
Remediation of Metals-Contaminated Soils and Groundwater

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FOREWORD

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TABLE OF CONTENTS

	<u>Page</u>
1.0 SUMMARY	1
2.0 PROBLEM DESCRIPTION	2
2.1 Metals at Contaminated Sites	2
2.2 Sources of Contaminants	3
2.2.1 Airborne Sources	3
2.2.2 Process Solid Wastes	3
2.2.3 Sludges	4
2.2.4 Soils	4
2.2.5 Direct Ground-Water Contamination	4
2.3 Definitions of Contaminant Concentrations	4
2.4 Chemical Fate and Mobility	5
2.4.1 Lead	7
2.4.2 Chromium	7
2.4.3 Arsenic	8
2.4.4 Zinc	9
2.4.5 Cadmium	9
2.4.6 Copper	10
2.4.7 Mercury	10
2.5 Influence of Soil Properties on Mobility	11
2.5.1 Chemical Properties	11
2.5.2 Physical Properties	13
3.0 AVAILABLE TECHNOLOGIES AND PERFORMANCE	14
3.1 Site Characterization and Establishment of Remediation Goals	14
3.2 General Remediation Approaches	14
3.2.1 Isolation	14
3.2.1.1 Capping	16
3.2.1.2 Subsurface Barriers	16
3.2.2 Immobilization	18
3.2.2.1 Solidification/Stabilization	18
3.2.2.2 Vitrification	20

TABLE OF CONTENTS (cont.)

	<u>Page</u>
3.2.3 Toxicity and/or Mobility Reduction	21
3.2.3.1 Chemical Treatment	21
3.2.3.2 Permeable Treatment Walls	22
3.2.3.3 Biological Treatment	23
3.2.4 Physical Separation	25
3.2.5 Extraction	26
3.2.5.1 Soil Washing	26
3.2.5.2 Pyrometallurgical Extraction	28
3.2.5.3 <i>In Situ</i> Soil Flushing	29
3.2.5.4 Electrokinetic Treatment	29
3.3 Performance of Available Commercial Technologies	29
3.3.1 Superfund Innovative Technology Evaluation (SITE) Demonstration and Best Demonstrated Available Technology (BDAT) Status	30
3.3.2 Containment	30
3.3.3 Ex Situ Remediation	31
3.3.3.1 Solidification/Stabilization	32
3.3.3.2 Soil Washing	33
3.3.3.3 Vitrification	34
3.3.3.4 Pyrometallurgical Separation	35
3.3.4 <i>In Situ</i> Remediation	36
3.3.4.1 Solidification/Stabilization	36
3.3.4.2 Vitrification	37
3.3.4.3 <i>In Situ</i> Soil Flushing	37
3.3.4.4 Electrokinetic Extraction	39
3.3.4.5 Biological Treatment	40
3.4 Best Technology by Metal	40
4.0 COST ESTIMATES	42
4.1 Containment	42
4.2 Solidification/Stabilization	43
4.3 Vitrification	43

TABLE OF CONTENTS (cont.)

	<u>Page</u>
4.4 Soil Washing	43
4.5 <i>In Situ</i> Soil Flushing	43
4.6 Electrokinetic Treatment	43
5.0 REGULATORY/POLICY REQUIREMENTS AND ISSUES	44
6.0 LESSONS LEARNED AND TECHNOLOGY DIRECTIONS	46
7.0 REFERENCES	47

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page</u>
1	Metals Most Commonly Present in all Matrices at Superfund Sites	2
2	Metal Adsorption to Hydrous Iron Oxide Gels	6
3	Typical pH edges for (a) cation sorption and (b) anion sorption	12
4	Estimated Operating Costs of Available Remediation Technologies for Metal-Contaminated Soils	42

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page</u>
1	Remediation Technologies Matrix for Metals in Soil and Ground-Water	15
2	Example Containment Applications at Metals-Contaminated Superfund Sites	31
3	Example Solidification/Stabilization Applications at Selected Metals-Contaminated Superfund Sites	33
4	Example Soil Washing Applications at Metals-Contaminated Superfund Sites	34
5	Approximate Vapor Pressures and Glass Solubility Limits for Metals	35
6	Example <i>In Situ</i> Solidification/Stabilization Applications at Metals-Contaminated Superfund Sites	36
7	Example <i>In Situ</i> Vitrification Applications at Metals-Contaminated Superfund Sites	37
8	Example <i>In Situ</i> Soil Flushing Applications at Metals-Contaminated Superfund Sites	38
9	Example Electrokinetic Applications at Metals-Contaminated Sites	39
10	Summary of Best Demonstrated Available Technologies (BDATs) for RCRA Wastes	41
11	Examples of U.S. Cleanup Goals/Standards for Selected Metals in Soils	45
12	Examples of U.S. Cleanup Goals/Standards for Selected Metals in Groundwater	45

1.0 SUMMARY

Metals contamination is a persistent problem at many contaminated sites. In the U.S., the most commonly occurring metals at Superfund sites are lead, chromium, arsenic, zinc, cadmium, copper, and mercury. The presence of metals in groundwater and soils can pose a significant threat to human health and ecological systems. The chemical form of the metal contaminant influences its solubility, mobility, and toxicity in ground-water systems. The chemical form of metals depends on the source of the metal waste and the soil and ground-water chemistry at the site. A detailed site characterization must be performed to assess the type and level of metals present and allow evaluation of remedial alternatives.

Typically metals are relatively immobile in subsurface systems as a result of precipitation or adsorption reactions. For this reason, remediation activities at metals-contaminated sites have focused on the solid-phase sources of metals, i.e., contaminated soils, sludges, wastes, or debris.

A range of technologies is available for remediation of metals-contaminated soil and groundwater at Superfund sites. General approaches to remediation of metal contamination include isolation, immobilization, toxicity reduction, physical separation and extraction. These general approaches can be used for many types of contaminants but the specific technology selected for treatment of a metals-contaminated site will depend on the form of the contamination and other site-specific characteristics. One or more of these approaches are often combined for more cost-effective treatment. A number of the available technologies have been demonstrated in full-scale applications and are presently commercially available. A comprehensive list of these technologies is available (U.S. EPA, 1996a). Several other technologies are being tested for application to metals-contaminated sites. This report summarizes remediation technologies for metals-contaminated soil and groundwater whose performance at full-scale has been verified under the United States Environmental Protection Agency (U.S. EPA) Superfund Innovative Technology Evaluation (SITE) program for evaluation of emerging and demonstrated technologies. The focus of this program is the demonstration phase in which the technologies are field-tested and performance and cost data are collected. Technologies available for treatment of metals-contaminated soil and groundwater by each of the general approaches to remediation are presented, and the applicability of these technologies to different types of metal contamination and physical site characteristics are evaluated. Cost ranges are provided for a number of the technologies. The most promising emerging technologies are also examined.

Treatment of metals-contaminated groundwater has typically involved flushing and above-ground treatment, while treatment of contaminated solids most often has been performed by excavation followed by ex situ treatment or disposal. The most common ex situ treatment for excavated soils is solidification/stabilization. *In situ* treatment methods for metals-contaminated soil and groundwater are being tested and will be applied with increasing frequency.

2.0 PROBLEM DESCRIPTION

2.1 METALS AT CONTAMINATED SITES

Approximately 75% of Superfund sites for which Records of Decision (RODs) have been signed contain metals as a form of contamination. Some of these sites contain mixed metal-organic wastes for which metals might not be the primary contaminant of concern. The most common metals found at contaminated sites are (U.S. EPA, 1996b), in order: lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), and mercury (Hg). Figure 1 summarizes the frequency with which these metals occur at Superfund sites.

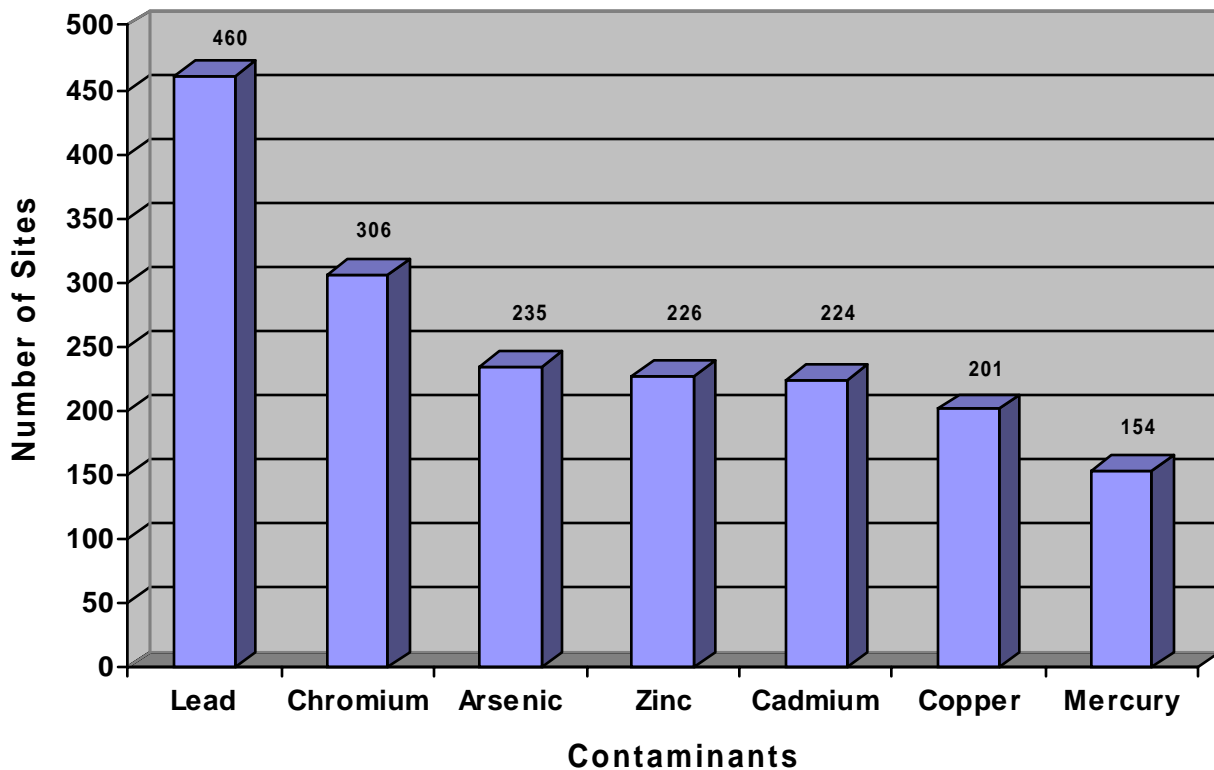


Figure 1. Metals Most Commonly Present in all Matrices at Superfund Sites (from U.S. EPA, 1996)

The specific type of metal contamination found at a Superfund site is directly related to the operation that occurred at the site. The range of contaminant concentrations and the physical and chemical forms of contaminants will also depend on activities and disposal patterns for contaminated wastes on the site. Other factors that may influence the form, concentration and distribution of metal contaminants include soil and ground-water chemistry and local transport mechanisms.

2.2 SOURCES OF CONTAMINANTS

Surface water and groundwater may be contaminated with metals from wastewater discharges or by direct contact with metals-contaminated soils, sludges, mining wastes, and debris. Metal-bearing solids at contaminated sites can originate from a wide variety of sources in the form of airborne emissions, process solid wastes, sludges or spills. The contaminant sources influence the heterogeneity of contaminated sites on a macroscopic and microscopic scale. Variations in contaminant concentration and matrix influence the risks associated with metal contamination and treatment options.

2.2.1 Airborne Sources

Airborne sources of metals include stack or duct emissions of air, gas, or vapor streams, and fugitive emissions such as dust from storage areas or waste piles. Metals from airborne sources are generally released as particulates contained in the gas stream. Some metals such as arsenic, cadmium, and lead can also volatilize during high-temperature processing. These metals will convert to oxides and condense as fine particulates unless a reducing atmosphere is maintained. (Smith et al., 1995)

Stack emissions can be distributed over a wide area by natural air currents until dry and/or wet precipitation mechanisms remove them from the gas stream. Fugitive emissions are often distributed over a much smaller area because emissions are made near the ground. In general, contaminant concentrations are lower in fugitive emissions compared to stack emissions. The type and concentration of metals emitted from both types of sources will depend on site-specific conditions.

2.2.2 Process Solid Wastes

Process solid wastes can result from a variety of industrial processes. These metal-bearing solid wastes are disposed above ground in waste piles or below ground or under cover in landfills. Examples of process solid wastes include slags, fly ash, mold sands, abrasive wastes, ion exchange resins, spent catalysts, spent activated carbon, and refractory bricks (Zimmerman and Coles, 1992). The composition of the process waste influences the density, porosity, and leach resistance of the waste and must be considered in evaluating the contaminated matrix.

Because waste piles are above ground, they are exposed to weathering which can disperse the waste pile to the surrounding soil, water and air and can result in generation of leachate which infiltrates into the subsurface environment. The ability of landfills to contain process solid wastes varies due to the range of available landfill designs. Uncontained landfills can release contaminants into infiltrating surface water or groundwater or via wind and surface erosion.

2.2.3 Sludges

The composition of sludges depends on the original waste stream and the process from which it was derived. Sludges resulting from a uniform wastestream, such as wastewater treatment sludges, are typically more homogeneous and have more uniform matrix characteristics. Sludge pits, on the other hand, often contain a mixture of wastes that have been aged and weathered, causing a variety of reactions to occur. Sludge pits often require some form of pretreatment before wastes can be treated or recycled (Smith et al., 1995).

2.2.4 Soils

Soil consists of a mixture of weathered minerals and varying amounts of organic matter. Soils can be contaminated as a result of spills or direct contact with contaminated waste streams such as airborne emissions, process solid wastes, sludges, or leachate from waste materials. The solubility of metals in soil is influenced by the chemistry of the soil and groundwater (Sposito, 1989; Evans, 1989). Factors such as pH, Eh, ion exchange capacity, and complexation/chelation with organic matter directly affect metal solubility.

