

SCANNED

Technology  
Evaluation Report

TE-98-01



# Phytoremediation

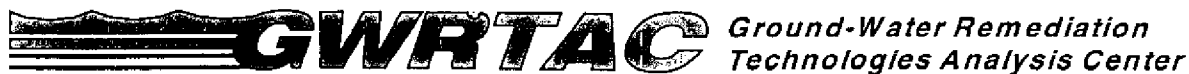
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## FOREWORD

### **About GWRTAC**

The Ground-Water Remediation Technologies Analysis Center (GWRTAC) is a national environmental technology transfer center that provides information on the use of innovative technologies to clean-up contaminated groundwater.

Established in 1995, GWRTAC is operated by Concurrent Technologies Corporation (CTC) in association with the University of Pittsburgh's Environmental Engineering Program through a Cooperative Agreement with the U.S. Environmental Protection Agency's (EPA) Technology Innovation Office (TIO). CTC, an independent nonprofit organization, is committed to assisting industry and government achieve world-class competitiveness. Through a unique concurrent engineering framework, CTC provides comprehensive solutions that improve product quality, productivity, and cost effectiveness.

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## 1.0 SUMMARY

Phytoremediation is the use of vegetation for *in situ* treatment of contaminated soils, sediments, and water. It is best applied at sites with shallow contamination of organic, nutrient, or metal pollutants that are amenable to one of five applications: Phytotransformation, Rhizosphere Bioremediation, Phytostabilization, Phytoextraction, or Rhizofiltration. In this Technology Evaluation report, it is shown that phytoremediation has been utilized at a number of pilot and full-scale field demonstration tests. It is an emerging technology that should be considered for remediation of contaminated sites because of its cost effectiveness, aesthetic advantages, and long-term applicability. Phytoremediation is well-suited for use at very large field sites where other methods of remediation are not cost-effective or practicable; at sites with low concentrations of contaminants where only "polishing treatment" is required over long periods of time; and in conjunction with other technologies where vegetation is used as a final cap and closure of the site. There are limitations to the technology that need to be considered carefully before it is selected for site remediation. These include limited regulatory acceptance, long duration of time sometimes required for clean-up to below action levels, potential contamination of the vegetation and food chain, and difficulty establishing and maintaining vegetation at some toxic waste sites.

Plants have shown the capacity to withstand relatively high concentrations of organic chemicals without toxic effects, and they can uptake and convert chemicals quickly to less toxic metabolites in some cases. In addition, they stimulate the degradation of organic chemicals in the rhizosphere by the release of root exudates, enzymes, and the build-up of organic carbon in the soil. For metal contaminants, plants show the potential for phytoextraction (uptake and recovery of contaminants into above-ground biomass), filtering metals from water onto root systems (rhizofiltration), or stabilizing waste sites by erosion control and evapotranspiration of large quantities of water (phytostabilization).

In this technology evaluation, recent field tests of phytoremediation are reported on wastes containing petroleum hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX) and polycyclic aromatic hydrocarbons (PAHs), pentachlorophenol, polychlorinated biphenyls (PCBs), chlorinated aliphatics (trichloroethylene, tetrachloroethylene, and 1,1,2,2-tetrachloroethane), ammunition wastes (2,4,6-trinitrotoluene or TNT, and RDX), metals (lead, cadmium, zinc, arsenic, chromium, selenium), pesticide wastes and runoff (atrazine, cyanazine, alachlor), radionuclides (cesium-137, strontium-90, and uranium), and nutrient wastes (ammonia, phosphate, and nitrate). Different species of plants have been used in various applications including: *Salix* spp. (hybrid poplars, cottonwoods, and willow), grasses (rye, Bermuda grass, sorghum, fescue, bullrush), legumes (clover, alfalfa, and cowpeas), aquatic plants (parrot feather, duckweed, arrowroot, cattail, pondweed), and hyperaccumulators for metals (sunflowers, Indian mustard, and *Thlaspi* spp.).

Key findings of this technology evaluation show that phytoremediation has successfully been applied at a brownfields site for remediation of soil contaminated with lead; a small pond at Chernobyl with uranium contamination; a riparian zone buffer strip at Amana, Iowa for nitrate and atrazine removal from agricultural runoff; and at an engineered wetland at Milan, Tennessee for TNT removal. In addition, many successful applications have involved remediation actions at small sites, such as agricultural cooperatives with pesticide and ammonia spills where state agencies have jurisdiction. At these sites, few funds are available for long-term compliance monitoring, and it is not to the advantage of the owners to pay for monitoring voluntarily. Therefore, long-term monitoring and evaluation of phytoremediation technology is still needed to demonstrate efficacy, to further define suitable plants and applications, and to gain acceptance from regulatory agencies.

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## 2.0 TECHNOLOGY DESCRIPTION

### 2.1 PHYTOTRANSFORMATION

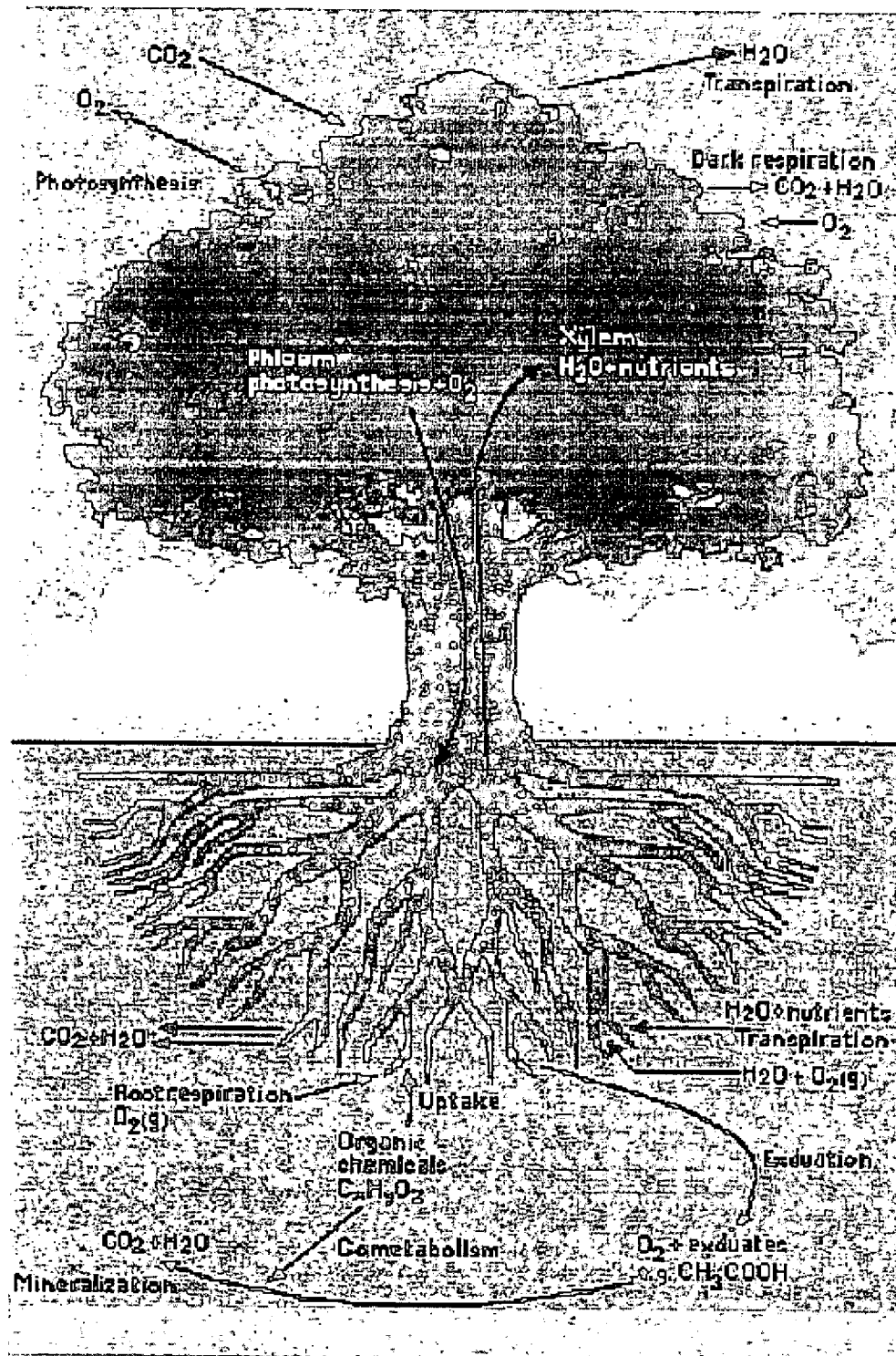
Phytotransformation refers to the uptake of organic and nutrient contaminants from soil and ground-water and the subsequent transformation by plants. Phytotransformation depends on the direct uptake of contaminants from soil water and the accumulation of metabolites in plant tissue. For environmental application, it is important that the metabolites which accumulate in vegetation be non-toxic or at least significantly less toxic than the parent compound.

Potential applications include phytotransformation of petrochemical sites and storage areas, ammunition wastes, fuel spills, chlorinated solvents, landfill leachates (including biochemical oxygen demand (BOD) and chemical oxygen demand (COD)), and agricultural chemicals (pesticides and fertilizers). Many times, phytoremediation is not the sole treatment option, but rather it is used in conjunction with other approaches such as removal actions or ex situ treatment of highly contaminated wastes, or as a polishing treatment.

Figure 1 is a schematic of mass flows through a woody, flood-tolerant tree species (Schnoor et al., 1995). Oxygen, water and carbon transport mechanisms can vary among plant species. Plants supply oxygen to the soil rhizosphere, but roots also demand oxygen for respiration. Root turnover is a key mechanism that adds organic carbon to the soil profile. Seedlings in the laboratory can transport considerable quantities of oxygen to roots in the rhizosphere ( $0.5 \text{ mol O}_2 \text{ per m}^2 \text{ of soil surface per day}$ ) (Shimp et al., 1993). Plants are able to take-up contaminants directly from the soil water or release exudates that help to degrade organic pollutants via cometabolism in the rhizosphere (see Rhizosphere Bioremediation).

Direct uptake of organics by plants is a surprisingly efficient removal mechanism from sites contaminated at a shallow depth with moderately hydrophobic organic chemicals (octanol-water partition coefficients,  $\log K_{ow} = 1 \text{ to } 3.5$ ). This includes most BTEX chemicals, chlorinated solvents, and short-chain aliphatic chemicals. Hydrophobic chemicals ( $\log K_{ow} > 3.5$ ) are bound so strongly to the surface of roots and soils that they cannot be easily translocated within the plant; and chemicals which are quite water soluble ( $\log K_{ow} < 1.0$ ) are not sufficiently sorbed to roots nor actively transported through plant membranes (Briggs et al., 1982). Very hydrophobic chemicals ( $\log K_{ow} > 3.5$ ) are candidates for phytostabilization and/or rhizosphere bioremediation.

Figure 1  
Schematic of oxygen, water, and chemical flows through a woody tree



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The direct uptake of chemical into the plant through roots depends on the uptake efficiency, transpiration rate, and the concentration of chemical in soil water (Burken and Schnoor, 1996). Uptake efficiency, in turn, depends on physical-chemical properties, chemical speciation, and the plant itself. Transpiration is a key variable that determines the rate of chemical uptake for a given phytoremediation design; it depends on the plant type, leaf area, nutrients, soil moisture, temperature, wind conditions, and relative humidity.

Once an organic chemical is translocated, the plant may store the chemical and its fragments into new plant structures via lignification (covalent bonding of chemical or its fragments into lignin of the plant); or it can volatilize, metabolize, or mineralize the chemical completely to carbon dioxide and water. Chlorinated aliphatic compounds such as trichloroethylene (TCE) have been reported to be mineralized to CO<sub>2</sub> and less toxic aerobic metabolites (trichloroethanol, trichloroacetic acid, and dichloroacetic acid by Newman et al., 1997). These products are consistent with those found in the human liver for TCE destruction by cytochrome P450, which is an abundant enzyme in plants as well as humans. Thus, plants are sometimes viewed as "green livers" in terms of their enzyme biochemistry.

Another form of phytotransformation is *phytovolatilization*, whereby volatile chemicals or their metabolic products are released to the atmosphere through plant transpiration. Many organic chemicals that are recalcitrant in the subsurface environment react rapidly in the atmosphere with hydroxyl radicals, an oxidant formed in the photochemical cycle. The transfer of contaminants from the soil or groundwater to the atmosphere is not as desirable as *in situ* degradation, but it may be preferable to prolonged exposure in the soil environment and the risk of ground-water contamination.

Nitroreductase and laccase enzymes in plants can break down ammunition wastes such as TNT (2,4,6-trinitrotoluene), and they may incorporate the broken ring structures into new plant material or organic detritus that becomes a part of sediment organic matter. Detoxification mechanisms may transform the parent chemical to non-phytotoxic metabolites that are stored in plant tissues (Schnoor et al., 1995). A thorough understanding of pathways and end-products of enzymatic processes will simplify toxicity investigations of *in situ* phytoremediation.

A summary of typical plants used in various applications of phytoremediation is presented in Table 1.

## 2.2 RHIZOSPHERE BIOREMEDIATION

Phytoremediation of the rhizosphere increases soil organic carbon, bacteria, and mycorrhizal fungi, all factors that encourage degradation of organic chemicals in soil. Rhizosphere bioremediation is also known as *phytostimulation* or *plant-assisted bioremediation*. Jordahl et al. (1997) showed that the numbers of beneficial bacteria increased in the root zone of hybrid poplar trees relative to an unplanted reference site. Denitrifiers, *Pseudonomad* spp., BTEX degrading organisms, and general heterotrophs were enhanced. Also, plants may release exudates to the soil environment that help to stimulate the degradation of organic chemicals by inducing enzyme systems of existing bacterial populations, stimulating growth of new species that are able to degrade the wastes, and/or increasing soluble substrate concentrations for all microorganisms. Leakage of sugars, alcohols, and acids from the plant and root turnover can amount to 10 to 20% of plant photosynthesis on an annual basis (Foth, 1990). Researchers have characterized the molecular weight distribution of organic

Table 1. Typical Plants Used in Various Phytoremediation Applications

Application	Media	Contaminants	Typical Plants
1. Phytotransformation	Soil, Groundwater, Landfill leachate, Land application of wastewater	<ul style="list-style-type: none"> <li>Herbicides (atrazine, alachlor)</li> <li>Aromatics (BTEX)</li> <li>Chlorinated aliphatics (TCE)</li> <li>Nutrients (<math>\text{NO}_3^-</math>, <math>\text{NH}_4^+</math>, <math>\text{PO}_4^{3-}</math>)</li> <li>Ammunition wastes (TNT, RDX)</li> </ul>	<ul style="list-style-type: none"> <li>Phreatophyte trees (poplar, willow, cottonwood, aspen);</li> <li>Grasses (rye, Bermuda, sorghum, fescue);</li> <li>Legumes (clover, alfalfa, cowpeas)</li> </ul>
2. Rhizosphere Bioremediation	Soil, Sediments, Land application of wastewater	<ul style="list-style-type: none"> <li>Organic contaminants (pesticides, aromatics, and polynuclear aromatic hydrocarbons [PAHs])</li> </ul>	<ul style="list-style-type: none"> <li>Phenolics releasers (mulberry, apple, osage orange);</li> <li>Grasses with fibrous roots (rye, fescue, Bermuda) for contaminants 0-3 ft deep;</li> <li>Phreatophyte trees for 0-10 ft;</li> <li>Aquatic plants for sediments</li> </ul>
3. Phytostabilization	Soil, Sediments	<ul style="list-style-type: none"> <li>Metals (Pb, Cd, Zn, As, Cu, Cr, Se, U)</li> <li>Hydrophobic Organics (PAHs, PCBs, dioxins, furans, pentachlorophenol, DDT, dieldrin)</li> </ul>	<ul style="list-style-type: none"> <li>Phreatophyte trees to transpire large amounts of water for hydraulic control;</li> <li>Grasses with fibrous roots to stabilize soil erosion;</li> <li>Dense root systems are needed to sorb/bind contaminants</li> </ul>
4. Phytoextraction	Soil, Brownfields, Sediments	<ul style="list-style-type: none"> <li>Metals (Pb, Cd, Zn, Ni, Cu) with EDTA addition for Pb Selenium (volatilization)</li> </ul>	<ul style="list-style-type: none"> <li>Sunflowers</li> <li>Indian mustard</li> <li>Rape seed plants</li> <li>Barley, Hops</li> <li>Crucifers</li> <li>Serpentine plants</li> <li>Nettles, Dandelions</li> </ul>
5. Rhizofiltration	Groundwater, Water and Wastewater in Lagoons or Created Wetlands	<ul style="list-style-type: none"> <li>Metals (Pb, Cd, Zn, Ni, Cu)</li> <li>Radionuclides (<math>^{137}\text{Cs}</math>, <math>^{90}\text{Sr}</math>, U)</li> <li>Hydrophobic organics</li> </ul>	<ul style="list-style-type: none"> <li>Aquatic Plants: <ul style="list-style-type: none"> <li>Emergents (bullrush, cattail, coontail, pondweed, arrowroot, duckweed);</li> <li>Submergents (algae, stonewort, parrot feather, Eurasian water milfoil, Hydrilla)</li> </ul> </li> </ul>

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exudates from root systems of hybrid poplar trees. Exudates include short chain organic acids, phenolics, and small concentrations of high molecular weight compounds (enzymes and proteins).

