



## Engineering Bulletin

# Technology Alternatives for the Remediation of Soils Contaminated with As, Cd, Cr, Hg, and Pb

### Purpose

Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the U.S. Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practical" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants, and contaminants as a principal element." The *EPA Engineering Bulletins* are a series of documents that summarize the available information on selected treatment and site remediation technologies and related issues. They provide summaries and references of the latest information to help remedial project managers, on-scene coordinators, contractors, and other site cleanup managers understand the type of data and site characteristics needed to evaluate a technology for potential applicability to their hazardous waste sites. Documents that describe individual site remediation technologies focus on remedial investigation scoping needs. Addenda are issued periodically to update the original bulletins.

### Introduction

This bulletin provides remedial project managers, on-scene coordinators, and other state or private remediation managers and their technical support personnel with information to facilitate the selection of appropriate remedial alternatives for soil contaminated with arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb). This bulletin primarily condenses information that is included in a more comprehensive Technical Resource Document (TRD) entitled "Contaminants and Remedial Options at Selected Metal-Contaminated Sites [1]".

Common compounds, transport, and fate are discussed for each of the five elements. A general description of metal-con-

taminated Superfund soils is provided. The technologies covered are immobilization [containment (caps, vertical barriers, horizontal barriers), solidification/stabilization (cement-based, polymer microencapsulation), and vitrification]; and separation and concentration (soil washing, pyrometallurgy, and soil flushing). Use of treatment trains is also addressed.

Electrokinetics is addressed in the technical resource document, but not here, since it had not been demonstrated at full scale in the U.S. for metals remediation. Also, an update on the status of in situ electrokinetics for remediation of metal-contaminated soil is in progress and should be available in the near fu-

Contents	
Section	Page
Purpose .....	1
Introduction .....	1
Overview of As, Cd, Cr, Hg, Pb, and Their Compounds .....	2
General Description of Superfund Soils Contaminated with As, Cd, Cr, Hg, and Pb .....	3
Soil Cleanup Goals for As, Cd, Cr, Hg, and Pb .....	3
Technologies for Containment and Remediation of As, Cd, Cr, Hg, and Pb in Soils .....	4
Specific Remedial Technologies .....	5
Use of Treatment Trains .....	15
Cost Ranges of Remedial Technologies .....	16
Sources of Additional Information .....	17
Acknowledgements .....	18
References .....	18

ture [2]. Another change from the original technical resource document is that physical separation is addressed in the bulletin under soil washing, whereas it was previously covered as a separate topic.

It is assumed that users of this bulletin will, as necessary, familiarize themselves with (1) the applicable or relevant and appropriate regulations pertinent to the site of interest; (2) applicable health and safety regulations and practices relevant to the metals and compounds discussed; and (3) relevant sampling, analysis, and data interpretation methods. The majority of the information on which this bulletin is based was collected during 1992 to 1994. Information on Pb battery (Pb, As), wood preserving (As, Cr), pesticide (Pb, As, Hg), and mining sites is limited, as it was in the original technical resource document. Most of these site types have been addressed in other EPA Superfund documents [3][4][5][6][7][8]. The greatest emphasis is on remediation of inorganic forms of the metals of interest. Organometallic compounds, organic-metal mixtures, and multimetal mixtures are briefly addressed.

At the time of this printing, treatment standards for Resource Conservation and Recovery Act (RCRA) wastes that contain metals (in 40 CFR 268) and for contaminated media (in 40 CFR 269) are being investigated for potential revisions. These revisions may impact the selection of the technology for remediating sites containing these metal-bearing wastes.

## Overview of As, Cd, Cr, Hg, and Pb and Their Compounds

This section provides a brief, qualitative overview of the physical characteristics and mineral origins of the five metals, and factors affecting their mobility. More comprehensive and quantitative reviews of the behavior of these five metals in soil can be found in other readily available EPA Superfund documents [1][9][10].

### Overview of Physical Characteristics and Mineral Origins

**As** is a semimetallic element or metalloid that has several allotropic forms. The most stable allotrope is a silver-gray, brittle, crystalline solid that tarnishes in air. As compounds, mainly  $As_2O_3$ , can be recovered as a by-product of processing complex ores mined mainly for copper, Pb, zinc, gold, and silver. As occurs in a wide variety of mineral forms, including arsenopyrite ( $FeAsS_4$ ), which is the main commercial ore of As worldwide.

**Cd** is a bluish-white, soft, ductile metal. Pure Cd compounds rarely are found in nature, although occurrences of greenockite ( $CdS$ ) and otavite ( $CdCO_3$ ) are known. The main sources of Cd are sulfide ores of Pb, zinc, and copper. Cd is recovered as a by-product when these ores are processed.

**Cr** is a lustrous, silver-gray metal. It is one of the less common elements in the earth's crust, and occurs only in compounds. The chief commercial source of Cr is the mineral chromite ( $FeCr_2O_4$ ). Cr is mined as a primary product and is not recovered as a by-product of any other mining operation. There are no chromite ore reserves, nor is there primary production of chromite in the U.S..

**Hg** is a silvery, liquid metal. The primary source of Hg is cinnabar ( $HgS$ ), a sulfide ore. In a few cases, Hg occurs as the principal ore product; it is more commonly obtained as the by-product of processing complex ores that contain mixed sulfides, oxides, and chloride minerals (these are usually associated with

base and precious metals, particularly gold). Native or metallic Hg is found in very small quantities in some ore sites. The current demand for Hg is met by secondary production (i.e., recycling and recovery).

**Pb** is a bluish-white, silvery, or gray metal that is highly lustrous when freshly cut but tarnishes when exposed to air. It is very soft and malleable, has a high density ( $11.35 \text{ g/cm}^3$ ) and low melting point ( $327.4^\circ\text{C}$ ), and can be cast, rolled, and extruded. The most important Pb ore is galena ( $PbS$ ). Recovery of Pb from the ore typically involves grinding, flotation, roasting, and smelting. Less common forms of the mineral are cerussite ( $PbCO_3$ ), anglesite ( $PbSO_4$ ), and crocoite ( $PbCrO_4$ ).

### Overview of Behavior of As, Cd, Cr, Pb, and Hg

Since metals cannot be destroyed, remediation of metal-contaminated soil consists primarily of manipulating (i.e., exploiting, increasing, decreasing, or maintaining) the mobility of metal contaminant(s) to produce a treated soil that has an acceptable total or leachable metal content. Metal mobility depends upon numerous factors. As noted in reference [9]:

"Metal mobility in soil-waste systems is determined by the type and quantity of soil surfaces present, the concentration of metal of interest, the concentration and type of competing ions and complexing ligands, both organic and inorganic, pH, and redox status. Generalization can only serve as rough guides of the expected behavior of metals in such systems. Use of literature or laboratory data that do not mimic the specific site soil and waste system will not be adequate to describe or predict the behavior of the metal. Data must be site specific. Long term effects must also be considered. As organic constituents of the waste matrix degrade, or as pH or redox conditions change, either through natural processes of weathering or human manipulation, the potential mobility of the metal will change as soil conditions change."

Based on the above description of the number and type of factors affecting metal mobility, it is clear that a comprehensive and quantitative description of mobility of the five metals under all conditions is well beyond the scope of this bulletin. Thus, the behavior of the five metals are described below, but for a limited number of conditions.

Cd, Cr (III), and Pb are present in cationic forms under natural environmental conditions [9]. These cationic metals generally are not mobile in the environment and tend to remain relatively close to the point of initial deposition. The capacity of soil to adsorb cationic metals increases with increasing pH, cation exchange capacity, and organic carbon content. Under the neutral to basic conditions typical of most soils, cationic metals are strongly adsorbed on the clay fraction of soils and can be adsorbed by hydrous oxides of iron, aluminum, or manganese present in soil minerals. Cationic metals will precipitate as hydroxides, carbonates, or phosphates. In acidic, sandy soils, the cationic metals are more mobile. Under conditions that are atypical of natural soils (e.g., pH  $<5$  or  $>9$ ; elevated concentrations of oxidizers or reducers; high concentrations of soluble organic or inorganic complexing or colloidal substances), but may be encountered as a result of waste disposal or remedial processes, the mobility of these metals may be substantially increased. Also, competitive adsorption between various metals has been observed in experiments involving various solids with oxide surfaces ( $\gamma\text{-FeOOH}$ ,  $\alpha\text{-SiO}_2$ , and  $\gamma\text{-Al}_2\text{O}_3$ ). In several experiments, Cd adsorption was decreased by the addition of Pb or Cu for all three of these sol-

ids. The addition of zinc resulted in the greatest decrease of Cd adsorption. Competition for surface sites occurred when only a few percent of all surface sites were occupied [11].

As, Cr (VI), and Hg behaviors differ considerably from Cd, Cr (III), and Pb. As and Cr(VI) typically exist in anionic forms under environmental conditions. Hg, although it is a cationic metal, has unusual properties (e.g., liquid at room temperature, easily transforms among several possible valence states).

In most As-contaminated sites, As appears as  $\text{As}_2\text{O}_3$  or as anionic As species leached from  $\text{As}_2\text{O}_3$ , oxidized to As (V), and then sorbed onto iron-bearing minerals in the soil. As may be present also in organometallic forms, such as methylarsenic acid ( $\text{H}_2\text{AsO}_3\text{CH}_3$ ) and dimethylarsenic acid ( $(\text{CH}_3)_2\text{AsO}_2\text{H}$ ), which are active ingredients in many pesticides, as well as the volatile compounds arsine ( $\text{AsH}_3$ ) and its methyl derivatives [i.e., dimethylarsine ( $\text{HAs}(\text{CH}_3)_2$ ) and trimethylarsine ( $\text{As}(\text{CH}_3)_3$ )]. These As forms illustrate the various oxidation states that As commonly exhibits (-III, 0, III, and V) and the resulting complexity of its chemistry in the environment.

