

*Recent Developments for In Situ Treatment of Metal
Contaminated Soils*

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ABSTRACT

Metals contamination is a common problem at hazardous waste sites. This report assists the remedy selection process by providing information on four in situ technologies for treating soil contaminated with metals. The four approaches are electrokinetic remediation, phytoremediation, soil flushing, and solidification/stabilization. The report discusses different techniques currently in practice or under development; identifies vendors and summarizes performance data; and discusses technology attributes that should be considered during early screening of potential remedies.

EXECUTIVE SUMMARY

Metals are prevalent at most Superfund sites. At sites with signed Records of Decision (ROD), metals are the sole contaminants (approximately 16 percent) or are found in combination with other contaminants are found such as volatile or semi-volatile organic compounds (approximately 49 percent). In general, in situ remedies are often capable of providing cost savings, when compared with traditional treatment methods, and are being selected more frequently at Superfund sites. However, relatively few alternatives exist for the in situ treatment of metals. This report presents an overview of four of the most promising technologies for in situ soil treatment:

- i. Electrokinetics
- ii. Phytoremediation
- iii. Soil Flushing
- iv. Solidification/stabilization

The report is intended to assist in screening new technologies early in the remedy evaluation and selection process.

Electrokinetics

Electrokinetic remediation relies on the application of low intensity direct current between electrodes placed in the soil. Contaminants are mobilized in the form of charged species, particles, or ions. Several organizations are developing technologies for the enhanced removal of metals by transporting contaminants to the electrodes where they are removed and subsequently treated above ground. A variation of the technique involves treatment without removal by transporting contaminants through specially designed treatment zones that are created between electrodes. This process is undergoing early field testing and is initially being targeted to treat chlorinated volatile compounds in low-permeability clay. Electrokinetics also can be used to slow or prevent migration of contaminants by configuring cathodes and anodes in a manner that causes contaminants to flow toward the center of a contaminated area of soil. The

practice has been named “electrokinetic fencing.”

Experience with this technology is limited to bench and pilot scales, with the notable exception of a metal removal process that has been commercially operated by a single vendor in Europe and recently licensed in the United States. Limited performance data from this vendor illustrate the potential for achieving removals greater than 90 percent for some contaminants.

The range of potential metals is broad. The commercial applications in Europe treated copper, lead, zinc, arsenic, cadmium, chromium, and nickel. There is also potential applicability for radionuclides and some types of organic compounds. The electrode spacing and duration of remediation is site-specific. The process requires adequate soil moisture in the vadose zone, so the addition of a conducting pore fluid may be required (particularly due to a tendency for soil drying near the anode). Specially designed pore fluids also are added to enhance the migration of target contaminants. The pore fluids are added at either the anode or cathode, depending on the desired effects.

Phytoremediation

This technology is in the early stage of commercialization for treatment of soils contaminated with metals, and in the future may provide a low cost option under specific circumstances. At the current stage of development, this process is best suited for sites with widely dispersed contamination at low concentrations where only treatment of soils at the surface (in other words, within depth of the root zone) is required.

Two basic approaches for metals remediation include phytoextraction and phytostabilization. Phytoextraction relies on the uptake of contaminants from the soil and their translocation into aboveground plant tissue, which is harvested and treated. Although hyperaccumulating trees, shrubs, herbs, grasses, and crops have potential, crops seem to be most promising because of their greater biomass

production. Nickel and zinc appear to be the most easily absorbed, although preliminary tests with copper and cadmium are encouraging. Significant uptake of lead, a commonly occurring contaminant, has not been demonstrated in any of the plants tested thus far. However, one researcher is experimenting with soil amendments that would facilitate uptake of lead by the plants.

Phytostabilization achieves risk reduction by stabilizing contaminants located near the surface. This result is achieved by the secretion of compounds by plants to affect soil pH and to form metal complexes with reduced solubility. In addition, the plants help control surface erosion and reduce leaching through increased evapotranspiration. Laboratory studies indicate the potential effectiveness of this approach for lead.

Soil Flushing

This technology involves extraction of contaminants from soil using water or other suitable aqueous solutions. Although additives such as acids and chelating agents have had some commercial use for full-scale ex situ soil washing projects, they have not been demonstrated as feasible for in situ applications.

Soil flushing has been selected at seven Superfund sites with metals present; however, at six of those sites, organic contaminants are the primary targets. For metals, soil flushing would be most effective in removing water-soluble species, such as hexavalent chrome. Two soil flushing remedies are currently ongoing at Superfund sites, with some preliminary data available from a hexavalent chrome application.

Leached contaminants are typically recovered from the underlying ground water by pump-and-treat methods. Site-specific conditions must be carefully considered to address the possible spread of contamination.

Solidification/stabilization

This process (also referred to as immobilization) changes the physical and chemical characteristics of the waste in order to immobilize contaminants. Metals are commonly remediated by ex situ solidification with pozzolans and sometimes other additives. This technology has been adapted to in situ applications through the use of various proprietary augers which provide reagent delivery and mixing. In situ treatment will likely have a cost advantage over ex situ applications for larger volumes and for depths greater than 10 feet. However, this technology has been only occasionally selected for Superfund use, largely because of concerns with long-term reliability.

A second solidification technique involves vitrification where an electrical current is passed between electrodes to melt soil and incorporate metals into a vitrified product. This technology is commercially available and has been successfully used at two Superfund sites, one of which was contaminated with metals.

Both processes are broadly applicable to a range of metals. Vitrification uses a hood to capture mercury and other volatile metals, such as lead and arsenic, which may be partially vaporized during operations. Vitrification is best suited for wastes that are difficult to treat, such as mixtures of organics and metals.

INTRODUCTION

Metals account for much of the contamination found at hazardous waste sites. They are present in the soil and ground water at approximately 65 percent of the Superfund sites for which the U.S. Environmental Protection Agency (EPA) has signed records of decisions (ROD). The metals most frequently identified are lead, arsenic, chromium, cadmium, nickel, and zinc. Other metals often identified as contaminants include copper and mercury. Figure 1 shows the most common contaminants in all matrices at Superfund sites. In addition to the Superfund program, metals make up a significant portion of the contamination requiring remediation under the Resource Conservation and Recovery Act (RCRA) and contamination present at federal facilities, notably those that are the responsibility of the Department of Defense (DoD) and the Department of Energy (DOE).

Since the reauthorization of Superfund in 1986, there has been a significant increase in the treatment of soil at Superfund sites. In the early days of the program, EPA selected conventional technologies (for example, incineration, solidification and stabilization, and groundwater pump-and-treat systems). Subsequently, new and improved processes were developed, especially for soils, that are capable of providing more cost-effective cleanups. In fiscal year 1993, EPA for the first time selected innovative technologies as remedies more frequently than conventional processes. The innovative technologies most often selected are in situ soil vapor extraction, various bioremediation processes, and thermal desorption for soils and in situ air sparging and bioremediation for ground water. All of these technologies target the treatment of organic compounds.

Experience under the Superfund program clearly demonstrates the successful development of new technologies to treat organic compounds. In addition, statistics show that more than half of the new technologies selected for soil treatment are in situ processes. In situ techniques have the potential to provide significant cost savings and are generally considered to represent a promising direction for the development of new technologies.

Few commercial alternatives exist, however, to treat metals in soil, especially in situ. The most frequently selected treatment process in the Superfund program is solidification/stabilization, which was selected 203 times through fiscal year 1994. This accounts for nearly 30 percent of all soil treatment technologies. By contrast, other technologies available to address metals in soil were selected only 18 times. No treatment technologies have been selected for sites with low-level radioactive metals, where excavation and either on-site or off-site disposal are typically chosen.

The difference between the availability of new technologies for the treatment of metals versus new technologies for the treatment of organic compounds is illustrated by data from EPA's Vendor Information System for Innovative Treatment Technologies (VISITT). The system, which is distributed on request to more than 12,000 users, contains information submitted by vendors of new technologies about the capabilities of their processes. EPA recently released the fifth version of the database, which contains information on 346 innovative technologies offered by more than 210 vendors. Information provided by vendors indicates that 226 technologies treat volatile organics, 208 technologies treat semi-volatile organics, and 66 technologies treat metals (some technologies can treat several waste groups). While a substantial portion (about 40 percent) of the organic treatment technologies are in situ processes, only 9 of the 66 technologies that treat metals are designed to treat soil or groundwater in situ.

1.0 PURPOSE

This document surveys treatment technologies with the potential for providing in situ treatment of soil contaminated with metals. The report updates project managers and cleanup professionals about the status of four technologies which are currently available or under active development. The information should be useful in screening technologies early in the remedy evaluation and selection process.

Most Common Contaminants in All Matrices at Superfund Sites

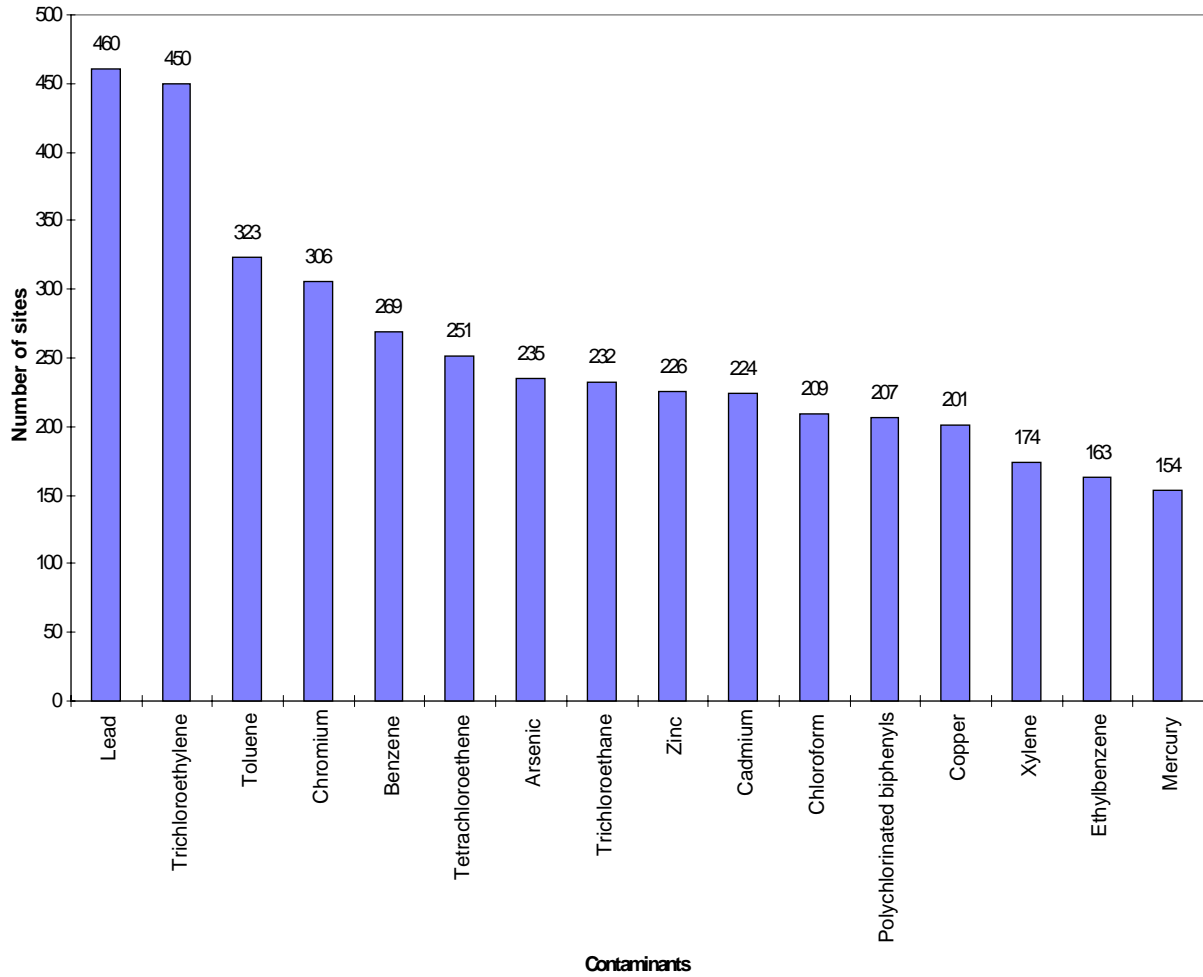


Figure 1. Contaminants Most Commonly Present in All Matrices at Superfund Sites

This document is not meant to provide a rigorous scientific examination. This document focuses only on contamination in soils; EPA recently published a series of booklets summarizing bench- and field-scale efforts for in situ treatment of organics and metals in groundwater. [*In Situ Remediation Technology Status Reports. EPA542-K-94-003/005/006/007/009. April 1995*]

2.0 REPORT ORGANIZATION

This document focuses on the treatment of metals, such as cadmium, copper, chromium, lead, mercury, arsenic, nickel, and zinc. The four in situ technologies presented are electrokinetic remediation, phytoremediation, soil flushing, and solidification/stabilization (S/S) techniques. The second chapter of this document presents a brief summary of the attributes of these technologies. Electrokinetic remediation, discussed in the third chapter separates contaminants from soil through selective migration upon application of an electric current. Phytoremediation, discussed in the fourth chapter is an emerging technology that uses plants to isolate or stabilize contaminants. Soil flushing techniques, described in the fifth chapter promote mobility and migration of metals by solubilizing contaminants so that they can be recovered. The sixth chapter describes two types of S/S techniques, one based on

addition of reagents and the other based on the use of energy.

The four chapters that address specific in situ technologies are organized in four sections. The first table of each technology chapter presents an overview of the technology. The general characteristics of the technology are summarized in the table, and are discussed in greater detail in Section 4 of the chapter, Analysis of Applications. Section 1, Description, provides a detailed description of the principle of the technology. The approaches described in the summary are discussed further in Section 2, Overview of Status. The available performance data for each of the technologies are provided in Section 3, Performance and Cost Summary.

Appendix A contains a description of the methodology followed in the preparation of this report and includes a list of technical experts that were contacted. It also contains treatment options not discussed here, such as the use of treatment trains. Appendix B contains an excerpt of a draft copy of an engineering bulletin titled *Technology Alternatives for the Remediation of Soils Contaminated with Arsenic, Cadmium, Chromium, Mercury, and Lead*. This bulletin provides a background description of physical properties of metals and discussions of S/S, soil washing, and soil flushing.

OVERVIEW OF IN SITU TECHNOLOGIES FOR REMEDIATION OF SOILS CONTAMINATED WITH METALS

This chapter presents an overview comparison of the four in situ technologies. The key factors that were considered in this analysis are: status, range of metals treated, major limiting factor, and site-specific considerations. Status refers to the stage of development of the technology. Range of metals treated specifies whether the technology can address a broad range of metals or focuses on a limited range of metals. Major limiting factor refers to process considerations which may limit broad use of the technology. Site-specific considerations refers to those site characteristics that can influence the effectiveness of the technology. Table 1 provides an overview of the key factors for each of the four technologies.

As Table 1 indicates, electrokinetics, soil flushing, and solidification/stabilization are in

more advanced stages of development than phytoremediation. Soil flushing currently is applicable to a limited range of metals. Soil flushing requires consideration of the potential risk of aquifer contamination by residual flushing solution at the site. The permeability of the soil and the characteristics of the groundwater flow are the main site-specific considerations affecting the applicability of soil flushing. Electrokinetics is most applicable to sites at which the soil is homogeneous and the moisture level is relatively high. Phytoremediation requires longer treatment times than other treatment technologies and may potentially be applied at sites at which the contamination is shallow and the concentration of the contaminants relatively low. Solidification/stabilization is limited by the lack of data concerning the long-term integrity of the treated material. The technology is most effective at sites at which little or no debris is present.