Research at the U.S. Environmental Protection (EPA) Laboratory in Athens, Georgia, has examined five plant enzyme systems in sediments and soils (dehalogenase, nitroreductase, peroxidase, laccase, and nitrilase). Dehalogenase enzymes are important in dechlorination reactions of chlorinated hydrocarbons. Nitroreductase is needed in the first step for degradation of nitroaromatics, while laccase enzyme serves to break aromatic ring structures in organic contaminants. Peroxidase and nitrilase are important in oxidation reactions. Enzymes are active in rhizosphere soils in close proximity to the root (1 mm) for transformation of organic contaminants that would not occur in the absence of the plant. The addition of plant root systems creates an ecology in soils that is suitable for bioremediation. When plants are grown in soil or sediment slurries, pH is buffered, metals are biosorbed or chelated, and enzymes remain protected inside the plant or sorbed to plant surfaces. In EPA studies of TNT breakdown, plants like hornwort increase soil water pH from 3 to 7 and sorb high concentrations of metals that would usually inhibit bacteria, while the plants remain healthy and viable. Overall, plants and their root systems can accommodate mixed wastes (organic and metals) and other harsh conditions (Schnoor et al., 1995).

Anderson et al. (1993) have demonstrated the importance of biodegradation in the rhizosphere. Plants help with microbial transformations in many ways.

- Mycorrhizae fungi associated with plant roots metabolize the organic pollutants
- Plant exudates stimulate bacterial transformations (enzyme induction)
- Build-up of organic carbon increases microbial mineralization rates (substrate enhancement)
- Plants provide habitat for increased microbial populations and activity
- Oxygen is pumped to roots ensuring aerobic transformations

Fletcher et al. (1995) have reported that flavonoids and coumarin are released by root turnover from trees like mulberry, osage orange, and apple which select and stimulate PCB and PAH degrading organisms.

Fungi, growing in symbiotic association with the plant, have unique enzymatic pathways that help to degrade organics that could not be transformed solely by bacteria. In addition to soluble exudates, the rapid decay of fine root biomass can become an important addition of organic carbon to soils which serves to retard organic chemical transport. Microbial mineralization of atrazine is directly related to the fraction of organic carbon in the soil (Nair and Schnoor, 1993). Microbial assemblages are abundant in the rhizosphere, and typical communities may comprise  $5 \times 10^6$  bacteria,  $9 \times 10^5$  actinomycetes, and  $2 \times 10^3$  fungi per gram of air dried soil; bacteria live in colonies that cover as much as 4 to 10% of the root surface area (Foth, 1990).

### 2.3 PHYTOSTABILIZATION

Phytostabilization refers to the holding of contaminated soils and sediments in place by vegetation, and to immobilizing toxic contaminants in soils. Establishment of rooted vegetation prevents



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windblown dust, an important pathway for human exposure at hazardous waste sites. Hydraulic control is possible, in some cases, due to the large volume of water that is transpired through plants which prevents migration of leachate towards groundwater or receiving waters. Phytostabilization is especially applicable for metal contaminants at waste sites where the best alternative is often to hold contaminants in place. Metals do not ultimately degrade, so capturing them *in situ* is sometimes the best alternative at sites with low contamination levels (below risk thresholds) or vast contaminated areas where a large-scale removal action or other *in situ* remediation is not feasible. Vigorously growing plants are necessary to exert hydraulic control and immobilization at the site; plants cannot die or be removed during the phytostabilization design period. Low-level radionuclide contaminants can also be held in place by phytostabilization, and this alternative can result in significant risk reduction if their half-lives are not too long. Soil amendments such as phosphate, lime, and organic matter are sometimes needed to immobilize toxic metals such as lead, cadmium, zinc, and arsenic. Cadmium is readily translocated to leaves in many plants, which represents a risk to the food chain, and this pathway may be the limiting consideration in applying phytostabilization at some metals contaminated sites.

## 2.4 PHYTOEXTRACTION

Phytoextraction refers to the use of metal-accumulating plants that translocate and concentrate metals from the soil in roots and above ground shoots or leaves. It has been used effectively by Phytotech® at brownfields sites with relatively low level lead and cadmium contamination for soil remediation to below action levels (McGinty, 1996). It has also been proposed for extraction of radionuclides from sites with mixed wastes. Phytoextraction offers significant cost advantages over alternative schemes of soil excavation and treatment or disposal. An important issue in phytoextraction is whether the metals can be economically recovered from the plant tissue or whether disposal of the waste is required. Design considerations include the accumulation factor (ratio of metal in the plant tissue to that in the soil) and the plant productivity (kg of dry matter that is harvestable each season). In order to have a practicable treatment alternative, one needs a vigorously growing plant (>3 tons dry matter/ha-yr) that is easily harvested and which accumulates large concentrations of metal in the harvestable portion (>1000 mg/kg metal).

As a general rule, readily bioavailable metals for plant uptake include cadmium, nickel, zinc, arsenic, selenium, and copper. Moderately bioavailable metals are cobalt, manganese, and iron; while lead, chromium, and uranium are not very bioavailable. Lead can be made greatly more bioavailable by the addition of EDTA to soils. Lead, chromium and uranium can be removed by binding to soils and root mass via rhizofiltration.

## 2.5 RHIZOFILTRATION

Rhizofiltration refers to the use of plant roots to sorb, concentrate, and precipitate metal contaminants from surface or groundwater. Roots of plants are capable of sorbing large quantities of lead and chromium from soil water or from water that is passed through the root zone of densely growing vegetation. The potential for treatment of radionuclide contaminants has received a great deal of attention in the press. Rhizofiltration has been employed by Phytotech® using sunflowers at a U.S. Department of Energy (DOE) pilot project with uranium wastes at Ashtabula, Ohio, and on water from a pond near the Chernobyl nuclear plant in the Ukraine.

Table 2. Phytoremediation Applications and Demonstrations in the Field

Location	Application	Plants	Contaminants	Performance	Contacts
Chernobyl, Ukraine	Rhizofiltration demonstration pond near nuclear disaster	Sunflowers <i>Helianthus annuus</i>	<sup>137</sup> Cs, <sup>90</sup> Sr	90% Reduction in 2 weeks. Roots concentrated 8,000 fold	I. Raskin, Rutgers U.
Ashtabula, OH	Rhizofiltration demonstration DOE energy wastes	Sunflowers <i>Helianthus annuus</i>	U	95% removal in 24 hours from 350 ppb to < 5 ppb	B. Ensley, Phytotech
Trenton, NJ	Phytoextraction demonstration 200 ft x 300 ft plot brownfield location	Indian mustard <i>Brassica juncea</i>	Pb	Pb cleaned-up to below action level in one season SITE program	B. Ensley, Phytotech
Rocky Flats, CO	Rhizofiltration from landfill leachate	Sunflowers and mustard	U and nitrate	Just beginning SITE program	Rock, 1997
Dearing, KS	Phytostabilization demonstration one acre test plot abandoned smelter, barren land	Poplars <i>Populus</i> spp.	Pb, Zn, Cd Concs. > 20,000 ppm for Pb and Zn	50% survival after 3 years. Site was successfully revegetated.	G. Pierzynski, Kansas St.
Whitewood Cr., SD	Phytostabilization demonstration one acre test plot mine wastes	Poplars <i>Populus</i> spp.	As, Cd	95% of trees died. Inclement weather, deer browse, toxicity caused die-off.	J. Shnoor, U. of Iowa
Pennsylvania	Phytoextraction pilot mine wastes	<i>Thlaspi caerulescens</i>	Zn, Cd	Uptake is rapid but difficult to decontaminate soil	R. Chaney, USDA Beltsville, MD Brown 1995
San Francisco, CA	Phytovolatilization refinery wastes and agricultural soils	<i>Brassica</i> sp.	Se	Selenium is partly taken-up and volatilized, but difficult to decontaminate soil	G. Banuelos, USDA Salinity Lab, Riverside, CA
Aberdeen, MD J-field site	Phytotransformation groundwater capture on 1 acre plot	Hybrid poplars <i>Populus</i> spp.	TCE, PCA (1,1,2,2-tetrachloroethane)	Only in second year Demonstration Project	H. Compton, EPA/ERT, Edison, NJ
Carswell AFB Ft. Worth, TX	Phytotransformation groundwater capture on 4 acre plot	Hybrid poplars <i>Populus</i> spp.	TCE	Only in second year SITE Project	G. Harvey, Ohio Wright-Patterson AFB

Table 2. Phytoremediation Applications and Demonstrations in the Field (cont.)

Location	Application	Plants	Contaminants	Performance	Contacts
Milan, TN	Phytotransformation engineered wetland at army ammunition plant	Elodeia Bullrush Canary Grass	TNT, RDX	> 90% removal	D. Bader, U.S. Army Aberdeen Proving Ground, MD
Middletown, IA	Phytotransformation created wetland and surrounding soil	Pondweed Coontail Arrowroot Hybrid poplars	TNT, RDX	Just beginning	J. Schnoor, U. of Iowa K. Howe, Army COE Omaha
Ogden, UT	Phytotransformation (groundwater and soil) petrochemical wastes 4 acre site	Hybrid Poplar	BTEX, TPH	Only in second year SITE Program	A. Ferro, Phytokinetics
Portland, OR	Phytotransformation on wastes of wood preservative	Hybrid Poplar	PCP, PAH	Only in second year SITE Program	A. Ferro, Phytokinetics
Martell, IA Clarence, IA Amana, IA	Phytotransformation agricultural runoff and agricultural co-op sites	Hybrid Poplar	atrazine, nitrates	90% reduction in groundwater of NO <sub>3</sub> atrazine reductions	Licht, Ecotree Paterson and Schnoor (1992)

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Shallow lagoons have been engineered as wetlands and maintained as facultative microbial systems with low dissolved oxygen in the sediment. Groundwater or wastewater is pumped through the system for the removal of contaminants by rhizofiltration. Usually this technology is intended for metals or mixed wastes, but it is suitable for ammunition wastes as well. 2,4,6-Trinitrotoluene (TNT) is an organic contaminant that sorbs strongly to roots and is not translocated to any appreciable degree. An engineered wetland technology has been used at the Milan, Tennessee, and Volunteer Army Ammunition Plants with bullrush (Table 2). In addition, an engineered wetland has been approved for full scale treatment of a CERCLA site at the Iowa Army Ammunition Plant at Middletown, Iowa, for TNT and RDX polishing of soil and groundwater after removal actions.

Wetlands have been used with great success in treating nutrients, metals, and organic contaminants for many years (Young, 1996). Long-term utilization of wetland plants and sulfate-reducing conditions result in an increase in pH and a decrease in toxic metals concentrations for treatment of acid mine drainage (Wieder, 1993; Walski, 1993). Root systems and sediments in wetlands are facultative (aerobic and anaerobic zones) which facilitates sorption and precipitation of toxic metals.

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## 3.0 APPLICATIONS AND PERFORMANCE

### 3.1 LIMITATIONS

Limitations of phytoremediation include the difficulty with treating wastes greater than three meters deep, possible uptake of contaminants into leaves and release during litter fall, inability to assure clean-up below action levels in a short period of time, difficulty in establishing the vegetation due to toxicity at the site, and possible migration of contaminants off-site by macropore flow or by binding with soluble plant exudates. Regulatory restrictions sometimes will not allow contaminants to be left in place, even when a vegetative cover prevents erosional or hydrological pathways of exposure. Phytoremediation is most effective at sites with shallow contaminated soils where contaminants can be treated in the rhizosphere and by root uptake. Sites where contamination is relatively deep and those with pools of nonaqueous phase liquids (NAPL) would not be good applications. However, deep ground-water contaminants or leachate pond effluent can be treated by pumping and irrigation on plantations of trees. Degradation of organics may be limited by mass transfer, i.e., desorption and mass transport of chemicals from soil particles to the aqueous phase may become the rate determining step. Therefore, phytoremediation may require more time to achieve clean-up standards than other more costly alternatives such as excavation and treatment or disposal, especially for hydrophobic pollutants that are tightly bound to soil particles. In many cases, phytoremediation may serve as a final "polishing step" to close sites after other clean-up technologies have been used to treat the hot spots.

Winter operations may pose problems for phytoremediation when deciduous vegetation loses its leaves, transformation and uptake cease, and soil water is no longer transpired. Mathematical modeling of the hydrology and contaminant transport is recommended in order to ensure that migration of contaminants and/or leaching to groundwater during seasonal periods of vegetation dormancy does not preclude the phytoremediation option.

### 3.2 PERFORMANCE

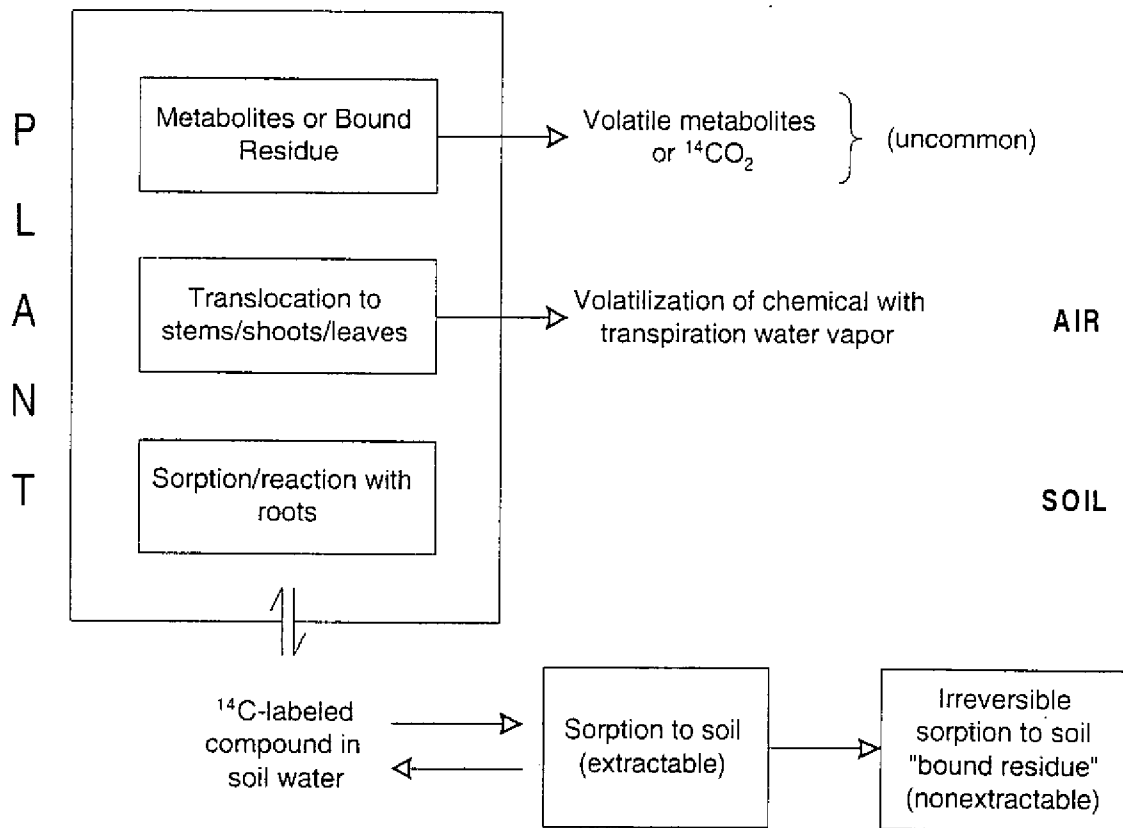
#### Phytotransformation

The concept of phytotransformation for organic compounds has been verified in the laboratory, greenhouse, and small plots. Contaminants are either immobilized as bound residues in the soil or plant, metabolized, or volatilized as shown in Figure 2.

Mass balance studies have been completed using  $^{14}\text{C}$ -labeled compounds, and the fate and transport of the chemicals through plants has been documented (Newman et al., 1997; Burken and Schnoor, 1997; Dushenkov et al., 1995; Ferro et al., 1994).

Newman et al. (1997) have demonstrated that TCE is transformed to trichloroethanol, trichloroacetic acid, and dichloroacetic acid by hybrid poplar trees. This observation is indicative of an aerobic transformation, such as that in the human liver by cytochrome P-450 enzymes (mono-oxygenase). Trace quantities of  $^{14}\text{CO}_2$  were released by the plant demonstrating partial mineralization of TCE. Mineralization is fairly unusual, however, and there are no reports in the literature of aromatic compounds being completely mineralized by plants.

Figure 2  
Fate and Transport of Organic Chemicals in Phytoremediation Laboratory Experiments with Radiolabeled  $^{14}\text{C}$ -isotopes



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Burken and Schnoor (1997) showed that the aromatic pesticide atrazine was uptaken and transformed to ammeline, a fully hydroxylated and dealkylated metabolite, but there was no indication of mineralization to  $^{14}\text{CO}_2$ . A fraction (~ 15%) of the ring-labeled atrazine was incorporated into biomass as bound residue.