As (V) is less mobile (and less toxic) than As (III). As (V) exhibits anionic behavior in the presence of water, and hence its aqueous solubility increases with increasing pH, and it does not complex or precipitate with other anions. As(V) can form low solubility metal arsenates. Calcium arsenate ( $\text{Ca}_3(\text{AsO}_4)_2$ ) is the most stable metal arsenate in well-oxidized and alkaline environments, but it is unstable in acidic environments. Even under initially oxidizing and alkaline conditions, absorption of  $\text{CO}_2$  from the air will result in formation of  $\text{CaCO}_3$  and release of arsenate. In sodic soils, sufficient sodium is available, such that the mobile compound  $\text{Na}_3\text{AsO}_4$  can form. The slightly less stable manganese arsenate ( $\text{Mn}_2(\text{AsO}_4)_2$ ) forms in both acidic and alkaline environments, while iron arsenate is stable under acidic soil conditions. In aerobic environments,  $\text{H}_3\text{AsO}_4$  predominates at pH <2 and is replaced by  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$  as pH increases to about 2, 7, and 11.5, respectively. Under mildly reducing conditions,  $\text{H}_3\text{AsO}_3$  is a predominant species at low pH, but is replaced by  $\text{H}_2\text{AsO}_3^-$ ,  $\text{HAsO}_3^{2-}$ , and  $\text{AsO}_3^{3-}$  as pH increases. Under still more reducing conditions and in the presence of sulfide,  $\text{As}_2\text{S}_3$  can form.  $\text{As}_2\text{S}_3$  is a low-solubility, stable solid.  $\text{AsS}_2$  and  $\text{AsS}_2^-$  are thermodynamically unstable with respect to  $\text{As}_2\text{S}_3$  [12]. Under extreme reducing conditions, elemental As and volatile arsine ( $\text{AsH}_3$ ) can occur. Just as competition between cationic metals affects mobility in soil, competition between anionic species (chromate, arsenate, phosphate, sulfate, etc.) affects anionic fixation processes and may increase mobility.

The most common valence states of Cr in the earth's surface and near-surface environment are +3 (trivalent or Cr(III)) and +6 (hexavalent or Cr(VI)). The trivalent Cr (discussed above) is the most thermodynamically stable form under common environmental conditions. Except in leather tanning, industrial applications of Cr generally use the Cr(VI) form. Due to kinetic limitations, Cr (VI) does not always readily reduce to Cr (III) and can remain present over an extended period of time.

Cr (VI) is present as the chromate ( $\text{CrO}_4^{2-}$ ) or dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) anion, depending on pH and concentration. Cr (VI) anions are less likely to be adsorbed to solid surfaces than Cr (III). Most solids in soils carry negative charges that inhibit Cr (VI) adsorption. Although clays have high capacity to adsorb cationic metals, they interact little with Cr (VI) because of the similar charges carried by the anion and clay in the common pH range of soil and groundwater. The only common soil solid that adsorbs Cr(VI) is iron oxyhydroxide. Generally, a major

portion of Cr(VI) and other anions adsorbed in soils can be attributed to the presence of iron oxyhydroxide. The quantity of Cr(VI) adsorbed onto the iron solids increases with decreasing pH.

At metal-contaminated sites, Hg can be present in mercuric form ( $\text{Hg}^{2+}$ ), mercurous form ( $\text{Hg}_2^{2+}$ ), elemental form ( $\text{Hg}^0$ ), or alkylated form (e.g., methyl and ethyl Hg).  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$  are more stable under oxidizing conditions. Under mildly reducing conditions, both organically bound Hg and inorganic Hg compounds can convert to elemental Hg, which then can be readily converted to methyl or ethyl Hg by biotic and abiotic processes. Methyl and ethyl Hg are mobile and toxic forms.

Hg is moderately mobile, regardless of the soil. Both the mercurous and mercuric cations are adsorbed by clay minerals, oxides, and organic matter. Adsorption of cationic forms of Hg increases with increasing pH. Mercurous and mercuric Hg also are immobilized by forming various precipitates. Mercurous Hg precipitates with chloride, phosphate, carbonate, and hydroxide. At concentrations of Hg commonly found in soil, only the phosphate precipitate is stable. In alkaline soils, mercuric Hg precipitates with carbonate and hydroxide to form a stable (but not exceptionally insoluble) solid phase. At lower pH and high chloride concentration, soluble  $\text{HgCl}_2$  is formed. Mercuric Hg also forms complexes with soluble organic matter, chlorides, and hydroxides that may contribute to its mobility [9]. In strong reducing conditions,  $\text{HgS}$ , a very low solubility compound is formed.

## General Description of Superfund Soils Contaminated with As, Cd, Cr, Hg, and Pb

Soils can become contaminated with metals from direct contact with industrial plant waste discharges; fugitive emissions; or leachate from waste piles, landfills, or sludge deposits. The specific type of metal contaminant expected at a particular Superfund site would obviously be directly related to the type of operation that had occurred there. Table 1 lists the types of operations that are directly associated with each of the five metal contaminants.

Wastes at CERCLA sites are frequently heterogeneous on a macro and micro scale. The contaminant concentration and the physical and chemical forms of the contaminant and matrix usually are complex and variable. Of these, waste disposal sites collect the widest variety of waste types; therefore concentration profiles vary by orders of magnitude through a pit or pile. Limited volumes of high-concentration "hot spots" may develop due to variations in the historical waste disposal patterns or local transport mechanisms. Similar radical variations frequently occur on the particle-size scale as well. The waste often consists of a physical mixture of very different solids, for example, paint chips in spent abrasive.

Industrial processes may result in a variety of solid metal-bearing waste materials, including slags, fumes, mold sand, fly ash, abrasive wastes, spent catalysts, spent activated carbon, and refractory bricks [13]. These process solids may be found above ground as waste piles or below ground in landfills. Solid-phase wastes can be dispersed by well-intended but poorly controlled reuse projects. Waste piles can be exposed to natural disasters or accidents causing further dispersion.

## Soil Cleanup Goals for As, Cd, Cr, Hg, and Pb

Table 2 provides an overview of cleanup goals (actual and potential) for both total and leachable metals. Based on inspec-

**Table 1.** Principal Sources of As, Cd, Cr, Hg, and Pb Contaminated Soils

Contaminant	Principal Sources
As	Wood preserving As-waste disposal Pesticide production and application  Mining
Cd	Plating Ni-Cd battery manufacturing Cd-waste disposal
Cr	Plating Textile manufacturing Leather tanning Pigment manufacturing Wood preserving Cr-waste disposal
Hg	Chloralkali manufacturing Weapons production Copper and zinc smelting Gas line manometer spills Paint application Hg-waste disposal
Pb	Ferrous/nonferrous smelting Pb-acid battery breaking Ammunition production Leaded paint waste Pb-waste disposal Secondary metals production Waste oil recycling Firing ranges Ink manufacturing Mining Pb-acid battery manufacturing Leaded glass production Tetraethyl Pb production Chemical manufacturing

tion of the total metals cleanup goals, one can see that they vary considerably both within the same metal and between metals. Similar variation is observed in the actual or potential leachate goals. The observed variation in cleanup goals has at least two implications with regard to technology alternative evaluation and selection. First, the importance of identifying the target metal(s), contaminant state (leachable vs. total metal), the specific type of test and conditions, and the numerical cleanup goals early in the remedy evaluation process is made apparent. Depending on which cleanup goal is selected, the required removal or leachate reduction efficiency of the overall remediation can vary by several orders of magnitude. Second, the degree of variation in goals both within and between the metals, plus the many factors that affect mobility of the metals (discussed earlier in the bulletin), suggest that generalizations about effectiveness of a technology for meeting total or leachable treatment goals should be viewed with some caution.

## Technologies for Containment and Remediation of As, Cd, Cr, Hg, and Pb in Soils

Technologies potentially applicable to the remediation of soils contaminated with the five metals or their inorganic compounds

are listed below. Underlined technologies have been implemented (not necessarily in all applicable modes—ex situ, in situ, off-site, and onsite) on numerous metal-contaminated soils and are available from a substantial number of vendors. Bracketed technologies have been operated or demonstrated on metal-contaminated soil with some success at full scale on one to approximately five soils, and some cost and performance data are available. In situ horizontal barriers are difficult to implement but are included to address in situ containment options for all contaminated soil deposit surfaces. The remaining technology, electrokinetics, has been implemented at full-scale in Europe and not in the U.S. but is undergoing a Superfund Innovative Technology Evaluation (SITE) demonstration. As noted above, electrokinetics is not addressed in the bulletin. Other technologies (e.g., phytoremediation and bacterial remediation) are being evaluated and may provide low-cost remediation for low concentration, large volume wastes, but these technologies are not addressed here due to their early stage of development and application to metal-contaminated soils.

Technology Class	Specific Technology
Containment	<u>Caps, Vertical Barriers,</u> Horizontal Barriers
Solidification/ Stabilization	<u>Cement-Based</u> [Polymer Microencapsulation] [Vitrification]
Separation/ Concentration	[Soil Washing] [Soil Flushing (In Situ Only)] [Pyrometallurgy] Electrokinetics (Addressed in TRD only)

For each technology listed above, the following topics are discussed:

- Process description
- Site requirements for technology implementation
- Applicability
- Performance in treating metals in soil and Best Demonstrated Available Technology (BDAT) status
- Technologies in the SITE Demonstration Program
- EPA contact for the technology

The BDAT status of the technology (see fourth bullet above) refers to the determination under the RCRA of the BDAT for various industry-generated hazardous wastes that contain the metals of interest. Whether the characteristics of a Superfund metal-contaminated soil (or fractions derived from it) are similar enough to the RCRA waste to justify serious evaluation of the BDAT for a specific Superfund soil must be made on a site specific basis. Other limitations relevant to BDATs include (1) the regulatory basis for BDAT standards focus BDATs on proven, commercially available technologies at the time of the BDAT determination, (2) a BDAT may be identified, but that does not necessarily preclude the use of other technologies, and (3) a technology identified as BDAT may not necessarily be the current technology of choice in the RCRA hazardous waste treatment industry.

The EPA's SITE program (referred to in the fifth bullet above) evaluates many emerging and demonstrated technologies in order to promote the development and use of innovative technologies to clean up Superfund sites across the country. The major focus of SITE is the Demonstration Program, which is designed to provide engineering and cost data for selected technologies.

Cost is not discussed in each technology narrative; however, a summary table is provided at the end of the technology

**Table 2.** Cleanup Goals (Actual and Potential) for Total and Leachable Metals

Description	As	Cd	Cr (Total)	Hg	Pb
<b>Total Metals Goals (mg/Kg)</b>					
Background (Mean) [1]	5	0.06	100	0.03	10
Background (Range) [1]	1 to 50	0.01 to 0.70	1 to 1000	0.01 to 0.30	2 to 200
Superfund Site Goals from TRD [1]	5 to 65	3 to 20	6.7 to 375	1 to 21	200 to 500
Theoretical Minimum Total Metals to Ensure TCLP Leachate < Threshold (i.e., TCLP X 20)	100	20	100	4	100
California Total Threshold Limit Concentration [1]	500	100	500	20	1000
<b>Leachable Metals (µg/L)</b>					
TCLP Threshold for RCRA Waste (SW 846, Method 1311)	5000	1000	5000	200	5000
Extraction Procedure Toxicity Test (EP Tox) (Method 1310)	5000	1000	5000	200	5000
Synthetic Precipitate Leachate Procedure (Method 1312)	—	—	—	—	—
Multiple Extraction Procedure (Method 1320)	—	—	—	—	—
California Soluble Threshold Leachate Concentration	5000	1000	5000	200	5000
Maximum Contaminant Level <sup>a</sup>	50	5	100	2	15
Superfund Site Goals from TRD [1]	50	—	50	0.05 to 2	50

<sup>a</sup> Maximum Contaminant Level = The maximum permissible level of contaminant in water delivered to any user of a public system.