2.2.5 Direct Ground-Water Contamination

Groundwater can be contaminated with metals directly by infiltration of leachate from land disposal of solid wastes, liquid sewage or sewage sludge, leachate from mine tailings and other mining wastes, deep-well disposal of liquid wastes, seepage from industrial waste lagoons, or from other spills and leaks from industrial metal processing facilities (e.g., steel plants, plating shops, etc.). A variety of reactions may occur which influence the speciation and mobility of metal contaminants including acid/base, precipitation/dissolution, oxidation/reduction, sorption or ion exchange. Precipitation, sorption, and ion exchange reactions can retard the movement of metals in groundwater. The rate and extent of these reactions will depend on factors such as pH, Eh, complexation with other dissolved constituents, sorption and ion exchange capacity of the geological materials, and organic matter content. Ground-water flow characteristics also influence the transport of metal contaminants.

2.3 DEFINITIONS OF CONTAMINANT CONCENTRATIONS

Sludges, soils, and solid wastes are multiphase materials which may contain metals in the solid, gaseous, or liquid phases. This complicates analysis and interpretation of reported results. For example, the most common method for determining the concentration of metals contaminants in soil is via total elemental analysis (U.S. EPA Method 3050). The level of metal contamination determined by this method is expressed as mg metal/kg soil. This analysis does not specify requirements for the moisture content of the soil and may therefore include soil water. This measurement may also be reported on a dry soil basis.

The level of contamination may also be reported as leachable metals as determined by leach tests, such as the toxicity characteristic leaching procedure, or TCLP test (U.S. EPA

Method 1311) or the synthetic precipitation leaching procedure, or SPLP test (U.S. EPA Method 1312). These procedures measure the concentration of metals in leachate from soil contacted with an acetic acid solution (TCLP) or a dilute solution of sulfuric and nitric acid (SPLP). In this case, metal contamination is expressed in mg/L of the leachable metal.

Other types of leaching tests have been proposed (see summary by Environment Canada, 1990), including sequential extraction procedures (Tessier et al., 1979) and extraction of acid volatile sulfide (DiToro et al., 1992). Sequential procedures contact the solid with a series of extractant solutions that are designed to dissolve different fractions of the associated metal. These tests may provide insight into the different forms of metal contamination present (e.g., see Van Benschoten et al., 1994).

Contaminant concentrations can be measured directly in metals-contaminated water. These concentrations are most commonly expressed as total dissolved metals in mass concentrations (mg/L or $\mu\text{g/L}$) or in molar concentrations (moles/L). In dilute solutions, a mg/L is equivalent to one part per million (ppm), and a $\mu\text{g/L}$ is equivalent to one part per billion (ppb).

Ground-water samples are usually filtered with a 0.45 μm filter prior to analysis for metals, though this is not always required and has recently been prohibited by many states and some U.S. EPA programs that require analysis of total metals. Interest in measurement of total metal concentrations (dissolved and particulate-associated metals) usually derives from concern about possible transport of metals adsorbed on mobile colloidal particles (e.g., Kaplan et al., 1995). Research indicates that significant colloid-facilitated transport of metals can occur only under a fairly specialized set of conditions (Roy and Dzombak, 1997), but the conservative approach in monitoring system design is to try to capture any mobile colloids present. The problem with sampling groundwater without filtration is that particles from the well material, well slime coatings, or well pack may be sampled, and any subsequent analysis will not accurately reflect ground-water composition. To avoid such artifacts, but still permit sampling that can capture any mobile colloids present in the groundwater, monitoring wells are purged before sampling to remove the casing water and obtain representative ground-water samples. Low-flow purging and sampling techniques have been developed to minimize sample disturbances that may affect analysis (Puls, 1994; Puls and Paul, 1995).

2.4 CHEMICAL FATE AND MOBILITY

The fate and transport of a metal in soil and groundwater depends significantly on the chemical form and speciation of the metal (Allen et al., 1991). The mobility of metals in ground-water systems is hindered by reactions that cause metals to adsorb or precipitate, or chemistry that tends to keep metals associated with the solid phase and prevent them from dissolving. These mechanisms can retard the movement of metals and also provide a long-term source of metal contaminants (NRC, 1994). While the various metals undergo similar reactions in a number of aspects, the extent and nature of these reactions varies

under particular conditions. In Figure 2, for example, the extent of sorption of several metal cations and anions onto iron oxide is shown as a function of pH for a particular background electrolyte composition. It may be seen there that lead sorbs extensively at much lower pH values than zinc or cadmium (Kinniburgh et al., 1976).

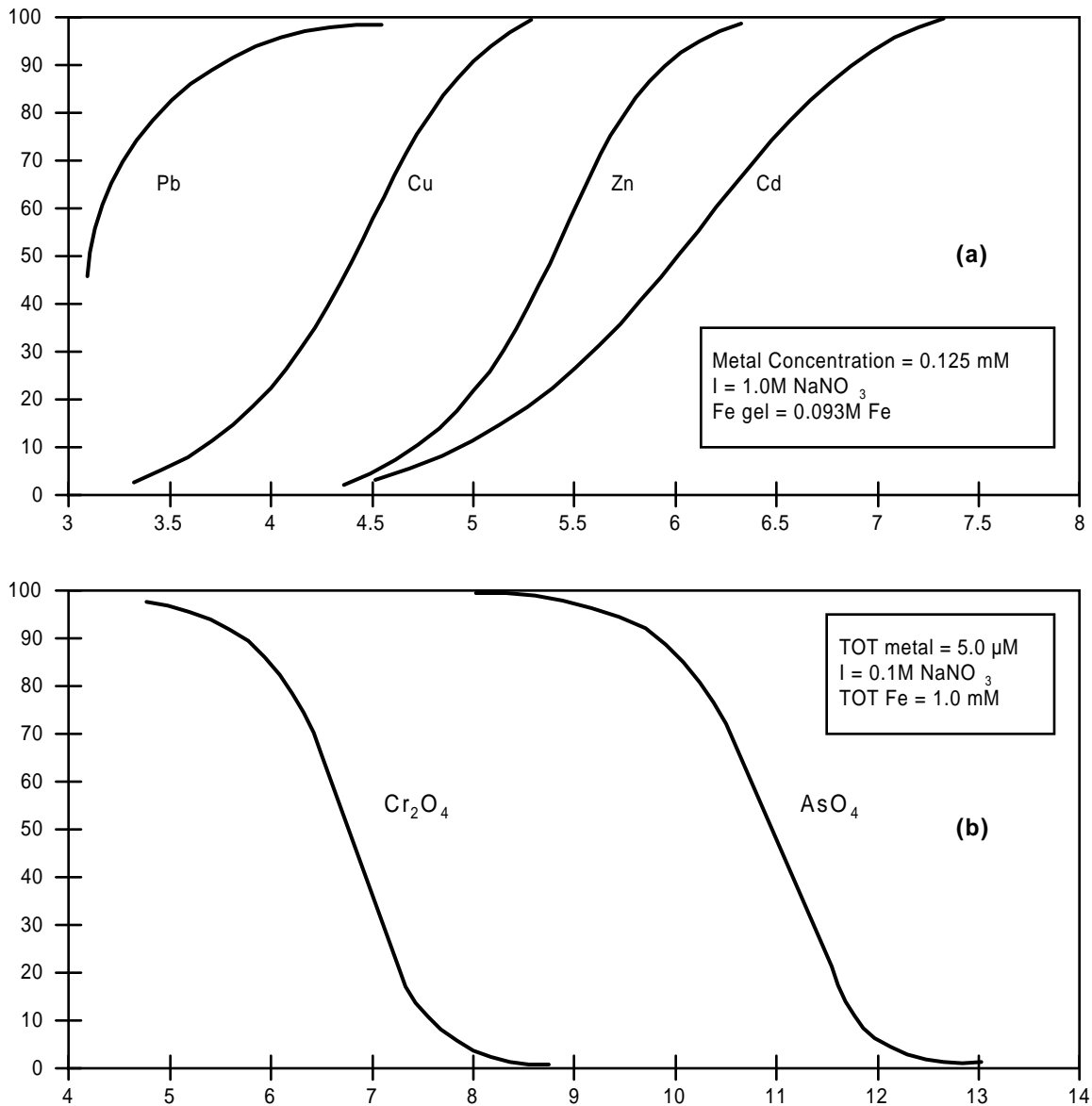


Figure 2. Metal Adsorption to Hydrous Iron Oxide Gels (a) Metal Cations (adapted from Kinniburgh et al., 1976) and (b) Metal Anions (adapted from Leckie et al., 1980; Honeyman et al., 1984)

The chemical form and speciation of some of the more important metals found at contaminated sites are discussed below. The influence of chemical form on fate and mobility of these compounds is also discussed.

2.4.1 Lead

The primary industrial sources of lead (Pb) contamination include metal smelting and processing, secondary metals production, lead battery manufacturing, pigment and chemical manufacturing, and lead-contaminated wastes. Widespread contamination due to the former use of lead in gasoline is also of concern. Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and lead-metal oxyanion complexes (Smith et al., 1995).

Lead occurs most commonly with an oxidation state of 0 or +II. Pb(II) is the more common and reactive form of lead and forms mononuclear and polynuclear oxides and hydroxides. Under most conditions Pb^{2+} and lead-hydroxy complexes are the most stable forms of lead (Smith et al., 1995). Low solubility compounds are formed by complexation with inorganic (Cl^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-}) and organic ligands (humic and fulvic acids, EDTA, amino acids) (Bodek et al., 1988). Lead carbonate solids form above pH 6 and PbS is the most stable solid when high sulfide concentrations are present under reducing conditions.

Most lead that is released to the environment is retained in the soil (Evans, 1989). The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater. The relatively volatile organolead compound tetramethyl lead may form in anaerobic sediments as a result of alkylation by microorganisms (Smith et al., 1995).

The amount of dissolved lead in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. In surface water and ground-water systems, a significant fraction of lead is undissolved and occurs as precipitates ($PbCO_3$, Pb_2O , $Pb(OH)_2$, $PbSO_4$), sorbed ions or surface coatings on minerals, or as suspended organic matter.

2.4.2 Chromium

Chromium(Cr) is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$. Major sources of Cr contamination include releases from electroplating processes and the disposal of chromium containing wastes (Smith et al., 1995).

Cr(VI) is the form of chromium commonly found at contaminated sites. Chromium can also occur in the +III oxidation state, depending on pH and redox conditions. Cr (VI) is the dominant form of chromium in shallow aquifers where aerobic conditions exist. Cr(VI) can be reduced to Cr(III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions often encountered in deeper groundwater. Major Cr(VI) species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) which precipitate readily in the presence of metal cations

(especially Ba^{2+} , Pb^{2+} , and Ag^+). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Cr(III) is the dominant form of chromium at low pH (<4). Cr^{3+} forms solution complexes with NH_3 , OH^- , Cl^- , F^- , CN^- , SO_4^{2-} , and soluble organic ligands. Cr(VI) is the more toxic form of chromium and is also more mobile. Cr(III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of $\text{Cr}(\text{OH})_3(\text{s})$ (Chrotowski et al., 1991).

Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and unadsorbed chromium complexes can leach from soil into groundwater. The leachability of Cr(VI) increases as soil pH increases. Most of chromium released into natural waters is particle associated, however, and is ultimately deposited into the sediment (Smith et al., 1995).

2.4.3 Arsenic

Arsenic (As) is a semimetallic element that occurs in a wide variety of minerals, mainly as As_2O_3 , and can be recovered from processing of ores containing mostly copper, lead, zinc, silver and gold. It is also present in ashes from coal combustion. Arsenic exhibits fairly complex chemistry and can be present in several oxidation states (-III, 0, III, V) (Smith et al., 1995).

In aerobic environments, As(V) is dominant, usually in the form of arsenate (AsO_4^{3-}) in various protonation states: H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-} . Arsenate, and other anionic forms of arsenic behave as chelates and can precipitate when metal cations are present (Bodek et al., 1988). Metal arsenate complexes are stable only under certain conditions. As(V) can also coprecipitate with or adsorb onto iron oxyhydroxides under acidic and moderately reducing conditions. Coprecipitates are immobile under these conditions but arsenic mobility increases as pH increases (Smith et al., 1995).

Under reducing conditions As(III) dominates, existing as arsenite (AsO_3^{3-}) and its protonated forms: H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} . Arsenite can adsorb or coprecipitate with metal sulfides and has a high affinity for other sulfur compounds. Elemental arsenic and arsine, AsH_3 , may be present under extreme reducing conditions. Biotransformation (via methylation) of arsenic creates methylated derivatives of arsine, such as dimethyl arsine $\text{HAs}(\text{CH}_3)_2$ and trimethylarsine $\text{As}(\text{CH}_3)_3$ which are highly volatile.

Since arsenic is often present in anionic form, it does not form complexes with simple anions such as Cl^- and SO_4^{2-} . Arsenic speciation also includes organometallic forms such as methylarsinic acid $(\text{CH}_3)\text{AsO}_2\text{H}_2$ and dimethylarsinic acid $(\text{CH}_3)_2\text{AsO}_2\text{H}$.

Many arsenic compounds sorb strongly to soils and are therefore transported only over short distances in groundwater and surface water. Sorption and coprecipitation with hydrous

iron oxides are the most important removal mechanisms under most environmental conditions (Krause and Ettel, 1989; Pierce and Moore, 1982). Arsenates can be leached easily if the amount of reactive metal in the soil is low. As(V) can also be mobilized under reducing conditions that encourage the formation of As(III), under alkaline and saline conditions, in the presence of other ions that compete for sorption sites, and in the presence of organic compounds that form complexes with arsenic (Smith et al., 1995).

2.4.4 Zinc

Zinc (Zn) does not occur naturally in elemental form. It is usually extracted from mineral ores to form zinc oxide (ZnO). The primary industrial use for Zinc is as a corrosion-resistant coating for iron or steel (Smith et al., 1995).

Zinc usually occurs in the +II oxidation state and forms complexes with a number of anions, amino acids and organic acids. Zn may precipitate as $Zn(OH)_2(s)$, $ZnCO_3(s)$, $ZnS(s)$, or $Zn(CN)_2(s)$.

Zinc is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values. At higher pH values, zinc can form carbonate and hydroxide complexes which control zinc solubility. Zinc readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations, and may coprecipitate with hydrous oxides of iron or manganese (Smith et al., 1995).

Sorption to sediments or suspended solids, including hydrous iron and manganese oxides, clay minerals, and organic matter, is the primary fate of zinc in aquatic environments. Sorption of zinc increases as pH increases and salinity decreases.