TABLE 1

**OVERVIEW OF IN SITU TECHNOLOGIES FOR REMEDIATION OF SOILS
CONTAMINATED WITH METALS**

	TECHNOLOGY			
EVALUATION FACTOR	ELECTROKINETICS	PHYTOREMEDIATION	SOIL FLUSHING	SOLIDIFICATION/ STABILIZATION
Status	Full-scale applications in Europe Recently licensed in U.S.	Pilot-scale Currently being field-tested in Trenton, NJ; Butte, MT; INEL at Fernald, OH; and Chernobyl, Ukraine	Commercial Selected at 4 Superfund sites	Commercial
Range of Metals Treated	Broad	Broad	Limited	Broad
Major Limiting Factor(s)	State-of-the-art	State-of-the-art Longer time required for treatment Crop yields and growth patterns	Potential contamination of the aquifer from residual flushing solution	Concern with long-term integrity
Site-Specific Considerations	Homogeneity of soil Moisture level in soil	Depth of contamination Concentration of contamination	Permeability of soil Groundwater flow and depth	Debris Depth of contamination

STATUS OF ELECTROKINETIC REMEDIATION TECHNOLOGY

Electrokinetic remediation involves the application of low density direct current between electrodes placed in the soil to mobilize contaminants in the form of charged species. Attempts to leach metals from soils by electro-osmosis date back to the 1930s. In the past, research focused on removing unwanted salts from agricultural soils. Electrokinetics has been used for dewatering of soils and sludges since the first recorded use in the field in 1939 [1]. Electrokinetic extraction has been used in the former Soviet Union since the early 1970s to concentrate metals and to explore for minerals in deep soils. By 1979, research had shown that the content of soluble ions increased substantially in electro-osmotic consolidation of polluted dredgings, while metals were not found in the effluent [2]. By the mid-1980s, numerous researchers had realized independently that electrokinetic separation of metals from soils was a potential solution to contamination [3].

Table 2 presents an overview of two variations of electrokinetic remediation technology. Geokinetics International, Inc.; Battelle Memorial Institute; Electrokinetics, Inc.; and Isotron Corporation all are developing variations of technologies categorized under Approach #1, Enhanced Removal. The consortium of Monsanto, E.I. du Pont de Nemours and Company, General Electric, DOE, and the EPA Office of Research and Development is developing the Lasagna Process, which is categorized under Approach #2, Treatment Without Removal.

1.0 DESCRIPTION

Electrokinetic remediation, also referred to as electrokinetic soil processing, electromigration, electrochemical decontamination, or electroreclamation, can be used to extract radionuclides, metals, and some types of organic wastes from saturated or unsaturated soils, slurries, and sediments [4]. This in situ soil processing technology is primarily a separation and removal technique for extracting contaminants from soils. An in situ bioremediation technology by electrokinetic

injection is under development, with support from EPA and DOE [16].

The principle of electrokinetic remediation relies upon application of a low-intensity direct current through the soil between two or more electrodes. Most soils contain water in the pores between the soil particles and have an inherent electrical conductivity that results from salts present in the soil [5]. The current mobilizes charged species, particles, and ions in the soil by the following processes [6]:

- Electromigration (transport of charged chemical species under an electric gradient)
- Electro-osmosis (transport of pore fluid under an electric gradient)
- Electrophoresis (movement of charged particles under an electric gradient)
- Electrolysis (chemical reactions associated with the electric field)

Figure 2 presents a schematic diagram of a typical conceptual electrokinetic remediation application.

Electrokinetics can be efficient in extracting contaminants from fine-grained, high-permeability soils. A number of factors determine the direction and extent of the migration of the contaminant. Such factors include the type and concentration of the contaminant, the type and structure of the soil, and the interfacial chemistry of the system [7]. Water or some other suitable salt solution may be added to the system to enhance the mobility of the contaminant and increase the effectiveness of the technology. (For example, buffer solutions may change or stabilize pore fluid pH). Contaminants arriving at the electrodes may be removed by any of several methods, including electroplating at the electrode, precipitation or coprecipitation at the electrode, pumping of water near the electrode, or complexing with ion exchange resins [7].

Electrochemistry associated with this process involves an acid front that is generated at the anode if water is the primary pore fluid present.

TABLE 2

OVERVIEW OF ELECTROKINETIC REMEDIATION TECHNOLOGY

General Characteristics	
<ul style="list-style-type: none"> • Depth of soil that is amenable to treatment depends on electrode placement. • Best used in homogeneous soils with high moisture content and high permeability. 	
Approach #1 - Enhanced Removal	Approach #2 - Treatment Without Removal
<p><u>Description:</u> Electrokinetic transport of contaminants toward the polarized electrodes to concentrate the contaminants for subsequent removal and ex-situ treatment.</p>	<p><u>Description:</u> Electro-osmotic transport of contaminants through treatment zones placed between the electrodes. The polarity of the electrodes is reversed periodically, which reverses the direction of the contaminants back and forth through treatment zones. The frequency with which electrode polarity is reversed is determined by the rate of transport of contaminants through the soil.</p>
<p><u>Status:</u> Demonstration projects using full-scale equipment are reported in Europe. Bench- and pilot-scale laboratory studies are reported in the U.S. and at least two full-scale field studies are ongoing in the U.S.</p>	<p><u>Status:</u> Demonstrations are ongoing.</p>
<p><u>Applicability:</u> Pilot scale: lead, arsenic, nickel, mercury, copper, zinc.</p> <p>Lab scale: lead, cadmium, chromium, mercury, zinc, iron, magnesium, uranium, thorium, radium.</p> <p>No performance data available for completed full-scale applications.</p>	<p><u>Applicability:</u> Technology developed for organic species. Research underway for metals.</p>
<p><u>Comments:</u> The efficiency and cost-effectiveness of the technique have not been fully evaluated at full scale in the U.S. by any federal agency. Field studies are under evaluation or recently have been initiated by EPA, DOE, DoD, and Electric Power Research Institute (EPRI). The technique primarily would require addition of water to maintain the electric current and facilitate migration; however, there is ongoing work in application of the technology in partially saturated soils.</p>	<p><u>Comments:</u> This technology is being developed for deep clay formations.</p>

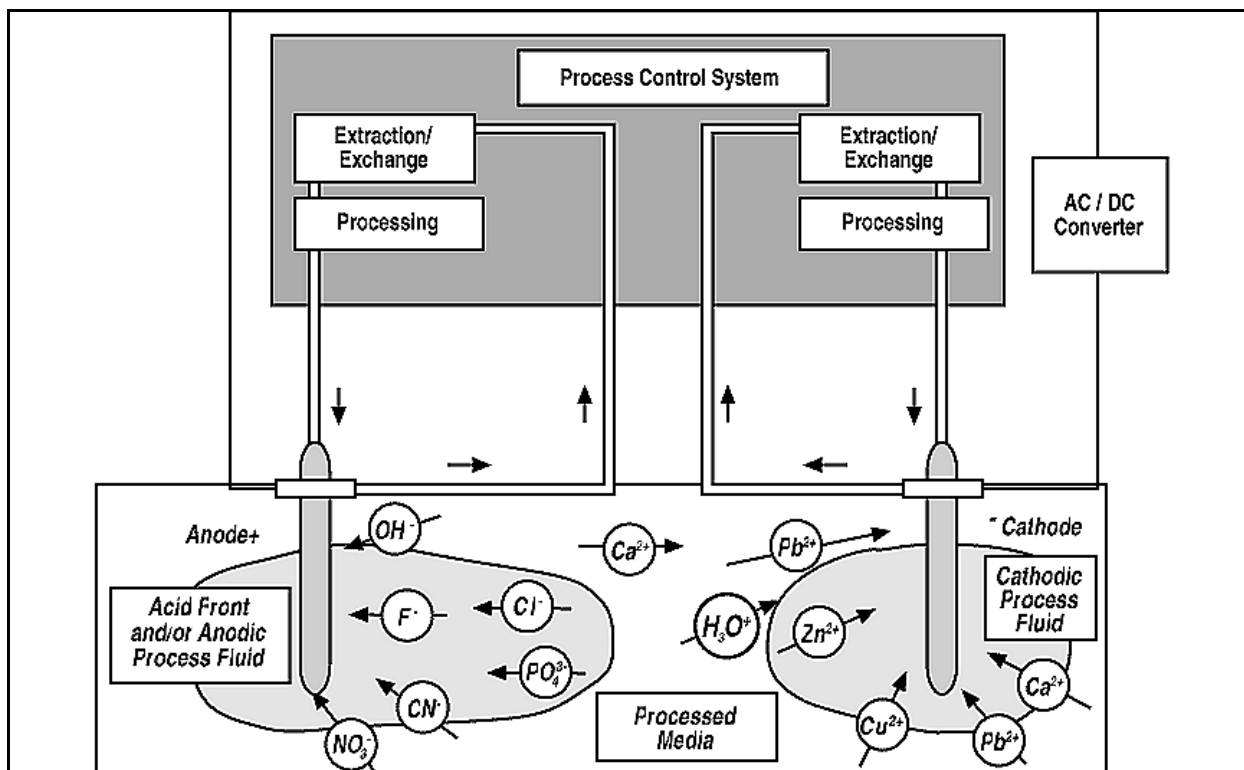


Figure 2. Schematic Diagram of One Electrode Configuration and Geometry Used in Field Implementation of Electrokinetic Remediation [13, 23]

The variation of pH at the electrodes results from the electrolysis of the water. The solution becomes acidic at the anode because hydrogen ions are produced and oxygen gas is released, and the solution becomes basic at the cathode, where hydroxyl ions are generated and hydrogen gas is released [8]. At the anode, the pH could drop to below 2, and it could increase at the cathode to above 12, depending on the total current applied. The acid front eventually migrates from the anode to the cathode. Movement of the acid front by migration and advection results in the desorption of contaminants from the soil [4]. The process leads to temporary acidification of the treated soil, and there are no established procedures for determining the length of time needed to reestablish equilibrium. Studies have indicated that metallic electrodes may dissolve as a result of electrolysis and introduce corrosion products into the soil mass. However, if inert electrodes, such as carbon, graphite, or platinum, are used, no residue will be introduced in the treated soil mass as a result of the process. The electrodes

can be placed horizontally or vertically, depending on the location and shape of the plume of contamination.

Before electrokinetic remediation is undertaken at a site, a number of different field and laboratory screening tests must be conducted to determine whether the particular site is amenable to the treatment technique.

- Field conductivity surveys: The natural geologic spatial variability should be delineated because buried metallic or insulating material can induce variability in the electrical conductivity of the soil and, therefore, the voltage gradient. In addition, it is important to assess whether there are deposits that exhibit very high electrical conductivity, at which the technique may be inefficient.

- Chemical analysis of water: The pore water should be analyzed for dissolved major anions and cations, as well as for the predicted concentration of the contaminant(s). In addition, electrical conductivity and pH of the pore water should be measured.
- Chemical analysis of soil: The buffering capacity and geochemistry of the soil should be determined at each site.
- pH effects: The pH values of the pore water and the soil should be determined because they have a great effect on the valence, solubility, and sorption of contaminant ions.
- Bench-scale test: The dominant mechanism of transport, removal rates, and amounts of contamination left behind can be examined for different removal scenarios by conducting bench-scale tests. Because many of these physical and chemical reactions are interrelated, it may be necessary to conduct bench-scale tests to predict the performance of electrokinetics remediation at the field scale [3,4].

2.0 OVERVIEW OF STATUS

Various methods, developed by combining electrokinetics with other techniques, are being applied for remediation. This section describes different types of electrokinetic remediation methods currently under development for use at contaminated sites. The methods discussed were developed by Electrokinetics, Inc.; Geokinetics International, Inc.; Isotron Corporation; Battelle Memorial Institute; a consortium effort; and P&P Geotechnik GmbH.

2.1 Electrokinetics, Inc.

Electrokinetics, Inc. operates under a licensing agreement with Louisiana State University. The technology is patented by and assigned to Louisiana State University [17] and a complementing process patent is assigned to Electrokinetics, Inc. [18]. As depicted in Figure 2, groundwater and/or a processing fluid

(supplied externally through the boreholes that contain the electrodes) serves as the conductive medium. The additives in the processing fluid, the products of electrolysis reactions at the electrodes, and the dissolved chemical entities in the contaminated soil are transported across the contaminated soil by conduction under electric fields. This transport, when coupled with sorption, precipitation/dissolution, and volatilization/complexation, provides the fundamental mechanism that can affect the electrokinetic remediation process.

Electrokinetics, Inc. accomplishes extraction and removal by electrodeposition, evaporation/condensation, precipitation, or ion exchange, either at the electrodes or in a treatment unit that is built into the system that pumps the processing fluid to and from the contaminated soil [20]. Pilot-scale testing was carried out with support from the EPA under the Superfund Innovative Technology Evaluation (SITE) program, and a design and analysis package for the process was developed with the support of the Gulf Coast Hazardous Substance Research Center of the EPA Office of Research and Development [19].

2.2 Geokinetics International, Inc.

On July 18, 1995, Geokinetics International, Inc. (GII) was awarded a patent for an electroreclamation process. The key claims in the patent are the use of electrode wells for both anodes and cathodes and the management of the pH and electrolyte levels in the electrolyte streams of the anode and the cathode. The patent also includes claims for the use of additives to dissolve different types of contaminants [9]. Fluor Daniel is licensed to operate GII's metal removal process in the United States.

GII has developed an alternative that combines containment, remediation, and prevention in electrokinetic fencing. Laboratory experiments have demonstrated that, with an electrokinetic fence, it is possible to:

- Capture electrically charged (polar) contaminants while treated water passes through the fence

- Influence the pH and redox potential of the groundwater
- Introduce microorganisms and nutrients through the electrode system or injection well
- Increase soil temperatures in the area inside the fence to accelerate biodegradation processes
- Retard and prevent migration

Electrokinetic fences can be installed both horizontally and vertically and at any depth [10], as Figure 3 shows.

Another alternative developed by GII, electroheating, uses heat generated by electrokinetics in combination with extraction methods to remove volatile and semivolatile compounds. Figure 4 presents a schematic and performance data for this electroheating process. Electroheating and extraction can be used to remove dense non-aqueous phase liquids

(DNAPL), such as chlorinated solvents, that have sunk deep into the aquifer. Field trials by GII using electrical current have shown that soil and groundwater between the electrodes are heated uniformly. In combination with vacuum or groundwater extraction, the vendor claims the removal of the contaminants identified above can be accomplished very effectively [10].

GII has developed and patented electrically conductive ceramic material (EBONEX[®]) that has an extremely high resistance to corrosion. It has a lifetime in soil of at least 45 years and is self-cleaning. GII also has developed a batch electrokinetic remediation (BEK[®]) process. The process which incorporates electrokinetic technology, normally requires 24 to 48 hours for complete remediation of the substrate. BEK[®] is a mobile unit that remediates ex situ soils on site. GII also has developed a solution treatment technology (EIX[®]) that allows removal of contamination from the anode and the cathode solutions up to a thousand times faster than can be achieved through conventional means [14].