— No specified level and no example cases identified.

discussion section that illustrates technology cost ranges and treatment train options.

## Specific Remedial Technologies

### Containment

Containment technologies for application at Superfund sites include landfill covers (caps), vertical barriers, and horizontal barriers [1]. For metal remediation, containment is considered an established technology except for in situ installation of horizontal barriers. This bulletin does not address construction of onsite landfill liners for placement of excavated material from the site.

**Process Description**—Containment ranges from a surface cap that limits infiltration of uncontaminated surface water to subsurface vertical or horizontal barriers that restrict lateral or vertical migration of contaminated groundwater. In addition to the containment documents referenced in this section, six other EPA containment documents are noted in the final section of this engineering bulletin on covers, liners, Quality Assurance/Quality Control (QA/QC) for geomembrane seams, and QA/QC for containment construction. Containment is covered primarily by reference in the original technical resource document. The text provided here is primarily from reference [5] on remediation of wood preserving sites.

**Caps**—Capping systems reduce surface water infiltration; control gas and odor emissions; improve aesthetics; and provide a stable surface over the waste. Caps can range from a simple native soil cover to a full RCRA Subtitle C, composite cover.

Cap construction costs depend on the number of components in the final cap system (i.e., costs increase with the addition of barrier and drainage components). Additionally, cost escalates as a function of topographic relief. Side slopes steeper than 3 horizontal to 1 vertical can cause stability and equipment problems that dramatically increase the unit cost.

**Vertical Barriers**—Vertical barriers minimize the movement of contaminated groundwater off-site or limit the flow of uncontaminated groundwater onsite. Common vertical barriers include slurry walls in excavated trenches; grout curtains formed by injecting grout into soil borings; vertically-injected, cement-bentonite grout-filled borings or holes formed by withdrawing beams driven into the ground; and sheet-pile walls formed of driven steel.

Certain compounds can affect cement-bentonite barriers. The impermeability of bentonite may significantly decrease when it is exposed to high concentrations of creosote, water-soluble salts (copper, Cr, As), or fire retardant salts (borates, phosphates, and ammonia). Specific gravity of salt solutions must be greater than 1.2 to impact bentonite [14][15]. In general, soil-bentonite blends resist chemical attack best if they contain only 1 percent bentonite and 30 to 40 percent natural soil fines. Treatability tests should evaluate the chemical stability of the barrier if adverse conditions are suspected.

Carbon steel used in pile walls quickly corrodes in dilute acids, slowly corrodes in brines or salt water, and remains mostly unaffected by organic chemicals or water. Salts and fire retardants can reduce the service life of a steel sheet pile; corrosion-resistant coatings can extend their anticipated life. Major steel suppliers will provide site-specific recommendations for cathodic protection of piling.

Construction costs for vertical barriers are influenced by the soil profile of the barrier material used and by the method of placing it. The most economical shallow vertical barriers are soil-bentonite trenches excavated with conventional backhoes; the most economical deep vertical barriers consist of a cement-bentonite wall placed by a vibrating beam.

**Horizontal Barriers**—In situ horizontal barriers can underlie a sector of contaminated materials onsite without removing the hazardous waste or soil. Established technologies use grouting techniques to reduce the permeability of underlying soil layers. Studies performed by the U.S. Army Corps of Engineers (COE) [16] indicate that conventional grout technology cannot produce an impermeable horizontal barrier because it cannot ensure uniform lateral growth of the grout. These same studies found greater success with jet grouting techniques in soils that contain fines sufficient to prevent collapse of the wash hole and that present no large stones or boulders that could deflect the cutting jet.

Since few in situ horizontal barriers have been constructed, accurate costs have not been established. Work performed by COE for EPA has shown that it is very difficult to form effective horizontal barriers. The most efficient barrier installation used a jet wash to create a cavity in sandy soils into which cement-bentonite grouting was injected. The costs relate to the number of borings required. Each boring takes at least one day to drill.

**Site Requirements**—In general, the site must be suitable for a variety of heavy construction equipment including bulldozers, graders, backhoes, multi-shaft drill rigs, various rollers, vibratory compactors, forklifts, and seaming devices [18]. When capping systems are being utilized, onsite storage areas are necessary for the materials to be used in the cover. If site soils are adequate for use in the cover, a borrow area needs to be identified and the soil tested and characterized. If site soils are not suitable, it may be necessary to truck in other low-permeability soils [18]. In addition, an adequate supply of water may also be needed in order to achieve the optimum soil density.

The construction of vertical containment barriers, such as slurry walls, requires knowledge of the site, the local soil and hydrogeologic conditions, and the presence of underground utilities [17]. Preparation of the slurry requires batch mixers, hydration ponds, pumps, hoses, and an adequate supply of water. Therefore, onsite water storage tanks and electricity are necessary. In addition, areas adjacent to the trench need to be available for the storage of trench spoils (which could potentially be contaminated) and the mixing of backfill. If excavated soils are not acceptable for use as backfill, suitable backfill must be trucked onto the site [17].

**Applicability**—Containment is most likely to be applicable to (1) wastes that are low-hazard (e.g., low toxicity or low concentration) or immobile; (2) wastes that have been treated to produce low hazard or low mobility wastes for onsite disposal; or (3) wastes whose mobility must be reduced as a temporary measure to mitigate risk until a permanent remedy can be tested and implemented. Situations where containment would not be applicable include (1) wastes for which there is a more permanent and protective remedy that is cost-effective, (2) where effective placement of horizontal barriers below existing contamination is difficult; and (3) where drinking water sources will be adversely affected if containment fails, and if there is inadequate confidence in the ability to predict, detect, or control harmful releases due to containment failure.

Important advantages of containment are (1) surface caps and vertical barriers are relatively simple and rapid to implement at low cost and can be more economical than excavation and removal of waste; (2) caps and vertical barriers can be applied to large areas or volumes of waste; (3) engineering control (containment) is achieved, and may be a final action if metals are well immobilized and potential receptors are distant; (4) a variety of barrier materials are available commercially; and (5) in some cases it may be possible to create a land surface that can support vegetation and/or be applicable for other purposes. Disadvantages of containment include (1) design life is uncertain; (2) contamination remains onsite, available to migrate should containment fail; (3) long-term inspection, maintenance and monitoring is required; (4) site must be amenable to effective monitoring; and (5) placement of horizontal barriers below existing waste is difficult to implement successfully.

**Performance and BDAT Status**—Containment is widely accepted as a means of controlling the spread of contamination and preventing the future migration of waste constituents. Table 3 shows a list of selected sites where containment has been selected for remediating metal-contaminated solids.

The performance of capping systems, once installed, may be difficult to evaluate [18]. Monitoring well systems or infiltration monitoring systems can provide some information, but it is often not possible to determine whether the water or leachate originated as surface water or groundwater.

With regard to slurry walls and other vertical containment barriers, performance may be affected by a number of variables including geographic region, topography, and material availability. A thorough characterization of the site and a compatibility study are highly recommended [17].

Containment technologies are not considered “treatment technologies” and hence no BDATs involving containment have been established.

**Table 3.** Containment Selections/Applications at Selected Superfund Sites With Metal Contamination

Site Name/State	Specific Technology	Key Metal Contaminants	Associated Technology	Status <sup>a</sup>
Ninth Avenue Dump, IN	Containment-Slurry Wall	Pb	Slurry Wall/Capping	S
Industrial Waste Control, AK	Containment-Slurry Wall	As, Cd, Cr, Pb	Capping/French Drain	I
E.H. Shilling Landfill, OH	Containment-Slurry Wall	As	Capping/Clay Berm	S
Chemtronic, NC	Capping	Cr, Pb	Capping	S
Ordnance Works Disposal, WV	Capping	As, Pb	Capping	S
Industriplex, MA	Capping	As, Pb, Cr	Capping	I

<sup>a</sup> Status codes as of February 1996: S = selected in ROD; I = in operation.

**SITE Program Demonstration Projects**—Ongoing SITE demonstrations applicable to soils contaminated with the metals of interest include

- Morrison Knudsen Corporation (High clay grouting technology)
- RKK, Ltd. (Frozen soil barriers)

**Contact**—Technology-specific questions regarding containment may be directed to Mr. David Carson (NRMRL) at (513) 569-7527.

## **Solidification/Stabilization Technologies**

Solidification/stabilization (S/S), as used in this engineering bulletin, refers to treatment processes that mix or inject treatment agents into the contaminated material to accomplish one or more of the following objectives:

- Improve the physical characteristics of the waste by producing a solid from liquid or semiliquid wastes.
- Reduce the contaminant solubility by formation of sorbed species or insoluble precipitates (e.g., hydroxides, carbonates, silicates, phosphates, sulfates, or sulfides).
- Decrease the exposed surface area across which mass transfer loss of contaminants may occur by formation of a crystalline, glassy, or polymeric framework which surrounds the waste particles.
- Limit the contact between transport fluids and contaminants by reducing the material's permeability [1].

S/S technology usually is applied by mixing contaminated soils or treatment residuals with a physical binding agent to form a crystalline, glassy, or polymeric framework surrounding the waste particles. In addition to the microencapsulation, some chemical fixation mechanisms may improve the waste's leach resistance. Other forms of S/S treatment rely on macroencapsulation, where the waste is unaltered but macroscopic particles are encased in a relatively impermeable coating [19], or on specific chemical fixation, where the contaminant is converted to a solid compound resistant to leaching. S/S treatment can be accomplished primarily through the use of either inorganic binders (e.g., cement, fly ash, and/or blast furnace slag) or by organic binders such as bitumen [1]. Additives may be used, for example, to convert the metal to a less mobile form or to counteract adverse effects of the contaminated soil on the S/S mixture (e.g., accelerated or retarded setting times, and low physical strength). The form of the final product from S/S treatment can range from a crumbly, soil-like mixture to a monolithic block. S/S is more commonly done as an ex situ process, but the in situ option is available. The full range of inorganic binders, organic binders, and additives is too broad to be covered here. The emphasis in this bulletin is on ex situ, cement-based S/S, which is widely used; in situ, cement-based S/S, which has been applied to metals at full-scale; and polymer microencapsulation, which appears applicable to certain wastes that are difficult to treat via cement-based S/S.

Additional information and references on solidification/stabilization of metals can be found in the source technical resource document for this bulletin [1] and *Engineering Bulletin: Solidification and Stabilization of Organics and Inorganics*, EPA/540/S-92/015 [20]. Also, *Chemical Fixation and Solidification of Hazardous Wastes* [21] is probably the most comprehensive reference on S/S of metals (692 pages total, 113 pages specifically

on fixation of metals). It is available in several EPA libraries. Innovative S/S technologies (e.g., sorption and surfactant processes, bituminization, emulsified asphalt, modified sulfur cement, polyethylene extrusion, soluble silicate, slag, lime, and soluble phosphates) are addressed in *Innovative Site Remediation Technology—Solidification/Stabilization*, Volume 4 [22].