Hydrophobic chemicals ( $\log K_{ow} > 3.5$ ) are expected to be sorbed strongly to soils and not bioavailable to plants for translocation. Phytoremediation of hydrophobic compounds such as PCBs and PAHs may be possible by enhancement of rhizosphere microbial degradation processes and sorption to roots. Moderately hydrophobic chemicals ( $\log K_{ow} = 1$  to 3.5) are expected to be taken-up by plants and metabolized, volatilized, or incorporated into plant tissues as nonextractable bound residue. Bound residues are generally viewed as much less toxic to animals (non-bioavailable) in the food chain, but further research may be necessary to confirm this for some compounds. Volatile organic chemicals (VOCs) may be transpired by the plant, and simple air toxics models can be used to determine if they pose an unacceptable risk to the atmosphere. In the case of TCE, the half-life in aerobic soil and groundwater is on the order of years; in the atmosphere, it reacts with the hydroxyl radical yielding a half-life of hours to days.

Hydrophilic chemicals ( $\log K_{ow} < 1$ ) are not expected to be taken up or sorbed by plants. However, exceptions do exist and treatability studies are recommended. Phytoremediation may be a viable option for some hydrophilic chemicals that are quite mobile in the subsurface environment and not amenable to microbial degradation.

Table 2 lists information on field demonstrations of phytoremediation. Despite a number of investigations in the lab and greenhouse, very few documented cases of full scale clean-up by phytotransformation exist. There are no Superfund Innovative Technology Evaluations (SITE Program by EPA) that have been completed, however five are currently in progress (Steve Rock, EPA Cincinnati, personal communication). These include demonstrations or evaluations of phytoremediation for lead, uranium, nitrate, TCE, BTEX, total petroleum hydrocarbons (TPH), pentachlorophenol, and PAHs (Table 2). Many other demonstration projects are underway, but they do not have detailed reporting requirements. A dozen small sites (such as pesticide dealerships) have utilized phytoremediation where states held the lead in hazardous waste programs. But these small projects generally do not have the funds necessary to document the extent of remediation in the field. Usually, ground-water monitoring is the only requirement placed upon the principal responsible party in these cases, and it is not in their self interest to conduct detailed monitoring at the site.

#### Rhizosphere Bioremediation

Rhizosphere bioremediation has been demonstrated in the field at Oak Ridge National Laboratory by Anderson (1992) and Anderson et al. (1993) for TCE contaminated soils. It was not possible to perform mass balance studies, but the project did show disappearance of TCE over time and differences among five different plant species. Aerobic rhizosphere bioremediation is thought to be effective for aromatic hydrophobic chemicals such as PAHs, BTEX, and phenolics (Hedge and Fletcher, 1996) at sites with shallow contamination (Hsu et al., 1992).

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### Phytostabilization

Phytostabilization is a potentially effective remediation strategy for hydrophobic chemicals and metals at contaminated sites where removal or treatment is not practical or as a polishing step where contaminant concentrations are below regulatory action levels. Hse (1996) reports on phytoremediation of metals at two locations: a mine tailings Superfund site in South Dakota with up to 1,000 mg/kg of arsenic (and lesser amounts of cadmium); and an abandoned smelter in Kansas with up to 200,000 mg/kg of zinc and 20,000 mg/kg of lead. The goal at each site was to stabilize soils and to decrease vertical migration of leachate to groundwater using deep-rooted hybrid poplar trees. At the South Dakota site, the trees died due to harsh climatic conditions, deer browse, and possible toxic stress. At the Kansas site, survival of the trees has been greater than 50% in the third year, and the effort is successful to date. Sites with high concentrations of metals are difficult to phytostabilize due to soil toxicity, but it is inexpensive relative to excavation and treatment or disposal. Soil amendments such as phosphate, lime, N/P/K, and organic matter (sewage sludge, compost, aged manure, straw, leaves, etc.) are usually required. Treatability and toxicity studies in small pots in a greenhouse are recommended.

### Phytoextraction

Phytoextraction has been proven effective at a brownfields site in Trenton, New Jersey for remediation of lead-contaminated shallow soils (Blaylock et al., 1996). Approximately 50% of the lead was removed from the surface soil (~ 700 mg/kg) in order to achieve clean-up standards (400 mg/kg) in one year using *Brassica juncea*, a relative of the mustard family. For phytoextraction to be effective, one needs vigorously growing plants (> 3 tons dry matter/acre-yr), an easily harvestable above-ground portion, and a plant that accumulates large amounts of metals (~ 1000 mg/kg) in above-ground biomass. To achieve clean-up within three to five years, the plant must accumulate about ten times the level in soil (for example, if the level in soil is 500 mg/kg, then the concentration in the plant must be almost 5000 mg/kg to clean-up the soil in a few years). Some sites have metals that are bioavailable while others do not. Generally, cadmium, nickel, zinc, arsenic, and copper are relatively bioavailable while lead, chromium, and uranium are not taken-up and translocated to the harvestable biomass. Plants which accumulate nickel, cobalt, copper, manganese, lead, zinc, and selenium have been reported in the literature (Kumar et al., 1995). Zinc and boron are phytotoxic to some plants at levels above 200 mg/kg in soil. Addition of EDTA (0.5 to 10 µg EDTA/kg soil) has greatly enhanced the bioavailability of lead, but the enhancement must be weighed against the increased probability of lead migration to groundwater. Mathematical modeling of water movement and metals transport may be required to further understand the fate of lead under these conditions.

### Rhizofiltration

Rhizofiltration has been pioneered by Ilya Raskin and the group at Rutgers University (Dushkenov, et al. 1995). It is effective in cases where wetlands can be created and all of the contaminated water allowed to come into contact with roots. Contaminants should be those that sorb strongly to roots such as hydrophobic organics, lead, chromium (III), uranium, and arsenic (V).



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## 4.0 DESIGN

Design of a phytoremediation system varies according to the contaminant(s), the conditions at the site, the level of clean-up required, and the plant(s) that are used. Clearly, phytoextraction has different design requirements than phytostabilization or rhizosphere bioremediation. Nevertheless, it is possible to specify a few design considerations that are a part of most phytoremediation efforts. These include:

- Plant selection;
- Treatability;
- Planting density and pattern;
- Irrigation, agronomic inputs, and maintenance;
- Ground-water capture zone and transpiration rate;
- Contaminant uptake rate and clean-up time required; and,
- Analysis of failure modes.

### 4.1 PLANT SELECTION

Plants are selected according to the needs of the application and the contaminants of concern. For phytotransformation of organics, the design requirements are that vegetation is fast growing and hardy, easy to plant and maintain, utilizes a large quantity of water by evapotranspiration (if groundwater is an issue), and transforms the contaminants of concern to non-toxic or less toxic products. In temperate climates, phreatophytes (e.g., hybrid poplar, willow, cottonwood, aspen) are often selected because of fast growth, a deep rooting ability down to the surface of groundwater, large transpiration rates, and the fact that they are native throughout most of the country. At the Iowa Army Ammunition Plant CERCLA site (Table 2), design requirements included the use of native plants (to avoid introduction of nuisance species) and species which showed nitroreductase activity. In pre-screening ELISA immunoassays for transformation of TNT. Hybrid poplar was selected for the terrestrial species and pondweed, arrowroot, and coontail were selected for the aquatic species. At petrochemical sites, other trees (mulberry, apple, and osage orange) have been selected for their ability to release flavonoids and phenolics (via fine root turnover), compounds that are known to induce enzymes in PCB and PAH-degrading organisms (Fletcher, 1995). Hybrid poplars have been shown to uptake and transform TCE. A screening test or knowledge from the literature of plant attributes will aid the design engineer in selection of plants. Engineers should work in interdisciplinary teams which includes a botanist and/or agricultural specialist to identify and select plants that will grow well at the site.

Grasses are often planted in tandem with trees at sites with organic contaminants or as the primary remediation method. They provide a tremendous amount of fine roots in the surface soil which is effective at binding and transforming hydrophobic contaminants such as TPH, BTEX, and PAHs. Grasses are often planted between rows of trees to provide for soil stabilization and protection against wind-blown dust that can move contaminants off-site. Legumes such as alfalfa, alsike clover, and peas can be used to restore nitrogen to poor soils. Fescue, rye, and reed canary grass have been used successfully at several sites, especially those contaminated with petrochemical wastes. The grasses are harvested periodically and disposed to compost or burned. Hydrophobic contaminants do not translocate appreciably, so the top portion of grasses are not contaminated. The system achieves phytoremediation via rhizosphere processes and sorption to roots.

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Selection of plants for phytoremediation of metals depends on the application: phytostabilization, rhizofiltration, or phytoextraction. In phytoextraction, one is seeking to concentrate the metal(s) in the above-ground portion of the biomass, and to harvest and recover metals from the biomass, if practicable. Plants used to date in phytoextraction remedies include sunflowers and Indian mustard plants for lead; *Thlaspi* spp. for zinc, cadmium, and nickel; and sunflowers and aquatic plants for radionuclides (Table 2). Screening tests for hyperaccumulators around the world have been led by Alan J.M. Baker, University of Sheffield, UK. Ilya Raskin, Rutgers University, has led a development effort for screening plants for phytoextraction capabilities in the laboratory. Recovery of metals from vegetation has centered on incineration and recovery from ash, or wet extraction techniques. Even if it is not practicable to recover the metals from plant biomass or ash, they will have been concentrated into a much smaller volume for ultimate disposal.

Aquatic plants are used in created wetlands applications. They fall into two categories: emergent and submerged species. Emergent vegetation transpires water, and it is easier to harvest the vegetation if desired. Submerged species do not transpire water, but they provide more biomass within the aquatic portion of the system for uptake and sorption of contaminants. Aquatic species in created wetlands have included bullrush, cattail, coontail, duckweed, arrowroot, pondweed, parrot feather, Eurasian water milfoil, stonewort, and *Potamogeton* spp.

#### 4.2 TREATABILITY

It is necessary to utilize treatability studies prior to design in order to assure that the phytoremediation system will achieve desired results. Toxicity and transformation data are obtained in treatability studies. There is a large amount of variation in toxicity and transformation rates that can be expected from one plant species to another, and even from one variety or cultivar to another. Boron, zinc, ammonium, some metals and salts are especially toxic to plants. Thus, it is critical to obtain treatability information in the laboratory or greenhouse, if prior knowledge has not been reported for the waste with that plant. The sequence of design information that is required typically ranges from hydroponic studies, to small pot studies with soils from the site in a greenhouse, to plot studies (up to 15 x 15 m). Different concentrations of contaminant can be analyzed for toxicity, and plant tissues can be harvested for metabolite or parent compound analysis. Regulators may require total mass balance information which necessitates use of radiolabeled compounds in the laboratory.

Treatability laboratory studies may be needed to assess the fate of the contaminant(s) in the plant system. For example, the potential for volatile compounds such as benzene and trichloroethylene to move through the plant and become transpired to the atmosphere as air toxics must be examined. Volatiles are often transpired to the atmosphere by plants, in which case, air toxics calculations would be needed to estimate the atmospheric concentrations and whether these emissions would be considered acceptable. Similarly, moderately hydrophobic organics ( $\log K_{ow} = 1$  to 3.5) are often translocated to the leaves of the plant and metabolized. Measurement of leaf concentrations of parent compound and metabolites would be needed in this case to determine if acceptable levels are exceeded.

#### 4.3 PLANT DENSITY AND PATTERN

Planting density depends on the application. Louis Licht, Ecolotree, has pioneered the use of hybrid poplar trees as riparian zone buffer strips, landfill caps, and at hazardous waste sites. For hybrid poplar trees, 1000 to 2000 trees per acre are typically planted with a conventional tree

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planter at 12 to 18 inches depth or in trenched rows one to six feet deep. Poplars have the ability to root along the entire buried depth. If a row conformation is used, the trees may be spaced with two feet between trees and ten feet between rows. The poplars are planted simply as "sticks", long cuttings that will root and grow rapidly in the first season. Several phreatophytes in the *Salix* family, such as willow and cottonwood, can be planted in a similar manner. Hardwood trees and evergreens may require a lower planting density initially. A high initial planting density assures a significant amount of evapotranspiration in the first year which is normally desirable, but the trees will naturally thin themselves by competition to 600 to 800 trees per acre over the first six years. If desirable, hybrid poplars can be harvested on a six-year rotation and sold for fuelwood or pulp and paper, and the trees will grow back from the cut-stump (coppicing trait). The dense, deep root system stays in place to sustain growth for the next year. The lifetime of hybrid poplars such as *Populus deltoides* x *nigra* DN-34 (Imperial Carolina) is on the order of 30 years which is usually sufficient as the design life of the project.

Grasses are usually drilled or broadcast for planting at waste sites. Biomass densities (above ground) of 200 to 600 g/m<sup>2</sup> are achieved by the second crop, with 1 to 3 crops per year depending on climate and water availability.

The initial planting density of aquatic species in a created or natural wetland is normally three plants to a pod, located on three foot centers. Replanting and maintenance should be estimated in the cost of the project. One should consider that at least 30 percent of the plants may need to be replanted in the second or third year, as a contingency. At Milan, Tennessee, the final plant density in four created wetlands cells ranges from 2400 to 4000 g/m<sup>2</sup> with addition of 350 to 700 mg/L of fertilizer addition (N = 3.6%, P = 0.7%, K = 2.4%, O.C. = 43.7%, trace elements = Mg, Na, Si, S, Fe, Zn, Mn). The application of large amounts of organic fertilizer at the Milan site ensured that most of the TNT treatment was due to anaerobic microbiological processes rather than by plant uptake and phytotransformation.

#### **4.4 IRRIGATION, AGRONOMIC INPUTS AND MAINTENANCE**

For terrestrial phytoremediation applications, it is often desirable to include irrigation costs in the design, on the order of 10 to 20 inches of water per year. Irrigation of the plants ensures a vigorous start to the system even in a drought. On the other hand, hydrologic modeling may be required to estimate the rate of percolation to groundwater under irrigation conditions. Over time, irrigation should be withdrawn from the site, provided the area receives sufficient rainfall to sustain the plants. Operation and maintenance (O&M) costs should be considered in the design of phytoremediation systems. Costs for mowing, replanting, pruning, harvesting, monitoring vegetation for contaminants, fertilizer costs, and performance monitoring should all be included in the initial estimated costs if they are needed.

Agronomic inputs include the nutrients necessary for vigorous growth of vegetation and rhizosphere bacteria. These include N/P/K from commercial fertilizer mixes, and carbon addition and soil conditioners such as aged manure, sewage sludge, compost, straw, or mulch. Typical application rates of fertilizer include 50 lbs P/acre and 100 lbs N/acre each year, especially for production of grasses and fine roots at petrochemical sites. It is critical that the site soils have sufficient water holding capacity to sustain vegetation. This is often not the case at mine tailings sites, abandoned smelters, and rocky terrains. In these cases, soil amendments are necessary to improve soil tilth and allow water to be absorbed. Sometimes it is desirable to neutralize pH by lime addition; a

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standard agronomic analysis of site soils will allow assessment of the necessity for pH adjustment.

Biomass production can be estimated at 7 tons dry matter/acre-yr for fast growing trees. The amount of nitrogen stored in woody tissue is typically 0.5 to 1.0%, so nitrogen uptake can be calculated. Stoichiometries of woody tissue and leaf tissue are available in the literature to estimate major nutrient uptake requirements.

In some cases, chemical inputs are a part of the total phytoremediation design. For phytostabilization, it is necessary to bind metals to soil particles so that they are not available for plant uptake or leaching. Phosphate rock or phosphate fertilizers are effective in binding lead and zinc. They can be added to trenches or disked into the soil prior to planting. For phytoextraction, the opposite effect is desired: metals must be bioavailable for plant uptake. In this case, chelates such as EDTA (0.5 to 10 µg EDTA/kg soil) have been added to soils in irrigation water to assure plant uptake and concentration from the soil to biomass (Raskin, 1996).

#### 4.5 GROUND-WATER CAPTURE AND TRANSPIRATION

One must understand where the water is moving at a site in order to estimate contaminant fate and transport. For applications involving ground-water remediation, a simple capture zone calculation (Domenico and Schwartz, 1997) can be used to estimate whether the phytoremediation "pump" can be effective at entraining the plume of contaminants. Trees can be grouped for consideration as average withdrawal points. The goal of such a phytoremediation effort is to create a water table depression where contaminants will flow to the vegetation for uptake and treatment. It is important to realize that organic contaminants are not taken-up at the same concentration as in the soil or groundwater, rather there is a transpiration stream concentration factor (a fractional efficiency of uptake) that accounts for the partial uptake of contaminant (due to membrane barriers at the root surface). The uptake rate is given by the following equation.

$$U = (\text{TSCF}) (T) (C) \quad (1)$$

where  $U$  = uptake rate of contaminant, mg/day

$\text{TSCF}$  = transpiration stream concentration factor, dimensionless

$T$  = transpiration rate of vegetation, L/day

$C$  = aqueous phase concentration in soil water or groundwater, mg/L

If the contaminant plume is not taken-up by the vegetation, the plume that emerges will be evapoconcentrated, i.e., the mass of contaminant in the plume will be less due to uptake by vegetation, but the concentration remaining will actually be greater. This is a potential concern for phytoremediation of ground-water plumes or with created wetlands, where a relatively hydrophilic contaminant can be concentrated on the downstream side of the phyto system.