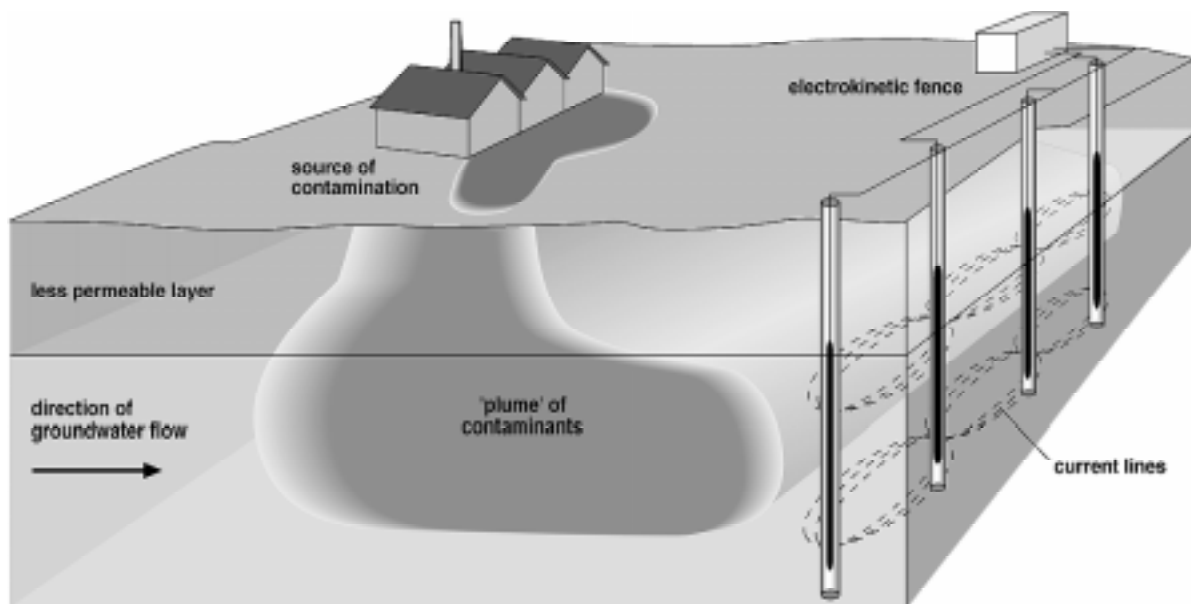


Figure 3. Schematic View of Contaminated Plume Stopped by An Electrokinetic Fence [10]

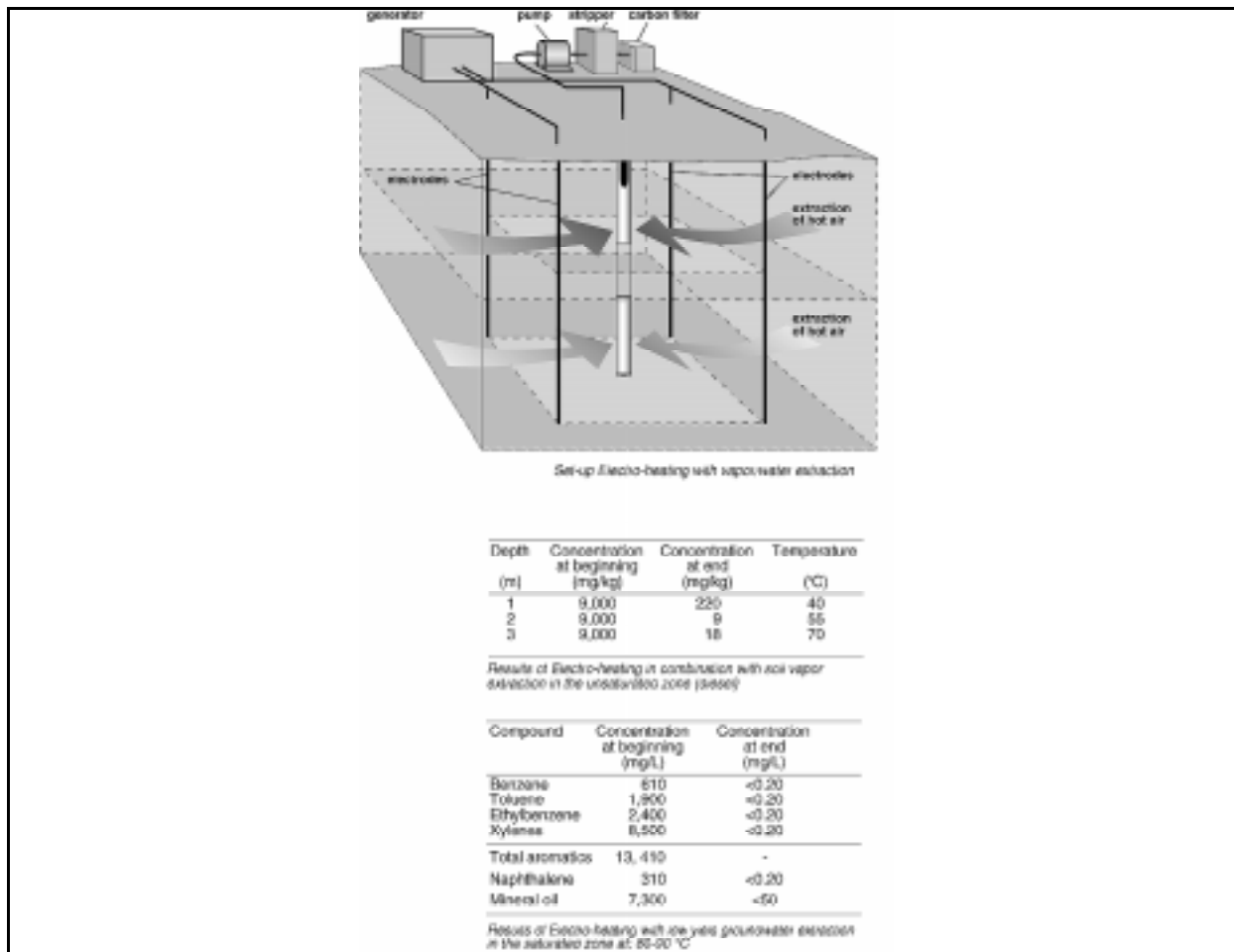


Figure 4. Setup of Electroheating with Vapor/Water Extraction: Results in Unsaturated Zone and in Saturated Zone [10]

2.3 Isotron Corporation

Isotron Corporation is participating in a pilot-scale demonstration of electrokinetic extraction supported by DOE's Office of Technology Development. The demonstration is taking place at the Oak Ridge K-25 facility in Tennessee. Laboratory tests completed in 1994 showed that the Isotron process could effect the movement and capture of uranium present in soil from the Oak Ridge site [12].

Isotron Corporation also is involved with Westinghouse Savannah River Company in an ongoing demonstration of electrokinetic remediation. The demonstration, supported by DOE's Office of Technology Development, is taking place at the old TNX basin at the Savannah River site in South Carolina. Isotron is using the Electrosorb^R process with a patented

cylinder to control buffering conditions in situ. An ion exchange polymer matrix called Isolock^R is being used to trap metal ions. The process is being tested for the removal of lead and chromium, although the low concentrations of mercury (5 milligrams per kilogram [mg/kg]) at the site have not been reduced appreciably [12].

2.4 Battelle Memorial Institute

Another method that uses electrokinetic technology is electroacoustical soil decontamination. This technology combines electrokinetics with sonic vibration. Through application of mechanical vibratory energy in the form of sonic or ultrasonic energy, the properties of a liquid contaminant in soil can be altered in a way that increases the level of removal of the contaminant. Battelle Memorial Institute of Columbus, Ohio developed the in situ treatment

process that uses both electrical and acoustical forces to remove floating contaminants, and possibly metals, from subsurface zones of contamination. The process was selected for EPA's SITE program; the technology demonstration was completed in May 1989 [13]. Figure 5 illustrates the process.

2.5 Consortium Process

Monsanto Company has coined the name Lasagna™ to identify its products and services that are based on the integrated in-situ remediation process developed by a consortium. The proposed technology combines electro-osmosis with treatment zones that are installed directly in the contaminated soils to form an integrated in-situ remedial process, as Figure 6 shows. The consortium consists of Monsanto, E.I. du Pont de Nemours and Company (DuPont), and General Electric (GE), with participation by the EPA Office of Research and Development and DOE, as Figure 7 shows.

The consortium's activities are being facilitated by Clean Sites, Inc., under a cooperative agreement with EPA's Technology Innovation Office (TIO) [12].

The in-situ decontamination process occurs as follows:

- Creates highly permeable zones in close proximity sectioned through the contaminated soil region and turns them into sorption-degradation zones by introducing appropriate materials (sorbents, catalytic agents, microbes, oxidants, buffers, and others).
- Uses electro-osmosis as a liquid pump to flush contaminants from the soil into the treatment zones of degradation.
- Reverses liquid flow, if desired, by switching the electrical polarity, a mode that increases the efficiency with which contaminants are removed from the soil; allows repeated passes through the treatment zones for complete sorption or destruction.

Initial field tests of the consortium process were conducted at DOE's gaseous diffusion plant in Paducah, Kentucky. The experiment tested the combination of electro-osmosis and in situ sorption in treatment zones. In November 1994, CDM Federal Programs Corporation installed field demonstration equipment [12]. Technology development for the degradation processes and their integration into the overall treatment scheme were carried out in 1994 and 1995 at bench and pilot scales, with field experiments of the full process planned for 1996 [11].

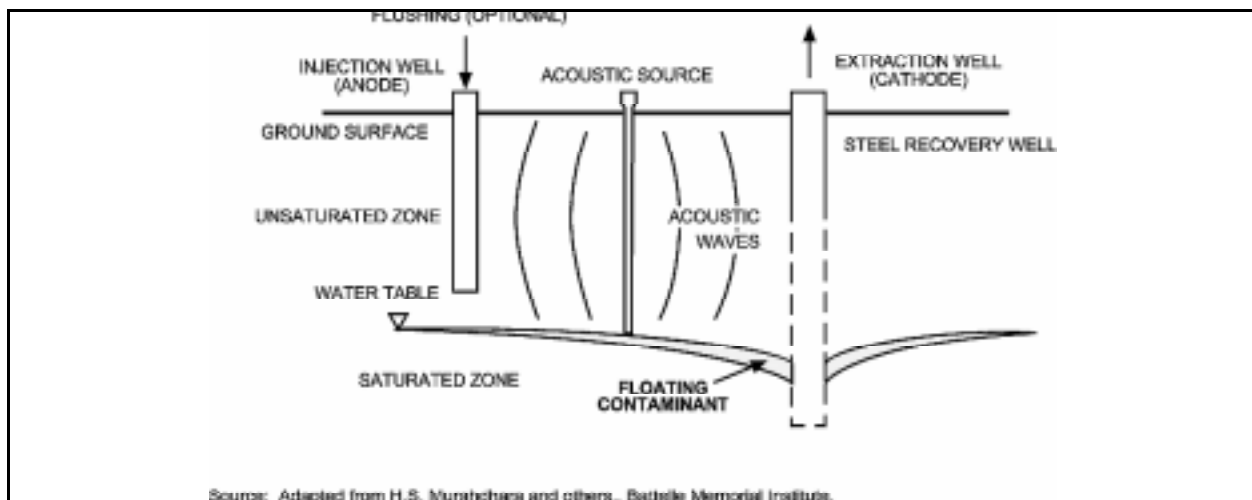


Figure 5. Electroacoustical Soil Decontamination Process [13]

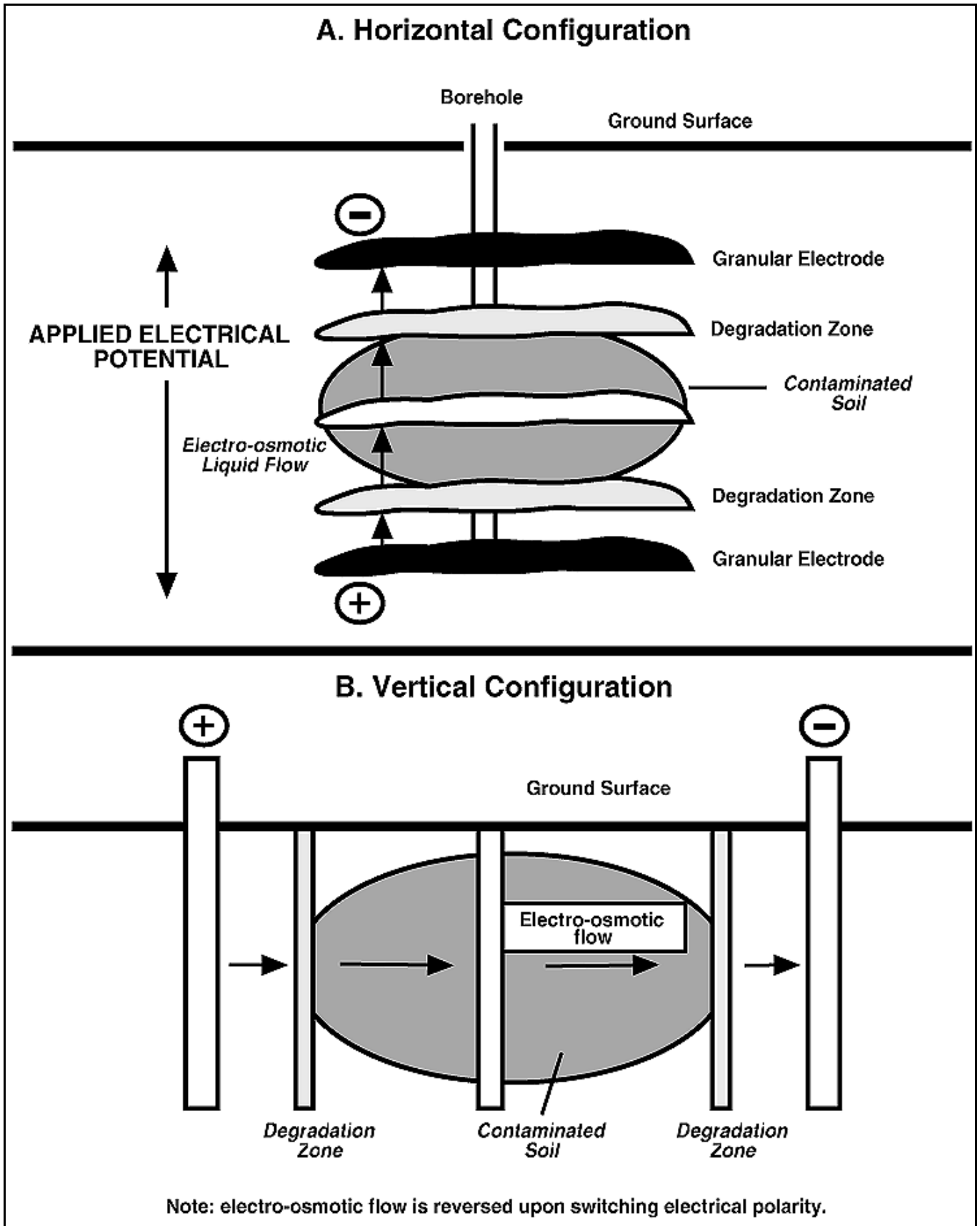


Figure 6. Schematic Diagram of the Lasagna™ Process [11]