2.4.5 Cadmium

Cadmium (Cd) occurs naturally in the form of CdS or $CdCO_3$. Cadmium is recovered as a by-product from the mining of sulfide ores of lead, zinc and copper. Sources of cadmium contamination include plating operations and the disposal of cadmium-containing wastes (Smith et al., 1995).

The form of cadmium encountered depends on solution and soil chemistry as well as treatment of the waste prior to disposal. The most common forms of cadmium include Cd^{2+} , cadmium-cyanide complexes, or $Cd(OH)_2$ solid sludge (Smith et al., 1995). Hydroxide ($Cd(OH)_2$) and carbonate ($CdCO_3$) solids dominate at high pH whereas Cd^{2+} and aqueous sulfate species are the dominant forms of cadmium at lower pH (<8). Under reducing conditions when sulfur is present, the stable solid CdS(s) is formed. Cadmium will also precipitate in the presence of phosphate, arsenate, chromate and other anions, although solubility will vary with pH and other chemical factors.

Cadmium is relatively mobile in surface water and ground-water systems and exists primarily as hydrated ions or as complexes with humic acids and other organic ligands (Callahan et al., 1979). Under acidic conditions, cadmium may also form complexes with chloride and sulfate. Cadmium is removed from natural waters by precipitation and sorption to mineral surfaces, especially oxide minerals, at higher pH values (>pH 6). Removal by these mechanisms increases as pH increases. Sorption is also influenced by the cation exchange capacity (CEC) of clays, carbonate minerals, and organic matter present in soils and sediments. Under reducing conditions, precipitation as CdS controls the mobility of cadmium (Smith et al., 1995).

2.4.6 Copper

Copper (Cu) is mined as a primary ore product from copper sulfide and oxide ores. Mining activities are the major source of copper contamination in groundwater and surface waters. Other sources of copper include algicides, chromated copper arsenate (CCA) pressure-treated lumber, and copper pipes.

Solution and soil chemistry strongly influence the speciation of copper in ground-water systems. In aerobic, sufficiently alkaline systems, CuCO_3 is the dominant soluble copper species. The cupric ion, Cu^{2+} , and hydroxide complexes, CuOH^+ and $\text{Cu}(\text{OH})_2$, are also commonly present. Copper forms strong solution complexes with humic acids. The affinity of Cu for humates increases as pH increases and ionic strength decreases. In anaerobic environments, when sulfur is present $\text{CuS}(\text{s})$ will form.

Copper mobility is decreased by sorption to mineral surfaces. Cu^{2+} sorbs strongly to mineral surfaces over a wide range of pH values (Dzombak and Morel, 1990).

The cupric ion (Cu^{2+}) is the most toxic species of copper. Copper toxicity has also been demonstrated for CuOH^+ and $\text{Cu}_2(\text{OH})_2^{2+}$ (LaGrega et al., 1994).

2.4.7 Mercury

The primary source of mercury is the sulfide ore cinnabar. Mercury (Hg) is usually recovered as a by-product of ore processing (Smith et al., 1995). Release of mercury from coal combustion is a major source of mercury contamination. Releases from manometers at pressure measuring stations along gas/oil pipelines also contribute to mercury contamination.

After release to the environment, mercury usually exists in mercuric (Hg^{2+}), mercurous (Hg_2^{2+}), elemental (Hg^0), or alkylated form (methyl/ethyl mercury). The redox potential and pH of the system determine the stable forms of mercury that will be present. Mercurous and mercuric mercury are more stable under oxidizing conditions. When mildly reducing conditions exist, organic or inorganic mercury may be reduced to elemental mercury, which may then be converted to alkylated forms by biotic or abiotic processes. Mercury is most

toxic in its alkylated forms which are soluble in water and volatile in air (Smith et al., 1995).

Hg(II) forms strong complexes with a variety of both inorganic and organic ligands, making it very soluble in oxidized aquatic systems (Bodek et al., 1988). Sorption to soils, sediments, and humic materials is an important mechanism for removal of mercury from solution. Sorption is pH-dependent and increases as pH increases. Mercury may also be removed from solution by coprecipitation with sulfides (Smith et al., 1995).

Under anaerobic conditions, both organic and inorganic forms of mercury may be converted to alkylated forms by microbial activity, such as by sulfur-reducing bacteria. Elemental mercury may also be formed under anaerobic conditions by demethylation of methyl mercury, or by reduction of Hg(II). Acidic conditions (pH<4) also favor the formation of methyl mercury, whereas higher pH values favor precipitation of HgS(s) (Smith et al., 1995).

2.5 INFLUENCE OF SOIL PROPERTIES ON MOBILITY

Chemical and physical properties of the contaminated matrix influence the mobility of metals in soils and groundwater. Contamination exists in three forms in the soil matrix: solubilized contaminants in the soil moisture, adsorbed contaminants on soil surfaces, and contaminants fixed chemically as solid compounds. The chemical and physical properties of the soil will influence the form of the metal contaminant, its mobility, and the technology selected for remediation (Gerber et al., 1991).

2.5.1 Chemical Properties

The presence of inorganic anions (carbonate, phosphate, sulfide) in the soil water can influence the soil's ability to fix metals chemically. These anions can form relatively insoluble complexes with metal ions and cause metals to desorb and/or precipitate in their presence.

Soil pH values generally range between 4.0 and 8.5 with buffering by Al at low pH and by CaCO₃ at high pH (Wild, 1988). Metal cations are most mobile under acidic conditions while anions tend to sorb to oxide minerals in this pH range (Dzombak and Morel, 1987). At high pH, cations precipitate or adsorb to mineral surfaces and metal anions are mobilized. The presence of hydrous metal oxides of Fe, Al, Mn can strongly influence metal concentrations because these minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation (Ellis and Fogg, 1985; Dzombak and Morel, 1987). As noted in the previous section, sorption of metal cations onto hydrous oxides generally increases sharply with pH and is most significant at pH values above the neutral range, while sorption of metal anions is greatest at low pH and decreases as pH is increased (Figure 3). Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations on a mineral surface and is often used to indicate the affinity of soils for uptake of cations such as metals. Anion exchange capacity (AEC) indicates the affinity of soils for uptake of anions, and is usually significantly lower than the CEC of the soil. In addition to hydrous oxides, clays are also important ion exchange materials for metals

(Sposito, 1989). The presence of natural organic matter (NOM) has been shown to influence the sorption of metal ions to mineral surfaces. NOM has been observed to enhance sorption of Cu^{2+} at low pH, and suppress Cu^{2+} sorption at high pH (Tipping et al., 1983; Davis, 1984).

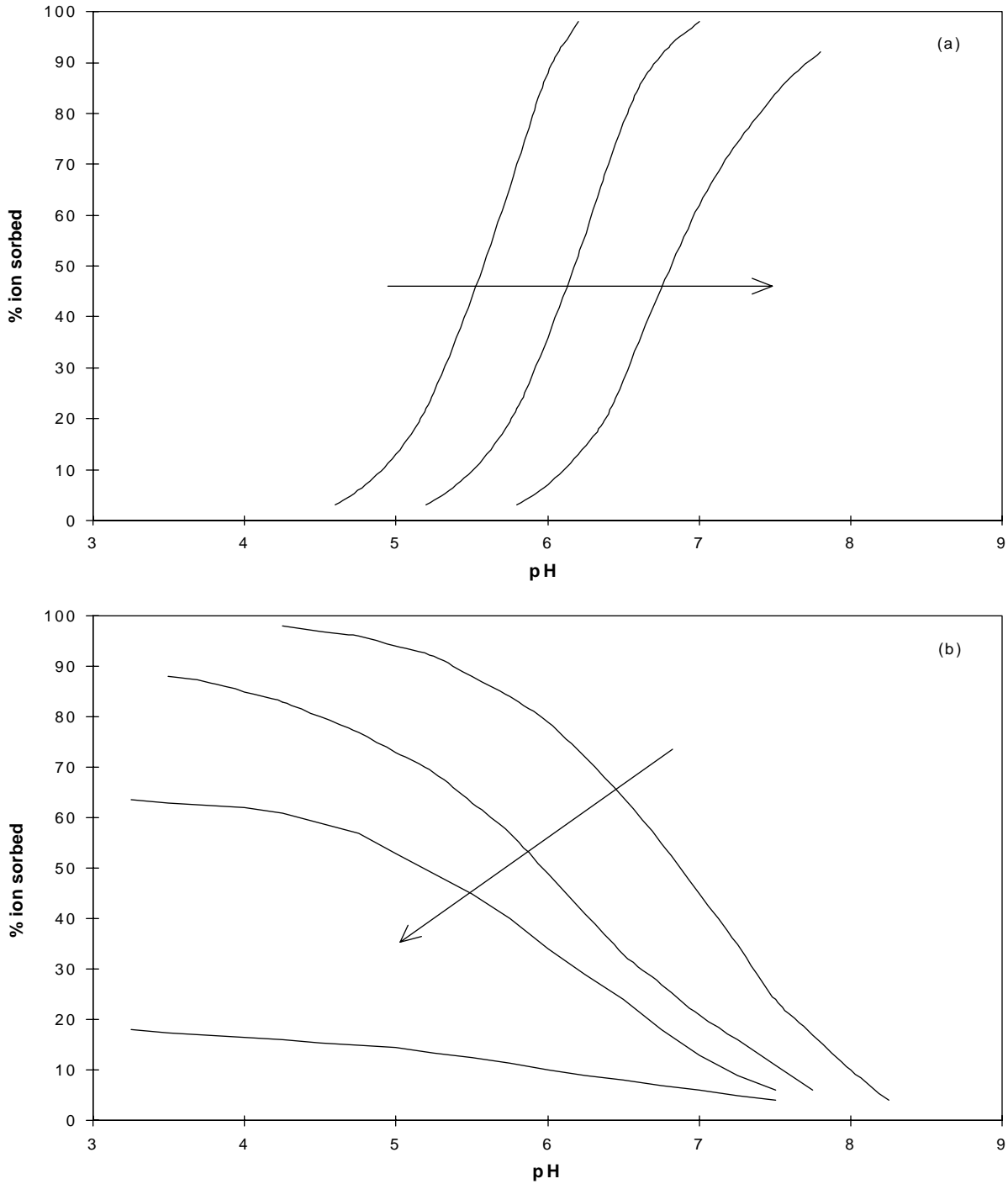


Figure 3. Typical pH edges for (a) cation sorption and (b) anion sorption. Arrows indicate direction of increasing sorbate/sorbent ratio. (From Dzombak, and Morel, 1990)

Organic matter, particularly humic materials, can complex metals and affect their removal from solution (Ali and Dzombak, 1996). Humic materials contain carboxylic and phenolic functional groups that can complex with metal ions.

2.5.2 Physical Properties

Particle size distribution can influence the level of metal contamination in a soil. Fine particles (<100 μm) are more reactive and have a higher surface area than coarser material. As a result, the fine fraction of a soil often contains the majority of contamination. The distribution of particle sizes with which a metal contaminant is associated can determine the effectiveness of a number of metal remediation technologies, e.g., soil washing (Dzombak et al., 1994).

Soil moisture influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water depends on the soil moisture content.

Soil structure describes the size, shape, arrangement and degree of development of soils into structural units. Soil structure can influence contaminant mobility by limiting the degree of contact between groundwater and contaminants.

3.0 AVAILABLE TECHNOLOGIES AND PERFORMANCE

3.1 SITE CHARACTERIZATION AND ESTABLISHMENT OF REMEDIATION GOALS

The physical and chemical form of the metal contaminant in soil or water strongly influences the selection of the appropriate remediation treatment approach. Information about the physical characteristics of the site and the type and level of contamination at the site must be obtained to enable accurate assessment of site contamination and remedial alternatives. The importance of adequate, well-planned site characterization to selection of an appropriate cost-effective remediation approach has been discussed many times (e.g., CII, 1995) but cannot be overemphasized. The contamination in the groundwater and soil should be characterized to establish the type, amount, and distribution of contaminants across different media.

Once the site has been characterized, the desired level of each contaminant in soil and groundwater must be determined. This is done by comparison of observed contaminant concentrations with soil and ground-water quality standards for a particular regulatory domain, or by performance of a site-specific risk assessment. Remediation goals for metals may be set as desired concentrations in groundwater, as total metal concentration in soil, as leachable metal in soil, or as some combination of these.

3.2 GENERAL REMEDIATION APPROACHES

Several technologies exist for the remediation of metals-contaminated soil and water. These technologies are contained within five categories of general approaches to remediation: isolation, immobilization, toxicity reduction, physical separation and extraction. These are the same general approaches used for many types of contaminants in the subsurface (LaGrega et al., 1994). As is usually the case, combinations of one or more of these approaches are often used for more cost-effective treatment of a contaminated site. Table 1 summarizes key factors discussed in this report that were found to influence the applicability and selection of available remediation technologies.

3.2.1 Isolation

Isolation technologies attempt to prevent the transport of contaminants by containing them within a designated area. These technologies can be used to prevent further contamination of groundwater when other treatment options are not physically or economically feasible for a site. Contaminated sites may also be isolated temporarily in order to limit transport during site assessment and site remediation.

Table 1. Remediation Technologies Matrix for Metals in Soils and Ground-Water

Remediation Technology	Metals Treated	Cost	Long-term Effectiveness/ Permanence	Commercial Availability	General Acceptance	Applicability to High Metals Concentrations	Applicability to Mixed Waste (metals & organics)	Toxicity Reduction	Mobility Reduction	Volume Reduction
Capping	1-3	+	«	+	+	«	+	«	+	«
Subsurface Barriers	1-3,5	+	«	+	+	«	+	«	+	«
Solidification/ Stabilization <i>Ex situ</i>	1-3,5	•	•	+	+	+	+	«	+	«
Solidification/ Stabilization <i>In situ</i>	1,2,4,6	+	•	+	+	+	+	«	+	«
Vitrification <i>Ex situ</i>	1-3,5	«	+	•	•	+	+	«	+	«
Vitrification <i>In situ</i>	1-3,7	«	+	•	•	+	+	«	+	«
Chemical Treatment	2	-	•	•	•	-	-	+	+	«
Permeable Treatment Walls	2	-	•	•	•	-	-	+	+	«
Biological Treatment	1-5	+	«	•	•	«	-	+	+	«
Physical Separation	1-6	•	+	+	+	+	«	«	«	+
Soil Washing	1-3,5-7	•	+	+	+	+	•	«	«	+
Pyrometallurgical Extraction	1-5,7	«	+	+	+	+	«	«	«	+
<i>In situ</i> Soil Flushing	1,2,7	+	«	+	+	+	+	«	«	+
Electrokinetic Treatment	1-6	•	+	+	+	+	-	«	«	+

1-Lead, 2-Chromium, 3-Arsenic, 4-Zinc, 5-Cadmium, 6-Copper, 7-Mercury
 + Good, • Average, « Marginal, - Inadequate Information

3.2.1.1 Capping

Capping systems are used to provide an impermeable barrier to surface water infiltration to contaminated soil for prevention of further release of contaminants to the surrounding surface water or groundwater. Secondary objectives include controlling gas and odor emissions, improving aesthetics, and providing a stable surface over a contaminated site. Capping also eliminates risks associated with dermal contact and/or incidental ingestion of surface soils, but if this is the primary goal for the site and surface water infiltration is not a concern, a less expensive permeable cover may be preferred.