A method for estimating the Transpiration Stream Concentration Factor (TSCF) for equation (1) is given in Table 3. The Root Concentration Factor is also defined in Table 3 as the ratio of the contaminant in roots to the concentration dissolved in soil water (µg/kg root per µg/L). It is important in estimating the mass of contaminant sorbed to roots in phytoremediation systems.

Table 3  
Estimating the Transpiration Stream Concentration Factor (TSCF)  
and Root Concentration Factor (RCF)  
for Some Typical Contaminants  
(from Burken and Schnoor, 1997b)

The TSCF and RCF for metals depends on their redox state and chemical speciation in soil and groundwater.

Chemical	*Log $K_{ow}$	*Solubility -Log $C_w^{sat}$ @ 25°C, (mol/l)	*Henry's Constant $k_{H^*}$ @25°C (dimensionless)	*Vapor Pressure -Log $P_v$ @ 25°C (atm)	Transpiration Stream Conc. Factor (TSCF)*	Root Conc. Factor, RCF† (L/kg)
benzene	2.13	1.64	0.2250	0.90	0.71	3.6
toluene	2.69	2.25	0.2760	1.42	0.74	4.5
ethylbenzene	3.15	2.80	0.3240	1.90	0.63	6.0
m-xylene	3.20	2.77	0.2520	1.98	0.61	6.2
TCE	2.33	2.04	0.4370	1.01	0.74	3.9
aniline	0.90	0.41	$2.2 \times 10^5$	2.89	0.26	3.1
nitrobenzene	1.83	1.77	0.0025 <sup>a</sup>	3.68	0.62	3.4
phenol	1.45	0.20	$>1.0 \times 10^5$	3.59	0.47	3.2
pentachloropheno	5.04	4.27	$1.5 \times 10^{-4}$ <sup>a</sup>	6.75 <sup>a</sup>	0.07	54
atrazine	2.69	3.81	$1.0 \times 10^{-7}$ <sup>a</sup>	9.40 <sup>a</sup>	0.74	4.5
1,2,4- trichlorobenzene	4.25	3.65	0.1130	3.21	0.21	19
RDX	0.87	4.57	---	---	0.25	3.1

\* Physical chemical properties (Schwarzenbach, et al., 1993) unless otherwise noted.

\*  $TSCF = 0.75 \exp \{ - [(\log K_{ow} - 2.50)^2 / 2.4] \}$  Burken & Schnoor, 1997b

†  $RCF = 3.0 + \exp (1.497 \log K_{ow} - 3.615)$  Burken & Schnoor, 1997b

<sup>a</sup> Source: (Schnoor, 1996)

Mature phreatophyte trees (poplar, willow, cottonwood, aspen, ash, alder, eucalyptus, mesquite, bald cypress, birch and river cedar) typically can transpire three to five acre-ft of water per year (36 to 60 inches of water per year). This is equivalent to about 600 to 1000 gallons of water per tree per year for a mature species planted at 1500 trees per acre. Transpiration rates in the first two years would be somewhat less, about 200 gallons per tree per year, and hardwood trees would transpire about half the water of a phreatophyte. Two meters of water per year is a practical maximum for transpiration in a system with complete canopy coverage (a theoretical maximum would be 4 m/yr based on the solar energy supplied at 40 °N on a clear day that is required to evaporate water). If evapotranspiration of the system exceeds precipitation, it is possible to capture water that is moving vertically through soil. Areas that receive precipitation in the wintertime (dormant season for deciduous trees) must be modeled to determine if the soil will be sufficiently dry to hold water for the next spring's growth period. The Corps of Engineers HELP model (Vicksburg, Mississippi) and other codes have been used to estimate vertical water movement and percolation to groundwater.

#### 4.6 CONTAMINANT UPTAKE RATE AND CLEAN-UP TIME

From equation (1) above, it is possible to estimate the uptake rate of the contaminant(s). First order kinetics can be assumed as an approximation for the time duration needed to achieve remediation goals. The uptake rate should be divided by the mass of contaminant remaining in the soil:

$$k = U/M_0 \quad (2)$$

where  $k$  = first order rate constant for uptake,  $\text{yr}^{-1}$   
 $U$  = contaminant uptake rate,  $\text{kg/yr}$   
 $M_0$  = mass of contaminant initially,  $\text{kg}$

Then, an estimate for mass remaining at any time is expressed by equation (3) below.

$$M = M_0 e^{-kt} \quad (3)$$

where  $M$  = mass remaining,  $\text{kg}$   
 $t$  = time,  $\text{yr}$

Solving for the time required to achieve clean-up of a known action level:

$$t = -(\ln M/M_0)/k \quad (4)$$

where  $t$  = time required for clean-up to action level,  $\text{yr}$   
 $M$  = mass allowed at action level,  $\text{kg}$   
 $M_0$  = initial mass of contaminant,  $\text{kg}$

#### 4.7 ANALYSIS OF FAILURE MODES

Phytoremediation systems are like any other treatment scheme; one cannot simply walk away from them and expect success. There are events that can cause failure that should be realistically assessed at the outset. These include killing frosts, wind storms, animals (voles, deer, beaver), disease or infestation (fungus, insects), and latent toxicity. A contingency fund should be provided for periodic replanting of a certain percentage of the site in order to ensure a viable vegetation system.

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## 5.0 EXAMPLES

Equations (1 through 4) from Section 4.0 can be applied to most sites where soil clean-up regulations are known for metals or organic contaminants. Two examples follow, one for TCE treatment by phytotransformation and another for lead removal by phytoextraction, which demonstrate the use of the design equations.

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### Organics - Example 1)

TCE residuals have been discovered in an unsaturated soil profile at a depth of 3 meters. From lysimeter samples, the soil water concentration is approximately 100 mg/L. Long cuttings of hybrid poplar trees will be planted through the waste at a density of 1500 trees per acre for uptake and phytotransformation of the TCE waste. By the second or third year, the trees are expected to transpire 3 acre ft/yr of water (36 in/yr) or about 600 gal/tree per year. Estimate the time required for clean-up if the mass of TCE per acre is estimated to be 1000 kg/acre, and the clean-up standard has been set at 100 kg/acre (90% clean-up).

$$U = (\text{TSCF}) (T) (C) \quad (1)$$

where TSCF = 0.74 from Table 3

$$T = (600 \text{ gal/tree-yr})(1500 \text{ tree/acre})(3.89 \text{ L/gal}) = 3.5 \times 10^6 \text{ L/acre-yr}$$

$$C = 100 \text{ mg/L (given)}$$

$$U = 2.59 \times 10^8 \text{ mg/acre-yr} = 259 \text{ kg/acre-yr}$$

$$k = U/M_o \quad (2)$$

$$k = (259 \text{ kg/yr})/1000 \text{ kg}$$

$$k = 0.259 \text{ yr}^{-1}$$

$$t = -(\ln M/M_o)/k \quad (4)$$

$$t = -(\ln 100/1000)/k$$

$$t = 8.9 \text{ yr}$$

Most of the TCE that is taken-up by the poplars is expected to volatilize slowly to the atmosphere. A portion will be metabolized by the leaves and woody tissue of the trees.

### Metals - Example 2)

Lead at a lightly contaminated Brownfield Site has a concentration in soil of 600 mg/kg to a depth of one foot. The clean-up standard has been set at 400 mg/kg. Indian mustard, *Brassica juncea*, will be planted, fertilized, and harvested three times each year for phytoextraction. Using small doses of EDTA, it is possible to achieve concentrations in the plant of 5000 mg/kg (dry weight basis), and harvestable densities of 3 tons dry matter per crop. Estimate the time required for clean-up.

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$$U = \text{Uptake Rate} = (5000 \text{ mg/kg}) (9 \text{ tons/acre-yr}) (908 \text{ kg/ton}) \\ = 4.09 \times 10^7 \text{ mg/acre-yr} = 40.9 \text{ kg/acre-yr}$$

$$M_o = \text{Mass of Pb in soil at a dry bulk density of } 1.5 \text{ kg/L}$$

$$M_o = (600 \text{ mg/kg})(1.5 \text{ kg/L})(1 \text{ ft})(43,560 \text{ ft}^3/\text{acre-ft})(28.32 \text{ L/ft}^3) \left( 10^{-6} \frac{\text{mg}}{\text{kg}} \right)$$

$$M_o = 1110 \text{ kg/acre (initial mass in soil)}$$

$$M = 740 \text{ kg/acre (clean-up standard of } 400 \text{ mg/kg)}$$

We assume zero-order kinetics (constant rate of Pb uptake each year) because EDTA will make the lead continue to be bioavailable to the sunflowers.

$$t = \frac{M_o - M}{U} = 9.0 \text{ yr}$$

The time to clean-up may actually be somewhat less than 9 years if Pb migrates down in the soil profile with EDTA addition, or if tillage practices serve to "smooth out" the hot spots. Regulatory clean-up levels are usually based on a limit that cannot be exceeded, such as 400 mg/kg, and soil concentrations would need to be analyzed to ensure compliance at the end of each year.

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## 6.0 COST

Phytoremediation is very competitive with other treatment alternatives. It is aesthetically pleasing and its public acceptability is high. Darlene Bader of the U.S. Army Environmental Center at Aberdeen Proving Ground, reports that two anaerobic wetlands cells followed by two aerobic cells with canary grass were successful in removing TNT at 30% of the cost of granular activated carbon treatment (Table 2). Tables 4 through 6 provide three different estimates for phytoremediation versus competing technologies. In Table 4, a five year cost comparison is made for a phytoremediation design versus a pump and treat system with reverse osmosis for nitrate contaminated groundwater. Phytoremediation is less than half the cost of the pump and treat technology. Table 5 shows the estimated cost advantage of phytoextraction for metals compared to *in situ* fixation, excavation and landfilling in a RCRA approved hazardous waste facility, and soil extraction. Phytoremediation is far less expensive, but it requires five years rather than shorter periods for the competing technologies. In Table 6, the advantage of phytoremediation on petrochemical wastes is shown relative to competing technologies. Once again, phytoremediation offers cost advantages, but the trade off is the amount of time that is required to achieve treatment to action levels.

Phytoremediation is most comparable to *in situ* bioremediation and natural attenuation. In these technologies, mathematical modeling and monitoring are necessary to demonstrate the effectiveness of the technology to regulatory agencies. The same will be true of phytoremediation.

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Table 4  
Five-Year Cost Comparison of Phytoremediation by Hybrid Poplar Trees  
versus Conventional Pump and Treat  
(Gatliff, E.G., 1996)

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1. Phytotransformation

Design and Implementation	\$ 50,000
Monitoring Equipment	
Capital	10,000
Installation	10,000
Replacement	5,000
5-Year Monitoring	
Travel and administration	50,000
Data collection	50,000
Reports (annual)	25,000
<u>Sample analysis</u>	<u>50,000</u>

TOTAL \$ 250,000

2. Pump and Treat (3 wells and Reverse Osmosis System)

Equipment	\$ 100,000
Consulting	25,000
Installation/Construction	100,000
5-Year Costs	
Maintenance	105,000
Operation (electricity)	50,000
Waste disposal	180,000
<u>Waste disposal liability</u>	<u>100,000</u>

TOTAL \$ 660,000

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Table 5  
Cost Advantage of Phytoextraction for Metals  
(Phytotech Technical Summary, 1997)

Type of Treatment	Cost/m <sup>3</sup> (\$)	Time Required (months)	Additional factors/expense	Safety Issues
Fixation	90-200	6-9	Transport/excavation Long-term monitoring	Leaching
Landfilling	100-400	6-9	Long-term monitoring	Leaching
Soil extraction, leaching	250-500	8-12	5,000 m <sup>3</sup> minimum Chemical recycle	Residue disposal
Phytoextraction	15-40	18-60	Time/land commitment	Residue disposal

Table 6  
Cost Advantage of Phytoremediation (Rhizosphere Bioremediation)  
of Soils Using Fine-Rooted Grasses Compared to Other Techniques  
(E. Drake, Exxon, Anandale, NJ, personal communication)

Type of Treatment	Range of Costs \$/Ton
Phytoremediation	\$10-35
In situ Bioremediation	\$50-150
Soil Venting	\$20-220
Indirect Thermal	\$120-300
Soil Washing	\$80-200
Solidification/Stabilization	\$240-340
Solvent Extraction	\$360-440
Incineration	\$200-1,500

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## 7.0 REGULATORY ISSUES

Phytoremediation is too new to be approved by regulatory agencies in *pro forma* reviews. The design team needs to work with regulatory personnel early and often to obtain a satisfactory solution for all parties at the site. Experience dictates that EPA and state agency personnel appreciate being involved at the conceptualization stage because they are interested in testing this emerging technology also. The main question that regulators must answer is whether phytoremediation can remediate the site to standards and reduce risk to human health and the environment.

The answer to this question requires pilot studies and demonstrations on a variety of wastes. This process is beginning to occur with a number of demonstrations listed in Table 2. The questions that remain for most of these projects are the same as those for bioremediation or natural attenuation:

- Can it clean-up the site to below action levels? On what time scale?
- Does it create any toxic intermediates or products?
- Is it as cost-effective as alternative methods?
- Does the public accept the technology?

The answer to the latter two questions appears to be positive because phytoremediation has a large impetus at the present time. The answer to the first two questions will determine whether phytoremediation will become a major new technology in the future.

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## 8.0 CONCLUSIONS

Phytoremediation is an emerging technology for contaminated sites that is attractive due to its low cost and versatility. It is not a panacea for hazardous waste problems, but it shows tremendous potential in several applications for treatment of metals and organics at sites where contamination is shallow. The role of enzymes, metabolites, and the selection of plant systems for various wastes must be better understood. Plants have the ability to withstand relatively high concentrations of pollutants; they can sometimes take-up the chemicals and convert them to less toxic products, and they are known to stimulate degradation of organics in the rhizosphere. The technology has not been demonstrated conclusively at many sites to date, and it remains to be seen if it is effective at full scale. Table 7 is a summary of some of the key factors required for the success of phytoremediation.

Table 7. Summary of Phytoremediation Critical Success Factors and Conditions

Phytoremediation Process	Critical Success Factors/Design Considerations	Conditions for Optimum Likelihood of Success	Basis	Data Needs*	Vegetation
Phytotransformation	uptake by plant; bound residue or metabolism/volatilization required	$\log K_{ow} = 1-3.5$ ; nontoxic concentrations	moderately hydrophobic organics taken-up	toxicity, fate	trees, grasses
Rhizosphere Bioremediation	degradation by microbes; dense root system needed	compounds amenable to aerobic biodegradation	dense roots sorb chemicals and enhance microbial degradation	toxicity, fate	trees, grasses, legumes
Phytostabilization	hydraulic control, soil stabilization, immobilization	vigorously growing roots; hydrophobic or immobile chemicals	roots hold soil and water, immobilize metals	toxicity, fate	trees, grasses, legumes
Phytoextraction	plant productivity accumulation in harvestable portion of plant	>3 tons dry matter/acre-yr; >1,000 mg/kg metals lightly contaminated soil near to clean-up standard	vigorous plant growth provides acceptable uptake rate high ability to accumulate contaminants desirable	toxicity, fate	terrestrial plants or aquatic emergent plants for sediments
Rhizofiltration	sorption/filtration by roots; water in contact with roots; hydraulic detention time	plant densities 200-1000 grams/m <sup>2</sup> ; hydraulic detention time of several days	roots sorb and immobilize contaminants	toxicity, fate	aquatic emergent or submergent plants

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## 9.0 GLOSSARY

**Bound residues** - chemical contaminants that are not extractable from plant tissues by conventional methods (covalent bonding, polymerization, or lignification within the plant)

**Exudates** - release of soluble organic matter from the roots of plants to enhance availability of nutrients or as a by-product of fine root degradation

**Lignification** - the synthesis of lignin and woody tissue by plants which may incorporate chemical contaminants and immobilize them from the environment

**Macropores** - openings in the soil matrix caused by worms, burrowing animals, old root channels or soil properties that allow the relatively free flow of water and contaminants through soil

**Phytoextraction** - the use of plants at waste sites to accumulate metals into the harvestable, above-ground portion of the plant and, thus, to decontaminate soils

**Phytostabilization** - the use of plants to immobilize contaminants *in situ* by decreasing soil erosion and curtailing vertical migration of contaminants to groundwater by transpiration (hydraulic control)

**Phytotransformation** - the uptake and transformation (metabolism) or volatilization of organic chemical contaminants by plants as an *in situ* treatment technology

**Rhizofiltration** - the use of plant roots and rhizosphere to sorb, concentrate, transform, and precipitate organic and metal contaminants from surface water, groundwater, or wastewater

**Rhizosphere** - the soil profile in close contact with roots of plants, usually taken to be the soil within 1 mm of roots and fine roots

**Rhizosphere bioremediation** - the microbial transformations of organic contaminants by bacteria, fungi, and protozoans within the biologically-rich zone of the immediate vicinity around plant roots

**Root turnover** - the rapid decay of fine roots in the soil profile by endogenous respiration

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

Prepared for:

U.S. Environmental Protection Agency  
Office of Solid Waste and Emergency Response  
Technology Innovation Office  
Washington D.C. 20460

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## 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.