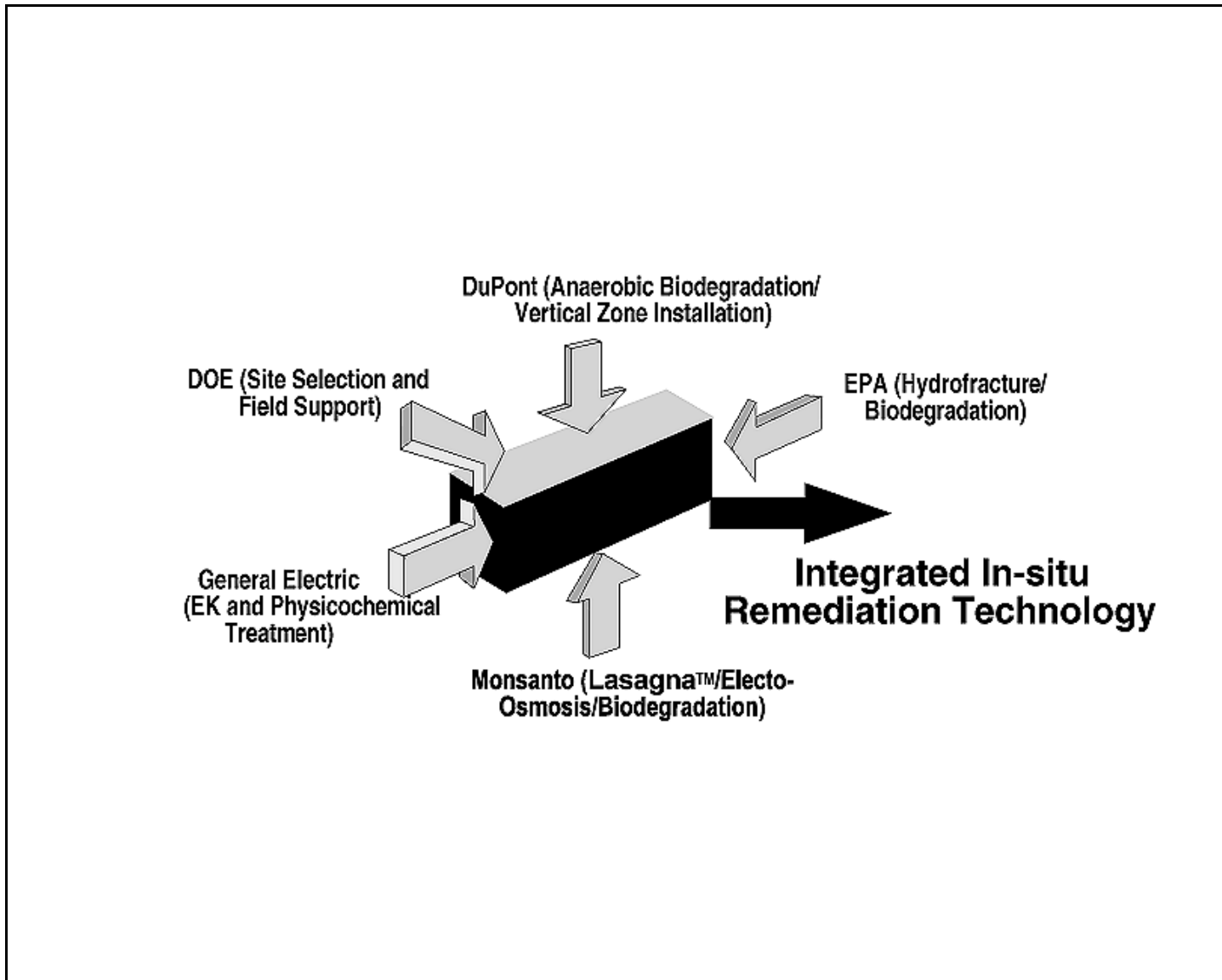


Figure 7. Integrated In-Situ Remediation: Consortium [11]

3.0 PERFORMANCE AND COST SUMMARY

Work sponsored by EPA, the U.S. Army Waterways Experiment Station (WES), DOE, the National Science Foundation, and private industry (for example, Dow Chemical, Du Pont, Monsanto, and GE), when coupled with the efforts of researchers from academic and public institutions (for example, Sandia National Laboratories, Argonne National Laboratory, Louisiana State University, the Massachusetts Institute of Technology, Texas A&M University, West Virginia University, and the University of Massachusetts Lowell [12]), have demonstrated the feasibility of moving electrokinetics remediation to pilot-scale testing and demonstration stages [4].

This section describes testing and cost summary results reported by Louisiana State University, Electrokinetics, Inc., GII, Battelle Memorial Institute, and the consortium.

3.1 Louisiana State University - Electrokinetics, Inc.

The Louisiana State University (LSU) - Electrokinetics, Inc. Group has conducted bench-scale testing on radionuclides and on organic compounds. Test results have been reported for lead, cadmium, chromium, mercury, zinc, iron, and magnesium. Radionuclides tested include uranium, thorium, and radium. Experimental data on the transport and removal of such polar organic compounds as phenol and acetic acid have been reported, and information about transport of nonpolar organic compounds such as benzene, toluene, ethylene, and xylene (BTEX) below their solubility values also has been disseminated.

In collaboration with EPA, the LSU-Electrokinetics, Inc. Group has completed pilot-scale studies of electrokinetic soil processing in the laboratory. WES, in partnership with Electrokinetics, Inc., is carrying out a site-specific pilot-scale study of the Electro-Klean™ electrical separation process. Pilot field studies also have been reported in the

Netherlands on soils contaminated with lead, arsenic, nickel, mercury, copper and zinc.

A pilot-scale laboratory study investigating the removal of 2,000 mg/kg of lead loaded onto kaolinite was completed in May 1993. Removal efficiencies of 90 to 95 percent were obtained. The electrodes were placed one inch apart in a two-ton kaolinite specimen for four months, at a total energy cost of about \$15 per ton [13].

Currently (in 1996), with the support of DoD's Small Business Innovative Research Program and in collaboration with WES, Electrokinetics, Inc. is carrying out a comprehensive demonstration study of lead extraction from a creek bed at a U.S. Army firing range in Louisiana. EPA is taking part in independent assessments of the results of that demonstration study under the SITE program. The soils are contaminated with levels as high as 4,500 mg/kg of lead; pilot-scale studies have demonstrated that concentrations of lead decreased to less than 300 mg/kg in 30 weeks of processing. The Toxicity Characteristic Leaching Procedure (TCLP) values dropped from more than 300 milligrams per liter (mg/L) to less than 40 mg/L within the same period. At the site of the demonstration study, Electrokinetics, Inc. is using the CADEX™ electrode system that promotes transport of species into the cathode compartment, where they are precipitated and/or electrodeposited directly. Electrokinetics, Inc. uses a special electrode material that is cost-effective and does not corrode. Under the supervision and support of the Electric Power Research Institute and power companies in the southern U.S., a treatability and a pilot-scale field testing study of soils in sites contaminated with arsenic has been initiated, in a collaborative effort between Southern Company Services Engineers and Electrokinetics, Inc [20].

With support from a Small Business Innovative Research (SBIR) Phase I grant from DOE, Electrokinetics, Inc., in collaboration with the Argonne National Laboratory, has initiated a project to assess the potential for electrokinetic transport processes to supplement, enhance, and engineer in situ bioremediation systems in contaminated soils that are characterized by

numerous zones of significantly different hydraulic and electrical conductivities [14]. Pilot-scale development of the project is underway at Electrokinetics, Inc., with support from the EPA's National Risk Management Research Laboratory in Cincinnati, Ohio, under the SITE program [20].

The processing cost of a system designed and installed by Electrokinetics, Inc. consists of energy cost, conditioning cost, and fixed costs associated with installation of the system. Power consumption is related directly to the conductivity of the soil across the electrodes. Electrical conductivity of soils can span orders of magnitude, from 30 micro reciprocal ohms per centimeter ($\mu\text{mhos/cm}$) to more than 3,000 $\mu\text{mhos/cm}$, with higher values being in saturated, high-plasticity clays. A mean conductivity value is often approximately 500 $\mu\text{mhos/cm}$. The voltage gradient often is held to approximately 1 volt per centimeter (V/cm) in an attempt to prevent adverse effects of temperature increases and for other practical reasons [4]. It may be cost-prohibitive to attempt to remediate high-plasticity soils that have high electrical conductivities. However, for most deposits having conductivities of 500 $\mu\text{mhos/cm}$, the daily energy consumption will be approximately 12 kilowatt hours (kWh)/cubic meter (m^3) per day or about $\$0.40/\text{m}^3$ per day, ($\$0.03/\text{kWh}$) and $\$12/\text{m}^3$ per month. The processing time will depend upon several factors, including the spacing of the electrodes, and the type of conditioning scheme that will be used. If an electrode spacing of 4 m is selected, it may be necessary to process the site over several months.

Ongoing pilot-scale studies using "real-world" soils indicate that the energy expenditures in extraction of metals from soils may be 500 kWh/m^3 or more at electrode spacings of 1.0 m to 1.5 m [19]. The vendor estimates that the direct cost of about $\$15/\text{m}^3$ ($\$0.03/\text{kWh}$) suggested for this energy expenditure, together with the cost of enhancement, could result in direct costs of $\$50/\text{m}^3$ or more. If no other efficient in situ technology is available to remediate fine-grained and heterogenous subsurface deposits contaminated with metals, this technique would remain potentially competitive.

3.2 Geokinetics International, Inc.

GII has successfully demonstrated in situ electrochemical remediation of metal-contaminated soils at several sites in Europe. Geokinetics, a sister company of GII, also has been involved in the electrokinetics arena in Europe. Table 3 summarizes the physical characteristics of five of the sites, including the size, the contaminant(s) present, and the overall performance of the technology at each site [22].

GII estimates its typical costs for 'turn key' remediation projects are in the range of $\$120$ - $\$200/\text{cubic yard}$ (yd^3) [22].

Demonstration of the electrokinetic remediation process in chromate-contaminated soil at the Sandia Chemical Waste Landfill is scheduled as part of the mixed waste landfill integrated demonstration. The demonstration is being conducted under the SITE program for the Sandia National Laboratories in New Mexico, Naval Air Station Alameda in California, and Electrokinetics, Inc. in Louisiana.

3.3 Battelle Memorial Institute

The technology demonstration through the SITE program was completed in May 1989 [13]. The results indicate that the electroacoustical technology is technically feasible for the removal of inorganic species from clay soils (and only marginally effective for hydrocarbon removal) [24].

3.4 Consortium Process

The Phase I-Vertical field test of the LasagnaTM process operated for 120 days and was completed in May 1995. Scale-up from laboratory units was successfully achieved with respect to electrical parameters and electro-osmotic flow. Soil samples taken throughout the test site before and after the test indicate a 98% removal of trichloroethylene (TCE) from a tight clay soil (i.e., hydraulic conductivity less

TABLE 3

PERFORMANCE SUMMARY OF ELECTROCHEMICAL SOIL REMEDIATION TECHNOLOGY APPLIED AT FIVE FIELD SITES IN EUROPE (1987-1994)

Site Description	Volume (ft ³)	Contaminant(s)	Initial Concentration (mg/kg)	Final Concentration (mg/kg)
Former paint factory	8,100 peat/clay soil	Cu Pb	1,220 >3,780	<200 <280
Operational galvanizing plant	1,350 clay soil	Zn	>1,400	600
Former timber plant	6,750 heavy clay soil	As	>250	<30
Temporary landfill	194,400 argillaceous sand	Cd	>180	<40
Military air base	68,000 clay	Cd Cr Cu Ni Pb Zn	660 7,300 770 860 730 2,600	47 755 98 80 108 289

than 1×10^{-7} cm/sec). TCE soil levels were reduced from the 100 to 500 mg/kg range to an average concentration of 1 mg/kg [25]. Various treatment processes are being investigated in the laboratory to address other types of contaminants, including heavy metals [25].

4.0 ANALYSIS OF APPLICATIONS

Electrokinetic remediation may be applied to both saturated and partially saturated soils. One problem to overcome when applying electrokinetic remediation to the vadose zone is the drying of soil near the anode. When an electric current is applied to soil, water will flow by electro-osmosis in the soil pores, usually toward the cathode. The movement of the water will deplete soil moisture adjacent to the anode, and moisture will collect near the cathode. However, processing fluids may be circulated at the electrodes. The fluids can serve both as a conducting medium and as a means to extract or exchange the species and introduce other species. Another use of processing fluids is to control, depolarize, or modify either or both electrode reactions. The advance of the process fluid (acid

or the conditioning fluid) across the electrodes assists in desorption of species and dissolution of carbonates and hydroxides. Electro-osmotic advection and ionic migration lead to the transport and subsequent removal of the contaminants. The contaminated fluid is then recovered at the cathode.

Spacing of the electrode will depend upon the type and level of contamination and the selected current voltage regime. When higher voltage gradients are generated, the efficiency of the process might decrease because of increases in temperature. A spacing that will generate a potential gradient in the order of one V/cm is preferred. The spacing of electrodes generally will be as much as three meters. The duration of the remediation will be site-specific. The remediation process should be continued until the desired removal is achieved. However, it should be recognized that, in cases in which the duration of treatment is reduced by increasing the electrical potential gradient, the efficiency of the process will decrease.

The advantage of the technology is its potential for cost-effective use for both in situ and ex situ applications. The fact that the technique requires the presence of a conducting pore fluid in a soil mass may have site-specific implication. Also, heterogeneities or anomalies found at sites, such

as submerged foundations, rubble, large quantities of iron or iron oxides, large rocks, or gravel; or submerged cover material, such as seashells, are expected to reduce removal efficiencies [4].

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The following vendors were contacted during the preparation of this report:

Name	Agency/Company	Telephone Number
Yalcin Acar	Electrokinetics, Inc. Louisiana State University South Stadium Drive Baton Rouge, Louisiana, 70803-6100	(504) 388-3992
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Robert Clark	Geokinetics International, Inc	(510) 254-2335
Dr. B. Mason Hughes (Project Manager) Lasagna™ Process	Monsanto	(314) 694-1466
Dr. Sa Ho (Contractor Principal Investigator) Lasagna™ Process	Monsanto Environmental Science Center St. Louis, Missouri 63167	(314) 694-5179

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**STATUS OF IN SITU
PHYTOREMEDIATION TECHNOLOGY**

Phytoremediation is the use of plants to remove, contain, or render harmless environmental contaminants. This definition applies to all biological, chemical, and physical processes that are influenced by plants and that aid in the cleanup of contaminated substances [1]. Plants can be used in site remediation, both to mineralize and immobilize toxic organic compounds at the root zone and to accumulate and concentrate metals and other inorganic compounds from soil into aboveground shoots

[2]. Although phytoremediation is a relatively new concept in the waste management community, techniques, skills, and theories developed through the application of well-established agro-economic technologies are easily transferable. The development of plants for restoring sites contaminated with metals will require the multidisciplinary research efforts of agronomists, toxicologists, biochemists, microbiologists, pest management specialists, engineers, and other specialists [1, 2]. Table 4 presents an overview of phytoremediation technology.

**TABLE 4
OVERVIEW OF PHYTOREMEDIATION TECHNOLOGY**

General Characteristics	
<ul style="list-style-type: none"> • Best used at sites with low to moderate disperse metals content and with soil media that will support plant growth. • Applications limited to depth of the root zone. • Longer times required for remediation compared with other technologies. • Different species have been identified to treat different metals. 	
Approach #1 - Phytoextraction (harvest)	Approach #2 - Phytostabilization (root-fixing)
<u>Description:</u> Uptake of contaminants from soil into aboveground plant tissue, which is periodically harvested and treated.	<u>Description:</u> Production of chemical compounds by the plant to immobilize contaminants at the interface of roots and soil. Additional stabilization can occur by raising the pH level in the soil.
<u>Status:</u> Field testing for effectiveness on radioactive metals is ongoing in the vicinity of the damaged nuclear reactor in Chernobyl, Ukraine. Field testing also is being conducted in Trenton, NJ and Butte, MT and by the Idaho National Engineering Laboratory (INEL) in Fernald, OH.	<u>Status:</u> Research is ongoing.
<u>Applicability:</u> Potentially applicable for many metals. Nickel and zinc appear to be most easily absorbed. Preliminary results for absorption of copper and cadmium are encouraging.	<u>Applicability:</u> Potentially applicable for many metals, especially lead, chromium, and mercury.
<u>Comments:</u> Cost affected by volume of biomass produced that may require treatment before disposal. Cost affected by concentration and depth of contamination and number of harvests required.	<u>Comments:</u> Long-term maintenance is required.

1.0 DESCRIPTION

Metals considered essential for at least some

forms of life include vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), and molybdenum (Mo) [2]. Because many metals are toxic in concentrations above minute levels, an organism must regulate the cellular concentrations of such metals. Consequently, organisms have evolved transport systems to regulate the uptake and distribution of metals. Plants have remarkable metabolic and absorption capabilities, as well as transport systems that can take up ions selectively from the soil. Plants have evolved a great diversity of genetic adaptations to handle potentially toxic levels of metals and other pollutants that occur in the environment. In plants, uptake of metals occurs primarily through the root system, in which the majority of mechanisms to prevent metal toxicity are found [4]. The root system provides an enormous surface area that absorbs and accumulates the water and nutrients essential for growth. In many ways, living plants can be compared to solar-powered pumps that can extract and concentrate certain elements from the environment [5].