Capping provides a range of design options that includes simple single-layer caps and more complex multilayer systems (Rumer and Ryan, 1995; U.S. EPA, 1991). Design selection depends on site characteristics, remedial objectives and risk factors associated with the site. A variety of materials are available for use in capping systems and choice of materials is site specific because local soils are often incorporated into parts of the cap. Synthetic membranes such as high-density polyethylene are also available for incorporation into capping systems. Surface water controls, such as ditches and dikes are usually included to help control drainage from the cap. Multilayered capping systems may also include a hard cover and/or a layer of topsoil to separate the underlying layers from the ground surface. Revegetation is promoted in order to reinforce the topsoil, to reduce soil erosion and runoff velocity, and to help remove water from the soil by evapotranspiration (Rumer and Ryan, 1995).

3.2.1.2 Subsurface Barriers

Subsurface barriers may be used to isolate contaminated soil and water by controlling the movement of groundwater at a contaminated site. These barriers are designed to reduce the movement of contaminated groundwater from the site, or to restrict the flow of uncontaminated groundwater through the contaminated site (Rumer and Ryan, 1995).

Vertical barriers are commonly used to restrict the lateral flow of groundwater. For effective isolation of the contaminated matrix, the barrier should extend and key into a continuous, low-permeability layer, such as clay or competent bedrock, below the contaminated area (U.S. EPA, 1985; Rumer and Ryan, 1995). If an impermeable layer is not available, a ground-water extraction system must be used to prevent transport of contaminants under the barrier. Vertical barriers may be installed upstream, downstream, or completely surrounding the site and are often implemented in conjunction with a capping system to control surface water infiltration. The use of circumferential barriers can prevent the escape of contamination from the site by using an infiltration barrier and collection system to create a hydraulic gradient in the inward direction. Vertical barriers are often limited to depths achievable with backhoe excavation technology for trenches, i.e., to about 30 feet (U.S. EPA, 1985).

Slurry walls are usually constructed in a vertical trench excavated under a slurry that is designed to prevent collapse and to form a filter cake on the walls of the trench to prevent

the loss of fluids to the surrounding soil (Xanthakos, 1979). A vibrating beam method (Slurry Systems, Inc.) is also available in which the beam penetrates the ground and slurry materials are injected into the soil (with assistance from a high pressure/low volume jet if needed). Two options exist for the slurry composition. The soil-bentonite (SB) slurry wall is the most common type, and comprises a bentonite-water slurry that is mixed with a soil engineered to harden upon addition to the slurry (Rumer and Ryan, 1995). The trench can also be excavated under a portland cement-bentonite-water slurry that is left to harden and form a cement-bentonite (CB) slurry wall (LaGrega et al., 1994). Available technologies for installation of slurry walls allow installation to depths up to 125 feet.

Slurry walls are the most common type of vertical barrier due to their low relative cost. The use of slurry walls can be limited by the topography, geology, and type of contamination at the site. For example, an SB slurry will flow unless the site and confining layer are nearly level. Also, some contaminants, such as concentrated organics and strong acids/bases, can degrade SB materials and prevent the application of SB slurry walls at some sites (Rumer and Ryan, 1995).

Other available vertical barriers include grout curtains and sheet piles. Grout curtains are constructed by drilling a borehole and injecting a fluid into the surrounding soil that is designed to solidify and reduce water flow through the contaminated region (U.S. EPA, 1985). The fluid is pressure-injected in rows of staggered boreholes that are designed to overlap once the fluid has permeated into the surrounding soil. Common materials used to construct grout curtains include cement, clays, alkali-silicate, and organic polymers (Rumer and Ryan, 1995). Clays are the most widely used grouting materials due to their low cost. This technique is more expensive than slurry walls and its use is therefore usually limited to sealing voids in existing rock.

Sheet piles usually comprise steel pilings that are driven into the formation to create a wall to contain the groundwater. Sheet piles are seldom used at contaminated sites due to concerns about wall integrity. This method is generally limited to isolation of shallow contamination (40-50 ft) distributed over a relatively small area (U.S. EPA, 1985), or used in conjunction with a soil-bentonite slurry when site conditions prevent the use of conventional slurry walls (Rumer and Ryan, 1995).

Technologies for the construction of horizontal barriers are under investigation. Horizontal barriers would enable control of the downward migration of contaminants by lining the site without requiring excavation of the contaminated matrix. The technologies under investigation include grout injection by vertical boring and horizontal drilling. The vertical boring method is similar to the construction of grout curtains except that the grout is injected at a fixed elevation over a tightly spaced grid of vertical boreholes to create an impermeable horizontal layer. Problems with this method include soil compaction by the large drill rigs situated over the contaminated area. Also, the vertical boreholes would provide access to the deeper layers and may therefore increase vertical migration of contaminants. Horizontal drilling involves the use of directional drilling techniques to create the horizontal grout layer.

Horizontal barriers may also be used in conjunction with vertical barriers at sites where a natural aquitard is not present. In this case, the vertical barrier could key into the horizontal barrier to prevent the transport of contaminants under the vertical barrier (Smith et al., 1995).

3.2.2 Immobilization

Immobilization technologies are designed to reduce the mobility of contaminants by changing the physical or leaching characteristics of the contaminated matrix. Mobility is usually decreased by physically restricting contact between the contaminant and the surrounding groundwater, or by chemically altering the contaminant to make it more stable with respect to dissolution in groundwater. The aqueous and solid phase chemistry of metals is conducive to immobilization by these techniques. A variety of methods are available for immobilization of metal contaminants, including those that use chemical reagents and/or thermal treatment to physically bind the contaminated soil or sludge. Most immobilization technologies can be performed *ex situ* or *in situ*. *In situ* processes are preferred due to the lower labor and energy requirements, but implementation *in situ* will depend on specific site conditions.

3.2.2.1 Solidification/Stabilization

Solidification and stabilization (S/S) immobilization technologies are the most commonly selected treatment options for metals-contaminated sites (Conner, 1990). Solidification involves the formation of a solidified matrix that physically binds the contaminated material. Stabilization, also referred to as fixation, usually utilizes a chemical reaction to convert the waste to a less mobile form. The general approach for solidification/stabilization treatment processes involves mixing or injecting treatment agents to the contaminated soils. Inorganic binders, such as cement, fly ash, or blast furnace slag, and organic binders such as bitumen are used to form a crystalline, glassy or polymeric framework around the waste. The dominant mechanism by which metals are immobilized is by precipitation of hydroxides within the solid matrix (Bishop et al., 1982; Shively et al., 1986).

S/S technologies are not useful for some forms of metal contamination, such as species that exist as anions (e.g., Cr(VI), arsenic) or metals that don't have low-solubility hydroxides (e.g., mercury). S/S may not be applicable at sites containing wastes that include organic forms of contamination, especially if volatile organics are present. Mixing and heating associated with binder hydration may release organic vapors. Pretreatment, such as air stripping or incineration, may be used to remove the organics and prepare the waste for metal stabilization/solidification (Smith et al., 1995). The application of S/S technologies will also be affected by the chemical composition of the contaminated matrix, the amount of water present, and the ambient temperature. These factors can interfere with the solidification/stabilization process by inhibiting bonding of the waste to the binding material, retarding the setting of the mixtures, decreasing the stability of the matrix, or reducing the strength of the solidified area (U.S. EPA, 1990b).

Cement-based binders and stabilizers are common materials used for implementation of S/S technologies (Conner, 1990). Portland cement, a mixture of Ca-silicates, aluminates, aluminoferrites, and sulfates is an important cement-based material. Pozzolanic materials which consist of small spherical particles formed by coal combustion (such as fly ash) and in lime and cement kilns, are also commonly used for S/S. Pozzolans exhibit cement-like properties, especially if the silica content is high. Portland cement and pozzolans can be used alone or together to obtain optimal properties for a particular site (U.S. EPA, 1989).

Organic binders may also be used to treat metals through polymer microencapsulation. This process uses organic materials such as bitumen, polyethylene, paraffins, waxes and other polyolefins as thermoplastic or thermosetting resins. For polymer encapsulation, the organic materials are heated and mixed with the contaminated matrix at elevated temperatures (120° to 200°C). The organic materials polymerize, agglomerate the waste and the waste matrix is encapsulated (U.S. EPA, 1989). Organics are volatilized and collected and the treated material is extruded for disposal or possible reuse (e.g., as paving material) (Smith et al., 1995). The contaminated material may require pretreatment to separate rocks and debris and dry the feed material. Polymer encapsulation requires more energy and more complex equipment than cement-based S/S operations. Bitumen (asphalt) is the cheapest and most common thermoplastic binder (U.S. EPA, 1989).

S/S is achieved by mixing the contaminated material with appropriate amounts of binder/stabilizer and water. The mixture sets and cures to form a solidified matrix and contain the waste. The cure time and pour characteristics of the mixture and the final properties of the hardened cement depend upon the composition (amount of cement, pozzolan, water) of the binder/stabilizer.

Ex situ S/S can be easily applied to excavated soils because methods are available to provide the vigorous mixing needed to combine the binder/stabilizer with the contaminated material. Pretreatment of the waste may be necessary to screen and crush large rocks and debris. Mixing can be performed via in-drum, in-plant or area mixing processes. In-drum mixing may be preferred for treatment of small volumes of waste or for toxic wastes. In-plant processes utilize rotary drum mixers for batch processes or pug mill mixers for continuous treatment. Larger volumes of waste may be excavated and moved to a contained area for area mixing. This process involves layering the contaminated material with the stabilizer/binder, and subsequent mixing with a backhoe or similar equipment. Mobile and fixed treatment plants are available for ex situ S/S treatment. Smaller pilot-scale plants can treat up to 100 tons of contaminated soil per day, while larger portable plants typically process 500 to over 1000 tons per day (Smith et al., 1995).

S/S techniques are available to provide mixing of the binder/stabilizer with the contaminated soil *in situ*. *In situ* S/S is less labor and energy intensive than ex situ process that require excavation, transport and disposal of the treated material. *In situ* S/S is also preferred if volatile or semi volatile organics are present because excavation would expose these contaminants to the air (U.S. EPA, 1990a). However the presence of bedrock, large boulders,

cohesive soils, oily sands and clays may preclude the application of *in situ* S/S at some sites. It is also more difficult to provide uniform and complete mixing through *in situ* processes.

Mixing of the binder and contaminated matrix may be achieved using in-place mixing, vertical auger mixing or injection grouting. In-place mixing is similar to ex situ area mixing except that the soil is not excavated prior to treatment. The *in situ* process is useful for treating surface or shallow contamination and involves spreading and mixing the binders with the waste using conventional excavation equipment such as draglines, backhoes or clamshell buckets. Vertical auger mixing uses a system of augers to inject and mix the binding reagents with the waste. Larger (6-12 ft diameter) augers are used for shallow (10-40 ft) drilling and can treat 500-1000 cubic yards per day (Ryan and Walker, 1992; Jasperse and Ryan, 1992). Deep stabilization/solidification (up to 150 ft) can be achieved by using ganged augers (up to 3 ft in diameter each) that can treat 150-400 cubic yards per day. Finally injection grouting may be performed to inject the binder containing suspended or dissolved reagents into the treatment area under pressure. The binder permeates the surrounding soil and cures in place (Smith et al., 1995).

3.2.2.2 Vitrification

The mobility of metal contaminants can be decreased by high-temperature treatment of the contaminated area that results in the formation of vitreous material, usually an oxide solid. During this process, the increased temperature may also volatilize and/or destroy organic contaminants or volatile metal species (such as Hg) that must be collected for treatment or disposal. Most soils can be treated by vitrification and a wide variety of inorganic and organic contaminants can be targeted. Vitrification may be performed ex situ or *in situ*, although *in situ* processes are preferred due to the lower energy requirements and cost (U.S. EPA, 1992a).

Typical stages in ex situ vitrification processes may include excavation, pretreatment, mixing, feeding, melting and vitrification, off-gas collection and treatment, and forming or casting of the melted product. The energy requirement for melting is the primary factor influencing the cost of ex situ vitrification. Different sources of energy can be used for this purpose, depending on local energy costs. Process heat losses and water content of the feed should be controlled in order to minimize energy requirements. Vitrified material with certain characteristics may be obtained by using additives such as sand, clay and/or native soil. The vitrified waste may be recycled and used as clean fill, aggregate, or other reusable materials (Smith et al., 1995).

In situ vitrification (ISV) involves passing electric current through the soil using an array of electrodes inserted vertically into the contaminated region. Each setting of four electrodes is referred to as a melt. If the soil is too dry, it may not provide sufficient conductance and a trench containing flaked graphite and glass frit (ground glass particles) must be placed between the electrodes to provide an initial flow path for the current. Resistance heating in

the starter path melts the soil. The melt grows outward and down as the molten soil usually provides additional conductance for the current. A single melt can treat up to 1000 tons of contaminated soil to depths of 20 feet, at a typical treatment rate of 3 to 6 tons per hour. Larger areas are treated by fusing together multiple individual vitrification zones. The main requirement for *in situ* vitrification is the ability of the soil melt to carry current and solidify as it cools. If the alkali content (as Na₂O and K₂O) of the soil is too high (≥ 1.4 wt%) the molten soil may not provide enough conductance to carry the current (Buel and Thompson, 1992).