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**

EVALUATION FACTOR	TECHNOLOGY			
	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.

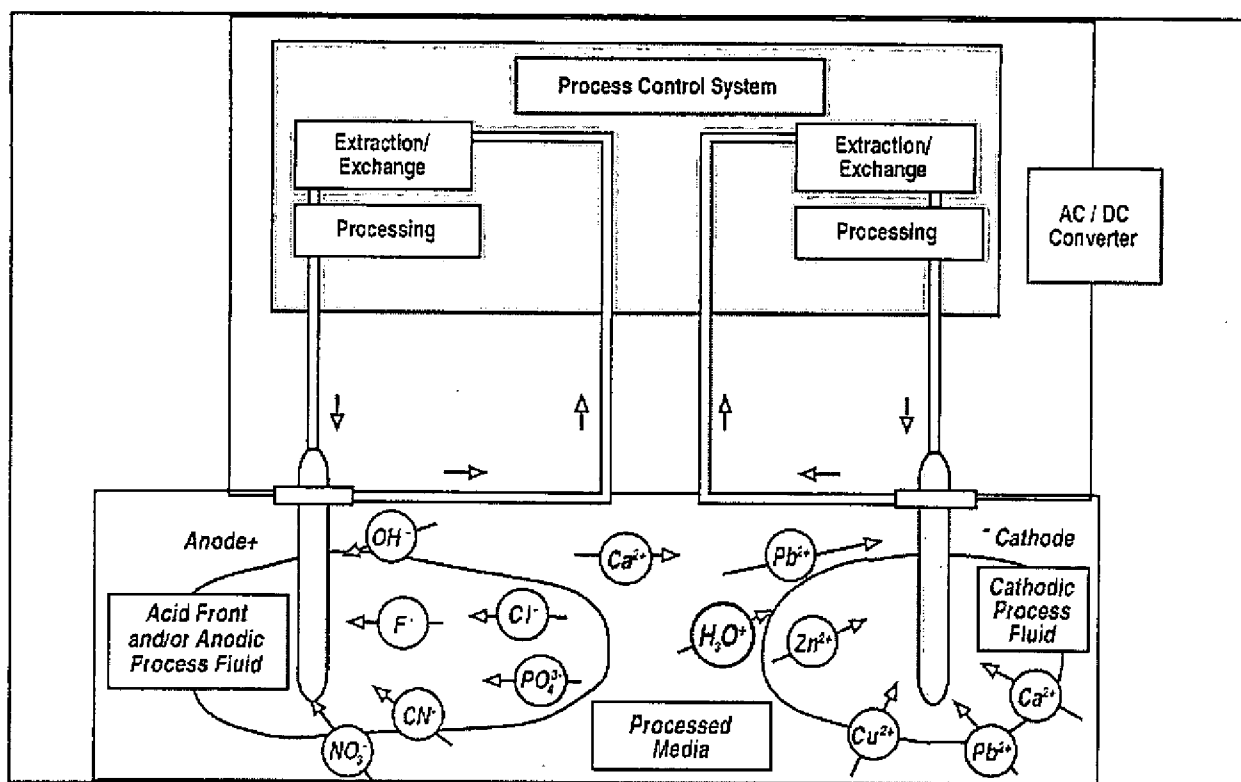
Electrokinetics can be efficient in extracting contaminants from fine-grained, high-permeability soils. A number of factors determine the direction and extent of the migration of the contaminant. Such factors include the type and concentration of the contaminant, the type and structure of the soil, and 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"> <li>• Depth of soil that is amenable to treatment depends on electrode placement.</li> <li>• Best used in homogeneous soils with high moisture content and high permeability.</li> </ul>	
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 Electrokinesis 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<sup>®</sup>) 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<sup>®</sup>) process. The process which incorporates electrokinetic technology, normally requires 24 to 48 hours for complete remediation of the substrate. BEK<sup>®</sup> is a mobile unit that remediates ex situ soils on site. GII also has developed a solution treatment technology (EIX<sup>®</sup>) 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].

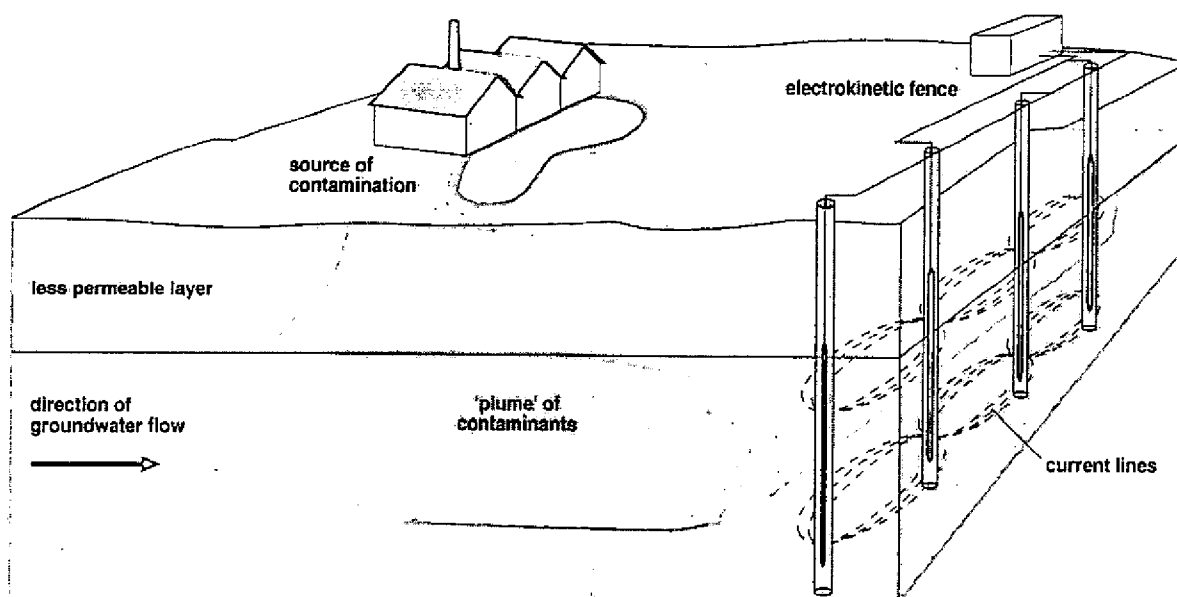
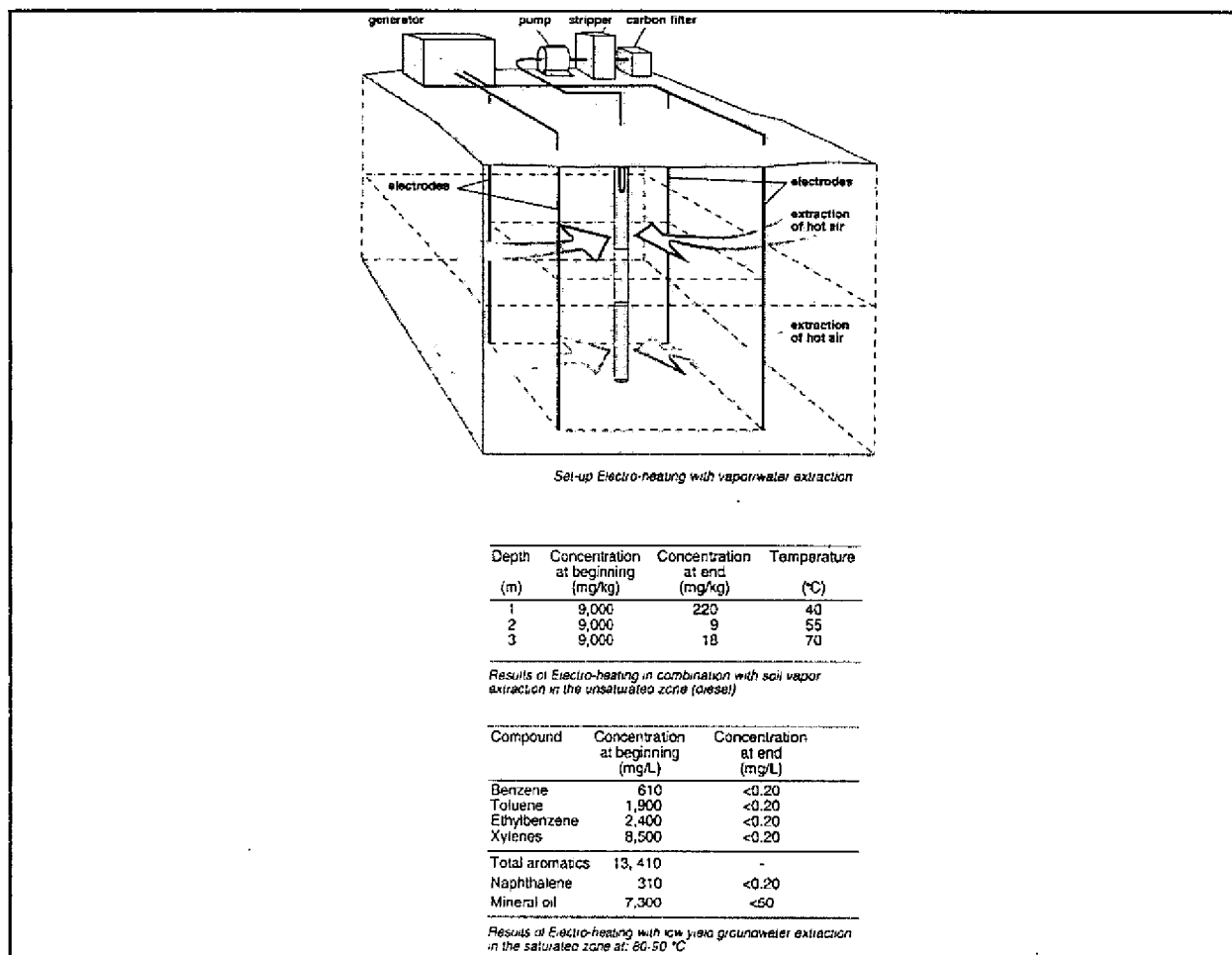


Figure 3. Schematic View of Contaminated Plume Stopped by An Electrokinetic Fence [10]



**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<sup>R</sup> process with a patented cylinder to control buffering conditions in situ.

An ion exchange polymer matrix called IsoLock<sup>R</sup> 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].

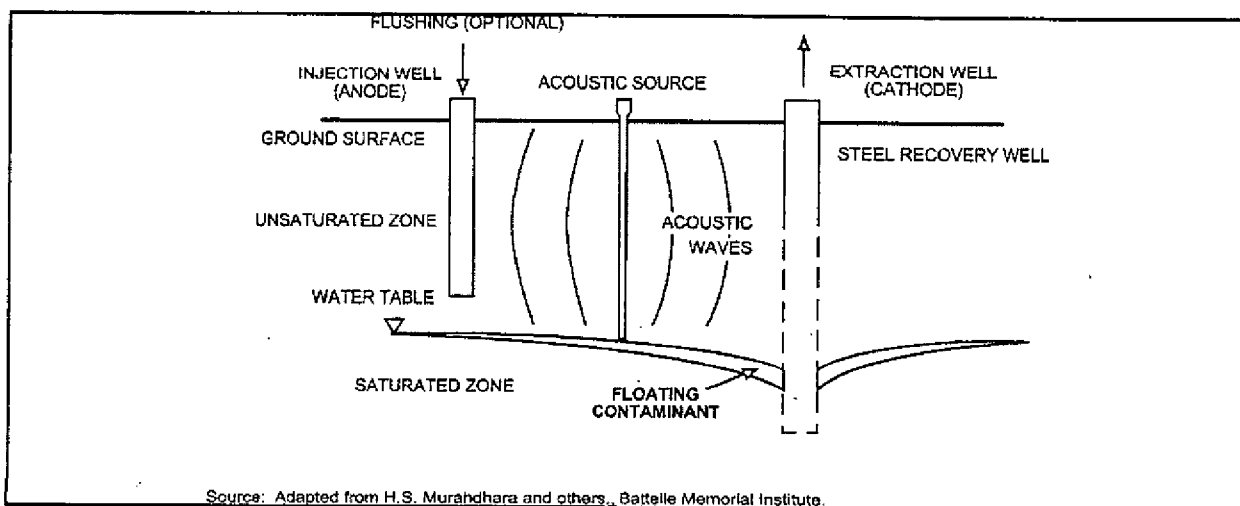


Figure 5. Electroacoustical Soil Decontamination Process [13]

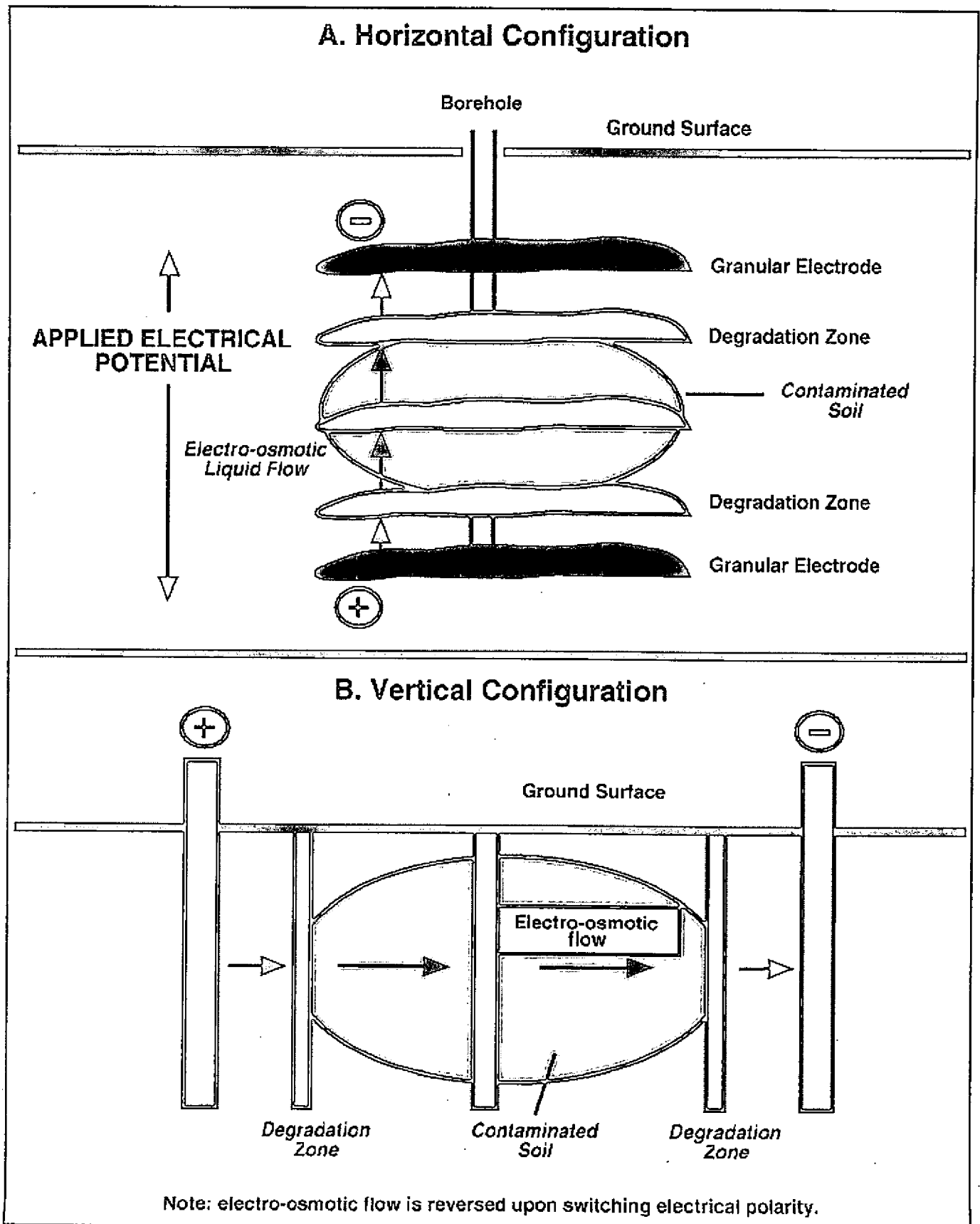


Figure 6. Schematic Diagram of the Lasagna™ Process [11]