**Process Description—Ex situ, cement-based S/S** is performed on contaminated soil that has been excavated and classified to reject oversize. Cement-based S/S involves mixing contaminated materials with an appropriate ratio of cement or similar binder/stabilizer, and possibly water and other additives. A system is also necessary for delivering the treated wastes to molds, surface trenches, or subsurface injection. Off-gas treatment (if volatiles or dust are present) may be necessary. The fundamental materials used to perform this technology are Portland-type cements and pozzolanic materials. Portland cements are typically composed of calcium silicates, aluminates, aluminoferrites, and sulfates. Pozzolans are very small spheroidal particles that are formed in combustion of coal (fly ash) and in lime and cement kilns, for example. Pozzolans of high silica content are found to have cement-like properties when mixed with water. Cement-based S/S treatment may involve using only Portland cement, only pozzolanic materials, or blends of both. The composition of the cement and pozzolan, together with the amount of water, aggregate, and other additives, determines the set time, cure time, pour characteristics, and material properties (e.g., pore size, compressive strength) of the resulting treated waste. The composition of cements and pozzolans, including those commonly used in S/S applications, are classified according to American Society for Testing and Materials (ASTM) standards. S/S treatment usually results in an increase (>50% in some cases) in the treated waste volume. Ex situ treatment provides high throughput (100 to 200 yd<sup>3</sup>/day/mixer).

Cement-based S/S reduces the mobility of inorganic compounds by formation of insoluble hydroxides, carbonates, or silicates; substitution of the metal into a mineral structure; sorption; physical encapsulation; and perhaps other mechanisms. Cement-based S/S involves a complex series of reactions, and there are many potential interferences (e.g., coating of particles by organics, excessive acceleration or retardation of set times by various soluble metal and inorganic compounds; excessive heat of hydration; pH conditions that solubilize anionic species of metal compounds, etc.) that can prevent attainment of S/S treatment objectives for physical strength and leachability. While there are many potential interferences, Portland cement is widely used and studied, and a knowledgeable vendor may be able to identify, and confirm via treatability studies, approaches to counteract adverse effects by use of appropriate additives or other changes in formulation.

**In situ, cement-based solidification/stabilization** has only two steps: (1) mixing and (2) off-gas treatment. The processing rate for in situ S/S is typically considerably lower than for ex situ processing. In situ S/S is demonstrated to depths of 30 feet and may be able to extend to 150 feet. The most significant challenge in applying S/S in situ for contaminated soils is achieving complete and uniform mixing of the binder with the contaminated matrix [23]. Three basic approaches are used for in situ mixing of the binder with the matrix: (1) vertical auger mixing; (2) in-place mixing of binder reagents with waste by conventional earthmoving equipment, such as draglines, backhoes, or clamshell buckets; and (3) injection grouting, which involves forcing a binder containing dissolved or suspended treatment agents into the subsurface, allowing it to permeate the soil. Grout injection can be applied to contaminated formations lying well below the ground surface. The injected grout cures in place to produce an in situ treated mass.

**S/S by polymer microencapsulation** can include application of thermoplastic or thermosetting resins. Thermoplastic materials are the most commonly used organic-based S/S treatment materials. Potential candidate resins for thermoplastic encapsulation include bitumen, polyethylene and other polyolefins, paraffins, waxes, and sulfur cement. Of these candidate thermoplastic resins, bitumen (asphalt) is the least expensive and by far the most commonly used [24]. The process of thermoplastic encapsulation involves heating and mixing the waste material and the resin at elevated temperature, typically 130°C to 230°C in an extrusion machine. Any water or volatile organics in the waste boil off during extrusion and are collected for treatment or disposal. Because the final product is a stiff, yet plastic resin, the treated material typically is discharged from the extruder into a drum or other container.

S/S process quality control requires information on the range of contaminant concentrations; potential interferences in waste batches awaiting treatment; and treated product properties such as compressive strength, permeability, leachability, and in some instances, toxicity [20].

**Site Requirements**—The site must be prepared for the construction, operation, maintenance, decontamination, and decommissioning of the equipment. The size of the area required for the process equipment depends on several factors, including the type of S/S process involved, the required treatment capacity of the system, and site characteristics, especially soil topography and load-bearing capacity. A small mobile ex situ unit occupies space for two, standard flatbed trailers. An in situ system requires a larger area to accommodate a drilling rig as well as a larger area for auger decontamination.

**Applicability**—This section addresses expected applicability based on the chemistry of the metal and the S/S binders. The soil-contaminant-binder equilibrium and kinetics are complicated, and many factors influence metal mobility, so there may be exceptions to the generalizations presented below.

For **cement-based S/S**, if a single metal is the predominant contaminant in soil, then Cd and Pb are the most amenable to cement-based S/S. The predominant mechanism for immobilization of metals in Portland and similar cements is precipitation of hydroxides, carbonates, and silicates. Both Pb and Cd tend to form insoluble precipitates in the pH ranges found in cured cement. They may resolubilize, however, if the pH is not carefully controlled. For example, Pb in aqueous solutions tends to resolubilize as  $\text{Pb}(\text{OH})_3^-$  around pH 10 and above. Hg, while it is a cationic metal like Pb and cadmium, does not form low solubility precipitates in cement, so it is difficult to stabilize reliably by cement-based processes, and this difficulty would be expected to be greater with increasing Hg concentration and with organomercury compounds. As, due to its formation of anionic species, also does not form insoluble precipitates in the high pH cement environment, and cement-based solidification is generally not expected to be successful. Cr(VI) is difficult to stabilize in cement due to formation of anions that are soluble at high pH. However, Cr(VI) can be reduced to Cr(III), which does form insoluble hydroxides. Although Hg and As(III and V) are particularly difficult candidates for cement-based S/S, this should not necessarily eliminate S/S (even cement-based) from consideration since (1) as with Cr(VI) it may be possible to devise a multistep process that will produce an acceptable product for cement-based S/S; (2) a non-cement based S/S process (e.g., lime and sulfide for Hg; oxidation to As(V) and coprecipitation with iron) may be applicable; or (3) the leachable concentration of the contaminant may be sufficiently low that a highly efficient S/S process may not be required to meet treatment goals.

The discussion of applicability above also applies to **in situ, cement-based S/S**. If in situ treatment introduces chemical agents into the ground, this chemical addition may cause a pollution problem in itself, and may be subject to additional requirements under the Land Disposal Restrictions.

**Polymer microencapsulation** has been mainly used to treat low-level radioactive wastes. However, organic binders have been tested or applied to wastes containing chemical contaminants such as As, metals, inorganic salts, polychlorinated biphenyls (PCBs), and dioxins [24]. Polymer microencapsulation is particularly well suited to treating water-soluble salts such as chlorides or sulfates that generally are difficult to immobilize in a cement-based system [25]. Characteristics of the organic binder and extrusion system impose compatibility requirements on the waste material. The elevated operating temperatures place a limit on the quantity of water and volatile organic chemicals (VOCs) in the waste feed. Low volatility organics will be retained in the bitumen but may act as solvents causing the treated product to be too fluid. The bitumen is a potential fuel source so the waste should not contain oxidizers such as nitrates, chlorates, or perchlorates. Oxidants present the potential for rapid oxidation, causing immediate safety concerns, as well as slow oxidation that results in waste form degradation.

Wastes containing more than one metal are not addressed here, other than to say that cement-based solidification/stabilization of multiple metal wastes will be particularly difficult if a set of treatment and disposal conditions cannot be found that simultaneously produces low mobility species for all the metals of concern. For example, the relatively high pH conditions that favor Pb immobilization would tend to increase the mobility of As. On the other hand, the various metal species in a multiple metal waste may interact (e.g., formation of low solubility compounds by combination of Pb and arsenate) to produce a low mobility compound.

Organic contaminants are often present with inorganic contaminants at metal-contaminated sites. S/S treatment of organic-contaminated waste with cement-based binders is more complex than treatment of inorganics alone. This is particularly true with VOCs where the mixing process and heat generated by cement hydration reactions can increase vapor losses [26][27][28][29]. However, S/S can be applied to wastes that contain lower levels of organics, particularly when inorganics are present and/or the organics are semivolatile or nonvolatile. Also, recent studies indicate the addition of silicates or modified clays to the binder system may improve S/S performance with organics [19].

**Performance and BDAT status**—S/S with cement-based and pozzolan binders is a commercially available, established technology. Table 4 shows a selected list of sites where S/S has been selected for remediating metal-contaminated solids. At 12 of the 19 sites, S/S has been either completely or partially implemented. Note that S/S has been used to treat all five metals (Cr, Pb, As, Hg, and Cd). Although it would not generally be expected (for the reasons noted in the previous section) that cement-based S/S would be applied to As and Hg contaminated soils, it was beyond the scope of this project to examine in detail the characterization data, S/S formulations, and performance data upon which the selections were based, so the selection/implementation data are presented without further comment.

Applications of polymer microencapsulation have been limited to special cases where the specific performance features are required for the waste matrix, and contaminants allow reuse of the treated waste as a construction material [30].

S/S is a BDAT for the following waste types:



**Table 4.** Solidification/Stabilization Selections/Applications at Selected Superfund Sites With Metal Contamination

Site Name/State	Specific Technology	Key Metal Contaminants	Associated Technology	Status <sup>a</sup>
DeRural Chemical, NJ	Solidification	Cr, Cd, Pb	GW pump and treatment	S
Marathon Battery Co., NY	Chemical fixation	Cd, Ni	Dredging, off-site disposal	I
Nascolite, Millville, NJ	Stabilization of wetland soils	Pb	On-site disposal of stabilized soils; excavation and off-site disposal of wetland soils	S
Roebing Steel, NJ	Solidification/stabilization (34-acre slag area)	As, Cr, Pb	Capping	S
Waldick Aerospace, NJ	S/S, 4,000 cy	Cd, Cr	LTTD, off-site disposal	C
Aladdin Plating, PA	Stabilization, 12,000 cy	Cr	Off-site disposal	C
Palmerton Zinc, PA	Stabilization, fly ash, lime, potash	Cd, Pb	—	I
Tonolli Corp., PA	S/S	As, Pb	In situ chemical limestone barrier	S
Whitmoyer Laboratories, PA	Oxidation/fixation	As	GW pump and treatment, capping, grading, and revegetation	S
Bypass 601, NC	S/S	Cr, Pb	Capping, regrading, revegetation, GW pump and treatment	S
Flowood, MS	S/S, 6,000 cy	Pb	Capping	C
Independent Nail, SC	S/S	Cd, Cr	Capping	C
Pepper's Steel and Alloys, FL	S/S	As, Pb	On-site disposal	C
Gurley Pit, AR	In situ S/S	Pb		C
Pesses Chemical, TX	Stabilization	Cd	Concrete capping	C
E.I. Dupont de Nemours, IA	S/S	Cd, Cr, Pb	Capping, regrading, and revegetation	C
Shaw Avenue Dump, IA	S/S	As, Cd	Capping, groundwater monitoring	C
Frontier Hard Chrome, WA	Stabilization	Cr		S
Gould Site, OR	S/S	Pb	Capping, regrading, and revegetation	I

<sup>a</sup> Status codes as of February 1996: S = selected in ROD; I = in operation, not complete; C = completed.