3.2.3 Toxicity and/or Mobility Reduction

Chemical and/or biological processes can be used to alter the form of metal contaminants in order to decrease their toxicity and/or mobility.

3.2.3.1 Chemical Treatment

Chemical reactions can be initiated that are designed to decrease the toxicity or mobility of metal contaminants. The three types of reactions that can be used for this purpose are oxidation, reduction, and neutralization reactions. Chemical oxidation changes the oxidation state of the metal atom through the loss of electrons. Commercial oxidizing agents are available for chemical treatment, including potassium permanganate, hydrogen peroxide, hypochlorite and chlorine gas. Reduction reactions change the oxidation state of metals by adding electrons. Commercially available reduction reagents include alkali metals (Na, K), sulfur dioxide, sulfite salts, and ferrous sulfate. Changing the oxidation state of metals by oxidation or reduction can detoxify, precipitate, or solubilize the metals (NRC, 1994). Chemical neutralization is used to adjust the pH balance of extremely acidic or basic soils and/or groundwater. This procedure can be used to precipitate insoluble metal salts from contaminated water, or in preparation for chemical oxidation or reduction.

Chemical treatment can be performed *ex situ* or *in situ*. However *in situ* chemical agents must be carefully selected so that they do not further contaminate the treatment area. The primary problem associated with chemical treatment is the nonspecific nature of the chemical reagents. Oxidizing/reducing agents added to the matrix to treat one metal will also target other reactive metals and can make them more toxic or mobile (NRC, 1994). Also, the long-term stability of reaction products is of concern since changes in soil and water chemistry might reverse the selected reactions.

Chemical treatment is often used as pretreatment for S/S and other treatment technologies. Reduction of Cr(VI) to Cr(III) is the most common form of chemical treatment and is necessary for remediation of wastes containing Cr(VI) by precipitation or S/S. Chromium in its Cr(III) form is readily precipitated by hydroxide over a wide range of pH values. Acidification may also be used to aid in Cr(VI) reduction. Arsenic may be treatable by chemical oxidation since arsenate, As(V), is less toxic, soluble and mobile than arsenite, As(III). Bench-scale work has indicated that arsenic stabilization may be achieved by precipitation and coprecipitation with Fe(III) (Smith et al., 1995).

3.2.3.2 Permeable Treatment Walls

Treatment walls remove contaminants from groundwater by degrading, transforming, precipitating or adsorbing the target solutes as the water flows through permeable trenches containing reactive material within the subsurface (Vidic and Pohland, 1996). Several methods are available for installation of permeable treatment walls, some of which employ slurry wall construction technology to create a permeable reactive curtain. The reactive zone can use physical, chemical and biological processes, or a combination of these. The ground-water flow through the wall may be enhanced by inducing a hydraulic gradient in the direction of the treatment zone or channeling ground-water flow toward the treatment zone (NRC, 1994).

Several types of treatment walls are being tried for arresting transport of metals in groundwater at contaminated sites. Trench materials being investigated include zeolite, hydroxyapatite, elemental iron, and limestone (Vidic and Pohland, 1996). Applications of elemental iron for chromium (VI) reduction and limestone for lead precipitation and adsorption are described below.

Elemental Iron

Trenches filled with elemental iron have shown promise for remediation of metals-contaminated sites. While investigations of this technology have focused largely on treatment of halogenated organic compounds, studies are being performed to assess the applicability to remediation of inorganic contaminants (Powell et al., 1994).

Low oxidation-state chemical species can serve as electron donors for the reduction of higher oxidation-state contaminants. This ability can be exploited to remediate metals that are more toxic and mobile in higher oxidation states, such as Cr(VI). Results of column experiments performed by Powell et al. (1994) and batch experiments performed by Cantrell et al. (1995) showed that chromate reduction was enhanced in systems containing iron filings in addition to the natural aquifer material. A field experiment has been initiated by researchers at the U.S. EPA National Risk Management Research Laboratory to investigate the use of zero-valent iron for chromium remediation at the U.S. Coast Guard air support base near Elizabeth City, North Carolina. Preliminary results indicate that the test barrier has reduced chromate in the groundwater to below detection limits (Wilson, 1995).

Limestone Barriers

The use of limestone treatment walls has been proposed for sites with metals contamination, in particular former lead acid battery recycling sites which have lead and acid contamination in groundwater and soil. In such cases, a limestone trench can provide neutralization of acidic groundwater. The attendant rise in pH promotes immobilization of any dissolved lead through precipitation and/or adsorption onto minerals. A limestone trench system is in design for implementation at the Tonolli Superfund site in Nesquehoning, Pennsylvania (U.S. EPA, 1992b)

There is some experience in the coal mining industry with use of limestone in the manner anticipated for the Tonolli site. Most of this experience has been acquired since 1990, when the concept of “anoxic limestone drains” was introduced (Turner and McCoy, 1990). Since that time, numerous limestone drain systems have been installed at Appalachian coal field sites (primarily in Kentucky, West Virginia, and Pennsylvania) in an attempt to control acid mine drainage. Summaries of installations and evolving design considerations are provided in Hedin and Nairn (1992), Hedin et al. (1994), and Hedin and Watzlaf (1994).

Design and operating guidelines for the anoxic limestone drains have for the most part been developed from trial and observation. Briefly, the systems in use employ fairly large, #3 or #4 (baseball size) limestone rocks. Anoxic mine water is directed to the limestone drain, which is installed with a soil cover to inhibit contact with air. Hedin and Nairn (1992) report that “some systems constructed with limestone powder and gravel have failed, apparently because of plugging problems.” Preliminary review of the literature on design of anoxic limestone drains indicates primary concern with maintenance of anoxic conditions in the drains. If high dissolved concentrations of Fe are present and aerobic conditions develop, insoluble ferric hydroxide can form and coat the limestone, rendering it ineffective. High concentrations of aluminum are also a concern, as aluminum hydroxide can precipitate and yield the same kind of coating problems. With use of large diameter stones, plugging is prevented even if precipitation occurs and the stones become coated with precipitate.

Available operating data for anoxic limestone drains indicate that they can be effective in raising the pH of strongly acidic water. Hedin and Watzlaf (1994) reviewed operating data for 21 limestone drain systems. The data they compiled showed fairly consistent increases in pH of highly acidic mine drainage (at pH 2.3 to 3.5) to pH values in the range of 6.0 to 6.7. Thus, there is clearly precedent for employing the limestone drain approach with some confidence of success in raising pH of highly acidic water. Long term (i.e., greater than 10 years) performance cannot be predicted with confidence as there has been relatively short duration operating experience. However, experience to date indicates clearly that limestone drain systems can operate effectively under appropriate conditions, especially anoxic or low-oxygen groundwater, for at least several years.

3.2.3.3 Biological Treatment

Biological treatment technologies are available for remediation of metals-contaminated sites. These technologies are commonly used for the remediation of organic contaminants and are beginning to be applied for metal remediation, although most applications to date have been at the bench and pilot scale (Schnoor, 1997). Biological treatment exploits natural biological processes that allow certain plants and microorganisms to aid in the remediation of metals. These processes occur through a variety of mechanisms, including adsorption, oxidation and reduction reactions, and methylation (Means and Hinchee, 1994).

Bioaccumulation

Bioaccumulation involves the uptake of metals from contaminated media by living organisms or dead, inactive biomass. Active plants and microorganisms accumulate metals as the result of normal metabolic processes via ion exchange at the cell walls, complexation reactions at the cell walls, or intra- and extracellular precipitation and complexation reactions. Adsorption to ionic groups on the cell surface is the primary mechanism for metal adsorption by inactive biomass. Accumulation in biomass has been shown to be as effective as some ion exchange resins for metals removal from water (Means and Hinchee, 1994).

Phytoremediation

Phytoremediation refers to the specific ability of plants to aid in metal remediation. Some plants have developed the ability to remove ions selectively from the soil to regulate the uptake and distribution of metals. Most metal uptake occurs in the root system, usually via absorption, where many mechanisms are available to prevent metal toxicity due to high concentration of metals in the soil and water. Potentially useful phytoremediation technologies for remediation of metals-contaminated sites include phytoextraction, phytostabilization and rhizofiltration (U.S. EPA, 1996b).

Phytoextraction

Phytoextraction employs hyperaccumulating plants to remove metals from the soil by absorption into the roots and shoots of the plant. A hyperaccumulator is defined as a plant with the ability to yield $\geq 0.1\%$ chromium, cobalt, copper or nickel or $\geq 1\%$ zinc, manganese in the aboveground shoots on a dry weight basis. The aboveground shoots can be harvested to remove metals from the site and subsequently disposed as hazardous waste or treated for the recovery of the metals.

Phytostabilization

Phytostabilization involves the use of plants to limit the mobility and bioavailability of metals in soil. Phytostabilizers are characterized by high tolerance of metals in surrounding soils but low accumulation of metals in the plant. This technique may be used as an interim containment strategy until other remediation techniques can be developed, or as treatment at sites where other methods would not be economically feasible.

Rhizofiltration

Rhizofiltration removes metals from contaminated groundwater via absorption, concentration and precipitation by plant roots. This technique is used to treat contaminated water rather than soil and is most effective for large volumes of water with low levels of metal contamination. Terrestrial plants are more effective than aquatic plants because they develop a longer, more fibrous root system that provides a larger surface area for interaction.

Wetlands construction is a form of rhizofiltration that has been demonstrated as a cost-effective treatment for metals-contaminated wastewater.

Bioleaching

Bioleaching uses microorganisms to solubilize metal contaminants either by direct action of the bacteria, as a result of interactions with metabolic products, or both. Bioleaching can be used *in situ* or *ex situ* to aid the removal of metals from soils. This process is being adapted from the mining industry for use in metals remediation. The mechanisms responsible for bioleaching are not fully defined, but in the case of mercury bioreduction (to elemental mercury) is thought to be responsible for mobilization of mercury salts (Means and Hinchee, 1994).

Biochemical Processes

Microbially mediated oxidation and reduction reactions can be manipulated for metal remediation. Some microorganisms can oxidize/reduce metal contaminants directly while others produce chemical oxidizing/reducing agents that interact with the metals to effect a change in oxidation state. Mercury and cadmium have been observed to be oxidized through microbial processes, and arsenic and iron are readily reduced in the presence of appropriate microorganisms. The mobility of metal contaminants is influenced by their oxidation state. Redox reactions can therefore be used to increase or decrease metal mobility (Means and Hinchee, 1994).

Methylation involves attaching methyl groups to inorganic forms of metal ions to form organometallic compounds. Methylation reactions can be microbially mediated. Organometallic compounds are more volatile than inorganic metals and this process can be used to remove metals through volatilization and subsequent removal from the gas stream. However, organometallics are also more toxic and mobile than other metal forms and may potentially contaminate surrounding surface waters and groundwater (Means and Hinchee, 1994).

3.2.4 Physical Separation

Physical separation is an *ex situ* process that attempts to separate the contaminated material from the rest of the soil matrix by exploiting certain characteristics of the metal and soil. Physical separation techniques are available that operate based on particle size, particle density, surface and magnetic properties of the contaminated soil. These techniques are most effective when the metal is either in the form of discrete particles in the soil or if the metal is sorbed to soil particles that occur in a particular size fraction of the soil. Physical separation is often used as a form of pretreatment in order to reduce the amount of material requiring subsequent treatment (Rosetti, 1993). Several techniques are available for physical separation of contaminated soils including screening, classification, gravity concentration, magnetic separation and froth flotation.

Screening separates soils according to particle size by passing the matrix through a sieve with particular size openings. Smaller particles pass through the sieve and leave larger particles behind, however, the separation is not always complete. Screening may be performed as a stationary process or with motion using a wet or dry process stream (Smith et al., 1995).

Classification involves separation of particles based upon the velocity with which they fall through water (hydroclassification) or air (air classification). Hydroclassification is more common for soil separation and may be performed using a non-mechanical, mechanical or a hydraulic classifier (Rosetti, 1993).

Gravity concentration relies on gravity and one or more other forces (centrifugal force, velocity gradients, etc.) that may be applied to separate particles on the basis of density differences. Gravity concentration may be achieved through the use of a hydrocyclone, jig, spiral concentrator, or shaking table (Rosetti, 1993).

Froth flotation uses air flotation columns or cells to remove particles from water. In this process, air is sparged from the bottom of a tank or column that contains a slurry of the contaminated material. Some metals and minerals attach to the air bubbles due to particular surface properties, such as hydrophobicity. Froth flotation can be used to remove metals that attach to air bubbles, or to remove other minerals while the metal remains in the slurry (Rosetti, 1993).

Magnetic separation subjects particles to a strong magnetic field using electromagnets or magnetic filters and relies on differences in magnetic properties of minerals for separation. Low intensity wet magnetic separators are the most common magnetic separation devices. This process can recover a wide variety of minerals and is particularly successful for separating ferrous from nonferrous minerals (Allen and Torres, 1991).

3.2.5 Extraction

Metals-contaminated sites can be remediated using techniques designed to extract the contaminated fraction from the rest of the soil, either *in situ* or *ex situ*. Metal extraction can be achieved by contacting the contaminated soil with a solution containing extracting agents (soil washing and *in situ* soil flushing) or by electrokinetic processes. The contaminated fraction of soil and/or process water is separated from the remaining soil and disposed or treated.

3.2.5.1 Soil Washing

Soil washing can be used to remove metals from the soil by chemical or physical treatment methods in aqueous suspension. Soil washing is an *ex situ* process that requires soil excavation prior to treatment. Chemical treatment involves addition of extraction agents that react with the contaminant and leach it from the soil (Elliot and Brown, 1989; Ellis and

Fogg, 1985; Tuin and Tels, 1990). The liquid containing the contaminants is separated from the soil resulting in a clean solid phase. Physical treatment is achieved by particle size separation technologies adapted from mineral processing to concentrate the contaminant in a particular size fraction (Allen and Torres, 1991).

Fine particles (<63 µm) often contain the majority of contaminated material because they bind contaminants strongly due to their large and reactive surface area. Many current soil washing approaches attempt to separate the fine fraction from the remainder of the soil in order to reduce the amount of material for subsequent treatment or disposal (Rosetti, 1993). Particle size separation techniques may not be successful if fine particle, e.g., metal oxide, coatings are present on particles in larger size fractions (Van Ben Schoten et al., 1994).