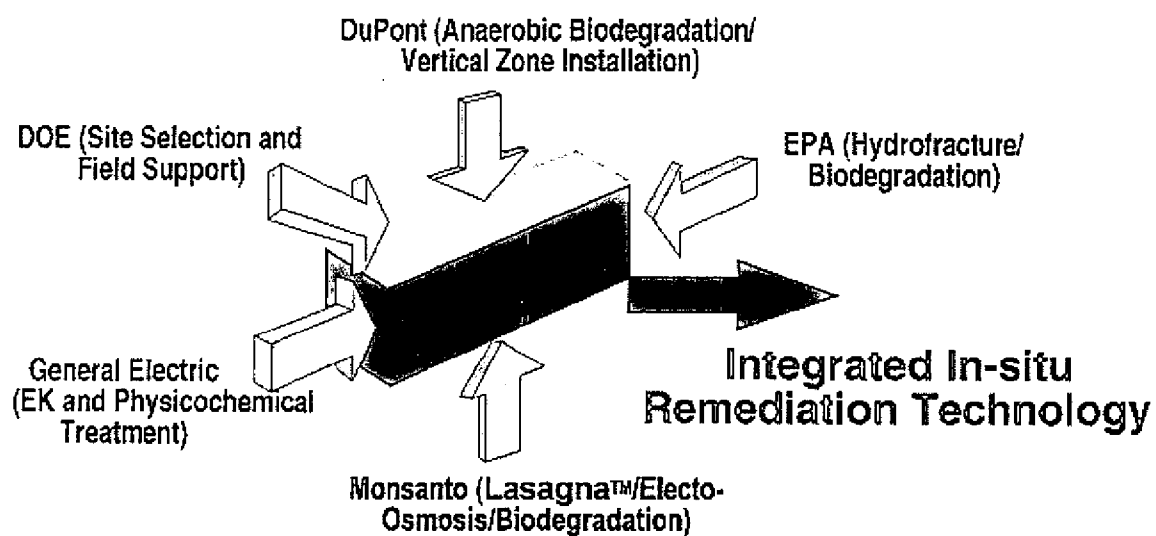


Figure 7. Integrated In-Situ Remediation: Consortium [11]

### 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 ( $\text{m}^3$ ) per day or about \$0.40/ $\text{m}^3$  per day, (@ \$0.03 /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/ $\text{m}^3$  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 /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/cubic yard ( $\text{yd}^3$ ) [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 Lasagna<sup>TM</sup> 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 <sup>3</sup> )	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  $1 \times 10^{-7}$  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
Steve Clark	Geokinetics International, Inc.	(510) 254-2335
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**

<b>General Characteristics</b>	
<ul style="list-style-type: none"> <li>• Best used at sites with low to moderate disperse metals content and with soil media that will support plant growth.</li> <li>• Applications limited to depth of the root zone.</li> <li>• Longer times required for remediation compared with other technologies.</li> <li>• Different species have been identified to treat different metals.</li> </ul>	
<b>Approach #1 - Phytoextraction (harvest)</b>	<b>Approach #2 - Phytostabilization (root-fixing)</b>
<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**

<b>METAL</b>	<b>PLANT SPECIES</b>	<b>PERCENTAGE OF METAL IN DRY WEIGHT OF LEAVES (%)</b>	<b>NATIVE LOCATION</b>
Zn	<i>Thlaspi calaminare</i>	<3	Germany
	<i>Viola species</i>	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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## 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].

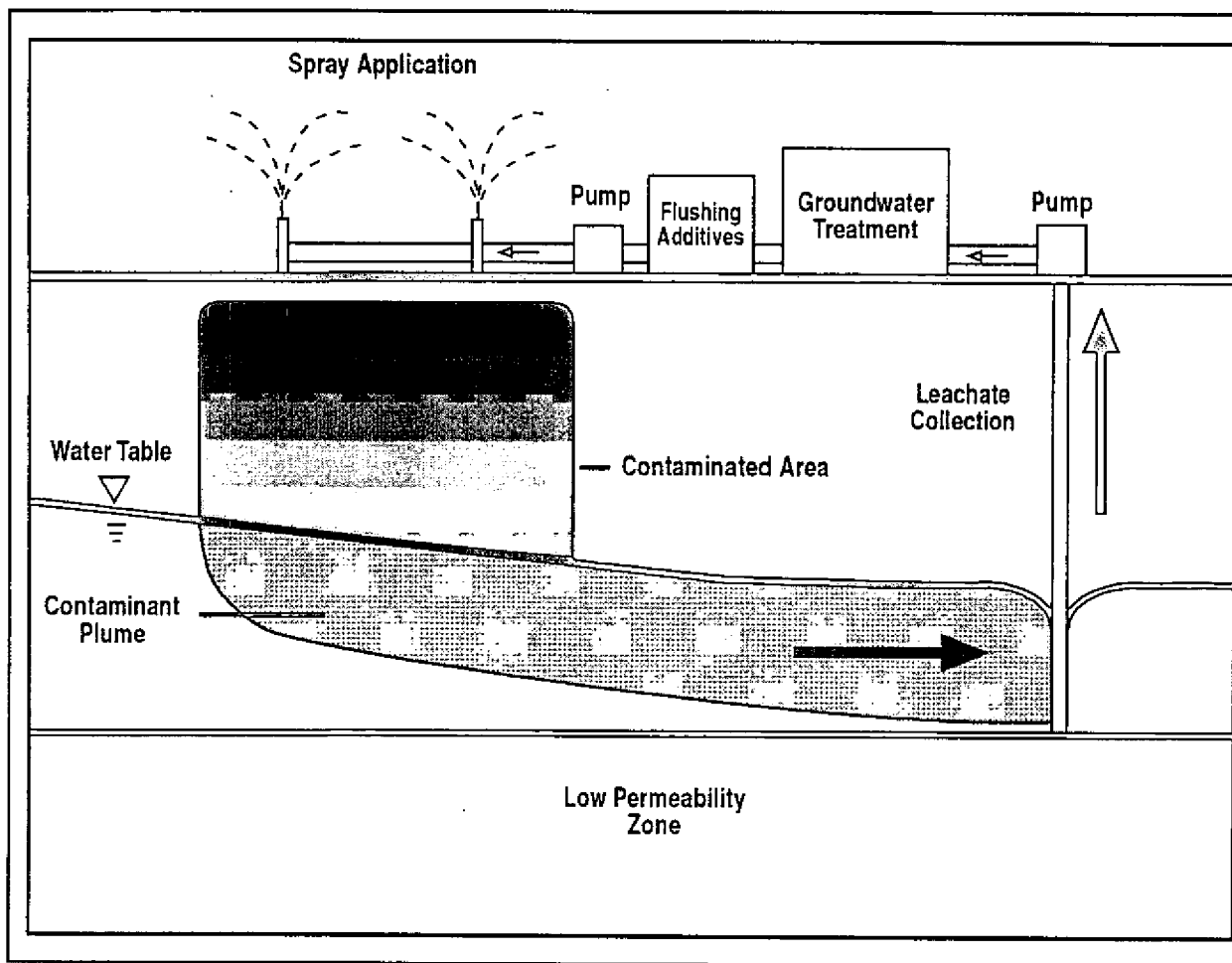
Once the infiltrated or percolated solution has flushed the contaminants to a certain location, the contaminated fluids must be extracted. Extraction techniques include vacuum extraction methods in the vadose zone and pump-and-treat systems in the saturated zone.

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**

<b>General Characteristics</b> <ul style="list-style-type: none"> <li>• Best used in soils with high permeability.</li> <li>• Different delivery systems available to introduce flushing solutions.</li> <li>• Cost is primarily influenced by potential need for interim containment, the depth of contamination, and the time required for operation.</li> <li>• 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.</li> </ul>	
<b>Approach #1 - Water flushing</b>	<b>Approach #2 - Reagent flushing</b>
<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"> <li>- 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.</li> <li>- pH adjusters and chemical binders also are being studied for potential applicability to metals.</li> <li>- Surfactants are primarily targeted for removal of organic contaminants.</li> </ul>



**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 ( $\text{CaCl}_2$ ) 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  $\text{CaCl}_2$ . 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  $\text{CaCl}_2$ , 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<sup>®</sup> 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 CaCl<sub>2</sub> 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 (CaCl<sub>2</sub>) [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.

#### 5.0 REFERENCES

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  $1 \times 10^{-3}$  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**

<b>General Characteristics</b> <ul style="list-style-type: none"> <li>• Commercially available</li> <li>• Cost is affected by the depth of the contamination, the degree of homogeneity of soil, the presence of debris, and excess moisture.</li> </ul>	
<b>Approach #1 - Reagent-based In Situ Stabilization</b>	<b>Approach #2 - Vitrification</b>
<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  $1 \times 10^{-6}$  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

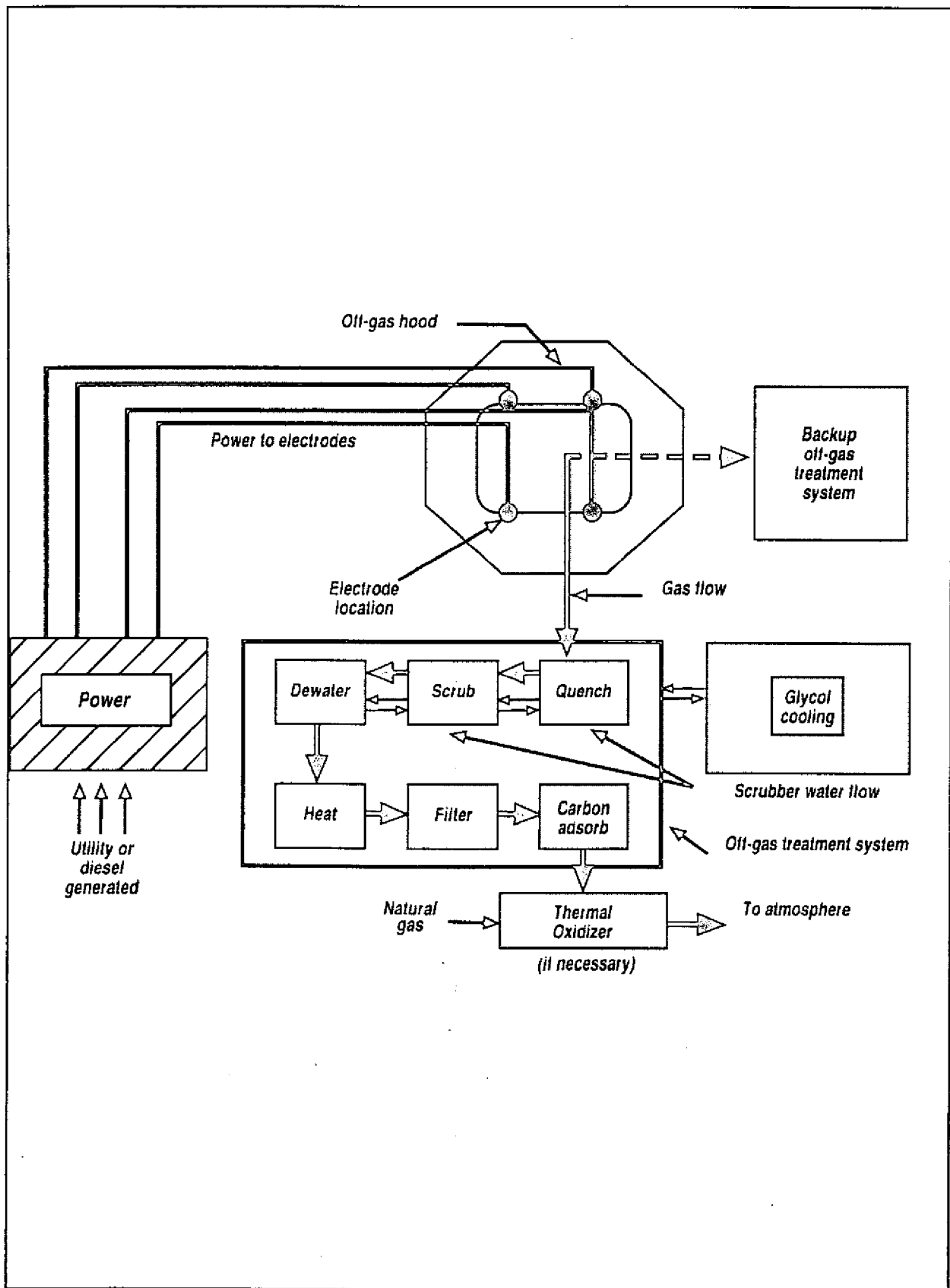


Figure 9. Geosafe In Situ Vitrification Process [3]

### **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
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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

### Name

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#### Electrokinetics

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Trish Erickson	EPA - NRMRL
Bob Thurnau	EPA - NRMRL
Mike Royer	EPA - NRMRL
Jeff Marquesse	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  
REMEDIATION 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  $\text{As}_2\text{O}_3$ , 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 ( $\text{FeAsS}_4$ ), 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 ( $\text{CdS}$ ) and otavite ( $\text{CdCO}_3$ ) 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 ( $\text{FeCr}_2\text{O}_4$ ). 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 ( $\text{HgS}$ ), 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 ( $11.35 \text{ g/cm}^3$ ) and low melting point ( $327.4^\circ\text{C}$ ), and can be cast, rolled, and extruded. The most important lead ore is galena ( $\text{PbS}$ ). Recovery of lead from the ore typically involves grinding, flotation, roasting, and smelting. Less common forms of the mineral are cerussite ( $\text{PbCO}_3$ ), anglesite ( $\text{PbSO}_4$ ), and crocoite ( $\text{PbCrO}_4$ ).

### 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 ( $\gamma$ -FeOOH,  $\alpha$ -SiO<sub>2</sub>, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). 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 As<sub>2</sub>O<sub>3</sub> or as anionic arsenic species leached from As<sub>2</sub>O<sub>3</sub>, 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 (H<sub>2</sub>AsO<sub>3</sub>CH<sub>3</sub>) and dimethylarsinic acid ((CH<sub>3</sub>)<sub>2</sub>AsO<sub>2</sub>H), which are active ingredients in many pesticides, as well as the volatile compounds arsine (AsH<sub>3</sub>) and its methyl derivatives [i.e., dimethylarsine (HAs(CH<sub>3</sub>)<sub>2</sub>) and trimethylarsine (As(CH<sub>3</sub>)<sub>3</sub>)]. 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 (Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>) 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 CO<sub>2</sub> from the air will result in formation of CaCO<sub>3</sub> and release of arsenate. In sodic soils, sufficient sodium is available, such that the mobile compound Na<sub>3</sub>AsO<sub>4</sub> can form. The slightly less stable manganese arsenate (Mn<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>) forms in both acidic and alkaline environments, while iron arsenate is stable under acidic soil conditions. In aerobic environments, H<sub>3</sub>AsO<sub>4</sub> predominates at pH <2 and is replaced by H<sub>2</sub>AsO<sub>4</sub>, HAsO<sub>4</sub><sup>2-</sup> and AsO<sub>4</sub><sup>3-</sup> as pH increases to about 2, 7, and 11.5, respectively. Under mildly reducing conditions, H<sub>3</sub>AsO<sub>3</sub> is a predominant species at low pH, but

is replaced by  $\text{H}_2\text{AsO}_3^-$ ,  $\text{HAsO}_3^{2-}$ , and  $\text{AsO}_3^{3-}$  as pH increases. Under still more reducing conditions and in the presence of sulfide,  $\text{As}_2\text{S}_3$  can form.  $\text{As}_2\text{S}_3$  is a low-solubility, stable solid.  $\text{AsS}_2^-$  and  $\text{AsS}_3^{3-}$  are thermodynamically unstable with respect to  $\text{As}_2\text{S}_3$ . Under extreme reducing conditions, elemental arsenic and volatile arsine ( $\text{AsH}_3$ ) can occur. Just as competition between cationic metals affects mobility in soil, competition between anionic species (chromate, arsenate, phosphate, sulfate, etc.) affects anionic fixation processes and may increase mobility.

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

At metal-contaminated sites, mercury can be present in mercuric form ( $\text{Hg}^{2+}$ ), mercurous form ( $\text{Hg}_2^{2+}$ ), elemental form ( $\text{Hg}^0$ ), or alkylated form (e.g., methyl and ethyl mercury).  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$  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  $\text{HgCl}_2$  is formed. Mercuric mercury also forms complexes with soluble organic matter, chlorides, and hydroxides that may contribute to its mobility. In strong reducing conditions,  $\text{HgS}$ , a very low solubility compound is formed.



## **TYPING CONTROL SHEET**

Work Assignment No. : 256\01107707.TD  
Directory Name : O:\256\01107707.TD  
Document Name : metals2.rpt

**TYPIST** **DATE**

KO 04/09/97

## **WORDPERFECT 7.0 DOCUMENT**

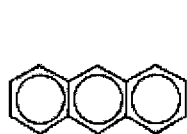
## Land Remediation

### Part I - Introduction

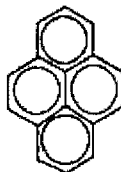
Throughout the industrial era, mining, manufacturing and chemical works have contaminated the land which they have exploited, or on which they have been built. The most common contamination at such sites is by heavy metals (e.g. Pb, Cd, Hg) or by cocktails of organic compounds (including polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pesticides). Typically, these sites have been abandoned, either on completion of mineral exploitation (in the case of mining), or when the manufacturing and chemical companies have either gone bankrupt or moved on. However, as available land within cities becomes increasingly scarce, and prices rise, the rehabilitation of contaminated land becomes more and more economical viable. In addition, such land recycling has environmental advantages over using ever more rural land - provided contamination of the site can be reduced to a level acceptable to legal and health authorities.