Plant roots cause changes at the soil-root interface as they release inorganic and organic compounds (root exudates) in the area of the soil immediately surrounding the roots (the rhizosphere) [6]. Root exudates affect the number and activity of microorganisms, the aggregation and stability of soil particles around the root, and the availability of elements. Root exudates can increase (mobilize) or decrease (immobilize) directly or indirectly the availability of elements in the rhizosphere. Mobilization and immobilization of elements in the rhizosphere can be caused by: 1) changes in soil pH; 2) release of complexing substances, such as metal-chelating molecules; 3) changes in oxidation-reduction potential; and 4) increase in microbial activity [7].

Phytoremediation technologies can be developed for different applications in environmental cleanup and are classified into three types:

- Phytoextraction
- Phytostabilization

- Rhizofiltration

1.1 Phytoextraction

Phytoextraction technologies use hyperaccumulating plants to transport metals from the soil and concentrate them into the roots and aboveground shoots that can be harvested [1, 2, 6]. A plant containing more than 0.1 percent of Ni, Co, Cu, Cr, or one percent of Zn and Mn in its leaves on a dry weight basis is called a hyperaccumulator, regardless of the concentration of metals in the soil [2, 10].

Almost all metal-hyperaccumulating species known today were discovered on metal-rich soils, either natural or artificial, often growing in communities with metal excluders [2, 11]. Actually, almost all metal-hyperaccumulating plants are endemic to such soils, suggesting that hyperaccumulation is an important ecophysiological adaptation to metal stress and one of the manifestations of resistance to metals. The majority of hyperaccumulating species discovered so far are restricted to a few specific geographical locations [2, 10]. For example, Ni hyperaccumulators are found in New Caledonia, the Philippines, Brazil, and Cuba. Ni and Zn hyperaccumulators are found in southern and central Europe and Asia Minor.

Dried or composted plant residues or plant ashes that are highly enriched with metals can be isolated as hazardous waste or recycled as metal ore. The goal of phytoextraction is to recycle as "bio-ores" metals reclaimed from plant ash in the feed stream of smelting processes. Even if the plant ashes do not have enough concentration of metal to be useful in smelting processes, phytoextraction remains beneficial because it reduces by as much as 95 percent the amount of hazardous waste to be landfilled [14]. Several research efforts in the use of trees, grasses, and crop plants are being pursued to develop phytoremediation as a cleanup technology. The following paragraphs briefly discuss these three phytoextraction techniques.

The use of trees can result in extraction of significant amounts of metal because of their high biomass production. However, the use of

trees in phytoremediation requires long-term treatment and may create additional environmental concerns about falling leaves. When leaves containing metals fall or blow away, recirculation of metals to the contaminated site and migration off site by wind transport or through leaching can occur [15].

Some grasses accumulate surprisingly high levels of metals in their shoots without exhibiting toxic effects. However, their low biomass production results in relatively low yield of metals. Genetic breeding of hyperaccumulating plants that produce relatively large amounts of biomass could make the extraction process highly effective; however, such work has not yet begun.

It is known that many crop plants can accumulate metals in their roots and aboveground shoots, potentially threatening the food chain. For example, in May 1980 regulations proposed under RCRA for hazardous waste (now codified at 40 CFR Part 264) include limits on the amounts of cadmium and other metals that can be applied to crops. Recently, however, the potential use of crop plants for environmental remediation has been under investigation. Using crop plants to extract metals from the soil seems practical because of their high biomass production and relatively fast rate of growth. Other benefits of using crop plants are that they are easy to cultivate and they exhibit genetic stability [14].

1.2 Phytostabilization

Phytostabilization uses plants to limit the mobility and bioavailability of metals in soils. Ideally, phytostabilizing plants should be able to tolerate high levels of metals and to immobilize them in the soil by sorption, precipitation, complexation, or the reduction of metal valences. Phytostabilizing plants also should exhibit low levels of accumulation of metals in shoots to eliminate the possibility that residues in harvested shoots might become hazardous wastes [5]. In addition to stabilizing the metals present in the soil, phytostabilizing plants also can stabilize the soil matrix to minimize erosion and migration of sediment. Dr. Gary Pierzynski of Kansas State University is studying

phytostabilization in poplar trees, which were selected for the study because they can be deep-planted and may be able to form roots below the zone of maximum contamination.

Since most sites contaminated with metals lack established vegetation, metal-tolerant plants are used to revegetate such sites to prevent erosion and leaching [16]. However, that approach is a containment rather than a remediation technology. Some researchers consider phytostabilization an interim measure to be applied until phytoextraction becomes fully developed. However, other researchers are developing phytostabilization as a standard protocol of metal remediation technology, especially for sites at which removal of metals does not seem to be economically feasible. After field applications conducted by a group in Liverpool, England, varieties of three grasses were made commercially available for phytostabilization [5]:

- *Agrostis tenuis*, cv *Parys* for copper wastes
- *Agrosas tenuis*, cv *Coginan* for acid lead and zinc wastes
- *Festuca rubra*, cv *Merlin* for calcareous lead and zinc wastes

1.3 Rhizofiltration

One type of rhizofiltration uses plant roots to absorb, concentrate, and precipitate metals from wastewater [5], which may include leachate from soil. Rhizofiltration uses terrestrial plants instead of aquatic plants because the terrestrial plants develop much longer, fibrous root systems covered with root hairs that have extremely large surface areas. This variation of phytoremediation uses plants that remove metals by sorption, which does not involve biological processes. Use of plants to translocate metals to the shoots is a slower process than phytoextraction [16].

Another type of rhizofiltration, which is more fully developed, involves construction of

wetlands or reed beds for the treatment of contaminated wastewater or leachate. The

technology is cost-effective for the treatment of large volumes of wastewater that have low concentrations of metals [16]. Since rhizofiltration focuses on treatment of contaminated water, it is not discussed further in this report.

Table 5 presents the advantages and disadvantages of each of the types of phytoremediation currently being researched that are categorized as either phytoextraction or phytostabilization [5].

TABLE 5
TYPES OF PHYTOREMEDIATION TECHNOLOGY:
ADVANTAGES AND DISADVANTAGES

TYPE OF PHYTOREMEDIATION	ADVANTAGES	DISADVANTAGES
Phytoextraction by trees	High biomass production	Potential for off-site migration and leaf transportation of metals to surface Metals are concentrated in plant biomass and must be disposed of eventually.
Phytoextraction by grasses	High accumulation	Low biomass production and slow growth rate Metals are concentrated in plant biomass and must be disposed of eventually.
Phytoextraction by crops	High biomass and increased growth rate	Potential threat to the food chain through ingestion by herbivores Metals are concentrated in plant biomass and must be disposed of eventually.
Phytostabilization	No disposal of contaminated biomass required	Remaining liability issues, including maintenance for indefinite period of time (containment rather than removal)
Rhizofiltration	Readily absorbs metals	Applicable for treatment of water only Metals are concentrated in plant biomass and must be disposed of eventually.

1.4 Future Development

Faster uptake of metals and higher yields of metals in harvested plants may become possible through the application of genetic engineering and/or selective breeding techniques. Recent laboratory-scale testing has revealed that a genetically altered species of mustard weed can uptake mercuric ions from the soil and convert them to metallic mercury, which is transpired through the leaves [23, 24, 25]. Improvements in phytoremediation may be attained through research and a better understanding of the principles governing the processes by which plants affect the geochemistry of their soils. In addition, future testing of plants and microflora may lead to the identification of plants that have metal accumulation qualities that are far superior to those currently known [17].

2.0 OVERVIEW OF STATUS

Plants have been used to treat wastewater for more than 300 years, and plant-based remediation methods for slurries of dredged material and soils contaminated with metals have been proposed since the mid-1970s [1, 13]. Reports of successful remediation of soils contaminated with metals are rare, but the suggestion of such application is more than a decade old, and progress is being made at a number of pilot test sites [11]. Successful phytoremediation must meet cleanup standards in order to be approved by regulatory agencies.

No full-scale applications of phytoremediation have been reported. One vendor, Phytotech, Inc., is developing phytostabilization for soil remediation applications. Phytotech also has patented strategies for phytoextraction and is conducting several field tests in Trenton, New Jersey and in Chernobyl, Ukraine [14]. Also, as was previously mentioned, a group in Liverpool, England has made three grasses commercially available for the stabilization of lead, copper, and zinc wastes [5].

3.0 PERFORMANCE AND COST SUMMARY

Currently, because it has not been used in any full scale applications, the potential of phytoremediation for cleanup of contaminated sites cannot be completely ascertained. However, a variety of new research approaches and tools are expanding understanding of the molecular and cellular processes that can be employed through phytoremediation [3].

3.1 Results of Testing

Potential for phytoremediation (phytoextraction) can be assessed by comparing the concentration of contaminants and volume of soil to be treated with the particular plant's seasonal productivity of biomass and ability to accumulate contaminants. Table 6 lists selected examples of plants identified as metal hyperaccumulators and their native countries. [10, 12]. If plants are to be effective remediation systems, one ton of plant biomass, costing from several hundred to a few thousand dollars to produce, must be able to treat large volumes of contaminated soil. For metals that are removed from the soil and accumulated in aboveground biomass, the total amount of biomass per hectare required for soil cleanup is determined by dividing the total weight of metal per hectare to be remediated by the accumulation factor, which is the ratio of the accumulated weight of the metal to the weight of the biomass containing the metal. The total biomass per acre then can be divided by the productivity of the plant (tons[t]/hectare[ha]/year[yr]) to determine the number of years required to achieve cleanup standards--a major determinant of the overall cost and feasibility of phytoremediation [3].

As discussed earlier, the amount of biomass is one of the factors that determines the practicality of phytoremediation. Under the best climatic conditions, with irrigation, fertilization, and other factors, total biomass productivity can approach 100 t/ha/yr. One unresolved issue is the trade-off between accumulation of toxic elements and productivity [20]. In practice, a maximum harvest biomass yield of 10 to 20

TABLE 6
EXAMPLES OF METAL HYPERACCUMULATORS

METAL	PLANT SPECIES	PERCENTAGE OF METAL IN DRY WEIGHT OF LEAVES (%)	NATIVE LOCATION
Zn	<i>Thlaspi calaminare</i>	<3	Germany
	<i>Viola</i> species	1	Europe
Cu	<i>Aeolanthus biformifolius</i>	1	Zaire
Ni	<i>Phyllanthus serpentinus</i>	3.8	New Caledonia
	<i>Alyssum bertoloni</i> and 50 other species of alyssum	>3	Southern Europe and Turkey
	<i>Sebertia acuminata</i>	25 (in latex)	New Caledonia
	<i>Stackhousia tryonii</i>	4.1	Australia
Pb	<i>Brassuca juncea</i>	<3.5	India
Co	<i>Haumaniastrum robertii</i>	1	Zaire

t/ha/yr is likely, particularly for plants that accumulate metals.

These values for productivity of biomass and the metal content of the soil would limit annual capacity for removal of metals to approximately 10 to 400 kg/ha/yr, depending on the pollutant, species of plant, climate, and other factors. For a target soil depth of 30 cm (4,000 t/ha), this capacity amounts to an annual reduction of 2.5 to 100 mg/kg of soil contaminants. This rate of removal of contamination often is acceptable, allowing total remediation of a site over a period of a few years to several decades [3].

3.2 Cost

The practical objective of phytoremediation is to achieve major reductions in the cost of cleanup of hazardous sites. Salt and others [5] note the cost-effectiveness of phytoremediation with an example: Using phytoremediation to clean up one acre of sandy loam soil to a depth of 50 cm typically will cost \$60,000 to \$100,000, compared with a cost of at least \$400,000 for excavation and disposal storage without

treatment [5]. One objective of field tests is to use commercially available agricultural equipment and supplies for phytoremediation to reduce costs. Therefore, in addition to their remediation qualities, the agronomic characteristics of the plants must be evaluated.

The processing and ultimate disposal of the biomass generated is likely to be a major percentage of overall costs, particularly when highly toxic metals and radionuclides are present at a site. Analysis of the costs of phytoremediation must include the entire cycle of the process, from the growing and harvesting of the plants to the final processing and disposal of the biomass. It is difficult to predict costs of phytoremediation, compared with overall cleanup costs at a site. Phytoremediation also may be used as a follow-up technique after areas having high concentrations of pollutants have been mitigated or in conjunction with other remediation technologies, making cost analysis more difficult.

3.3 Future directions

Because metal hyperaccumulators generally produce small quantities of biomass, they are unsuited agronomically for phytoremediation. Nevertheless, such plants are a valuable store of genetic and physiologic material and data [1]. To provide effective cleanup of contaminated soils, it is essential to find, breed, or engineer plants that absorb, translocate, and tolerate levels of metals in the 0.1- to 1.0-percent range. It also is necessary to develop a methodology for selecting plants that are native to the area.

Currently, phytoremediation is generally not commercially available (although three grasses are commercially available for the stabilization of lead, copper, and zinc wastes [5]). Relatively few research projects and field tests of the technology have been conducted. An integrated approach that involves basic and applied research, along with consideration of safety, legal, and policy issues, will be necessary to establish phytoremediation as a practicable cleanup technology [1].

According to a 1994 DOE report titled "Summary Report of a Workshop on Phytoremediation Research Needs," three broad areas of research and development can be identified for the in situ treatment of soil contaminated with metals [3]:

- Mechanisms of uptake, transport, and accumulation: Research is needed to develop better understanding of the use of physiological, biochemical, and genetic processes in plants. Research on the uptake and transport mechanisms is providing improved knowledge about the adaptability of those systems and how they might be used in phytoremediation.
- Genetic evaluation of hyperaccumulators: Research is being conducted to collect plants growing in soils that contain high levels of metals and screen them for specific traits useful in phytoremediation. Plants that tolerate and colonize environments polluted with

metals are a valuable resource, both as candidates for use in phytoremediation and as sources of genes for classical plant breeding and molecular genetic engineering.

- Field evaluation and validation: Research is being conducted to employ early and frequent field testing to accelerate implementation of phytoremediation technologies and to provide data to research programs. Standardization of field-test protocols and subsequent application of test results to real problems also are needed.

Research in this area is expected to grow over the next decade as many of the current engineering technologies for cleaning surface soil of metals are costly and physically disruptive. Phytoremediation, when fully developed, could result in significant cost savings and in the restoration of numerous sites by a relatively noninvasive, solar-driven, in situ method that, in some forms, can be aesthetically pleasing [1].

4.0 ANALYSIS OF APPLICATIONS

Phytoremediation is in the early stage of development and is being field tested at various sites in the U.S. and overseas for its effectiveness in capturing or stabilizing metals, including radioactive wastes. Limited cost and performance data are currently available. Phytoremediation has the potential to develop into a practicable remediation option at sites at which contaminants are near the surface, are relatively nonleachable, and pose little imminent threat to human health or the environment [1]. The efficiency of phytoremediation depends on the characteristics of the soil and the contaminants; these factors are discussed in the sections that follow.

4.1 Site Conditions

The effectiveness of phytoremediation generally is restricted to surface soils within the rooting zone. The most important limitation to phytoremediation is rooting depth, which can be 20, 50, or even 100 cm, depending on the plant

and soil type. Therefore, one of the favorable site conditions for phytoremediation is contamination with metals that is located at the surface [3].

The type of soil, as well as the rooting structure of the plant relative to the location of contaminants can have strong influence on uptake of any metal substance by the plant. Amendment of soils to change soil pH, nutrient compositions, or microbial activities must be selected in treatability studies to govern the efficiency of phytoremediation. Certain generalizations can be made about such cases; however, much work is needed in this area [1]. Since the amount of biomass that can be produced is one of the limiting factors affecting phytoremediation, optimal climatic conditions, with irrigation and fertilization of the site, should be considered for increased productivity of the best plants for the site [3].