- Cd nonwastewaters (other than Cd-containing batteries)
- Cr nonwastewaters such as D007 and U032 [following reduction to Cr (III)]
- Pb nonwastewaters such as D008, P110, U144, U145, and U146
- Wastes containing low concentrations (< 260 mg/Kg) of elemental Hg—sulfide precipitation
- Plating wastes and steelmaking wastes

Although vitrification, not S/S, was selected as BDAT for RCRA As-containing nonwastewaters, EPA does not preclude the use of S/S for treatment of As (particularly inorganic As) wastes but recommends that its use be determined on a case-by-case basis. A variety of stabilization techniques including cement, silicate, pozzolan, and ferric coprecipitation were evaluated as candidate BDATs for As. Due to concerns about long-term stability and the waste volume increase, particularly with ferric coprecipitation, stabilization was not accepted as BDAT.

**SITE Program Demonstration Projects**—Completed or ongoing SITE demonstrations applicable to soils contaminated with the metals of interest include

*Completed*

- Advanced Remediation Mixing, Inc. (Ex situ S/S)
- Funderburk & Associates (Ex situ S/S)
- Geo-Con, Inc. (In situ S/S)
- Soliditech, Inc. (Ex situ S/S)
- STC Omega, Inc. (Ex situ S/S)
- WASTECH Inc. (Ex situ S/S)

*Ongoing*

- Separation and Recovery Systems, Inc. (Ex situ S/S)
- Wheelabrator Technologies Inc. (Ex situ S/S)

**Contact**—Technology-specific questions regarding S/S may be directed to Mr. Ed Barth (NRMRL) at (513) 569-7669.

## Vitrification

Vitrification applies high temperature treatment aimed primarily at reducing the mobility of metals by incorporation into a chemically durable, leach resistant, vitreous mass. Vitrification can be carried out on excavated soils as well as in situ.

**Process Description**—During the vitrification process, organic wastes are pyrolyzed (in situ) or oxidized (ex situ) by the melt front, whereas inorganics, including metals, are incorporated into the vitreous mass. Off-gases released during the melting process, containing volatile components and products of combustion and pyrolysis, must be collected and treated [1][31]. Vitrification converts contaminated soils to a stable glass and crystalline monolith [32]. With the addition of low-cost materials such as sand, clay, and/or native soil, the process can be adjusted to produce products with specific characteristics, such as chemical durability. Waste vitrification may be able to transform the waste into useful, recyclable products such as clean fill, aggregate, or higher valued materials such as erosion-control blocks, paving blocks, and road dividers.

*Ex situ vitrification* technologies apply heat to a melter through a variety of sources such as combustion of fossil fuels (coal, natural gas, and oil) or input of electric energy by direct joule heat, arcs, plasma torches, and microwaves. Combustion or oxidation of the organic portion of the waste can contribute significant energy to the melting process, thus reducing energy costs. The particle size of the waste may need to be controlled for some of the melting technologies. For wastes containing refractory compounds that melt above the unit's nominal processing temperature, such as quartz or alumina, size reduction may be required to achieve acceptable throughputs and a homogeneous melt. For high-temperature processes using arcing or plasma technologies, size reduction is not a major factor. For the intense melters using concurrent gas-phase melting or mechanical agitation, size reduction is needed for feeding the system and for achieving a homogeneous melt.

*In situ vitrification* (ISV) technology is based on electric melter technology, and the principle of operation is joule heating, which occurs when an electrical current is passed through a region that behaves as a resistive heating element. Electrical current is passed through the soil by means of an array of electrodes inserted vertically into the surface of the contaminated soil zone. Because dry soil is not conductive, a starter path of flaked graphite and glass frit is placed in a small trench between the electrodes to act as the initial flow path for electricity. Resistance heating in the starter path transfers heat to the soil, which then begins to melt. Once molten, the soil becomes conductive. The melt grows outward and downward as power is gradually increased to the full constant operating power level. A single melt can treat a region of up to 1000 tons. The maximum treatment depth has been demonstrated to be about 20 feet. Large contaminated areas are treated in multiple settings that fuse the blocks together to form one large monolith [1]. Further information on in situ vitrification can be found in the *Engineering Bulletin: In Situ Vitrification Treatment*, EPA/540/S-94/504 [33].

**Site Requirements**—The site must be prepared for the mobilization, operation, maintenance, and demobilization of the equipment. Site activities such as clearing vegetation, removing overburden, and acquiring backfill material are often necessary for ex situ as well as in situ vitrification. Ex situ processes will require areas for storage of excavated, treated, and possibly pre-

treated materials. The components of one ISV system are contained in three transportable trailers: an off-gas and process control trailer, a support trailer, and an electrical trailer. The trailers are mounted on wheels sufficient for transportation to and over a compacted ground surface [34].

The field-scale ISV system evaluated in the SITE program required three-phase electrical power at either 12,500 or 13,800 volts, which is usually taken from a utility distribution system [35]. Alternatively, the power may be generated onsite by means of a diesel generator. Typical applications require 800 kilowatt hours/ton (kWh/ton) to 1,000 kWh/ton [33].

**Applicability**—Setting cost and implementability aside, vitrification should be most applicable where nonvolatile metal contaminants have glass solubilities exceeding the level of contamination in the soil. Cr-contaminated soil should pose the least difficulties for vitrification, since it has low volatility, and a glass solubility between 1% and 3%. Vitrification may or may not be applicable for Pb, As, and Cd, depending on the level of difficulty encountered in retaining the metals in the melt, and controlling and treating any volatile emissions that may occur. Hg clearly poses problems for vitrification due to high volatility and low glass solubility (<0.1%) but may be allowable at very low concentrations (see Performance and BDAT section that follows).

Chlorides present in the waste in excess of about 0.5 weight percent typically will not be incorporated into and discharged with the glass but will fume off and enter the off-gas treatment system. If chlorides are excessively concentrated, salts of alkali, alkaline earths, and heavy metals will accumulate in solid residues collected by off-gas treatment. Separation of the chloride salts from the other residuals may be required before or during return of residuals to the melter. When excess chlorides are present, there is also a possibility that dioxins and furans may form and enter the off-gas treatment system.

Waste matrix composition affects the durability of the treated waste. Sufficient glass-forming materials ( $\text{SiO}_2$ ) (>30 wt %) and combined alkali (Na + K) (>1.4 wt %) are required for vitrification of wastes. If these conditions are not met, frit and/or flux additives typically are needed. Vitrification is also potentially applicable to soils contaminated with mixed metals and metal-organic wastes.

Specific situations where **ex situ vitrification** would not be applicable or would face additional implementation problems include (1) wastes containing > 25% moisture content cause excessive fuel consumption; (2) wastes where size reduction and classification are difficult or expensive; (3) volatile metals, particularly Cd and Hg, will vaporize and must be captured and treated separately; (4) As-containing wastes may require pre-treatment to produce less volatile forms; (5) metal concentrations in soil that exceed their solubility in glass; and (6) sites where commercial capacity is not adequate or transportation cost to a fixed facility is unacceptable.

Specific situations, in addition to those cited above, where **in situ vitrification** would not be applicable or would face additional implementation problems include (1) metal-contaminated soil where a less costly and adequately protective remedy exists; (2) projects that cannot be undertaken because of limited commercial availability; (3) contaminated soil <6 feet and >20 feet below the ground surface; (4) presence of an aquifer with high hydraulic conductivity (e.g., soil permeability >1 X 10<sup>-5</sup> cm/sec) limits economic feasibility due to excessive energy required; (5) contaminated soil mixed with buried metal that can result in a conductive path causing short circuiting of electrodes; (6) contaminated soil mixed with loosely packed rubbish or buried coal

can start underground fires and overwhelm off-gas collection and treatment system; (7) volatile heavy metals near the surface can be entrained in combustion product gases and not retained in melt; (8) sites where surface slope >5% may cause melt to flow; (9) in situ voids >150 m<sup>3</sup> interrupt conduction and heat transfer; and (10) underground structures and utilities <20 feet from the melt zone must be protected from heat or avoided.

Where it can be successfully applied, advantages of vitrification include (1) vitrified product is an inert, impermeable solid that should reduce leaching for long periods of time; (2) volume of vitrified product will typically be smaller than initial waste volume; (3) vitrified product *may be* usable; (4) a wide range of inorganic and organic wastes can be treated; and (5) there is both an ex situ and an in situ option available. A particular advantage of ex situ treatment is better control of processing parameters. Also, fuel costs may be reduced for ex situ vitrification by the use of combustible waste materials. This fuel cost-saving option is not directly applicable for in situ vitrification, since combustibles would increase the design and operating requirements for gas capture and treatment.

**Performance and BDAT Status**—In situ vitrification has been implemented to date at one metal-contaminated Superfund site (Parsons/ETM, Grand Ledge, MI) and was evaluated under the SITE Program [36]. The demonstration was completed in April 1994. About 3,000 cubic yards of soil were remediated. Some improvements are needed with melt containment and air emission control systems. The Innovative Technology Evaluation Report is now available from EPA [37]. ISV has been operated at a large scale ten times, including two demonstrations on radioactively contaminated sites at the DOE's Hanford Nuclear Reservation [31][38]. Pilot-scale tests have been conducted at Oak Ridge National Laboratory, Idaho National Engineering Laboratory, and Arnold Engineering Development Center. More than 150 tests and demonstrations at various scales have been performed on a broad range of waste types in soils and sludges. The technology has been selected as a preferred remedy at 10 private, Superfund, and DOD sites [39]. Table 5 provides a summary of ISV technology selection/application at metal-contaminated Superfund sites. A number of ex situ vitrification systems are under development. The technical resource document iden-

**Table 5.** In Situ Vitrification Selections/Applications at Selected Superfund Sites With Metal Contamination

Site Name/State	Key Metal Contaminants	Status <sup>a</sup>
Parsons Chemical, MI	Hg (low)	C
Rocky Mountain Arsenal, CO	As, Hg	S/D

<sup>a</sup> Status codes as of February 1996: C = completed; S/D = selected, but subsequently de-selected.

tified one full-scale ex situ melter that was reported to be operating on RCRA organics and inorganics.