Preliminary Screening

After excavation, the soil undergoes preliminary screening and preparation in order to separate large rocks and debris from the contaminated matrix. Residual fines may be adhered to the surface of large rocks and are often washed off prior to return of the large rocks to the site (Rosetti, 1993).

Secondary Screening

Most soil washing processes employ secondary screening to segregate the particles into different size fractions, usually between 5 mm and 60 mm. Most secondary screening processes involve making an aqueous slurry of the soil stream and wet screening/sieving of the slurry. The particles in this size range are considered less contaminated than the finer fraction and may be returned to the site as clean soil after separation from the water (Rosetti, 1993).

Chemical Treatment

Chemical treatment may be used to solubilize contaminants from the most contaminated fraction of the soil. Chemical treatment is performed in an aqueous slurry of the contaminated material to which an extracting agent is added. The extraction is performed in a mixing vessel or in combination with the physical treatment stage. The type of extractant used will depend on the contaminants present and the characteristics of the soil matrix. Many processes manipulate the acid/base chemistry of the slurry to leach contaminants from the soil (Tuin and Tels, 1990). However, if a very low pH is required concerns about dissolution of the soil matrix may arise. Chelating agents (e.g., EDTA) selectively bind with some metals and may be used to solubilize contaminants from the soil matrix (Elliot and Brown, 1989). Oxidizing and reducing agents (e.g., hydrogen peroxide, sodium borohydride) provide yet another option to aid in solubilization of metals since chemical oxidation/reduction can convert metals to more soluble forms (Assink and Rulkens, 1989; Tuin et al., 1987). Finally, surfactants may be used in extraction of metals from soil (U.S. EPA, 1996b).

Physical Treatment

Physical treatment is used to separate the contaminated fraction, usually the fine materials, from the rest of the soil matrix. Physical separation may be performed alone (Section 3.2.4) or in conjunction with chemical treatment, as in most soil washing processes. The most common method for physical separation in soil washing uses rotary attrition scrubbers to isolate the contaminated particles. The rotation of the slurry causes contact between large particles, resulting in attrition of the larger particles which releases the contaminant and contaminated fines to the slurry. The contaminant remains suspended in solution or sorbs to the reactive fine particles. Vibration units are also available to perform similar separations (Rosetti, 1993).

Hydrocyclones are the most common method used to separate fines from the clean soil. Other options are available for fine particle separation, including mechanical classifiers, gravity classifiers, spiral concentrators, and magnetic separators (Rosetti, 1993).

Froth flotation can be used to combine physical and chemical treatment processes into one step. For this method, extracting agent is added to the soil before it enters the froth flotation cell. The slurry is leached in the tanks to remove the contaminant and the fines (<50 µm) are then separated from coarse particles in the flotation unit (Rosetti, 1993).

Dewatering

After the contaminated fine particles are separated from the clean coarse particles, both fractions are dewatered. The fine fraction is usually dewatered using a belt filter or filter press and disposed of in a landfill. Larger particles are rinsed to remove residual extracting solution and contaminant and dewatered using belt and filter presses. This fraction is considered clean and can be returned to the site.

Water Treatment

The contaminated water from rinsing and dewatering steps is treated by manipulating the solution chemistry to separate the contaminant from the extractant if possible. Contaminants can then be removed from solution, most commonly by precipitation or sedimentation, and are dewatered before disposal with the contaminated fines. The extracting agent and process water can be recycled for reuse.

3.2.5.2 Pyrometallurgical Extraction

Pyrometallurgical technologies use elevated temperature extraction and processing for removal of metals from contaminated soils. Soils are treated in a high-temperature furnace to remove volatile metals from the solid phase. Subsequent treatment steps may include metal recovery or immobilization. Pyrometallurgical treatment requires a uniform feed material for efficient heat transfer between the gas and solid phases and minimization of

particulates in the off-gas. This process is usually preceded by physical treatment to provide optimum particle size. Pyrometallurgical processes usually produce a metal-bearing waste slag, but the metals can also be recovered for reuse (U.S. EPA, 1996c).

3.2.5.3 *In Situ Soil Flushing*

In situ soil flushing is used to mobilize metals by leaching contaminants from soils so that they can be extracted without excavating the contaminated materials. An aqueous extracting solution is injected into or sprayed onto the contaminated area to mobilize the contaminants usually by solubilization. The extractant can be applied by surface flooding, sprinklers, leach fields, vertical or horizontal injection wells, basin infiltration systems or trench infiltration systems (U.S. EPA, 1996b). After being contacted with the contaminated material the extractant solution is collected using pump-and-treat methods for disposal or treatment and reuse. Similar extracting agents are used for *in situ* soil flushing and soil washing, including acids/bases, chelating agents, oxidizing/reducing agents and surfactants/cosolvents. Also, water can be used alone to remove water-soluble contaminants such as hexavalent chromium. The applicability of *in situ* soil flushing technologies to contaminated sites will depend largely on site-specific properties, such as hydraulic conductivity, that influence the ability to contact the extractant with contaminants and to effectively recover the flushing solution with collection wells (NRC, 1994).

3.2.5.4 *Electrokinetic Treatment*

Electrokinetic remediation technologies apply a low density current to contaminated soil in order to mobilize contaminants in the form of charged species. The current is applied by inserting electrodes into the subsurface and relying on the natural conductivity of the soil (due to water and salts) to effect movement of water, ions and particulates through the soil. Water and/or chemical solutions can also be added to enhance the recovery of metals by this process. Positively charged metal ions migrate to the negatively charged electrode, while metal anions migrate to the positively charged electrode. Electrokinetic treatment concentrates contaminants in the solution around the electrodes. The contaminants are removed from this solution by a variety of processes, including electroplating at the electrodes, precipitation/coprecipitation at the electrodes, complexation with ion exchange resins, or by pumping the water from the subsurface and treating it to recover the extracted metals (Smith et al, 1995).

Electrokinetic treatment is most applicable to saturated soils with low ground-water flow rates and moderate to low permeability. The efficiency of metal removal by this process will be influenced by the type and concentration of contaminant, the type of soil, soil structure, and interfacial chemistry of the soil.

3.3 PERFORMANCE OF AVAILABLE COMMERCIAL TECHNOLOGIES

The following section focuses on commercially available technologies that have been demonstrated or implemented for metals-contaminated soils and groundwater. Ex situ

treatment technologies are examined only for soils. The full range of contaminated water treatment technologies is available for ex situ treatment of groundwater. For the most part, the technologies reported are those whose performance has been verified by the U.S. EPA under the Superfund Innovative Technology Evaluation (SITE) program which evaluates emerging and demonstrated technologies. Technologies currently in the SITE demonstration phase are also discussed.

3.3.1 Superfund Innovative Technology Evaluation (SITE) Demonstration and Best Demonstrated Available Technology (BDAT) Status

The 1986 Superfund Amendments and Reauthorization Act recognized a need for an “alternative or innovative technology research and demonstration program.” In response, the U.S. EPA established the Superfund Innovative Technology Evaluation (SITE) Program to encourage the development and implementation of innovative treatment technologies for remediation of hazardous waste sites and for monitoring and measurement. Innovative technologies are field-tested in the SITE Demonstration Program and engineering and cost data are collected to assess the performance of the technology. The demonstration stage also attempts to evaluate the applicability of the technology to different types of wastes and waste matrices, the need for pre- and post-processing of the waste stream, and potential operating problems. The SITE Program is administered by the U.S. EPA Office of Research and Development (ORD) National Risk Management Research Laboratory, headquartered in Cincinnati, Ohio.

The Resource Conservation and Recovery Act (RCRA) provides for determination of a Best Demonstrated Available Technology (BDAT) for treatment of hazardous wastes. BDATs have been established based upon critical analysis of performance data collected for treatment of various industry-generated wastes. BDAT status is given only to proven, commercially available technologies. Different BDATs and treatment standards are usually given for nonwastewater and wastewater forms of contamination. The applicability of a BDAT to metals-contaminated soil and water at a Superfund site must be evaluated on a site specific basis. The establishment of a BDAT does not prevent the use of other available technologies for treatment of these wastes.

3.3.2 Containment

Containment technologies are widely used to control the transport of hazardous materials and prevent the spread of contamination. Containment is the preferred remedial method for sites having low levels of wastes with low toxicity and low mobility, or wastes that have been pretreated to obtain these characteristics. Containment may also be used as a temporary measure to reduce the mobility of wastes that pose a high risk until a permanent remedy is selected and implemented. Advantages to containment technologies include relatively simple and rapid implementation often at lower cost than alternatives that require excavation; ability to treat large areas and volumes of waste; and the potential for successful containment as the final action at the site. Uncertainty regarding long-term effectiveness

and the need for long-term inspection because untreated contaminants remain onsite are among the disadvantages of containment technologies. Also, future use of the site may be limited if containment technologies are used. Containment has been selected as the remedial operation for soil contaminated with metals at a number of sites. Some example applications are summarized in Table 2.

Table 2. Example Containment Applications at Metals-Contaminated Superfund Sites (from U.S. EPA, 1996c)

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

^a Status codes as of February, 1996: I=in operation; S=selected

Capping systems have been selected for a number of sites with low levels of metal contamination. Monitoring wells and/or infiltration monitoring systems are often used to help assess the performance of capping systems.

Slurry walls have also been used for containment of metals-contaminated sites. The performance of vertical containment barriers also must be monitored. Performance can be influenced by geography, topography, and geology. The presence of certain compounds can also influence the long-term integrity of some cement-based vertical barriers by chemically attacking the soil-bentonite blends. Material availability can affect the application of slurry walls and other containment technologies.

There are no established BDAT's for containment technologies since they are not considered to be treatment technologies. Ongoing SITE demonstrations for remediation of metals by containment technologies include a high clay grouting procedure (Morrison Knudsen Corporation) and frozen soil barriers (RKK, Ltd.).

3.3.3 Ex Situ Remediation

The majority of the technologies that have been demonstrated for metals remediation to date are ex situ technologies. Ex situ remediation technologies demonstrated include solidification/stabilization, soil washing, vitrification and pyrometallurgic separation.

3.3.3.1 Solidification/Stabilization

Immobilization technologies, especially solidification/stabilization, are the most common methods selected for remediation of metal contamination, accounting for nearly 30 percent of all soil treatment technologies at Superfund sites. S/S techniques have been widely used to manage metal wastes at hazardous waste sites and to treat residues from other treatment processes (LaGrega et al., 1994). Benefits associated with immobilization treatments include their broad application to a wide variety of metals (Malone and Jones, 1985) and also to wastes that contain mixtures of metals and organics (U.S. EPA, 1996b).

Solidification/stabilization technologies using cement-based and pozzolan binders are available commercially and have been applied at several sites for a wide variety of metals, including chromium, lead, arsenic, mercury, and cadmium (Lo et al., 1988; Stanczyk and Senefelder, 1982; Zirschky and Piznar, 1988; Lister, 1996).

Examples of sites where ex situ S/S technologies have been selected and/or implemented for remediation of metals-contaminated soils are given in Table 3. Remediation has been completed for a number of these sites and S/S has been selected or initiated for several others. SITE demonstrations have been performed or are underway for various ex situ stabilization/solidification technologies.

Table 3. Example Solidification/Stabilization Applications at Selected Metals-Contaminated Superfund Sites (from U.S. EPA, 1996c)

Site Name/State	S/S Technology	Metal Contaminants	Secondary Technology	Status ^a
DeRewal Chemical, NJ	Solidification	Cr, Cd, Pb	GW pump and treat	S
Marathon Battery Co., NY	Stabilization	Cd, Ni	Dredging, off-site disposal	I
Nascolite, NJ	Stabilization	Pb	On-site disposal of stabilized soil, off-site disposal of wetland soil	S
Roebing Steel, NJ	S/S	As, Cr, Pb	Capping	S
Waldick Aerospace, NJ	S/S	Cd, Cr	Off-site disposal	C
Aladdin Plating, PA	Stabilization	Cr	Off-site disposal	C
Palmerton Zinc, PA	Stabilization	Cd, Pb	-	I
Tonolli Corp.	S/S	As, Pb	<i>In situ</i> chemical barrier	S
Whitmoyer Laboratories, PA	Oxidation/Stabilization	As	GW pump and treat, capping, grading, revegetation	S
Bypass 601, NC	S/S	Cr, Pb	GW pump and treat, capping, grading, revegetation	S
Flowood, MS	S/S	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
Pesses Chemical, TX	Stabilization	Cd	Capping	C
E.I. Dupont de Nemours, IA	S/S	Cd, Cr, Pb	Capping, regrading, revegetation	C
Shaw Avenue Dump, IA	S/S	As, Cd	Capping, GW monitoring	C
Frontier Hard Chrome, WA	Stabilization	Cr	-	S
Gould Site, OR	S/S	Pb	Capping, regrading, revegetation	I

^a Status codes as of February, 1996: C=completed; I=in operation; S=selected

Ex situ solidification/stabilization techniques have been determined to be the BDAT for a range of waste types, including cadmium nonwastewaters (other than Cd-containing batteries), chromium nonwastewaters (after reduction to Cr(III)), lead nonwastewaters, wastes with low (<260mg/kg) concentrations of elemental mercury, and plating and steel-making wastes. S/S can also be used to treat arsenic wastes even though vitrification was selected as the BDAT for arsenic-containing nonwastewaters (U.S. EPA, 1996c).

3.3.3.2 Soil Washing

Soil washing technologies are applicable to a range of soils containing a variety of metal contaminants. Soil washing is most easily implemented when a single metal contaminant occurs in a particular insoluble fraction of the soil which can be separated by particle size

classification. Soils with a minimum content of finer material (<20% of particles with diameters <2 mm) are easier to process. Soil washing has been used for remediation of metals-contaminated sites in Europe and has been selected and/or implemented at several U.S. Superfund sites. Table 4 gives examples of Superfund sites at which soil washing has been selected as the remediation technology.

