable and carbonate fractions for Cu and Zn was achieved during the first extraction stage, whereas it required two extraction stages for the same fractions for Pb. Removal of Pb, Cu, and Zn present as exchangeable, carbonates, and reducible oxides occurred between the fourth- and fifth-stage extractions. The overall removal of copper, lead, and zinc from the multiple-stage washing were 98.9%, 98.9%, and 97.2%, respectively. The concentration and operating conditions for the soil washing extractions were not necessarily optimized. If the conditions had been optimized and using a more representative Pb concentration ($\sim 12\,000$ mg/kg), it is likely that the TCLP and residual heavy metal soil concentrations could be achieved within two to three extractions. The results indicate that the J-Field contaminated soils can be successfully treated using a soil washing technique.

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