4.2 Waste Characteristics

Sites that have low to moderate contamination with metals might be suitable for growing hyperaccumulating plants, although the

most heavily contaminated soils do not allow plant growth without the addition of soil amendments. Unfortunately, one of the most difficult metal cations for plants to translocate is lead, which is present at numerous sites in need of remediation. Although significant uptake of lead has not yet been demonstrated, one researcher is experimenting with soil amendments that make lead more available for uptake [5].

Capabilities to accumulate lead and other metals are dependent on the chemistry of the soil in which the plants are growing. Most metals, and lead in particular, occur in numerous forms in the soil, not all of which are equally available for uptake by plants [1]. Maximum removal of lead requires a balance between the nutritional requirements of plants for biomass production and the bioavailability of lead for uptake by plants. Maximizing availability of lead requires low pH and low levels of available phosphate and sulfate. However, limiting the fertility of the soil in such a manner directly affects the health and vigor of plants [1].

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The following vendors were contacted during the preparation of this report:

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Burt Ensley	Phytotech, Inc. One Deer Park Drive Suite 1 Monmouth Junction, NJ 08852	(908) 438-0900
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STATUS OF SOIL FLUSHING TECHNOLOGY

One approach to treating contaminated sites is physical separation and removal of the contaminants from the soil. Physical separation can be achieved in situ by introducing a fluid to the soil that will flush out the contaminants, leaving the soil matrix intact. In situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. In situ soil flushing has been used most often at sites contaminated with organics. This chapter focuses on the application of in situ soil flushing to sites contaminated with metals.

Table 7 presents an overview of soil flushing technology.

1.0 DESCRIPTION

Soil flushing techniques promote mobility and migration of metals by solubilizing the contaminants so that they can be extracted. Soil flushing is an in situ process that is accomplished by applying the flushing fluid to the surface of the site or injecting it into the contaminated zone. The resulting leachate then typically is recovered from the underlying groundwater by pump-and-treat methods. Figure 8 presents schematics of different soil flushing systems [1, 2].

Soil flushing can solubilize contaminants using either water as the flushing fluid or chemical additives to enhance the solubility of the contaminant. Water alone can be used to remove certain water-soluble contaminants (for example, hexavalent chromium). The use of soil flushing chemicals may involve adjusting the soil pH, chelating metal contaminants, or displacing toxic cations with nontoxic cations. The in situ flushing process requires that the flushing fluids be percolated through the soil matrix. The fluids can be introduced by surface flooding, surface sprinklers, leach fields, vertical or horizontal injection wells, basin infiltration systems, or trench infiltration systems.

Several chemical and physical phenomena control the mobility of metals in soils. The

finer-sized soil fractions (clays, silts, iron and manganese oxides, and organic matter in soil) can bind metals electrostatically as well as chemically [3]. Numerous soil factors affect sorption of metals and their migration in the subsurface. Such factors include pH, soil type, cation exchange capacity (CEC), particle size, permeability, specific types and concentrations of metals, and types and concentrations of organic and inorganic compounds in solutions. Generally, as the soil pH decreases, solubility and mobility of cationic metals increase. In most cases, mobility and sorption of a metal are likely to be controlled by clay content in the subsoils and by the organic fraction in topsoils. Clays can adsorb metals present in the soils. It has been reported that surface soils high in organic matter retained significantly more metal than subsurface soils that contained less organic matter [4]. Organic matter in soil is of significant importance because of its effect on CEC [5]. CEC, which measures the extent to which cations in the soil can be exchanged, often is used as an indication of a soil's capacity to immobilize metals [6].

Once the infiltrated or percolated solution has flushed the contaminants to a certain location, the contaminated fluids must be extracted. Extraction techniques include vacuum extraction methods in the vadose zone and pump-and-treat systems in the saturated zone.

Recovered groundwater and flushing fluids containing the desorbed contaminants may require treatment to meet appropriate discharge standards before such fluids are recycled or released to publicly owned wastewater treatment works or receiving streams. If state regulations so allow, recovered fluids should be reused in the flushing process to reduce disposal costs.

The treatment system will be configured to remove specific contaminants of concern. For treatment of inorganics, the system may include standard precipitation systems, electrochemical exchange, ion exchange, or ultrafiltration systems. The contaminants of concern may

**TABLE 7
OVERVIEW OF SOIL FLUSHING TECHNOLOGY**

<p>General Characteristics</p> <ul style="list-style-type: none"> • Best used in soils with high permeability. • Different delivery systems available to introduce flushing solutions. • Cost is primarily influenced by potential need for interim containment, the depth of contamination, and the time required for operation. • Associated risk of contamination of underlying aquifer with unrecovered flushing solution that contains solubilized contaminants; best used at sites with aquifers that have low specific yields. 	
Approach #1 - Water flushing	Approach #2 - Reagent flushing
<u>Description:</u> Use of water to solubilize the contaminants prior to extraction.	<u>Description:</u> Use of a chemical reagent to solubilize the contaminants for extraction.
<u>Status:</u> Commercial.	<u>Status:</u> Limited research.
<u>Applicability:</u> Chromium (VI); potentially applicable for other water-soluble metals.	<u>Applicability:</u> Bench-scale: lead, uranium.
<u>Comments:</u> Applicable only for water-soluble metals; focus of water flushing often is on organics. In situ flushing has been selected at 4 Superfund sites at which soils are contaminated with metals (most of the sites also are contaminated with organics).	<u>Comments:</u> <ul style="list-style-type: none"> - Some small-scale testing has been conducted with chelators as the primary reagent for removal of metals from soils; the results of those tests have not led to further testing on a larger scale. - pH adjusters and chemical binders also are being studied for potential applicability to metals. - Surfactants are primarily targeted for removal of organic contaminants.

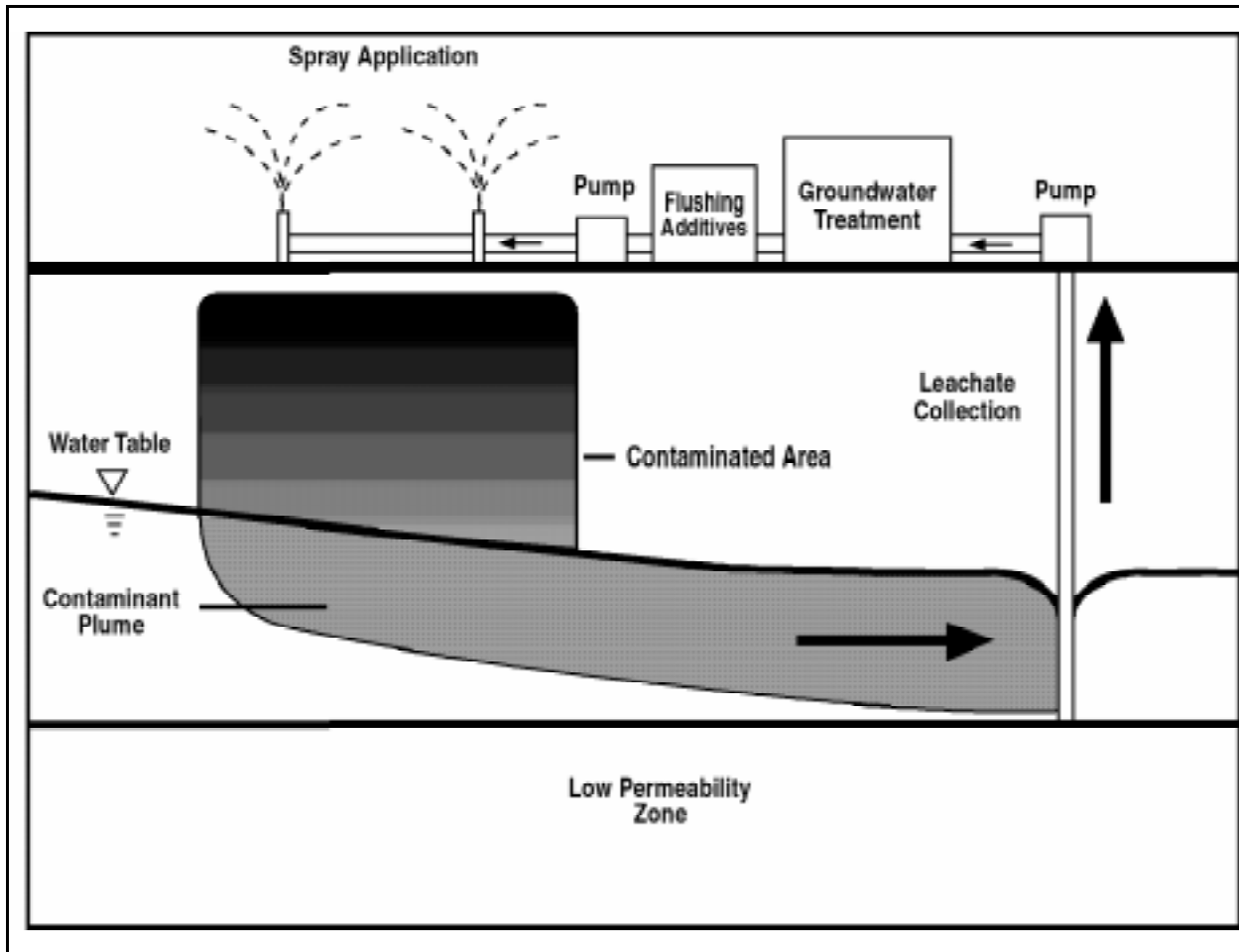


Figure 8. Typical Soil Flushing System (Surface Sprinklers)

include organics and inorganics in the same waste stream. In posttreatment, once the recovery system (that is, pump-and-treat system) has been shut down, it may be necessary to control infiltration through the use of caps or covers to prevent further migration of residual contaminants.

2.0 OVERVIEW OF STATUS

For treatment of metals, soil flushing has been employed for a limited number of projects, using the treated effluent from a pump-and-treat operation for reinjection and improved mobilization of contaminants. The use of chelating additives for treating metals in soil has not yet been found to be effective.

Limited information is available on the use of soil flushing to remediate soils contaminated

with metals. Most information is related to treatment of organic contaminants rather than metals. Soil flushing has been selected at seven Superfund sites which contain metals. At two sites, Lipari Landfill in New Jersey and the United Chrome Products site in Oregon, in situ soil flushing is operational [7]. At one other site, in situ soil flushing is listed as the technology in design, and at four other sites, in situ flushing is listed as the technology in the predesign stage [7].

One literature reference summarizes a bench-scale soil flushing technology called metal extraction that was developed by Scientific Ecology Group, Inc. of Pittsburgh, Pennsylvania for removing heavy and radioactive metals from soil and groundwater through cation displacement [10]. Another literature reference describes the bench-scale use of organic and

inorganic flushing agents to remove lead from in situ soils. Solutions of hydrochloric acid (HCl), ethylenediamine tetraacetic acid (EDTA), and calcium chloride (CaCl_2) were used as flushing agents [3]. A third literature reference describes an ongoing, full-scale in situ soil flushing technology that uses water as the flushing agent to treat chromium [8]. The information in these representative references is summarized in the following paragraphs.

2.1 Cation Displacement

The metal extraction method is based on demonstrated in situ uranium mining technology. Continuous injection and recapture of an extraction solution flushes heavy or radioactive metals from the subsurface. The metal extraction process consists of the following steps [11]:

- Introduction of extraction solution: The remedial process begins with the injection of a solution containing sufficient cation concentrations to displace the contaminants from the soil.
- Removal of contaminants: The solution migrates through the treatment zone, selectively displacing the target contaminants. Cations that occur naturally, or that are present in the extraction solution, remain in the soil.
- Recovery of solution: The contaminated solution is pumped to surface equipment through a network of recovery wells. A subsequent treatment process precipitates the contaminants.
- Stabilization of residual contaminants: If necessary, a stabilizing solution is injected after soil flushing has been completed. The solution reacts with the remaining contaminants, produces an immobile species, and prevents further migration of residual metals.

2.2 Lead Removal

Organic and inorganic flushing agents to remove lead have been tested on a small scale. In a bench-scale experiment, contaminated soil columns (coarse, sandy loam with a favorable hydraulic conductivity and relatively low organic content) were flushed separately with solutions of 0.1 moles per liter (M) HCl, 0.01 M EDTA, and 1.0 M CaCl_2 . Each soil column was packed under saturated conditions by maintaining the water level above each successive soil layer during the packing procedures. Significant amounts of lead were removed from the soil when HCl and EDTA were used. When HCl and EDTA were used as flushing solutions, the pH levels of the effluent appeared to be related directly to the rate of removal of lead. The mechanisms of lead removal appeared to be desorption caused by a decrease in pH, dissolution of $\text{Pb}(\text{OH})_2$ or other lead precipitates, metal chelation, and cation exchange for HCl, EDTA, and CaCl_2 , respectively [3].

This approach is not practical for use in full scale applications due to the high costs of reagents.

2.3 Chrome Flushing

A full-scale in situ soil flushing technology is being implemented at the United Chrome Products site, a Superfund site in Corvallis, Oregon. The site is a former industrial hard-chrome electroplating shop. Leaks from plating tanks and the discharge of rinse water into a disposal pit during the shop's operation from 1956 to 1985 contaminated soil and groundwater underlying the facility. Contamination of soil at levels higher than 60,000 mg/kg chromium and contamination of groundwater at levels exceeding 19,000 mg/L chromium were detected in areas adjacent to the plating tanks. In 1985, EPA began remediation activities that have continued to the present time (1996). Those activities include construction of two infiltration basins to flush contaminated soils, a 23-well groundwater extraction network in low-permeability soils, and an injection and groundwater extraction network in a deep gravel aquifer, as well as on-site treatment of wastewaters containing high concentrations of chromium [8].

At this site, Cr(III) is found in high concentrations in the soils of the upper zone, but, because of its very low solubility, it is only a minor groundwater contaminant. In contrast, Cr(VI), a potential carcinogen, is found in high concentrations in the upper zone, aquitard soils, and groundwater, because of its high solubility in water. EPA has established a maximum concentration level (MCL) of 0.05 mg/L (total chromium) as a drinking-water standard. Thus far, chromium levels in groundwater have been reduced from more than 5,000 mg/L to less than 50 mg/L in areas of high concentration [8].

This in situ, full-scale cleanup is unique because: 1) soil flushing has been applied in low-permeability silt soil, 2) both the shallow and deep aquifer have been treated, and 3) flushing of the clay aquitard has been accomplished indirectly by using the deep aquifer injection wells in conjunction with the upper zone extraction wells to create upward vertical gradients.

Three methods of infiltration have been employed: infiltration basins, an infiltration trench, and injection wells. The two basins are abovegrade structures that have open bottoms that permit infiltration of water to the underlying soils. They were placed at the sites of the highest observed levels of soil contamination (the former plating tank and disposal pit areas) [8]. The basins have been successful in delivering water to the upper zone, averaging approximately 7,600 gallons per day in Basin No. 1 and 3,000 gallons per day in Basin No. 2 during the dry summer months. During the winter months, infiltration rates decrease to 50 percent or less of the summer rates [8].

The infiltration trench was constructed approximately 22 months after the project began. The trench is positioned and operated primarily to increase discharge rates of the extraction wells along the longitudinal axis of the plume during the dry summer months. The trench is approximately 100 feet long and 8 feet deep, and a float valve maintains the water level at 4 feet below grade. Infiltration rates have averaged 2,500 gallons per day [8].

Another type of groundwater recharge used at the site is water injection. To reverse the downward vertical gradient present between the upper zone and the deep aquifer, clean water has been injected into the deep aquifer through two wells [9].

2.4 Twin Cities Army Ammunition Plant

In 1993, the Twin Cities Army Ammunition Plant (TCAAP) soil remediation demonstration project for removal and recovery of metals (lead was the main contaminant) began in New Brighton, Minnesota. The TCAAP project used the COGNIS TERRAMET^R process and was the first project in which cleaned soil from a soil washing process was returned on-site. Although the COGNIS process currently is operated as a soil washing system rather than an in situ soil flushing technology, research is being considered to assess the viability of adapting the COGNIS process for in situ remediation applications [10]. No process water is discharged during operation of the COGNIS process; all leachant is recycled within the plant. Targets for removal of lead were not achieved; therefore, the treatment was only partially successful.