Table 4. Example Soil Washing Applications at Metals-Contaminated Superfund Sites (from U.S. EPA, 1996c)

Site Name/State	Soil Washing Technology	Metal Contaminants	Secondary Technology	Status ^a
Ewan Property, NJ	Water washing	As, Cr, Cu, Pb	Solvent extraction to remove organics	S
GE Wiring Devices, PR	Water with KI solution additive	Hg	On-site disposal of clean soil	S
King of Prussia, NJ	Water with washing agents	Ag, Cr, Cu	Sludge disposal	C
Zanesville Well Field, OH	Water washing	As, Cr, Hg, Pb	On-site disposal of clean soil, SVE to remove organics	S
Twin Cities Army Ammunition Plant, MN	Acid leaching	Cd, Cr, Cu, Hg, Pb	Soil leaching	C
Sacramento Army Depot, CA	Water washing	As, Cr, Pb	Off-site treatment/disposal of wash liquid, on-site disposal of clean soil	S/D

^a Status codes as of February, 1996: C=completed; S=selected; S/D=selected but subsequently deselected

Remediation at the Twin Cities Army Ammunition Plant (TCAAP) in New Brighton, Minnesota is one of the two completed soil washing projects. The COGNIS TERRAMET® soil washing procedure used at this site employed a combination of particle sizing, gravity separation, and acid-leaching apparatus that was designed to remove lead, mercury, cadmium, chromium and copper from the soil. Preliminary studies have shown that the primary target metal at this site, lead, could be reduced from over 86000 mg/kg to less than 100 mg/kg, well below the target cleanup level of 300 mg/kg (Griffiths, 1995). Acid leaching soil washing procedures have been designated as the BDAT for mercury-contaminated soils. Several SITE demonstrations have been performed for soil washing of metals-contaminated soils (U.S. EPA, 1996c).

3.3.3.3 Vitrification

Vitrification is most applicable to sites containing low-volatility metals with high glass solubilities, and therefore appears to be well-suited for treatment of lead, chromium, arsenic,

zinc, cadmium and copper wastes (Table 5). The ability of a melt to retain these and other metals depends on the metal solubility in the soil at the site, and silica content of the soil. The metal concentration can be adjusted by adding soil or another source of silica to improve site characteristics for vitrification. The ability to control volatile emissions also influences the applicability of vitrification technologies. Mercury's high volatility and low glass solubility makes it unsuitable for vitrification, but treatment by vitrification may be allowed at sites containing very low mercury concentrations.

Ex situ vitrification may not be applicable for soils with greater than 25% moisture content due to excess fuel consumption, or at sites where size reduction and classification are not feasible. Several ex situ vitrification technologies are under development. SITE program demonstrations have been completed for two of these processes and a third demonstration is underway (U.S. EPA, 1996c). *Ex-situ* vitrification has also been demonstrated for treatment of cesium-contaminated tank wastes from the Oak Ridge Reservation (PNNL, 1997).

Table 5. Approximate Vapor Pressures and Glass Solubility Limits for Metals

Metal	Temperature [°C] at which Vapor Pressure=1mm Hg ^a	Maximum Allowed Oxide Content [%] for Sample Silicate Glass ^b
Pb	973	30
Cr	1840	2
As	372	5
Zn	487	20
Cd	394	1
Cu	1628	5
Hg	126.2	~ 0

^a CRC, 1991.

^b From Smith et al., 1995

3.3.3.4 Pyrometallurgical Separation

Mercury has a relatively high vapor pressure and is easily converted to its metallic form at elevated temperature, making it easily treated by pyrometallurgic methods. Pyrometallurgic treatment of lead, arsenic, cadmium and chromium may require pretreatment by reducing agents or fluxing agents to facilitate melting. Nonvolatile metals such as chromium can be tapped from the furnace as molten metal (U.S. EPA, 1996c).

Pyrometallurgic treatment is usually performed offsite because few mobile treatment units are available. This technology is most applicable to large volumes of highly-contaminated soils (metal concentrations >5%-20%, especially when metal recovery is expected. Low metal concentrations can be processed, especially for mercury since it is easy to volatilize and recover (Smith et al., 1995).

A number of pyrometallurgical process technologies are currently available for treatment of metals-contaminated soils. Pyrometallurgical treatment is a BDAT for cadmium-containing batteries, lead nonwastewaters, mercury wastes, mercury from wastewater treatment sludge, lead acid batteries, and zinc nonwastewaters. SITE demonstrations have been completed for thermal desorption (RUST Remedial Services, Inc.) and flame reactor (Horsehead Resource Development Company, Inc.) pyrometallurgical technologies.

3.3.4 *In Situ* Remediation

In situ remediation technologies offer the potential for significant cost savings over *ex situ* technologies because *in situ* techniques are usually associated with lower labor and energy requirements for implementation. This section discusses the status of *in situ* technologies which are currently available for metal remediation at contaminated sites.

3.3.4.1 *Solidification/Stabilization*

In situ S/S treatment appears to have been applied less frequently than *ex situ* techniques mostly due to concerns about uniformity of treatment and long-term reliability. These limitations are being reduced, however, through advances in chemical reagent delivery systems for large-diameter auger drilling devices (Jasperse, 1989; Walker, 1992). Examples of Superfund sites at which *in situ* S/S has been selected for remediation are given in Table 6. While *in situ* S/S technologies are well developed due to roots in construction techniques, data on the performance of *in situ* S/S are limited. Based upon preliminary data, *in situ* S/S appears likely to be an effective treatment option. *In situ* S/S typically will be most beneficial for sites with contamination at depths less than 8-10 feet and for larger volumes of waste because *ex situ* may prove to be cheaper for small volumes and shallow contamination due to high costs associated with mobilization and demobilization for *in situ* technologies. Deep soil mixing technology is also available for treating contaminated soils at greater depth (Ryan and Walker, 1992) but is more expensive than shallow soil mixing. The cost of *in situ* technologies is also affected by implementation concerns such as a level, stable base that is required for augering, and the presence of large rocks that can make large-diameter augering impossible. The use of dry reagents in soils with high moisture content is a well established method in Europe that is gaining interest in the U.S. and may expand the applicability of *in situ* S/S techniques (U.S. EPA, 1996b).

Table 6. Example *In situ* Solidification/Stabilization Applications at Metals-Contaminated Superfund Sites (from U.S. EPA, 1996c)

Site Name/State	S/S Technology	Metal Contaminants	Status ^a
Gurley Pit, AR	<i>In situ</i> S/S	Pb	C
General Electric Co., FL	<i>In situ</i> S/S	Pb, Cr, Cu, Zn	D

^a Status codes as of February, 1996: C=completed; D=demonstrated

3.3.4.2 Vitrification

In situ vitrification (ISV) technologies are currently offered commercially in the U.S. by a single vendor, Geosafe Corporation. The first full-scale application of ISV was demonstrated at the Parsons Chemical/ETM Enterprises Superfund site in Grand Ledge, Michigan under the EPA SITE program (Table 7). The Geosafe ISV process was used for treatment of soils and sediments contaminated with pesticides, metals (As, Cr, Hg, Pb), and dioxins. This treatment system required the use of eight melts which were each completed over a time frame of 10 to 20 days. This system also included an air emissions control system to treat volatilized contaminants, including mercury. While ISV is not recommended for remediation of mercury, this method can be used in conjunction with emissions control systems when Hg is present in mixed metal/organic wastes. This treatment was successful, meeting TCLP limits for all of the metals in the treated waste.

ISV has also been used successfully at two sites contaminated with organics (PCB, dioxin, pentachlorophenol, pesticides, herbicides), further demonstrating the applicability of this technology. Based upon observations from these limited applications, it appears that ISV may not be appropriate for sites with high levels of organics (> 10 % organics by weight) due to contamination of the off-gas, or inorganics (> 25 % metals by weight, or > 20 % by volume) due to concerns about exceeding glass solubility limits (U.S. EPA, 1996b).

Table 7. Example *In Situ* Vitrification Applications at Metals-Contaminated Superfund Sites (from U.S. EPA, 1996c)

Site Name/State	Vitrification Technology	Metal Contaminants	Status ^a
Parsons Chemical, MI	<i>In situ</i> vitrification	As, Cr, Hg, Pb	C
Rocky Mountain Arsenal, CO	<i>In situ</i> vitrification	As, Hg	S/D

^a Status codes as of February, 1996: C=completed; S/D=selected but subsequently deselected

3.3.4.3 *In Situ* Soil Flushing

In Situ soil flushing has been selected for treatment at several Superfund sites contaminated with metals. Some examples of sites where *in situ* soil flushing is currently operational are given in Table 8. *In situ* soil flushing is the technology in design or the predesign stage at least five other sites. This technology has been applied for a limited number of projects, mostly containing organic forms of contamination (NRC, 1994), and limited information is available on the application of this technology to metals-contaminated sites.

Table 8. Example *In Situ* Soil Flushing Applications at Metals-Contaminated Superfund Sites (from U.S. EPA, 1996c)

Site Name/State	<i>In situ</i> soil flushing Technology	Metal Contaminants	Secondary Technology	Status ^a
Lipari Landfill, NJ	Flushing of contained wastes with water	Cr, Hg, Pb	Slurry wall, cap, excavation of wetlands	I
United Chrome Products, OR	Soil flushing with water	Cr	Considering electrokinetic and chemical (reduction) treatment	I

^a Status codes as of February, 1996: I=in operation

The United Chrome Products Superfund site in Corvallis, Oregon is currently being remediated using *in situ* soil flushing technologies. The soil and groundwater at this site are heavily contaminated with chromium, with chromium levels in the soil as high as 60000 mg/kg and levels in the groundwater reaching up to 19000 mg/kg. The general approach to remediation of this site has been removal of the more soluble, mobile and toxic form of chromium, Cr(VI), by flushing the contaminated region with water to solubilize Cr(VI), with subsequent extraction of the chromium-containing water for treatment. Remediation at this site began in 1985 and has combined a variety of technologies to aid remediation by *in situ* soil flushing. The technologies used have included infiltration basins and trenches to flush contaminated soils, a 23-well ground-water extraction network to remove contaminated groundwater and recharge water, on-site treatment of wastewater, and off-site disposal of contaminated soil and debris (Sturges et al., 1992).

This full-scale application of *in situ* soil flushing with water as the flushing solution appears to be successful for removal of Cr(VI) from coarse soils of relatively high hydraulic conductivity. The *in situ* soil flushing procedure used at this site leaches contaminants from the unsaturated and saturated zones, and provides for recharge of the groundwater to the extraction wells. This cleanup operation has removed significant amounts of chromium from the soil and groundwater and the ground-water pumping strategy has achieved hydraulic containment of the plume. Cr(VI) levels in water retrieved by the extraction wells decreased from more than 5000 mg/L to approximately 50 mg/L during the first two and one half years of operation. Average chromium concentrations in the plume decreased from 1923 mg/L to 207 mg/L after flushing the first one and one half pore volumes (approximately 2.6 million gallons for one pore volume). These rapid removal rates are expected to continue for the first few pore volumes of treatment until Cr(VI) removal begins to tail off to the asymptotic level. Tailing results from slow desorption from soil particles, dissolution of solid phase contaminants, and release of contaminants from the fine pores in the soil matrix. Tailing is commonly observed in *in situ* soil flushing applications and usually represents the practical limit for remediation via pump and treat methods (Sturges et al., 1992).

3.3.4.4 Electrokinetic Extraction

The success of various electrokinetic remediation technologies has been illustrated for removal of metals from soils via bench and pilot scale experiments. Currently, several of these technologies are being implemented in comprehensive demonstration studies to further the use of electrokinetic techniques at contaminated sites.

Electrokinetic remediation of metals-contaminated sites has been demonstrated *in situ* at many sites in Europe using processes developed by Geokinetics International, Inc. (GII) (U.S. EPA, 1996b). Table 9 provides examples of sites in Europe for which this technology has been selected as the remediation technology. The success of electrokinetic remediation appears to vary depending on the metals present, and can remove up to 90% of the initial contamination. The first demonstration of this electrokinetic process in the U.S. is scheduled under the EPA SITE program for remediation of a chromium-contaminated soil at the Sandia Chemical Waste Landfill.

Table 9. Example Electrokinetic Applications at Metals-Contaminated Sites (from U.S. EPA, 1996c)

Site Description	Electrokinetic Technology	Metal Contaminants	Status ^a
Former paint factory	Electrochemical Remediation	Cu, Pb	C
Operational galvanizing plant	Electrochemical Remediation	Zn	C
Former timber plant	Electrochemical Remediation	As	C
Temporary landfill	Electrochemical Remediation	Cd	C
Military air base	Electrochemical Remediation	Cd, Cr, Cu, Ni, Pb, Zn	C

^a Status codes as of February, 1996: C=completed

Electrokinetics, Inc. is carrying out a SITE demonstration study of lead extraction from a creek bed at a U.S. Army firing range in Louisiana using their CADEX^ä electrode system. Soils at this site are contaminated with lead at concentrations up to 4500 mg/kg. In pilot-scale studies, the lead levels in the soil were reduced to below 300 mg/kg after 30 weeks of processing. The TCLP values for this soil were reduced from over 300 mg/L to less than 40 mg/L over this time. This technology is also being explored for remediation of sites contaminated with arsenic. Treatability and pilot-scale field testing studies for this application are under way.

Other electrokinetic techniques have been demonstrated for remediation of organics (TCE) and have accounted for removal of up to 98% of these wastes. The LASAGNA[™] process is being developed by a consortium consisting of Monsanto, E.I. DuPont deNemours & Co., Inc, and General Electric. LASAGNA[™] is an integrated, *in situ* process that uses

electrokinetics to transport contaminants in soil pore water into treatment zones. The treatment zones are designed to capture or decompose the organic contaminants. ManTech Environmental provides the ElectroChemical GeoOxidation (ECGO) process that has been used to successfully remediate organic-contaminated soil and groundwater in Germany. ECGO uses induced electric currents to create oxidation-reduction reactions that mineralize organic contaminants. These reactions may be useful for immobilization of inorganic contaminants as well. Attempts are being made to determine the potential for treatment of metals using these processes (U.S. EPA, 1996b).

3.3.4.5 Biological Treatment

Phytoremediation technologies are largely in the developmental stage and many are being field tested at a variety of sites in the U.S. and in Europe. Because full-scale applications of phytoremediation technologies are just being initiated, limited cost and performance data are available. Some techniques under development have shown potential for use at metals-contaminated sites. Phytostabilization and phytoextraction methods are being developed by Phytotech, Inc. and field tests for patented phytoextraction techniques are being performed. Some grasses have been made commercially available for phytostabilization of metals (lead, copper, zinc) (Salt, 1995). Nickel has been removed from plating wastes by bacteria (Wong and Kwok, 1992) and other organisms are being genetically engineered to remove metals such as cadmium, cobalt, copper and mercury (Smit and Atwater, 1991). Bioreduction has been demonstrated (for Hg) at the bench scale but has not been tested at pilot scale (Smith et al., 1995). A process has been developed for chromium reduction by H₂S produced by sulfate-reducing bacteria and reduction of Cr(VI) by direct metabolism is being investigated by several organizations (Smith et al., 1995).