#### Organic Compounds Commonly Found in Soil/Sediments

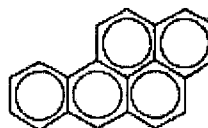
##### Polyaromatic Hydrocarbons (PAHs)



Anthracene

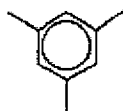


Pyrene

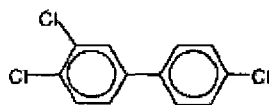


Benzo[a]pyrene

##### Other Organics



Trimethyl Benzene



Polychlorinated Biphenyl (PCB)  
-one of 209 possible isomers

At its simplest, land remediation involves removing the contaminated soil, taking it elsewhere, and replacing it with fresh topsoil. Such a technique however, does not address the underlying problem of contamination, merely moves it elsewhere in a largely unmodified form. The techniques examined in this report focus on either fractionating contaminants into a smaller mass, or chemically (or biologically) breaking them down into less toxic compounds.

This report is divided into two main parts. The following section critically examines the aims and objectives of the research program at Oxford University, being developed by Dr. Luet Wong. The final section presents a broader overview of other techniques for land remediation which are currently being studied or evaluated in other institutions in both Europe and the United States.

### Part II - Research at Oxford University

This part of the report is held on Fujita Research's secure web server at [pineapple.fujita.com](http://pineapple.fujita.com)

### Part III - Other Land Remediation Research

## 1.0 Phytoremediation

### 1.1 Phytoremediation of sites contaminated by metals

Research into the phytoremediation of sites contaminated by metals has largely focused on the use of hyper-accumulating plants - plants which take metals up into their leaves and root systems. Studies (including those by Dr. Bellhouse's group at Oxford), have shown that hyperaccumulators can accumulate very high levels of certain metals in their tissues. However, despite the excitement such hyperaccumulators have generated, they are only now (summer 1997) entering field trials on real-world contaminated sites. A major problem has traditionally been, that while up to 4% w/w of metals such as Zinc can be accumulated, the uptake of heavy metals such as lead and cadmium is often orders of magnitude less. In addition, many hyperaccumulators have tolerance only to a small number of metals. Many industrial sites are a cocktail of a number of inorganic pollutants, and some of these may kill off an otherwise metal-tolerant hyperaccumulator.

Although of little use in remediation of sites contaminated by heavy metals, hyperaccumulators which take up high levels of relatively non-toxic metals are beginning being to be used in phyto-mining - extraction of economically valuable metals into biomass (from which they are processed). Metals suitable for such phyto-mining include Ni, Cu, and precious metals such as Ag and Au. Although this field is only just beginning to develop, success has already been reported in the "phyto-mining" of Nickel.

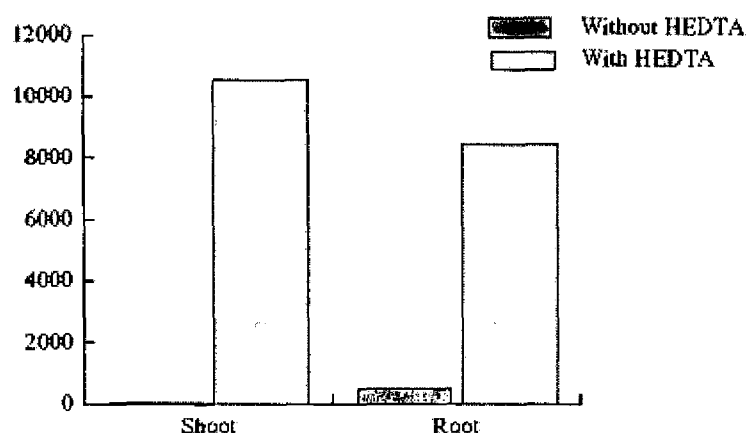
#### 1.1.1 Combination use of Chelates and Hyperaccumulators

One of the reasons that the accumulation of heavy metals in biomass is so low is that heavy metals adsorb strongly to soil particles, limiting their bio-availability. Therefore, one method of increasing uptake of such metals is simply to increase their bio-availability. Chelating solutions, such as Fe-EDTA have for some time been used in soil washing. They act to increase the solubility of metals in the soil, by causing metal ions to bind strongly to organic ligands rather than to the soil particles. Researchers at a number of universities, and at Phytotech, a New Jersey Company, have recently begun examining the combined use of chelates and hyperaccumulators in a series of field studies. These findings of these studies are now (September 1997) just beginning to be published in the scientific literature. They show that the effect of combining chelating compounds with hyperaccumulators has been remarkable. Not only have they succeeded in the primary aim of increasing Pb availability (and therefore uptake), but also in changing the way plants store the Pb they take up. With chelating compounds, Pb no longer accumulates in the roots of the plants, but in the foliage, making it easier to remove.

The Phytotech studies, undertaken at a brownfield site in New Jersey (formerly used by the makers of Magic Markers) showed the combination use of *Brassica juncea* (Indian mustard) and chelates resulted in foliage lead concentrations of 1.5% w/w. At this rate, levels of lead should be brought below legal requirements in just two summers.

In another recent paper, researchers from DuPont investigated uptake by corn and ragwort from a contaminated soil (Pb = 2 500 mg/kg), both with and without a chelating compound (HEDTA) applied. The effects of HEDTA treatment of the soil (at 2.0 g/kg) were similarly dramatic to those reported by other researchers. In soil not treated with HEDTA root concentration in corn did not exceed 500 mg/kg, and shoot concentrations were only 40 mg/kg. With HEDTA treatment Pb concentration increased to almost 8 500 mg/kg, with shoot concentrations at 10 600 mg/kg (1.6%). As a result of such rapid accumulation of such high levels of lead the plants died within one week. However this premature plant death was not considered important in light of the amount of lead transferred into the biomass (and thus removed from the soil). It is clear that plant biomass needs to be achieved prior to application of the chelating compound to the soil. Calculations based on the above field experiments suggest that reduction of lead levels from the 2500 mg/kg found at the site to the legal limit of 600 mg/kg would require 14-16 crops of corn (7-8 years at 2 crops/year).

Fig 4 Concentration (mg/kg) of Pb in roots and shoots of corn



The above experiments have shown the potential for the combined use of hyperaccumulators and chelating compounds in the removal of lead from contaminated land. However, there are other issues to be considered - particularly regarding the increased mobility of chelated lead. As the lead is no longer strongly sorbed to the soil it may penetrate to the water table or be washed off-site by rainwater.

Other work is being directed at the use of hyperaccumulators to remove Zinc and Cadmium - two metals which often exist as co-pollutants. The problem is often that Zinc accumulation inhibits uptake of Cadmium. Phytotech are working on this issue, and believe (through genetic modification) that they can develop strains of *Thlaspi caerulescens* which will accumulate up to 10 000 mg/kg (1%) Cd.

## 1.2 Phytoremediation of sites contaminated by organics

The phytoremediation of organic compounds in soil is a less straightforward process than that for inorganics, and can occur broadly through one of three main processes:

- (i) hyperaccumulation - analogous to the case for metals discussed previously
- (ii) phytovolatilization - where the contaminant is converted to a volatile form and enters the atmosphere
- (iii) phytodegradation - where the contaminant is broken down either by the plant or by associated bacteria

Since the late 1970s a number of studies (largely qualitative) have suggested that plants (or in the case of the third process - planting) can significantly reduce levels of certain organic compounds, particularly Organophosphates, polyaromatic hydrocarbons (PAHs), and organochlorines (such as PCBs, DDT, etc.). One, rather more rigorous study, has been undertaken by the Union Carbide Company, in association with Utah State University(3). Over three years, the study examined the efficiency of bioremediation (using a variety of grasses) of a clay soil contaminated with PAHs.

In the Union Carbide study, degradation of PAHs was thought to occur by one of three specific mechanisms:

- (i) cometabolism by root exudates and bacteria of higher molecular weight compounds (such as benzo[a]pyrene) which cannot be degraded by bacteria alone.
- (ii) ring cleavage in plant tissue to produce oxygenated PAH derivatives which are immobilized in the insoluble lignin fraction.
- (iii) complete degradation to CO<sub>2</sub> by plant seedlings.

Over the three year study, Verde Kleingrass was found to be particularly efficient at removing PAHs from the soil rootzone. Removal of the lower weight PAHs (Naphthalene (m/w = 128) through Fluoranthene (m/w=202)) was extremely successful (>90% removal). Removal of the higher molecular weight PAHs (Pyrenes, Chrysenes and

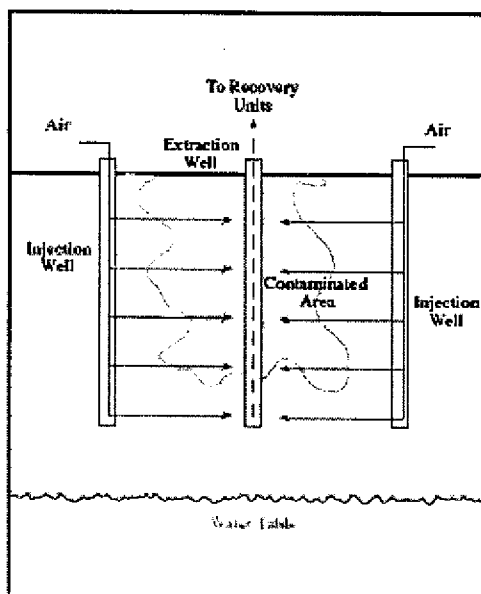
Benzopyrenes) was less dramatic (removal of about 50%). Although many other species of grasses proved equally effective at removing low weight PAHs from the root zone soil, all other species tested, showed increases in high molecular weight compounds over the unvegetated control sample (emphasizing the variability of phytoremediation, and the care with which plant species must be selected).

## 2.0 Air Stripping Methods

Air stripping is a well-established, in situ method for the removal of organic compounds from contaminated soils. Air is pumped down injection wells either side of the contamination zone and travels, due to pressure differential, to a central extraction well. From the extraction well, the contaminated air is processed by conventional methods - such as adsorption of pollutants onto charcoal. Air stripping is most effective at the treatment of the vadose region of the soil (i.e. the upper regions where water saturation is low and pore water is discontinuous). Soil permeability needs to be quite high, and contaminants need to be volatile or semivolatile. When the above conditions are met, contaminants exist in one of four phases: vapor, sorbed (soil), aqueous phase liquid, and non-aqueous phase liquid. The four phases are at equilibrium with one another; by lowering the vapor concentration (by injecting fresh air and removing the exhaust) contaminants are stripped from the soil. Recent research at the University of Calgary (4) has considered the effectiveness of air-stripping by using octane (C8) in laboratory studies and using the results in numerical models to estimate in situ behavior at a soil/air temperature of 20°C. Although affected by distance of air injection from the soil surface, depth of the water table and concentration of contaminants, air stripping seems likely to remove 60-65% of octane contamination. Clearly, higher temperatures and greater injection rates (the study adopted a Q value of 20kmol.s<sup>-1</sup>) would result in greater removal.

The results obtained suggest that air-stripping is a useful technique for removal of light, volatile organics, where total contaminant removal is not required, but levels are marginally too high to meet legal requirements.

Fig 5 Air Stripping of Contaminants



## 3.0 Soil Washing

Soil washing is the process of rinsing soils with liquid solutions (water, surfactants, organic solvents etc.) in order to remove contaminants. The soil washing may be accomplished in one of two ways - either ex situ or in situ. Ex situ washing requires the removal of the soil from the ground, sieving it, and feeding it through a washing unit (which can be on-site). Following washing the soil is dewatered and can be returned to the site. In Situ washing uses solvent extraction and reinjection to flush the soil, with minimal ground disturbance. Solvent is extracted from below the contaminated zone, treated, and reinjected upgradient of the contamination (or sprayed across the soil surface). As a result, one major consideration with in situ soil washing is potential contamination of the water table.

### 3.1 Aqueous Systems

The results of two studies on soil-washing in the United States have recently been published. (5,6) The first of these studies, based in the laboratory, examined the effects of volume of washing solution, addition of surfactants, and solution temperature on soil samples contaminated with ca. 1000 ppm PAHs. The results obtained suggested that under optimal conditions (a volume washing solution: weight of soil ratio of 4:1, 4% added surfactants, and a washing temperature of 60°C) approximately 70% of PAHs could be removed from the soil samples.

The second paper reports on the first full-scale soil washing for removal of inorganic compounds to be undertaken in the US. The method used was one which has previously been successfully used in the Netherlands. It exploits the fact that metal contamination is generally associated with fine grained particles. Soil and water are mixed to a slurry which is then placed into a hydrocyclone separator. Fine-grained material exits from the top of the separator, coarse-grained from the bottom. The fine grained is retained (as it is high in pollutants). The sandy, coarse, fraction is treated with surfactants in a air froth tank. The contaminated froth is added to the fine-grained contaminated material retained, while the sand, now relatively clean, is returned to the site.

The method was used to treat nearly 20 000 tonnes of soil on a contaminated site at New Jersey. Of these 20 000 tonnes 83% was returned to the soil, the other 17%, the highly contaminated fine sediment fraction, was removed for treatment off-site. Table 1 below shows the efficiency of such a clean-up.

Table 1 Soil Washing at New Jersey (all concentrations in mg/kg)

Contaminant	Untreated	Treated Sand	Fines (removed)
Chromium	500-5500	73	4700
Nickel	300-3500	25	2300
Copper	800-8500	110	5900

### 3.2 Supercritical Fluids

In analytical laboratories, the introduction of supercritical fluid extraction (SFE) has caused much excitement. A supercritical fluid is formed at high pressures and temperatures, and exhibits a behavior between that of a liquid and a gas. This behavior allows it interact more closely with adsorbed contaminants than liquids can. In addition supercritical extraction uses solvents which are non-toxic (most commonly CO<sub>2</sub>).

A paper recently published by researchers from Vanderbilt University has examined the feasibility of scaling-up SFE to deal with contaminated soil at industrial sites, using the results of a mathematical model based on laboratory scale experiments. There are difficulties arising from the pressures required for extraction of the soil, making semi-continuous feeding of soil into the unit (rather than continuous) a necessity. However, by extracting organics to activated carbon within the pressurized tank, many other pressure-related problems can be successfully overcome. Indeed such a unit has been used successfully in Germany at the pilot plant stage.

The findings were that the SFE process would be cheaper (\$US170/m<sup>3</sup>) than their calculated costs for bio-remediation (\$US300m<sup>3</sup>), and about 10% of the cost of incineration. Calculations by the research team suggest that a pilot plant would cost about \$US2.2 million. Such a plant would have a design life of 15 years, operating at 308K (35°C) at 120-330 bar pressure. Such a plant would treat about 20m<sup>3</sup> of soil per hour.

Clearly SFE is an emergent technology, but if laboratory removal of organics (99.8±0.2% of naphthalene and trimethylbenzene) could be achieved in the field, it would be a very attractive method for land remediation.

#### Conclusions

There are no simple conclusions to be drawn about land remediation, other than that is a field that will become more and more attractive as inner-city land prices continue to rise. There are many ideas about efficient ways to remediate contaminated sites, but all the technologies are at a relatively primitive stage. The ideal system has not been developed, and is likely it never will be. All have strengths and weaknesses, depending on the type of site contamination. However, this report shows some of the most promising technologies for major contaminant classes.

### ◉Bibliography

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## 4.5 Phytoremediation

(In Situ Soil Remediation Technology)

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Description	Synonyms	Applicability	Limitations
Data Needs	Performance	Cost	References
Site Information	Points of Contact	Vendor Information	Health & Safety

Technology	Description
<b>Soil, Sediment, and Sludge</b>	
<b>3.1 In Situ Biological Treatment</b>	
4.5 Phytoremediation	Phytoremediation is a process that uses plants to remove, transfer, stabilize, and destroy contaminants in soil and sediment. Contaminants may be either organic or inorganic.

### Description:

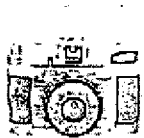


Figure 4-5:  
Typical In Situ  
Phytoremediation System

Phytoremediation is a process that uses plants to remove, transfer, stabilize, and destroy contaminants in soil and sediment. The mechanisms of phytoremediation include enhanced rhizosphere biodegradation, phyto-extraction (also called phyto-accumulation), phyto-degradation, and phyto-stabilization.

#### **Enhanced Rhizosphere Biodegradation**

Enhanced rhizosphere biodegradation takes place in the soil immediately surrounding plant roots. Natural substances released by plant roots supply nutrients to microorganisms, which enhances their biological activities. Plant roots also loosen the soil and then die, leaving paths for transport of water and aeration. This process tends to pull water to the surface zone and dry the lower saturated zones.

#### **Phyto-accumulation**

Phyto-accumulation is the uptake of contaminants by plant roots and the translocation/accumulation (phytoextraction) of contaminants into plant shoots and leaves.

#### **Phyto-degradation**



Phyto-degradation is the metabolism of contaminants within plant tissues. Plants produce enzymes, such as dehalogenase and oxygenase, that help catalyze degradation. Investigations are proceeding to determine if both aromatic and chlorinated aliphatic compounds are amenable to phyto-degradation.

#### **Phyto-stabilization**

Phyto-stabilization is the phenomenon of production of chemical compounds by plant to immobilize contaminants at the interface of roots and soil.