3.0 PERFORMANCE AND COST SUMMARY

According to Scientific Ecology Group, Inc., the metal extraction technology demonstrates removal efficiencies as high as 90 percent. Concentrations of uranium in groundwater of 5 to 20 mg/L were reduced to 1 to 2 mg/L. Groundwater contaminated with 250 to 500 mg/L of ammonium contained only 10 to 50 mg/L after treatment [11].

In the soil column experiment, initial concentrations of lead during the bench-scale study were 500 to 600 mg/kg. Lead removal efficiencies for HCl, EDTA, and CaCl₂ were 96, 93, and 78 percent, respectively. In the soil used in the study, background concentrations of lead were approximately 20 mg/kg. Final concentrations of lead, after flushing with the three test solutions, were 23.3 mg/kg (HCl), 37.8 mg/kg (EDTA), and 135.6 mg/kg (CaCl₂) [3]. It should be noted that, if the soils contain

relatively high levels of calcium, substantial amounts of the HCl flushing solution would be consumed in neutralization reactions.

At the United Chrome Products site, the use of water as a flushing solution to remove chromium (VI) from in situ soils appears to be a successful treatment option. The full-scale cleanup has achieved hydraulic containment of the plume, while extracting significant amounts of chromium from the subsurface. Table 8 presents a summary of recent available performance data [13].

The performance of the two infiltration basins constructed at the United Chrome Products site has been confirmed by the increase in pumping rates and concurrent decreases in concentrations of Cr(VI) observed in the extraction wells around the basins. In many of the wells, pumping rates have increased from less than 0.5 gallon per minute (gpm) to 2 or more gpm [8]. Concentrations of Cr(VI) decreased from more than 2,000 mg/L to approximately 18 mg/L [13].

According to the developers of the metal exchange process, the cost of such a project is estimated to be approximately 50 percent of that of a typical pump-and-treat method.

Because in situ soil flushing has had only limited field application, it is difficult to obtain comprehensive, detailed estimates of the cost of this treatment technology. The factors that most significantly affect costs are the initial and target concentrations of contaminants, permeability of the soil, and depth of the aquifer [11].

Capital costs for chemically enhanced solubilization (CES) are similar to those for traditional pump-and-treat systems, except for the initial expense of equipment needed to handle the flushing solution. Operating costs also are similar, except for the cost of handling and replacement of flushing solutions and additives. Overall, for the life of the treatment process, CES should be significantly less expensive than pump-and-treat systems because of the much shorter time frames for treatment and smaller volumes of water to be extracted and treated [2].

TABLE 8

**UNITED CHROME PRODUCTS SUPERFUND SITE
EXTRACTION AND TREATMENT SYSTEM SUMMARY
AUGUST 1988 THROUGH DECEMBER 1995**

Parameter	Total	Daily Average
Groundwater Extracted	58,000,000 gal	11,400 gal
Influent Cr (VI) Concentration Range	146 mg/L to 1,923 mg/L	
Mass of Cr (VI) Removed	31,200 lb	41 lb
Infiltration Recharge	4,700,000 gal	8,000 gal
Average Effluent Cr (VI) Concentration		1.7 mg/L (monthly)

A hypothetical analysis in a recent engineering monograph on soil washing and soil flushing compares cost and time estimates for CES with those for pump-and-treat systems. Based on interpretation of data from a test site, the effective aqueous solubility of a contaminant was compared to the amount of flushing solution needed to solubilize the contaminant. The pore volumes required by the two systems to attain similar levels of cleanup differed dramatically; the CES system would require 21 pore volumes and the pump-and-treat system would require more than 2,000 pore volumes. Likewise, the time frames for treatment using the two systems also differed. Using the specified injection rates of the two systems to calculate time required for treatment, the CES system would require 4 years and the pump-and-treat system would require 400 years. [2].

4.0 ANALYSIS OF APPLICATIONS

The performance of an in situ soil flushing system depends largely upon the amount of contact achieved between the flushing solution and the contaminants. The appropriateness of the flushing solution, the soil adsorption coefficients of the contaminants, and the permeability of the soil are also key factors.

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The following vendors were contacted during the preparation of this report:

CONTACTS

Name	Agency/Company	Telephone Number
Donald R. Justice	Horizontal Technologies, Inc. (Soil Flushing- In Situ)	813/995-8777
Ken Wyatt	Surtek, Inc. (Soil Flushing - In Situ Surfactant Enhanced Recovery)	303/278-0877

Best results will be achieved in highly permeable soils.

The following types of data are required to support selection of the flushing solution and to predict the effectiveness of soil flushing:

- Soil hydrogeology (physical and chemical properties of the soil), subsurface vertical and horizontal flow and velocity, characteristics of the aquifer, and vadose zone saturation
- Areal and vertical concentration gradients for contaminants.

Effective application of the process requires a sound understanding of soil chemistry (the manner in which target contaminants are bound to soil), relative permeability, and hydrogeology. In general, soil flushing is most effective in homogeneous, permeable soils (sands and silty sands with permeabilities greater than 1×10^{-3} centimeters per second [cm/sec]). The relationships among capillary processes, water content, and hydraulic conductivity must be understood before any flushing solution can be used effectively. In addition, because soil flushing increases the mobility of contaminants, the hydrology of the site must be well understood.

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**STATUS OF IN SITU
SOLIDIFICATION/STABILIZATION
TECHNOLOGY**

Solidification treatment processes change the physical characteristics of the waste to improve its handling and to reduce the mobility of the contaminants by creating a physical barrier to leaching. Solidification can be achieved through the use of conventional pozzolans, such as Portland cement. Stabilization (or immobilization) treatment processes convert contaminants to less mobile forms through chemical or thermal interactions.

(Vitrification of soil is an example of a solidification/stabilization (S/S) process that employs thermal energy.) S/S treatment processes can be performed in situ or ex situ.

Although many vendors provide S/S technologies for ex situ applications, relatively few companies offer in situ S/S treatment processes. This chapter focuses on the in situ applications of S/S remediation techniques.

Table 9 presents an overview of solidification/stabilization technology.

TABLE 9

OVERVIEW OF SOLIDIFICATION/STABILIZATION TECHNOLOGY

General Characteristics	
<ul style="list-style-type: none"> • Commercially available • Cost is affected by the depth of the contamination, the degree of homogeneity of soil, the presence of debris, and excess moisture. 	
Approach #1 - Reagent-based In Situ Stabilization	Approach #2 - Vitrification
<u>Description:</u> Addition of pozzolanic reagents with or without additives to physically and chemically convert contaminants to less mobile forms.	<u>Description:</u> Use of energy to melt soils and physically and chemically encapsulate contaminants into less mobile and more stable forms.
<u>Status:</u> Commercial.	<u>Status:</u> Commercial; one firm is licensed.
<u>Applicability:</u> Broad general applicability to most metals; applicability to arsenic and mercury should be tested on a case-by-case basis. Hexavalent chromium requires additives that ensure its conversion to the trivalent state during mixing.	<u>Applicability:</u> Broad general applicability to most metals. Full-scale: arsenic, lead, chromium. Potential: cadmium, copper, zinc, asbestos, radioactive metals.
<u>Comments:</u> Performance is highly dependent on mixing efficiency. Soils having high clay content or significant debris may be difficult to mix. Various auger sizes and mixing configurations can be used, and various reagents are available. In situ applications are less common than ex situ applications because it is difficult to verify whether mixing is sufficient.	<u>Comments:</u> It may be necessary to treat, remove, or filter mercury or other volatile metals from process off-gases. High moisture content will increase costs substantially. Debris or high concentrations of organic contaminants may decrease performance.

1.0 DESCRIPTION

S/S technologies are used to change the physical characteristics and leaching potential of waste. The term S/S refers to treatment processes that utilize treatment reagents or thermal energy to accomplish one or more of the following objectives [1]:

- Reduce the mobility or solubility of the contaminants to levels required by regulatory or other risk-based standards
- Limit the contact between site fluids (such as groundwater) and the contaminants by reducing the permeability of the waste, generally to less than 1×10^{-6} cm/sec
- Increase the strength or bearing capacity of the waste, as indicated by unconfined compressive strength (UCS) or measured by the California bearing ratio

There are two basic types of S/S treatment processes: reagent-based systems and thermal-based systems. Reagent-based systems use chemicals to solidify and stabilize the contaminants in the soil matrix. Thermal-based systems use heat to melt the soil to solidify and stabilize the contaminants after cooling.

1.1 Reagent-based S/S Processes

In situ reagent-based S/S technologies consist of a reagent formulation and a delivery system. With the exception of near-surface applications (that is, to depths of 15 feet deep), a reagent-based S/S delivery system usually consists of a slurry batch plant, delivery hoses, and one or more augers. Most reagent formulations for in situ S/S applications consist of ordinary pozzolanic reagents, although proprietary reagents are often used in conjunction with or instead of pozzolanic reagents [7]. Pozzolanic mixtures are based on siliceous volcanic ashes similar to substances used to produce hydraulic cement. Depending on the characteristics of the waste to be treated and the desired properties of the treated wastes, additives such as bentonite or silicates may be added to the cement and/or fly

ash mixture. For example, addition of bentonite increases the ease of pumping of the wet reagent slurry and decreases the permeability of the treated waste. Silicates form chemical complexes with metals, often providing greater insolubility than do hydroxide, carbonate, or sulfate precipitates. (Other additives or proprietary reagents, such as activated carbon or organophilic clays, can be used to stabilize semivolatile organic compounds in wastes).

Wastes containing lead can be stabilized with the addition of trisodium phosphate; the resulting lead phosphate precipitate is insoluble in water. Although solidification of the waste treated with trisodium phosphate is not necessary to provide a barrier to leaching, it may be done for other purposes such as providing sufficient bearing strength to support a cap. Additionally, lead phosphate is toxic by inhalation. Solidification or other means of encapsulation may be used to prevent air-borne particulates from escaping the treated waste. Alternatively, solidification may be used to provide a barrier to acids or alkaline solutions which could solubilize the lead phosphate.

Each of the vendors contacted has a patented auger consisting of blades or paddles studded with injection ports through which the reagent mixture flows. Some vendors emphasize the kneading and shearing action of their augers, while other vendors emphasize grout (reagent mixture) control and the capability to deliver two or more mixtures simultaneously. The vendors also differ with respect to the size of injection ports and their operating pressure.

Choice of auger diameter varies among the vendors of reagent-based S/S technologies, but generally depends on depth of drilling, consistency and hardness of the soil, and soil porosity. For example, augers from 4 to 12 feet in diameter generally can be used to a depth of 40 feet. The diameter selected will depend on the porosity of the soil. Augers of larger diameter may be used in sludges and sands, while silts and clays require augers of a smaller diameter. One vendor uses small-diameter augers for all depths because large-diameter augers affect mixing efficiencies. Beyond a

depth of 35 to 40 feet, a smaller-diameter auger

(from 2.5 to 4 feet in diameter) is suggested. Using a smaller auger permits treatment to depths as great as 100 feet or more. Only two of the five vendors contacted treat soil at depths of more than 40 feet; however, most soil contamination is encountered at depths of 10 to 20 feet and only rarely deeper than 40 feet [6] (although treatment to depths of more than 40 feet is becoming more common).

1.2 Thermal-based S/S Processes

The only thermal-based S/S treatment process commercially available is in situ vitrification. In situ vitrification uses electrical power to heat and melt soils contaminated with organic, inorganic, and metal-bearing wastes. The molten material cools to form a hard, monolithic, chemically inert, stable product of glass and crystalline material that incorporates and immobilizes the inorganic compounds and metals. The resultant vitrified product is a glassy material, with very low leaching characteristics. Organic wastes initially are vaporized or pyrolyzed by the process. Those contaminants migrate to the surface, where they are treated in an off-gas treatment system [2].

2.0 OVERVIEW OF STATUS

The vendors that were identified as potential providers of in situ S/S processes were contacted to determine whether they have available data that can be used in the status report for this technology. Vendors of ex situ stabilization equipment also were contacted to determine whether any has made progress in developing an in situ version of the technology.

A single vendor, Geocon, accounts for most of the in situ applications reported; however, little data on applications are available. Each vendor's system is well established, tracing its roots to established construction technologies. (Deep soil mixing and the installation of cement footers and grout curtains or slurry walls are construction techniques that have been employed for many years.) An emerging development for American vendors is the injection of dry reagents when high levels of moisture in the soil preclude the use of liquid reagents. Although this variation of

the technology has been employed in Europe for more than 20 years, only one U.S. vendor (Hayward Baker) has used it. Although conveying dry reagents pneumatically requires some expertise, both Millgard and Geocon currently are experimenting with the technique. It is notable that in situ application of dry reagents tends to decrease the effective depth of treatment for a given auger diameter and soil porosity. (Conversely, wet slurries help extend the depth of treatment.)

Only one vendor offers in situ thermal-based S/S treatment processes. Geosafe Corporation of Richland, Washington offers the in situ vitrification (ISV) technology commercially. Figure 9 is a schematic of the Geosafe ISV process. ISV uses electrical current to heat and vitrify the contaminated material in place. A pattern of electrically-conductive graphite

containing glass frit is placed in the soil between the electrodes. When power is supplied to the electrodes, the mixture of graphite and glass frit conducts the current through the soil, heating the surrounding area and melting the soil between and directly adjacent to the electrodes.

Molten soils are electrically conductive and can continue to transmit the electrical current, melting soil downward and outward. The electrodes are lowered further into the soil as the soil becomes molten, continuing the melting process to the desired depth of treatment. One setting of four electrodes is referred to as a melt. For the Geosafe system, the melting process occurs at an average rate of approximately three to four tons per hour.

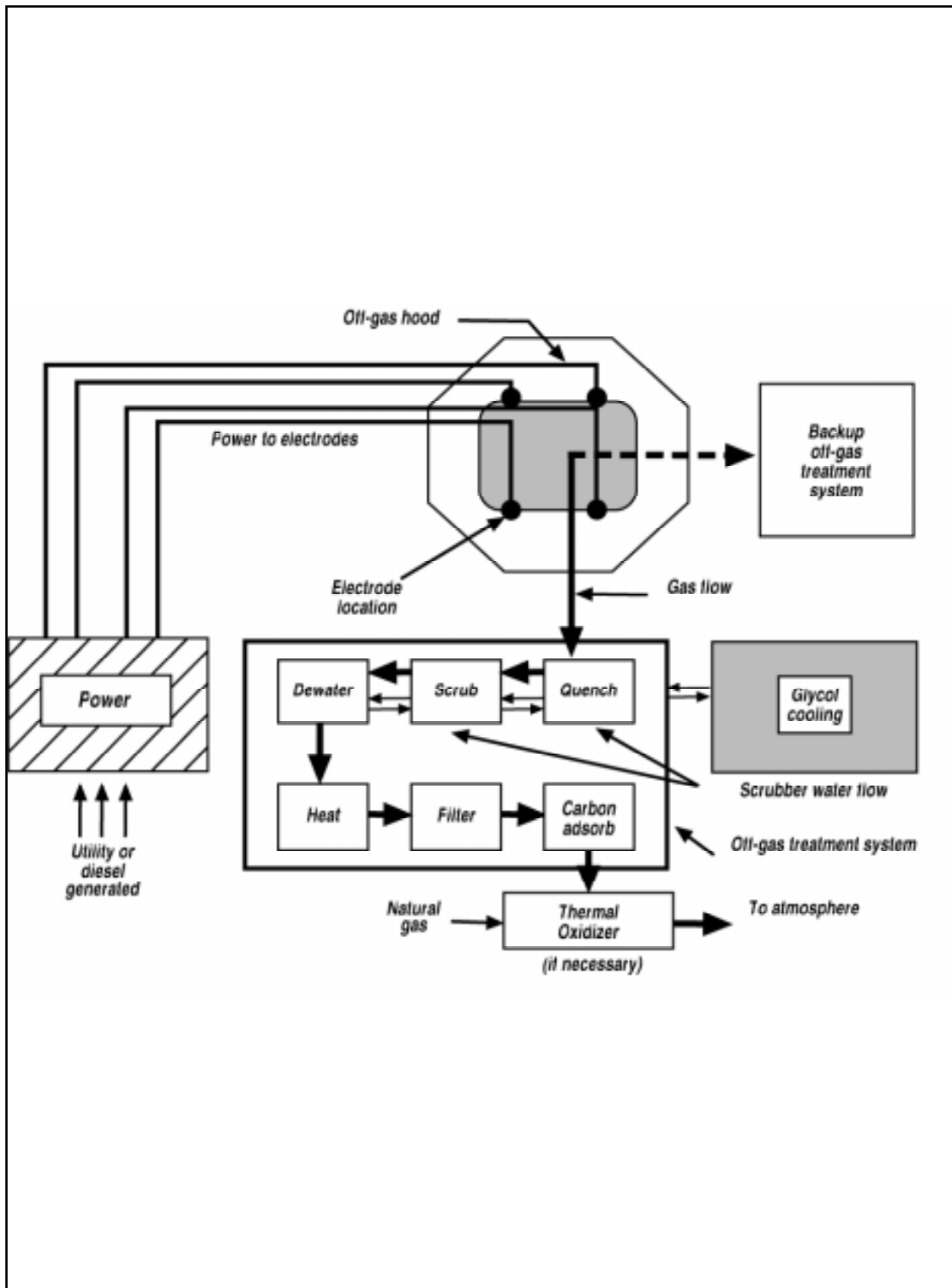


Figure 9. Geosafe In Situ Vitrification Process [3]

3.0 PERFORMANCE AND COST SUMMARY

Information on the testing and costs of reagent-based and thermal-based S/S processes are discussed separately in the following subsections.