Vitrification is a BDAT for the following waste types: As-containing wastes including K031, K084, K101, K102, D004, and As-containing P and U wastes.

**SITE Program Demonstration Projects**—Completed or ongoing SITE demonstrations applicable to soils contaminated with the metals of interest include

#### Completed

- Babcock & Wilcox Co. (Cyclone furnace—ex situ vitrification)
- Retech, Inc. (Plasma arc—ex situ vitrification)
- Geosafe Corporation (In situ vitrification)

#### Ongoing

- Vortec Corporation (Ex situ oxidation and vitrification process)

Three additional projects were completed in the SITE Emerging Technology program.

**Contact**—Technology-specific questions regarding vitrification may be directed to Ms. Teri Richardson (NRMRL) at (513) 569-7949.

## Soil Washing

Soil washing is an ex situ remediation technology that uses a combination of physical separation and aqueous-based separation unit operations to reduce contaminant concentrations to site-specific remedial goals [40]. Although soil washing is sometimes used as a stand-alone treatment technology, more often it is combined with other technologies to complete site remediation. Soil washing technologies have successfully remediated sites contaminated with organic, inorganic, and radioactive contaminants [40]. The technology does not detoxify or significantly alter the contaminant but transfers the contaminant from the soil into the washing fluid or mechanically concentrates the contaminants into a much smaller soil mass for subsequent treatment.

Further information on soil washing can be found in Innovative Site Remediation Technology—Soil Washing/Soil Flushing, Vol. 3, EPA 542-B-93-012 [41]. Revised versions of an EPA Engineering Bulletin and a soil washing treatability study guide are currently in preparation.

**Process Description**—Soil washing systems are quite flexible in terms of the number, type, and order of processes involved. Soil washing is performed on excavated soil and may involve some or all of the following, depending on the contaminant-soil matrix characteristics, cleanup goals, and specific process employed: (1) mechanical screening to remove various oversize materials, (2) crushing to reduce applicable oversize to suitable dimensions for treatment; (3) physical processes (e.g. soaking, spraying, tumbling, and attrition scrubbing) to liberate weakly bound agglomerates (e.g. silts and clays bound to sand and gravel) followed by size classification to generate coarse-grained and fine-grained soil fraction(s) for further treatment; (4) treatment of the coarse-grained soil fraction(s); (5) treatment of the fine-grained fraction(s); and (6) management of the generated residuals.

Step 4 above (i.e., treatment of the coarse-grained soil fraction) typically involves additional application of physical separation techniques and possibly aqueous-based leaching techniques. Physical separation techniques (e.g., sorting, screening, elutriation, hydrocyclones, spiral concentrators, flotation) exploit physical differences (e.g., size, density, shape, color, wetability) between contaminated particles and soil particles in order to produce a clean (or nearly clean) coarse fraction and one or more metal-concentrated streams. Many of the physical separation processes listed above involve the use of water as a transport medium, and if the metal contaminant has significant water solu-

bility, then some of the coarse-grained soil cleaning will occur as a result of transfer to the aqueous phase. If the combination of physical separation and unaided transfer to the aqueous phase cannot produce the desired reduction in the soil's metal content, which is frequently the case for metal contaminants, then solubility enhancement is an option for meeting cleanup goals for the coarse fraction. Solubility enhancement can be accomplished in several ways: (1) converting the contaminant into a more soluble form (e.g., oxidation/reduction, conversion to soluble metal salts); (2) using an aqueous-based leaching solution (e.g., acidic, alkaline, oxidizing, reducing) in which the contaminant has enhanced solubility; (3) incorporating a specific leaching process into the system to promote increased solubilization via increased mixing, elevated temperatures, higher solution/soil ratios, efficient solution/soil separation, multiple stage treatment, etc.; or (4) a combination of the above. After the leaching process is completed on the coarse-grained fraction, it will be necessary to separate the leaching solution and the coarse-grained fraction by settling. A soil rinsing step may be necessary to reduce the residual leachate in the soil to an acceptable level. It may also be necessary to re-adjust soil parameters such as pH or redox potential before replacement of the soil on the site. The metal-bearing leaching agent must also be treated further to remove the metal contaminant and permit reuse in the process or discharge, and this topic is discussed below under management of residuals.

Treatment of fine-grained soils (Step 5 above) is similar in concept to the treatment of the coarse-grained soils, but the production rate would be expected to be lower and hence more costly than for the coarse-grained soil fraction. The reduced production rate arises from factors including (1) the tendency of clays to agglomerate, thus requiring time, energy, and high water/clay ratios to produce a leachable slurry; and (2) slow settling velocities that require additional time and/or capital equipment to produce acceptable soil/water separation for multi-batch or countercurrent treatment, or at the end of treatment. A site-specific determination needs to be made whether the fines should be treated to produce clean fines or whether they should be handled as a residual waste stream.

Management of generated residuals (Step 6 above) is an important aspect of soil washing. The effectiveness, implementability, and cost of treating each residual stream is important to the overall success of soil washing for the site. Perhaps the most important of the residual streams is the metal-loaded leachant that is generated, particularly if the leaching process recycles the leaching solution. Furthermore, it is often critical to the economic feasibility of the project that the leaching solution be recycled. For these closed or semi-closed loop leaching processes, successful treatment of the metal-loaded leachant is imperative to the successful cleaning of the soil. The leachant must (1) have adequate solubility for the metal so that the metal reduction goals can be met without using excessive volumes of leaching solution; and (2) be readily, economically, and repeatedly adjustable (e.g., pH adjustment) to a form in which the metal contaminant has very low solubility so that the recycled aqueous phase retains a favorable concentration gradient compared to the contaminated soil. Also, efficient soil-water separation is important prior to recovering metal from the metal-loaded leachant in order to minimize contamination of the metal concentrate. Recycling the leachant reduces logistical requirements and costs associated with makeup water, storage, permitting, compliance analyses, and leaching agents. It also reduces external coordination requirements and eliminates the dependence of the remediation on the ability to meet Publicly Owned Treatment Works (POTW) discharge requirements.

Other residual streams that may be generated and require proper handling include (1) untreatable, uncrushable oversize; (2) recyclable metal-bearing particulates, concentrates, or sludges from physical separation or leachate treatment; (3) non-recyclable metal-bearing particulates, concentrates, soils, sludges, or organic debris that fail toxicity characteristic leaching procedure (TCLP) thresholds for RCRA hazardous waste; (4) soils or sludges that are not RCRA hazardous wastes but are also not sufficiently clean to permit return to the site; (5) metal-loaded leachant from systems where leachant is not recycled; and (6) rinsate from treated soil. Options for residuals treatment are listed in Table 8 at the end of the technology section.

**Site Requirements**—The area required for a unit at a site will depend on the vendor system selected, the amount of soil storage space, and/or the number of tanks or ponds needed for washwater preparation and wastewater storage and treatment. Typical utilities required are water, electricity, steam, and compressed air; the quantity of each is vendor- and site-specific. It may be desirable to control the moisture content of the contaminated soil for consistent handling and treatment by covering the excavation, storage, and treatment areas. Climatic conditions such as annual or seasonal precipitation cause surface runoff and water infiltration; therefore, runoff control measures may be required. Since soil washing is an aqueous based process, cold weather impacts include freezing as well as potential effects on leaching rates.

**Applicability**—Soil washing is potentially applicable to soils contaminated with all five metals of interest. Conditions that particularly favor soil washing include (1) a single principal contaminant metal that occurs in dense, insoluble particles that report to a specific, small mass fraction(s) of the soil; (2) a single contaminant metal and species that is very water or aqueous leachant soluble and has a low soil/water partition coefficient; (3) soil containing a high proportion (e.g., >80%) of soil particles >2 mm are desirable for efficient contaminant-soil and soil-water separation.

Conditions that clearly do not favor soil washing include (1) soils with a high (i.e., >40%) silt and clay fraction; (2) soils that vary widely and frequently in significant characteristics such as soil type, contaminant type and concentration, and where blending for homogeneity is not feasible; (3) complex mixtures (e.g. multicomponent, solid mixtures where access of leaching solutions to contaminant is restricted; mixed anionic and cationic metals where pH of solubility maximums are not close); (4) high clay content, cation exchange capacity, or humic acid content, which would tend to interfere with contaminant desorption; (5) presence of substances that interfere with the leaching solution (e.g., carbonaceous soils would neutralize extracting acids; similarly, high humic acid content will interfere with an alkaline extraction); and (6) metal contaminants in a very low solubility, stable form (e.g., PbS) may require long contact times and excessive amounts of reagent to solubilize.

**Performance and BDAT Status**—Soil washing has been used at waste sites in Europe, especially in Germany, the Netherlands, and Belgium [42]. Table 6 lists selected Superfund sites where soil washing has been selected and/or implemented.

Acid leaching, which is a form of soil washing, is the BDAT for Hg (D009, K071, P065, P092, and U151).

**SITE Demonstrations and Emerging Technologies Program Projects**—Completed SITE demonstrations applicable to soils contaminated with the metals of interest include

- Bergmann USA (Physical separation/leaching)

**Table 6.** Soil Washing Selections/Applications at Selected Superfund Sites With Metal Contamination

Site Name/State	Specific Technology	Key Metal Contaminants	Associated Technology	Status <sup>a</sup>
Ewan Property, NJ	Water washing	As, Cr, Cu, Pb	Pretreatment by solvent extraction to remove organics	S
GE Wiring Devices, PR	Water with KI solution additive	Hg	Treated residues disposed onsite and covered with clean soil	S
King of Prussia, NJ	Water with washing agent additives	Ag, Cr, Cu	Sludges to be land disposed	C
Zanesville Well Field, OH	Soil washing	Hg, Pb	SVE to remove organics	S
Twin Cities Army Ammunition Plant, MN	Soil washing	Cd, Cr, Cu, Hg, Pb	Soil leaching	C
Sacramento Army Depot Sacramento, CA	Soil washing	Cr, Pb	Offsite disposal of wash liquid	S/D

<sup>a</sup> Status codes as of February 1996: S = selected in ROD; C = completed; S/D = selected, but subsequently de-selected.

- BioGenesis<sup>SM</sup> (Physical separation/leaching)
- Biotrol, Inc. (Physical separation)
- Brice Environmental Services Corp. (Physical separation)
- COGNIS, Inc. (Leaching)
- Toronto Harbour Commission (Physical separation/leaching)

Four SITE Emerging Technologies Program projects have been completed that are applicable to soils contaminated with the metals of interest.

**Contact**—Technology-specific questions regarding soil washing may be directed to Mr. Richard Griffiths at (513) 569-7832 or Mr. Michael Borst (NRMRL) at (908) 321-6631.