Treatment by wetlands has been studied under the U.S. EPA's SITE program. Full-scale demonstration of a constructed wetland is planned for the Burleigh Tunnel site, part of the Clear Creek/Central City Superfund site in Colorado.

Bioleaching is currently used to recover copper and uranium ores by heap or *in situ* leaching (Ehrlich, 1988) and is under development for a wide range of metals including cadmium, chromium, lead, mercury and nickel. Microorganisms have been tested for chemical reduction and removal of mercury salts from wastewater (Horn et al. 1992, Hansen and Stevens, 1992).

Phytoremediation technologies will likely be limited to use in shallow soils with relatively low levels of metal contamination. Based upon estimates of biomass productivity and metal content of soils, the annual removal rate of metals by phytoremediation would be limited to between 2.5 to 100 mg/kg of soil contaminants (U.S. EPA, 1996b).

3.4 BEST TECHNOLOGY BY METAL

The Best Demonstrated Available Technologies, BDATs (See Section 3.3.1) for metals-contaminated RCRA wastes are summarized in Table 10 according to the type of metal

contamination. These technologies can be used as guidelines to review treatment options for Superfund sites, but technology selection at Superfund sites should also consider site-specific characteristics and innovative technologies that may be available under the EPA SITE program.

Table 10. Summary of Best Demonstrated Available Technologies (BDATs) for RCRA Wastes (from Smith et al., 1995)

Metal Contaminant	Example BDATs for Metal Wastes	
	Nonwastewater	Wastewater
Lead	Stabilization or metal recovery	Chemical precipitation
Chromium	Chromium reduction and S/S	Chromium reduction and S/S
Arsenic	Vitrification	Chemical precipitation
Cadmium	Stabilization or metal recovery	Chemical precipitation
Mercury	Metal recovery (≥ 260 mg/kg) or acid leaching followed by chemical precipitation	Chemical precipitation with sulfide

4.0 COST ESTIMATES

The costs for implementing available technologies will vary significantly between sites because costs are influenced by a wide variety of factors. Figure 4 represents the ranges of operating costs that have been observed for remediation of metals-contaminated soils by a number of techniques that have been discussed. Some important factors influencing costs of specific treatment technologies are discussed below.

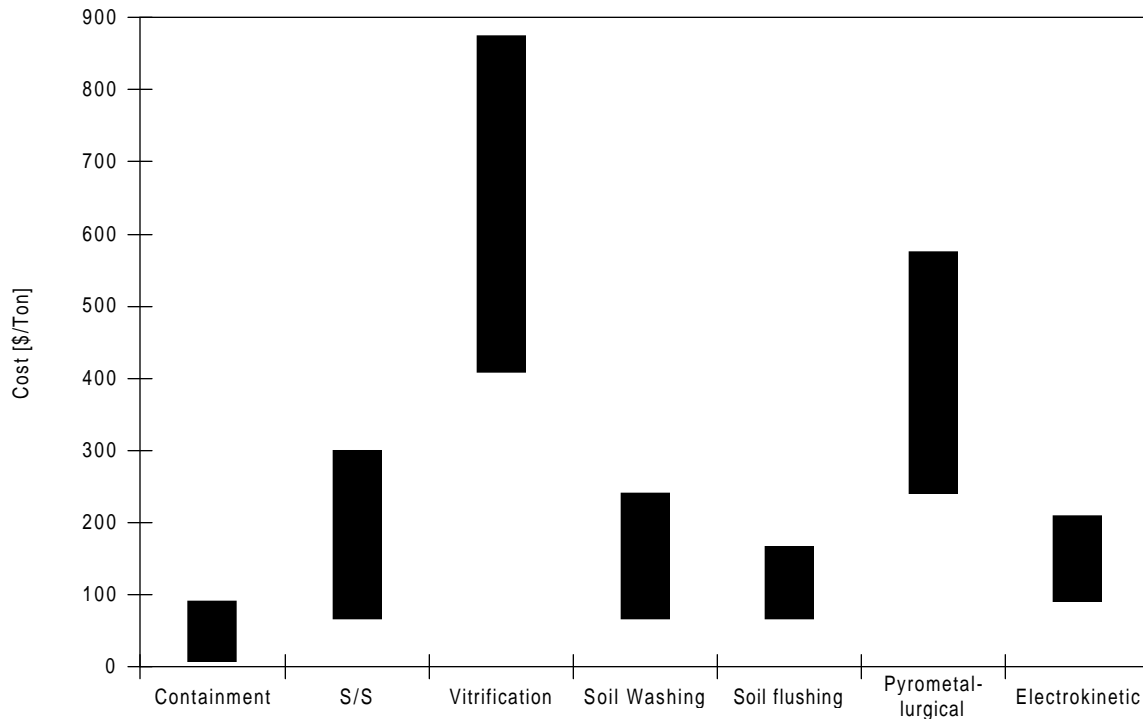


Figure 4. Estimated Operating Costs of Available Remediation Technologies for Metal-Contaminated Soils (U.S. EPA, 1996c)

4.1 CONTAINMENT

The costs associated with capping systems depend largely on the number of components included in the design (Rumer and Ryan, 1995). Barrier and drainage components can add significant amounts to the overall cost of this technology. Sites with steep slopes will also increase cost.

The cost of vertical barrier construction will be influenced by the type of barrier material and the method used to place it. Soil-bentonite trenches provide the most economical method for installation of shallow vertical barriers (Rumer and Ryan, 1995). The most economical deep vertical barrier is a cement-bentonite barrier constructed using a vibrating beam (U.S. EPA 1996b). Costs will also be influenced by ground-water or topographical conditions.

4.2 SOLIDIFICATION/STABILIZATION

Factors directly influencing the costs for implementation of S/S techniques include labor, equipment, energy requirements, testing and monitoring, and the types of reagents. *In situ* processing can lower labor and energy expenses associated with excavation, transport, and disposal of soil from the site.

4.3 VITRIFICATION

Treatment costs for ex situ vitrification of contaminated soils depend on the waste, throughput capacity of the glass melter, and local energy costs. Site location will affect the cost of transporting the material offsite or equipment transport onsite. As with most technologies, the *in situ* process may provide cost savings over ex situ implementation of this technology.

4.4 SOIL WASHING

Soil washing at a contaminated site can involve techniques ranging from physical separation and disposal of the contaminated fraction offsite to chemical leaching of contaminants from the entire soil matrix for onsite disposal. Soil washing costs depend largely on the extent to which the contaminated soils are processed.

4.5 IN SITU SOIL FLUSHING

In situ soil flushing involves pumping and treatment of contaminated water, sometimes with recharge of the treated water. The initial and target contaminant concentrations, soil permeability and the depth of the aquifer will influence costs. Chemically enhanced flushing systems will have additional costs associated with reagents and equipment needed to handle the flushing solution. Costs for above-ground treatment of the pumped water vary with contaminant type.

4.6 ELECTROKINETIC TREATMENT

The cost of remediating metals-contaminated soils using electrokinetic techniques is strongly influenced by soil conductivity because energy consumption is directly related to the conductivity of the soil between the electrodes. Electrokinetic treatment of soils with high electrical conductivities may not be feasible due to the high cost. Overall expenses for electrokinetic remediation will also be influenced by local energy costs, pretreatment costs, and fixed costs associated with installing the system.

5.0 REGULATORY/POLICY REQUIREMENTS AND ISSUES

Cleanup goals for remediation of metals-contaminated sites vary considerably depending on site-specific factors, especially those that affect the mobility of metals, and regulatory domain. Cleanup goals that are established for a site have a significant influence on determining the acceptability of different technologies for remediation of metals at the site. Thus, the application of remediation technologies to different sites may vary even if the types of contamination at the sites are the same.

A number of states have established soil and ground-water quality criteria that are the basis for cleanup goals. In the absence of such criteria (as in the U.S. Superfund program), or when the criteria are intended as default values, cleanup goals are established based upon site-specific human health and ecological risk assessments which consider the fate and transport of contaminants and possible exposure routes for humans and sensitive environmental receptors. The goals may be established in terms of the total metals in the soil/water or as leachable metals (as defined by various EPA testing procedures). Table 11 provides examples of established cleanup goals for total metals in soils and soil leachate at hazardous waste sites, and Table 12 gives examples of cleanup goals for metals in groundwater.

The use of risk assessment for establishment of site-specific or regional goals for metals in soil or groundwater is difficult because the chemistry of metals is so complex. The hydrogeochemistry of metals is affected by various geochemical and biogeochemical phenomena, including acid-base chemistry, complexation, precipitation/dissolution, adsorption/desorption, and oxidation/reduction. These processes are interlinked and not capable of being described with a simple model. In the case of adsorption/desorption reactions, for example, the speciation of metal ions and the aqueous solution composition determine the extent of reaction (Dzombak and Morel, 1987, 1990). These factors are not captured in a simple partitioning expression. Thus, exposure assessment modeling for metals in soil and groundwater demands the use of flow models integrated with complex chemical models. This requirement frequently has discouraged detailed exposure assessment for metals, resulting in the use of conservative assumptions with regard to metal fate and transport in subsurface systems.

The risk-based corrective action (RBCA) procedure developed by the Environmental Assessment Committee of the American Society for Testing and Materials (ASTM, 1994) may be applied to determine cleanup goals for soil and groundwater. The aim of RBCA is the establishment of cleanup goals based on risk reduction rather than generic cleanup concentrations. However, when regulatory screening levels are exceeded and fate and transport modeling is required as part of a Tier III assessment, there will still be the issue of adequate consideration of the complex chemistry of metals.

Table 11. Examples of U.S. Cleanup Goals/Standards for Selected Metals in Soils

DESCRIPTION	As	Cd	Cr (total)	Hg	Pb
Total Metals (mg metal/kg soil)					
Background (Mean) ^a	5	0.06	100	0.03	10
Background (Range) ^a	1 to 50	0.01 to 0.70	1 to 1000	0.01 to 0.30	2 to 200
Superfund Site Goals ^a	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 × 20) ^b	100	20	100	4	100
EPA Region III ^c : residential commercial	23 610	39 1000	390 Cr(VI) 10000	23 610	- -
California Total Threshold Limit Concentration ^a	500	100	500	20	1000
Pennsylvania ^d	3	20	300	20	500
Florida ^e : residential industrial	0.8 3.7	37 600	290 Cr(VI) 430	23 480	500 1000
Leachable Metals (mg/L)					
TCLP Threshold for RCRA Waste ^f	5	1	5	2	5
Synthetic Precipitation Leachate Procedure ^g	-	-	-	-	-
California Soluble Threshold Leachate Concentration ^a	5	1	5	2	5
Florida Leachability Standards ^e	5	1	5	2	5

^a from U.S. EPA, 1995

^f EPA Method 1311

^b from U.S. EPA, 1996c

^g EPA Method 1312

^c from EPA Region III Risk-Based Concentration Table

^d PA Department of Environmental Protection (DEP) Health-Based Standards, 1996

^e FL DEP Health-Based Standards, 1996

Table 12. Examples of U.S. Cleanup Goals/Standards for Selected Metals in Groundwater

DESCRIPTION	As	Cd	Cr	Hg	Pb
Metals (µg/L)					
Maximum Contaminant Level (MCL) ^a	50	5	100	2	15
Superfund Site Goals ^b	50	-	50	0.05 to 2	50
Pennsylvania Standard for Groundwater in aquifers (<2500 mg/L TDS) ^c	50	5	100	2	5
Wisconsin Ground-water Quality Enforcement Standards	50	5	100	2	15

^a MCL= the maximum permissible level of contaminant in water delivered to any user of a public system, established under the Safe Drinking Water Act.

^b from U.S. EPA, 1995

^c PA DEP Health-Based Standards, 1996

^d WI Department of Natural Resources (DNR) Ground-water Quality Standards Tables, 1996

6.0 LESSONS LEARNED AND TECHNOLOGY DIRECTIONS

Metals are typically relatively immobile in subsurface systems. For this reason, remediation activities at metals-contaminated sites have focused on the solid-phase sources or repositories of metals. Treatment has often involved excavation of contaminated soil, sludge, or debris followed by *ex situ* treatment or disposal. The most common *ex situ* treatment is solidification/stabilization through addition of chemical reagents, followed by replacement or off-site disposal of the treated material.

Several *in situ* remediation technologies have the potential to provide significant cost savings over *ex situ* techniques because they eliminate the need to excavate and dispose of contaminated solids or to pump and treat contaminated groundwater. *In situ* solidification/stabilization technologies have been demonstrated for treatment of shallow (8-10 ft below surface) wastes and are being implemented at greater depths. Favorable results have been attained using *in situ* vitrification for treatment of a variety of wastes, including metals when metal concentrations do not exceed their glass solubilities. Extraction using *in situ* soil flushing or electrokinetic techniques has been employed at a limited number of sites but may prove to be useful for a range of metal contaminants. Phytoremediation technologies offer promise for remediation of sites with low levels of contamination.

Treatment walls will be used increasingly for effective, low-cost, passive remediation of metal contamination in groundwater. Reactive wall installation will not address metal contamination in soils, but will enable treatment of groundwater contaminated from contact with metal-bearing solids.

Some soil washing technologies are being considered for adaptation to soil leaching/flushing technologies. Chemical additives are being developed to aid with *in situ* extraction of metals from soil.

In situ solidification/stabilization techniques are being employed and promise to gain popularity. Application of *in situ* S/S is being aided by development of wide-diameter auger drilling devices that are equipped with chemical reagent delivery systems.

Phytoremediation technologies have only recently gained attention for use in metal remediation. Additional research is needed in order to improve the applicability of phytoremediation for management of metals-contaminated sites. A variety of plants are being investigated for favorable metal accumulation qualities such as a fast rate of uptake.

The future of electrokinetic methods will depend on the efficiency and cost-effectiveness of the technique. Full-scale applications of *in situ* electrokinetic technologies have been initiated in the U.S. but detailed data are not yet available.

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