3.1 Reagent-based S/S Processes

In most cases involving in situ S/S, the site cleanup manager independently contracts with a testing laboratory to develop and optimize a suitable reagent formulation that will meet the desired performance objectives for the site of concern. Vendors then submit bids for delivering the specified formulation in situ. Occasionally, the vendor of the in situ technology will develop the formulation at the bench scale to achieve the desired immobilization of contaminants and posttreatment permeability and unconfined compressive strength. Therefore, testing at the bench scale consists of optimizing the reagent formulation. Testing at the pilot or full scale consists of quality control of grout and confirmation sampling to determine whether the treated material is meeting required performance specifications.

Although published data generally are limited to those developed in demonstration projects sponsored by EPA, in situ S/S is likely to be effective in reducing leachable concentrations of metals to within regulatory or risk-based limits. The goal of vendors (and site managers) is to meet the performance specifications at the lowest cost. Failure to meet the design specifications in the field most often stems from poor grout control (that is, inconsistently formulated slurries or clogged injection ports that cause incomplete mixing or a spray pattern that is not uniform).

Interviews with five vendors indicated that costs for in situ S/S are likely to be below ex situ treatment under certain circumstances. For contaminated depths of less than eight feet, excavation and ex situ treatment are likely to be cheaper. In situ S/S treatment is likely to be cheaper for larger volumes because of the high cost of mobilization and demobilization for in

situ S/S technologies (four to five times that of ex situ technologies.) For this reason, vendors of in situ S/S technologies are not likely to use augers or bid jobs in cases where the depth of treatment is 10 feet or less. (Geocon, for example, uses a backhoe-mounted attachment for depths to 10 feet). In addition, auguring requires a level, stable base. At sites that are not level, backfill must be brought in to level the site to support the auguring equipment. Eventually, the cost of bringing in backfill can make the cost of ex situ treatment competitive with that of in situ S/S.

According to the vendors consulted, the cost of in situ S/S can range from as low as \$20 to \$40 per cubic yard to as much as \$100 to \$200 per cubic yard, depending on the volume to be treated, the structure of the soil (porosity), the treatment depth, the type of contaminant, and the post-treatment objectives (leachability, permeability, or bearing ratio) desired. The low end of the cost range would apply to solidifying dredge spoils, while the high end would apply to treatment of high concentrations of contaminants at great depths. For application at a hazardous waste site consisting of sands to silts at a depth of 25 feet, \$75 to \$90 per cubic yard would be typical (20 percent of that figure would be the cost of reagent).

3.2 Thermal-based Processes

The Geosafe ISV process was demonstrated under the SITE program at the Parsons Chemical/ETM Enterprises Superfund site in Grand Ledge, Michigan from May 1993 to May 1994. The ISV system that was used at the Parsons site included an air emissions control and treatment system to treat the eight-melt operation. This project was the first application of in situ vitrification at a Superfund site to treat soils and sediments contaminated with pesticides, metals, and dioxins.

The Geosafe ISV system used at the Parsons site included eight melt cells and an air emissions control system. Because contamination was shallow, contaminated soil was excavated and staged at the site. The melt cells were installed in a treatment trench. Eight melts were

completed, ranging in duration from 10 to 20 days. Mercury concentrations in the treated waste were reduced by more than 98 percent when compared with untreated soil. In addition, TCLP concentrations of arsenic, chromium, lead, and mercury in the treated waste were below regulatory levels of concern.

ISV also subsequently was applied successfully the Wasatch Chemical Superfund site, where ISV was used to treat dioxin, pentachlorophenol, pesticides, and herbicides.

The major factors affecting cost of ISV are the amount of water present, the treatment zone, depth, combustible waste load, scale of operation and price of electricity. The vendor estimates costs between \$375 and \$425 per ton, which makes this process especially suited for hard to treat wastes, such as mixtures of metals and organics.

4.0 ANALYSIS OF APPLICATIONS

The most commonly stabilized metal contaminants for reagent-based systems are chromium, arsenic, and lead, followed by cadmium, copper, zinc, and mercury. Site managers may specify that hexavalent chromium be treated in two stages (the first to reduce the chromium and the second to stabilize it); however, vendors may add reducing agents to their formulations to treat hexavalent chromium in one stage.

Limited experience with ISV suggests that it should not be recommended at sites at which organic content in the soil exceeds 10 percent by weight. In addition, it is not recommended at sites at which metals in the soil exceed 25 percent by weight or where inorganic contaminants exceed 20 percent of the soil by volume. The cost of ISV is influenced principally by the need for electric power, which increases substantially with increasing moisture in the soil [8].

5.0 REFERENCES

The following vendors were contacted during the preparation of this report:

CONTACTS

Name	Agency/Company	Telephone Number
Steve Day	Geocon	(412) 856-7700
David Coleman	Millgard Environmental	(313) 261-9760
David Yang	S.M.W. Seiko	(510) 783-4105
George Burke	Hayward Baker	(410) 551-1995
Neville Kingham	Kiber Environmental Services, Inc.	(770) 455-3944
Kent Saugier	Brown & Root	(713) 575-4677
James Hansen	Geosafe Corporation	(509) 375-0710

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APPENDIX A
METHODOLOGY

METHODOLOGY

Technologies discussed in this report were chosen because they were at or near a point of being commercially available. The survey work to prepare this report consisted of the following activities:

- Literature searches of several on-line databases, including EPA's Clean Up Information Bulletin Board (CLU-IN) and Alternative Treatment Technology Information Center (ATTIC) databases
- Searches of the EPA record of decision (ROD) database
- Searches of back issues of various technical journals and shelf material in EPA's libraries not available on-line
- Communication with experts at federal agencies, such as DoD, the DOE, and the Bureau of Mines, who are involved in research and development of environmental restoration technologies
- Contacts with technology vendors identified in EPA's Vendor Information System for Innovative Treatment Technologies (VISITT)
- Interviews with authors of articles relevant to each technology

Several technology vendors and authors identified from the searches were contacted via telephone calls. They were asked to comment on the status of the technology, the amount of performance data available from field applications of the technology, and cost estimates for performing remedial actions with the technology. Vendors were chosen to contact to provide representative information on different technologies. Reference information on the vendors contacted is included in each technology chapter. No attempt was made to identify all vendors and their inclusion or exclusion is purely coincidental. Researchers and technical experts that were also contacted are listed on the following pages.

Researchers and Technical Experts

<u>Name</u>	<u>Agency/Company</u>
<u>Electrokinetics</u>	
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Trish Erickson	EPA - NRMRL
Bob Thurnau	EPA - NRMRL
Mike Royer	EPA - NRMRL
Jeff Marquette	U.S. Department of Defense Office of Assistant Deputy Under Secretary of Defense (Environmental Technology)
Len Zintak	EPA - Region 5 (Parsons project)
Terri Richardson	EPA - SITE Program (Parsons project)

APPENDIX B

**ENGINEERING BULLETIN: *TECHNOLOGY ALTERNATIVES FOR THE
REMEDICATION OF SOILS CONTAMINATED WITH ARSENIC,
CADIUM, CHROMIUM, MERCURY, AND LEAD***

Purpose

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

Introduction

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

Common compounds, transport, and fate are discussed for each of the five elements. A general description of metal-contaminated Superfund soils is provided. The technologies covered are: immobilization [containment (caps,

vertical barriers, horizontal barriers), solidification/stabilization (cement-based, polymer microencapsulation), and vitrification]; and separation and concentration (soil washing, pyrometallurgy, and soil flushing). Use of treatment trains is also addressed.

Electrokinetics is addressed in the technical resource document, but not here, since it had not been demonstrated at full-scale in the United States for metals remediation. Also, an update on the status of in situ electrokinetics for remediation of metal-contaminated soil is in progress and should be available in the near future. Another change from the original technical resource document is that physical separation is addressed in the bulletin under soil washing, whereas it was previously covered as a separate topic.

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

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

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

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

Overview of Physical Characteristics and Mineral Origins

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

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

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

Mercury is a silvery, liquid metal. The primary source of Hg is cinnabar (HgS), a sulfide ore. In a few cases, Hg occurs as the principal ore product; it is more commonly obtained as the by-product of process complex ores that contain mixed sulfides, oxides, and chloride minerals (these are usually associated with base and precious metals, particularly gold). Native or metallic Hg is found in very small quantities in some ore sites. The current demand for mercury

is met by secondary production (i.e., recycling and recovery).

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

Overview of Behavior of Arsenic, Cadmium, Chromium, Lead, and Mercury

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

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

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

Cadmium, chromium (III), and lead are present in cationic forms under natural environmental conditions. These cationic metals are not mobile in the environment and tend to remain relatively close to the point of initial deposition. The capacity of soil to adsorb cationic metals increases with increasing pH, cation exchange capacity, and organic carbon content. Under the neutral to basic conditions typical of most soils, cationic metals are strongly adsorbed on the clay fraction of soils and can be adsorbed by hydrous oxides of iron, aluminum, or manganese present in soil minerals. Cationic metals will precipitate as hydroxides, carbonates, or phosphates. In acidic, sandy soils, the cationic metals are more mobile. Under conditions that are atypical of natural soils (e.g., pH <5 or >9; elevated concentrations of oxidizers or reducers; high concentrations of soluble organic or inorganic complexing or colloidal substances), but may be encountered as a result of waste disposal or remedial processes, the mobility of these metals may be substantially increased. Also, competitive adsorption between various metals has been observed in experiments involving various solids with oxide surfaces (γ -FeOOH, α -SiO₂, and γ -Al₂O₃). In several experiments, Cd adsorption was decreased by the addition of Pb or Cu for all three of these solids. The addition of zinc resulted in the greatest decrease of Cd adsorption. Competition for surface sites occurred when only a few percent of all surface sites were occupied.

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

In most arsenic-contaminated sites, arsenic appears as As₂O₃ or as an anionic arsenic species leached from As₂O₃, oxidized to As (V), and then sorbed onto iron-bearing minerals in the soil. Arsenic may be present also in organometallic forms, such as methylarsenic acid (H₂AsO₃CH₃) and dimethylarsinic acid ((CH₃)₂AsO₂H), which are active ingredients in many pesticides, as well as the volatile compounds arsine (AsH₃) and its methyl derivatives [i.e., dimethylarsine (HAs(CH₃)₂) and trimethylarsine (As(CH₃)₃)]. These arsenic forms illustrate the various oxidation states that arsenic commonly exhibits (-III, 0, III, and V) and the resulting complexity of its chemistry in the environment.

As (V) is less mobile (and less toxic) than As (III). As (V) exhibits anionic behavior in the presence of water, and hence its aqueous solubility increases with increasing pH, and it does not complex or precipitate with other anions. As(V) can form low solubility metal arsenates. Calcium arsenate (Ca₃(AsO₄)₂) is the most stable metal arsenate in well-oxidized and alkaline environments, but it is unstable in acidic environments. Even under initially oxidizing and alkaline conditions, absorption of CO₂ from the air will result in formation of CaCO₃ and release of arsenate. In sodic soils, sufficient sodium is available, such that the mobile compound Na₃AsO₄ can form. The slightly less stable manganese arsenate (Mn₂(AsO₄)₂) forms in both acidic and alkaline environments, while iron arsenate is stable under acidic soil conditions. In aerobic environments, H₃AsO₄ predominates at pH <2 and is replaced by H₂AsO₄, HAsO₄²⁻ and AsO₄³⁻ as pH increases to about 2, 7, and 11.5, respectively. Under mildly reducing conditions, H₃AsO₃ is a predominant species at low pH, but is replaced by H₂AsO₃⁻, HAsO₃²⁻, and AsO₃³⁻ as pH increases. Under still more reducing conditions and in the presence of sulfide, As₂S₃ can form. As₂S₃ is a low-solubility, stable solid. AsS₂ and AsS₃ are thermodynamically unstable with respect to As₂S₃. Under extreme reducing conditions, elemental arsenic and volatile arsine (AsH₃) can occur. Just as competition between cationic metals affects mobility in soil, competition between anionic species (chromate,

arsenate, phosphate, sulfate, etc.) affects anionic fixation processes and may increase mobility.

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

Cr (VI) is present as the chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) anion, depending on pH and concentration. Cr (VI) anions are less likely to be adsorbed to solid surfaces than Cr (III). Most solids in soils carry negative charges that inhibit Cr (VI) adsorption. Although clays have high capacity to adsorb cationic metals, they interact little with Cr (VI) because of the similar charges carried by the anion and clay in the common pH range of soil and groundwater. The only common soil solid that adsorbs Cr(VI) is iron oxyhydroxide. Generally, a major portion of Cr(VI) and other anions adsorbed in soils can be attributed to the presence of iron oxyhydroxide. The quantity of Cr(VI) adsorbed onto the iron solids increases with decreasing pH.

At metal-contaminated sites, mercury can be present in mercuric form (Hg^{2+}) mercurous form (Hg_2^{2+}), elemental form (Hg^0), or alkylated form (e.g., methyl and ethyl mercury). Hg_2^{2+} and Hg^{2+} are more stable under oxidizing conditions. Under mildly reducing conditions, both organically bound mercury and inorganic mercury compounds can convert to elemental mercury, which then can be readily converted to methyl or ethyl mercury by biotic and abiotic processes. Methyl and ethyl mercury are mobile and toxic forms.

Mercury is moderately mobile, regardless of the soil. Both the mercurous and mercuric cations are adsorbed by clay minerals, oxides, and organic matter. Adsorption of cationic forms of mercury increases with increasing pH. Mercurous and mercuric mercury also are immobilized by forming various precipitates. Mercurous mercury precipitates with chloride, phosphate, carbonate, and hydroxide. At concentrations of Hg commonly found in soil, only the phosphate precipitate is stable. In alkaline soils, mercuric mercury precipitates with carbonate and hydroxide to form a stable (but not exceptionally insoluble) solid phase. At lower pH and high chloride concentration, soluble HgCl_2 is formed. Mercuric mercury also forms complexes with soluble organic matter, chlorides, and hydroxides that may contribute to its mobility. In strong reducing conditions, HgS , a very low solubility compound is formed.

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