## Soil Flushing

Soil flushing is the in situ extraction of contaminants from the soil via an appropriate washing solution. Water or an aqueous solution is injected into or sprayed onto the area of contamination, and the contaminated elutriate is collected and pumped to the surface for removal, recirculation, or onsite treatment and reinjection. The technology is applicable to both organic and inorganic contaminants, and metals in particular [1]. For the purpose of metals remediation, soil flushing has been operated at full-scale, but for a small number of sites.

**Process Description**—Soil flushing uses water, a solution of chemicals in water, or an organic extractant to recover contaminants from the in situ material. The contaminants are mobilized by solubilization, formation of emulsions, or a chemical reaction with the flushing solutions. After passing through the contamination zone, the contaminant-bearing fluid is collected by strategically placed wells or trenches and brought to the surface for disposal, recirculation, or onsite treatment and reinjection. During elutriation, the flushing solution mobilizes the sorbed contaminants by dissolution or emulsification.

One key to efficient operation of a soil flushing system is the ability to reuse the flushing solution, which is recovered along with groundwater. Various water treatment techniques can be

applied to remove the recovered metals and render the extraction fluid suitable for reuse. Recovered flushing fluids may need treatment to meet appropriate discharge standards prior to release to a POTW or receiving waters. The separation of surfactants from recovered flushing fluid, for reuse in the process, is a major factor in the cost of soil flushing. Treatment of the flushing fluid results in process sludges and residual solids, such as spent carbon and spent ion exchange resin, which must be appropriately treated before disposal. Air emissions of volatile contaminants from recovered flushing fluids should be collected and treated, as appropriate, to meet applicable regulatory standards. Residual flushing additives in the soil may be a concern and should be evaluated on a site-specific basis [43]. Subsurface containment barriers can be used in conjunction with soil flushing technology to help control the flow of flushing fluids. Further information on soil flushing can be found in the *Engineering Bulletin: In Situ Soil Flushing* [43] or *Innovative Site Remediation Technology—Soil Washing/Soil Flushing, Volume 3*, EPA 542-B-93-012 [41].

**Site Requirements**—Stationary or mobile soil-flushing systems are located onsite. The exact area required will depend on the vendor system selected and the number of tanks or ponds needed for washwater preparation and wastewater treatment. Certain permits may be required for operation, depending on the system being utilized. Slurry walls or other containment structures may be needed along with hydraulic controls to ensure capture of contaminants and flushing additives. Impermeable membranes may be necessary to limit infiltration of precipitation, which could cause dilution of the flushing solution and loss of hydraulic control. Cold weather freezing must also be considered for shallow infiltration galleries and above-ground sprayers [44].

**Applicability**—Soil flushing may be easy or difficult to apply, depending on the ability to wet the soil with the flushing solution and to install collection wells or subsurface drains to recover all the applied liquids. The achievable level of treatment varies and depends on the contact of the flushing solution with the contaminants and the appropriateness of the solution for contaminants, and the hydraulic conductivity of the soil. Soil flushing is most applicable to contaminants that are relatively soluble in the extracting fluid, and that will not tend to sorb onto soil as the metal-laden flushing fluid proceeds through the soil to the extraction point. Based on the earlier discussion of metal behavior, some potentially promising scenarios for soil flushing would in-

clude Cr(VI), As (III or V) in permeable soil with low iron oxide, low clay, and high pH; Cd in permeable soil with low clay, low cation exchange capacity (CEC), and moderately acidic pH; and, Pb in acid sands. A single target metal would be preferable to multiple metals, due to the added complexity of selecting a flushing fluid that would be reasonably efficient for all contaminants. Also, the flushing fluid must be compatible with not only the contaminant, but also the soil. Soils that counteract the acidity or alkalinity of the flushing solution will decrease its effectiveness. If precipitants occur due to interaction between the soil and the flushing fluid, then this could obstruct the soil pore structure and inhibit flow to and through sectors of the contaminated soil. It may take long periods of time for soil flushing to achieve cleanup standards.

A key advantage of soil flushing is that the contaminant is removed from the soil. Recovery and reuse of the metal from the extraction fluid may be possible in some cases, although the value of the recovered metal would not be expected to fully offset the costs of recovery. The equipment used for the technology is relatively easy to construct and operate. It does not involve excavation, treatment, and disposal of the soil, which avoids the expense and hazards associated with these activities.

**Performance and BDAT Status**—Table 7 lists the Superfund sites where soil flushing has been selected and/or implemented. Soil flushing has a more established history for removal of organics but has been used for Cr removal (e.g., United Chrome Products Superfund Site, near Corvallis, Oregon). In situ technologies, such as soil flushing, are not considered RCRA BDAT for any of the five metals.

Soil flushing techniques for mobilizing contaminants can be classified as conventional and unconventional. Conventional applications employ water only as the flushing solution. Unconventional applications that are currently being researched include the enhancement of the flushing water with additives, such as acids, bases, and chelating agents to aid in the desorption/dissolution of the target contaminants from the soil matrix to which they are bound.

Researchers are also investigating the effects of numerous soil factors on heavy metal sorption and migration in the subsurface. Such factors include pH, soil type, soil horizon, CEC, particle size, permeability, specific metal type and concentration, and type and concentrations of organic and inorganic compounds in solutions. Generally, as the soil pH decreases, cationic metal solubility and mobility increase. In most cases, metal mobility and sorption are likely to be controlled by the organic fraction in topsoils, and clay content in the subsoils.

**SITE Demonstration and Emerging Technologies Program Projects**—There are no in situ soil flushing projects re-

ported to be completed or ongoing either as SITE demonstration or Emerging Technologies Program Projects [44].

**Contact**—Technology-specific questions regarding soil flushing may be directed to Mr. Jerry N. Jones (NRMRL) at (405) 436-8593.

## Pyrometallurgical Technologies

Pyrometallurgy is used here as a broad term encompassing elevated temperature techniques for extraction and processing of metals for use or disposal. High-temperature processing increases the rate of reaction and often makes the reaction equilibrium more favorable, lowering the required reactor volume per unit output [1]. Some processes that clearly involve both metal extraction and recovery include roasting, retorting, or smelting. While these processes typically produce a metal-bearing waste slag, metal is also recovered for reuse. A second class of pyrometallurgical technologies included here is a combination of high temperature extraction and immobilization. These processes use thermal means to cause volatile metals to separate from the soil and report to the fly ash, but the metal in the fly ash is then immobilized, instead of recovered, and there is no metal recovered for reuse. A third class of technologies are those that are primarily incinerators for mixed organic-inorganic wastes, but which have the capability of processing wastes containing the metals of interest by either capturing volatile metals in the exhaust gases or immobilizing the nonvolatile metals in the bottom ash or slag. As noted in the introduction, mixed organic-metal waste is beyond the scope of this bulletin. However, since some of these systems may have applicability to some cases where metals contamination is the primary concern, a few technologies of this type are noted that are in the SITE program. Vitrification is addressed in a previous section. It is not considered pyrometallurgical treatment since there is typically neither a metal extraction nor a metal recovery component in the process.

**Process Description**—Pyrometallurgical processing usually is preceded by physical treatment to produce a uniform feed material and upgrade the metal content.

Solids treatment in a high-temperature furnace requires efficient heat transfer between the gas and solid phases while minimizing particulate in the off-gas. The particle-size range that meets these objectives is limited and is specific to the design of the process. The presence of large clumps or debris slows heat transfer, so pretreatment to either remove or pulverize oversize material normally is required. Fine particles also are undesirable because they become entrained in the gas flow, increasing the volume of dust to be removed from the flue gas. The feed material is sometimes pelletized to give a uniform size. In many cases a reducing agent and flux may be mixed in prior to pelletization to ensure good contact between the treatment agents and the contaminated material and to improve gas flow in the reactor [1].

**Table 7.** Soil Flushing Selections/Applications at Selected Superfund Sites With Metal Contamination

Site Name/State	Specific Technology	Key Metal Contaminants	Associated Technology	Status <sup>a</sup>
Lipari Landfill, NJ	Soil flushing of soil and wastes contained by slurry wall and cap; excavation from impacted wetlands	Cr, Hg, Pb	Slurry wall and cap	I
United Chrome Products, OR	Soil flushing with water	Cr	Electrokinetic Pilot test, Considering in situ reduction	I

<sup>a</sup> Status codes as of February 1996: I = in operation, not complete.

Due to its relatively low boiling point (357°C) and ready conversion at elevated temperature to its metallic form, Hg is commonly recovered through roasting and retorting at much lower temperatures than the other metals. Pyrometallurgical processing to convert compounds of the other four metals to elemental metal requires a reducing agent, fluxing agents to facilitate melting and to slag off impurities, and a heat source. The fluid mass often is called a melt, but the operating temperature, although quite high, often is still below the melting points of the refractory compounds being processed. The fluid forms as a lower-melting-point material due to the presence of a fluxing agent such as calcium. Depending on processing temperatures, volatile metals such as Cd and Pb may fume off and be recovered from the off-gas as oxides. Nonvolatile metals, such as Cr or nickel, are tapped from the furnace as molten metal. Impurities are scavenged by formation of slag [1]. The effluents and solid products generated by pyrometallurgical technologies typically include solid, liquid, and gaseous residuals. Solid products include debris, oversized rejects, dust, ash, and the treated medium. Dust collected from particulate control devices may be combined with the treated medium or, depending on analyses for carryover contamination, recycled through the treatment unit.

**Site Requirements**—Few pyrometallurgical systems are currently available in mobile or transportable configurations. Since this is typically an off-site technology, the distance of the site from the processing facility has an important influence on transportation costs. Off-site treatment must comply with EPA's off-site treatment policies and procedures. The off-site facility's environmental compliance status must be acceptable, and the waste must be of a type allowable under their operating permits. In order for pyrometallurgical processing to be technically feasible, it must be possible to generate a concentrate from the contaminated soil that will be acceptable to the processor. The processing rate of the off-site facility must be adequate to treat the contaminated material in a reasonable amount of time. Storage requirements and responsibilities must be determined. The need for air discharge and other permits must be determined on a site specific basis.

**Applicability**—With the possible exception of Hg, or a highly-contaminated soil, pyrometallurgical processing where metal recovery is the goal would not be applied directly to the contaminated soil, but rather to a concentrate generated via soil washing. Pyrometallurgical processing in conventional rotary kilns, rotary furnaces, or arc furnaces is most likely to be applicable to large volumes of material containing metal concentrations (particularly, Pb, Cd, or Cr) higher than 5 to 20%. Unless a very concentrated feed stream can be generated (e.g., approximately 60% for Pb), there will be a charge, in addition to transportation, for processing the concentrate. Lower metal concentrations can be acceptable if the metal is particularly easy to reduce and vaporize (e.g., Hg) or is particularly valuable (e.g., gold or platinum). As is the weakest candidate for pyrometallurgical recovery, since there is almost no recycling of As in the U.S. As [\$250 to \$500 per metric ton (mt)] for As trioxide) is also the least valuable of the metals. The reported price range [1] for the other metals are Cd (\$5,950/mt); Cr (\$7,830/mt); Pb (\$700 to \$770/mt); and, Hg (\$5,295 to \$8,490/mt).

**Performance and BDAT Status**—The technical resource document (1) contains a list of approximately 35 facilities/addresses/contacts that may accept concentrates of the five metals of interest for pyrometallurgical processing. Sixteen of the 35 facilities are Pb recycling operations, 7 facilities recover Hg, and the remainder address a range of RCRA wastes that contain the metals of interest. Due to the large volume of electric arc furnace (EAF) emission control waste (K061), extensive processing capability has been developed to recover Cd, Pb, and zinc from

solid waste matrices. Permitting is being expanded to cover other hazardous waste types. The currently available process technologies for K061 and similar materials include

- Waelz kiln process (Horsehead Resource Development Company, Inc.)
- Waelz kiln and calcination process (Horsehead Resource Development Company, Inc.)
- Flame reactor process (Horsehead Resource Development Company, Inc.)
- Inclined rotary kiln (Zia Technology)

Plasma arc furnaces currently are successfully treating K061 (EAF waste) at two steel plants. These are site-dedicated units that do not accept outside material for processing.

Pyrometallurgical recovery is a BDAT for the following waste types:

- Cd-containing batteries, D006
- Pb nonwastewaters such as K069 in the noncalcium sulfate subcategory
- Hg wastes, P065, P092, and D009 (organics) prior to retorting [45]
- Pb acid batteries such as D008
- Zinc nonwastewaters such as K061 in the high zinc subcategory
- Hg from wastewater treatment sludge such as K106 in the high-Hg subcategory
- Hg such as U151 in the high-Hg subcategory.

**SITE Demonstration and Emerging Technologies Program Projects**—Completed SITE demonstrations applicable to soils contaminated with the metals of interest include

- RUST Remedial Services, Inc. (X-Trax Thermal Desorption)
- Horsehead Resource Development Company, Inc. (Flame Reactor)

Four SITE Emerging Technology Program projects that are applicable to the metals of interest have been completed or are ongoing.

**Contact**—Technology-specific questions regarding pyrometallurgical treatment may be directed to Mrs. Marta K. Richards (NRMRL) at (513) 569-7692.

## Use of Treatment Trains

Several of the metal remediation technologies discussed are often enhanced through the use of treatment trains. Treatment trains use two or more remedial options applied sequentially to the contaminated soil and often increase the effectiveness while decreasing the cost of remediation. Processes involved in treatment trains include soil pretreatment, physical separation designed to decrease the amount of soil requiring treatment, additional treatment of process residuals or off-gases, and a variety of other physical and chemical techniques, which can greatly

**Table 8** Typical Treatment Trains

	Containment	S/S <sup>a</sup>	Vitrification <sup>a</sup>	Soil Washing	Pyrometallurgical	Soil Flushing
<b>Pretreatment</b>						
Excavation	•	E,P	I,E	•	•	
Debris removal		E,P	E	•	•	
Oversize reduction		E,P	E	•	•	
Adjust pH	•	I,E,P				
Reduction [e.g., Cr(VI) to Cr(III)]	•	I,E				
Oxidation [e.g., As(III) to As (V)]	•	I,E				
Treatment to remove or destroy organics		I,E				
Physical separation of rich and lean fractions		I,E,P	E	•	•	
Dewatering and drying for wet sludge	•	P	E		•	
Conversion of metals to less volatile forms [e.g., As <sub>2</sub> O <sub>3</sub> to Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ]			E			
Addition of high temperature reductants					•	
Pelletizing					•	
Flushing fluid delivery and extraction system						•
Containment barriers	•	I,E,P	I	•		•
<b>Post-treatment/Residuals Management</b>						
Disposal of treated solid residuals (preferably below the frost line and above the water table)		I,E,P	E		•	
Containment barriers		I,E,P	I,E			•
Off-gas treatment		I,E,P	I,E		•	
Reuse for onsite paving		P				
Metal recovery from extraction fluid by aqueous processing (ion exchange, electrowinning, etc.)				•		
Pyrometallurgical recovery of metal from sludge				•		
Processing and reuse of leaching solution				•	•	
S/S treatment of leached residual				•		
Disposal of solid process residuals (preferably below the frostline and above the water table)				•		
Disposal of liquid process residuals				•		•
S/S treatment of slag or fly ash					•	
Reuse of slag/vitreous product as construction material			E	•		
Reuse of metal or metal compound					•	
Further processing of metal or metal compound					•	
Flushing liquid/groundwater treatment/disposal						•

<sup>a</sup> Technology has been divided into the following categories: I = In Situ Process; E = Ex Situ Process; P= Polymer Microencapsulation (Ex Situ)

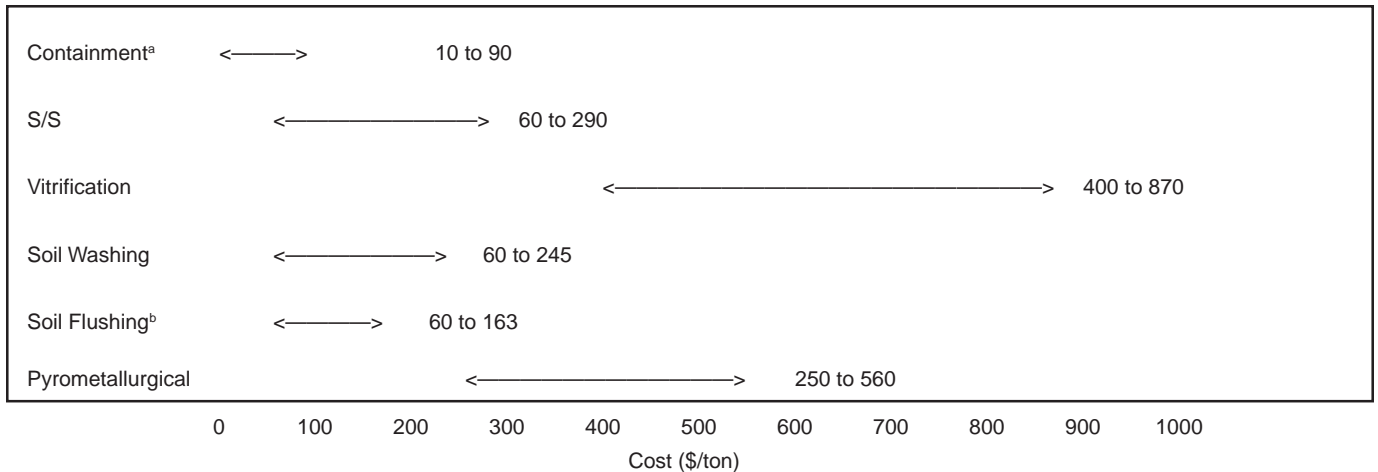
improve the performance of the remediation technology. Table 8 provides examples of treatment trains used to enhance each metal remediation technology that has been discussed.

### Cost Ranges of Remedial Technologies

Estimated cost ranges for the basic operation of the technology are presented in Figure 1. The information was compiled from EPA documents, including Engineering Bulletins, SITE Dem-

onstration Reports, and EPA electronic databases. The reader is cautioned that the cost estimates generally do not include pretreatment, site preparation, regulatory compliance costs, costs for additional treatment of process residuals (e.g., stabilization of incinerator ash or disposal of metals concentrated by solvent extraction), or profit. Since the actual cost of employing a remedial technology at a specific site may be significantly different than these estimates, data are best used for order-of-magnitude cost evaluations.





<sup>a</sup> Includes landfill caps and slurry walls. A slurry wall depth of 20' is assumed.

<sup>b</sup> Costs reported in \$/Yd<sup>3</sup>, assumed soil density of 100 lb/ft<sup>3</sup>

**Figure 1. Estimated Cost Ranges of Metals Remediation Technologies**  
[Source: VISITT (Ver. 3.0), various EPA Engineering Bulletins and TRD]

## Sources of Additional Information

The following databases, reports, and EPA hotlines offer additional information on the remediation of metal-contaminated soil. The reader is also encouraged to review sources referenced in this paper.

Alternative Treatment Technology Information Center (ATTIC) database. U.S. EPA Assistance, (908) 321-6677. ATTIC modem contact, (703) 908-2138 (1200 or 2400 baud), and the modem settings are no parity, 8 data bits, 1 stop bit, and full duplex.

The Clean-Up Information Bulletin Board System (CLU-IN). System Operator, (301) 589-8368. Online communication, (301) 589-8366.

EPA Online Library System (OLS). Includes the following applicable databases: The National Catalog, The Hazardous Waste Superfund Data Collection, and The Chemical Collection System. Online communication, (919) 549-0720. Public Information Center, (202) 260-2080.

Records of Decision System (RODS) database. RODS staff and registration, (703) 603-9091. RODS database searches, (703) 538-7234.

Subsurface Remediation Technology (SRT) Database. Database information, contact Dr. David S. Burden, (405) 436-8606.

Cost of Remedial Action (CORA). PC-based database available on disk.

Hazardous Waste Superfund Data Collection (HWSDC). PC-based database available on disk. For information, Felice Sacks, (202) 260-3121.

Risk Reduction Engineering Laboratory (RREL) Treatability Database. Available on disk and through the ATTIC database. Contact Glenn Shaul, (513) 569-7589.

Vendor Information System for Innovative Treatment Technologies (VISITT) database. PC-based database available on disk, (800) 245-4505 or (703) 883-8448.

ReOpt/Remedial Action Assessment System (RAAS) databases. U.S. Department of Energy. For government projects only—a contract number must be filed with PNL for each copy received.

EPA Home Page on World Wide Web (<http://www.epa.gov>).

Marks, Peter J., Walter J. Wujcik, and Amy F. Loncar. Remediation Technologies Screening Matrix and Reference Guide, Second Edition. U.S. Army Environmental Center. October 1994.

RCRA/Superfund Assistance Hotline. Washington, D.C., (800) 424-9346.

U.S. Environmental Protection Agency. Lining of Waste Containment and Other Impoundment Facilities, EPA/600/2-88-052. 1988.

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U.S. Environmental Protection Agency. Technical Guidance Document: Final Covers on Hazardous Waste Landfills and Surface Impoundments, EPA/530-SW-89-047. July 1989.

U.S. Environmental Protection Agency. Technical Guidance Document: Inspection Techniques for the Fabrica-

tion of Geomembrane Field Seams, EPA/530/SW-91/051. May 1991.

U.S. Environmental Protection Agency. Technical Guidance Document: Construction Quality Management for Remedial Action and Remedial Design Waste Containment Systems, EPA/540/R-92/073. October 1992.

U.S. Environmental Protection Agency. Technical Guidance Document: Quality Assurance and Quality Control for Waste Containment Facilities, EPA/600/R-93/182. 1993.

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