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#### **Synonyms:**

Vegetation-enhanced bioremediation.

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#### **Applicability:**

Phytoremediation may be applicable for the remediation of metals, pesticides, solvents, explosives, crude oil, PAHs, and landfill leachates.

Some plant species have the ability to store metals in their roots. They can be transplanted to sites to filter metals from wastewater. As the roots become saturated with metal contaminants, they can be harvested.

Hyper-accumulator plants may be able to remove and store significant amount of metallic contaminants.

Currently, trees are under investigation to determine their ability to remove organic contaminants from ground water, translocate and transpiration, and possibly metabolize them either to CO<sub>2</sub> or plant tissue.

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#### **Limitations:**

There are a number of limitations to phytoremediation in soil.

- The depth of the treatment zone is determined by plants used in phytoremediation. In most cases, it is limited to shallow soils.
- High concentrations of hazardous materials can be toxic to plants.
- It involves the same mass transfer limitations as other biotreatments.
- It may be seasonal, depending on location.
- It can transfer contamination across media, e.g., from soil to air.
- It is not effective for strongly sorbed (e.g., PCBs) and weakly sorbed contaminants.
- The toxicity and bioavailability of biodegradation products is not always known.
- Products may be mobilized into ground water or bioaccumulated in animals.
- It is still in the demonstration stage.
- It is unfamiliar to regulators.

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#### **Data Needs:**

A detailed discussion of these data elements is provided in Subsection 2.2.1 (Data Requirements for Soil, Sediment, and Sludge). In addition, detailed information is needed to determine the kinds of soil used for phytoremediation projects. Water movement, reductive oxygen concentrations, root growth, and root structure all affect the growth of plants and should be considered when implementing phytoremediation.

[Back to Top](#)**Performance Data:**

Currently, the Superfund Innovative Technology Evaluation (SITE) Program is attempting to demonstrate and evaluate the efficacy and cost of phytoremediation in the field at sites in Oregon, Utah, Texas, and Ohio.

USAEC is also leading the team of experts from EPA, Tennessee Valley Authority (TVA) and the Waterways Experimental Station (WES) to successfully demonstrate phytoremediation of explosive contaminated sites in Milan Army Ammunition Plant in Milan, TN.

[Back to Top](#)**Cost:**

US AEC estimated that the cost for phytoremediation of one acre of lead-contaminated soil to a depth of 50 cm was \$60,000 to \$100,000, whereas excavating and landfilling the same soil volume was \$400,000 to \$1,700,000.

[Back to Top](#)**References:**

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A comprehensive list of 850 references on phytoremediation are available at Remediation Technologies Development Forum (RTDF) Phytoremediation Action Team Web Site. Click to access

**RTDF Phytoremediation Bibliography**[Back to Top](#)**Site Information:**

- McCormick & Baxter SUPERFUND Site, Portland, OR (Wood treatment site)
- Argonne National Laboratory
- Cranev Island Fuel Terminal, U.S. Navv, Portsmouth, VA
- EPA S.I.T.E. Program, Ogden, Utah
- Ohio (Former metal plating site)
- DOE Demo: Savannah River Site, SC
- DOE Savannah River Site, SC

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# *Phytoremediation*

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## ABSTRACT

Phytoremediation is a relatively new (within the last 10 years) option for remediation of organic and inorganic contaminants in soil and sediment. Using plants for uptake, degradation or sequestration of contaminants is an aesthetically pleasing in-situ remediation alternative. It is also an economically pleasing option, in most cases, with the trade-off to lower costs being lengthy remediation.. Research into in-situ alternatives for heavy metal remediation led to the re-discovery of plants known as hyperaccumulators. Hyperaccumulators are plants that possess the inherent ability to take up heavy metals by as much as 5% of their own mass. In general these plants are tropical and lack the ability to propagate outside of their natural habitat. This inability for habitat adaptation has spurred research in genetic modification of indigenous plants for heavy metal uptake and/or sequestration. Other areas of research include biomass processing once metal uptake has occurred, biovolatilization and using plants for biomining and metals reclamation.

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## INTRODUCTION

We chose to look into phytoremediation because a recent talk given by one of the leading experts in the area of phytoremediation excited one of our team members. The idea of using plants for contaminant uptake was exceptionally appealing. It's non-invasive, non-destructive, aesthetically pleasing, and economically satisfying for those who need to do the remediation. The chemistry and physics of phytoremediation processes is inherent in some plants and the re-discovery of this ability lead to interest in applying phytoremediation to metal-contaminated sites. The capability of these plants, known as hyperaccumulators, to take up heavy metals has been genetically exploited and transformed into many different species of plants to expand the potential for phytoremediation. However, research continues in enhancing uptake rates and increasing the biomass capable of absorbing metals. Research also continues in expanding the applications of phytoremediation such as in the case of biomining, metals reclamation and biovolatilization. We used a variety of methods to obtain information about phytoremediation. As a result of attending the above mentioned talk, one of the team members received a large package of technical papers from the speaker. These papers, in turn, led to other literature sources of information from journals such as The Journal of Environmental Quality, Plant Physiology, and In vitro Cellular and Developmental Biology. The use of the Internet resulted in locating areas of research that are active in phytoremediation such as the University of Georgia, Rutgers University and UC-Berkeley. Books referred to in technical papers were consulted. And finally, a one-on-one interview with Scott D. Cunningham, Central Research and Development for the DuPont Company, produced useful information pertaining to current areas of research, obstacles that need to be overcome for widespread acceptance of phytoremediation and pronouncements on the future of phytoremediation.

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## RESULTS AND DISCUSSION

## I. Chemical and Physical Reactions

### 1. Processes of Phytoremediation

For plants to accumulate metals from the soil, the metals must mobilize into the soil solution[2]. Many metals, however, are bound in soils due to many factors such as, complexation with organic matter, sorption on oxides and clays, and precipitation of metals[3]. The bioavailability of metals is increased in soil through several means. One way plants achieve this is by secreting phytosidophores into the rhizosphere to chelate and solubilize metals that are soil-bound. Another technique to enhance metal uptake that plants use is the ability to reduce metals to a more soluble form amplifying the amount of bioavailable metals. By acidifying soil through the release of protons from their roots, plants can solubilize soil-bound heavy metals, as well[2]. These three factors account for natural means by which the bioavailability of heavy metals that were bound to soil can be increased. Much current phytoremediation research is concerned with manipulating the soil chemistry of contaminated sites to increase the bioavailability of metals in an effort to increase heavy metal uptake of plants. Because Lead is one of the most common and hazardous heavy metal contaminants, a large focus of research deals with its accumulation in plants. There are two main limiting factors involved with the phytoextraction of Pb. They are Pb's low bioavailability in soil and its poor translocation from the roots to shoots of a plant[4]. Research is also being done on the effects of altering the pH of soil through the use of ammonium containing fertilizers as well as organic acids like citric acid. Numerous studies show that decreasing the pH of soil lowers heavy metals ability to adsorb which then increases their bioavailability and hence phytoextraction.

- Comparison of phytoremediation vs. conventional technology(tech, cost, etc.)

### 2. Mechanisms of Metal Uptake

There are two pathways for solubilized heavy metals in soils to enter a plant. They are apoplastic (extracellular) and symplastic (intracellular). Apoplastic means are limited by a high cation exchange capacity of cell walls, however this can be somewhat avoided if metals are transported as non-cationic metal chelates[2]. Apoplastic transport is relatively unregulated, because water and dissolved substances can flow or diffuse without having to cross a membrane. Symplastic transport is more regulated due to the selectively permeable plasma membranes of the cells that control access to the symplast by specific or generic metal ion carriers or channels[1]. Although this means of access to the plant is more regulated than apoplastic entry, there is an apparent lack of selectivity in transmembrane carriers which allow non-essential heavy metals to compete with essential heavy metals from transport across a membrane. This also accounts for the phenomenon of non-essential heavy metals entering the cells via symplastic transport against a concentration gradient[2]. After heavy metal have entered the root they are either stored in the root or translocated to the shoots. Symplastic transport of heavy metals probably takes place in the xylem after they cross the Casparian strip which is the division between the endodermis and the epidermis. The vacuole is an important component for metal ion storage where they are often chelated either by organic acids or phytochelatins. Under certain conditions, the metal ions may form insoluble precipitates. Precipitation compartmentalization, and chelating are the most-likely major events that take place in resisting the damaging effects of metals. The mechanisms involved in transport of heavy metals in plants is not well understood, however phytoremediation is drawing attention to these processes and hyperaccumulating plants represent a wonderful test subject to enhance our understanding of the biology, chemistry and physics of plants and their transport. Organic complexes have been isolated from plants that bind to metals that are drawn into the plant tissue. Theories that explain this mechanism above is that metals exist as ions in water and when water passes through the membrane of the root of the plant, the metal ions are taken up as well. Thus osmosis is involved. The cortex of the root contains cellulose, which is associated with the water in the ground, thus water and inorganic salts can easily pass through. The next layer into the plant is the endodermis, which separates the cortex from the stele. The stele contain both the phloem, which conducts organic molecules, and the xylem, which conducts water and inorganic salts. Water and inorganic salts can not pass through the Casparian strip, which is a waxy material contained in the endodermis of the root. Instead the water passes through the

protoplasts. Therefore, any metals dissolved in water will pass through along with the water. It is believed that in order for water and the dissolved ions (salts and metals) to pass through the Casparian strip, active transport would be required. Ions cross the cortex through the inert cell walls, then through the endodermis by active transport. Ions cross the cell membranes of the epidermis, then through the cortex via cytoplasmic drift through plasmodesmata, which connect protoplasts of adjacent cells. However, still more studies need to be done in order to elucidate the exact mechanisms involved.

## **2. Complexation of metal in the tissue**

Chelators have been isolated from plants that are strongly involved in the uptake of heavy metals and the detoxification of them as well. Chelating agents like EDTA are applied to Pb contaminated soils that enhance Pb desorption from soil. This increases the amount of bioavailable Pb in the soil solution and a greater accumulation in plants is observed[4]. Research also shows that a more significant amount of Pb is translocated to the shoots when some synthetic Chelating agents are employed[4]. The mechanisms of these to results are poorly understood at this point, but the increase in bioavailability of Pb certainly pertains to the increase in phytoextraction. The biological response is proportional to the concentration of surface complexes. It indicates that the ligands tend to attenuate the biological response[12]. It is known that in many cases the chelators bind the heavy metals and most likely transport the complex into storage vesicles, such as vacuoles. Thus, cellular processes are not disturbed.

## **3. Detoxification**

Plant can change in the cell wall membrane to decrease permeability of roots to metals. Metals are taken up by plant but excreted through leaching, guttation, or shedding of leaf. Secretion of enzymes or molecules that render nearby environment of the roots favorable for bacteria to grow in order to detoxify heavy metals. Metals are changed into non-toxic compounds through its use in metabolism.

### **Related Websites:**

<http://www.anl.gov/LabDB/Current/Ext/H603-text.002.html> (Argonne National Laboratory).

<http://publish.uwrl.usu.edu>

<http://www.phytotech.com>

## **II. Toxicological Effect of Heavy Metals on Plants**

### **1. The effects of metal bioavailability on plants**

The nature of many "heavy metals" is such that they are toxic to plant life. For a plant to be a good remediator, it must be capable of resisting the toxic effects of "heavy metals."

- (1) displace essential metal ions from biomolecules
- (2) block essential functional groups of biomolecules
- (3) modify active conformation of biomolecules
- (4) disrupt integrity of biomolecules
- (5) modify some other biologically active agent

### **2. Plants resistant to the toxic effect of heavy metals**

Studies of plants in areas of naturally occurring high metal concentrations have focused on individual plant species. Characteristic plants have been recognized in soils overlying mineral ores. On the east

coast, high-nickel serpentinites are recognized by red cedar growths (Table 1). These trees have high nickel contents and low calcium/magnesium ratios. Other examples are known, but in most cases the use of plant species as an ore prospecting tool is only anecdotal. Recent work with tailings at abandoned mines in North Carolina and Wisconsin has also recognized plants that are characteristic of specific mineral-ore deposits. Some of these plants contain 1000's mg of copper, zinc, and lead per gram of plant material[6]. A multifloral system is present in each, indicating that these plants were introduced to the area recently.

### 3. Plants mechanism of resisting the toxic effects of heavy metals

Plants can survive in soils with high concentrations of heavy metals by one of two processes: tolerance and avoidance[7].

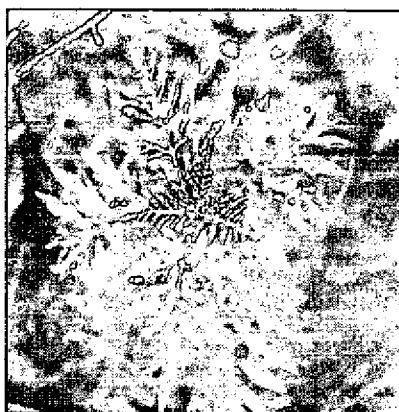
#### *Tolerance Mechanisms:*

- plant produces intracellular metal binding compounds (chelators)
- plant alters its metal compartmentation patterns ( storage in nonsensitive parts of the plant, where metabolic activities do not occur, e.g. old leaves)
- plant alters its cellular metabolism through increased enzyme activity and synthesis

#### *Avoidance Mechanisms:*

- plant alters its membrane permeability, as metals seem to saturate through root structures
- plant changes its metal binding capacity of cell walls (changes in the fixed charge of a cell wall's free space can decrease the diffusion rate of metals)
- plant exudes more natural chelating substances (more chelators in the soil can take up more heavy metals)

To survive and thrive in soils of high concentrations of heavy metals, the plants can either stabilize metal contaminants in the soil- avoidance (Figure 1), or they can take up the contaminants into their cellular structure- tolerance (Figure 2). Both of these methods are employed in phytoremediation techniques.



Plants currently used in Phytoremediation Two plants are currently being used in phytoremediation programs. Both use tolerance mechanism, and they are also termed hyperaccumulators. Common ragweed (left picture)

(<http://www.rce.rutgers.edu/weeddocu> and Dogbane (right picture)

(<http://chili.rt66.com/hrbmoore/Images> have been used to accumulate lead in industrial chemical sites. These sites once produced tetraethyl lead, which

was used as a gasoline additive. Lead concentrations of >1000ppm have been measured in these soils[8]. Far in excess of the normal background level of 70 ppm[9]. Some ragweed samples from these sites have concentrations in excess of 8000 ppm of lead. This further suggests that not only are these plants tolerant of heavy metals, they are also bioaccumulators.

### III. Consequences of No Remediation

Berti and Cunningham state that remediation criteria for Pb in soils are set primarily to protect children who may incidentally ingest small quantities of soil. It is thought that exposure to Pb can increase the risk of neurobehavioral damage at concentrations as low as 10 micrograms dL<sup>-1</sup> of blood. The Integrated Exposure Uptake Biokinetic Model for Lead in Children was designed to estimate Pb uptake from Pb in soil and dust that is ingested or inhaled. The default value for the bioavailability of Pb in soil that is ingested is 30% of the total Pb, meaning that 30% of the total Pb in the ingested soil enters the blood. On the question of differing points of view, Cunningham states that manipulating the chemistry of the soil to maximize Pb removal requires balancing plant -nutritional requirements for biomass production with the availability of Pb for uptake by plants. Further, he states that we have found these to be often competing processes. Maximizing Pb availability requires a lower pH and low solution levels of phosphate and sulfate, which directly impacts total plant biomass produced. The plant -nutritional status of the soil must be continuously balanced against the Pb-availability status to maximize total Pb removal.

#### **IV. Evaluation of Internet Data and Availability**

The majority of information used in constructing this site did not directly come from any specific web site. The subject of phytoremediation is so new that most sites dealing with the topic handle it only in a cursory manner. The available sites, however, provide a wealth of support in referencing the subject. This is mainly due to the high scientific integrity of these sites, many of which are federal, academic, or large industrial research centers.

#### **V. Interview with Dr. Scott Cunningham, DuPont Environmental Biotechnology Research Center**

Scott D. Cunningham, one of the leading experts on phytoremediation of heavy metals, gives his views on other notable research currently going on in the field of phytoremediation of heavy metals, opposition/obstacles that impede the progress of this remediation technique, and the future of using plants as a remediation or reclamation mechanism. Below are excerpts from an interview conducted November 3, 1997.

EC667: What are some of the most important areas of phytoremediation research and development? Who is involved with this research?

**Scott Cunningham (SC):** As I see it, the main areas of research with respect to heavy metals are in the actual application of phytoremediation techniques, using plants for metals reclamation, and biovolatilization of metals by plant off-gassing. Important research in genetic engineering of plants to increase amount and rate of metal uptake is also being conducted. Elie Orescan, out of Rutgers University, and Rufus Chaney, University of Georgia, are leading researchers in terms of actually using plants to suck up metals. Orescan, in conjunction with Bert Ensley, formerly of Envirogen, runs a small remediation company called Phytotech. Phytotech is responsible for actual field applications of phytoremediation techniques. Orescan is able to extract valuable information from the company's remediation sites. Business isn't as good now as it was 2-4 years ago, though. The risk assessment pendulum seems to have swung from "Remove all of it" towards "Remove what's bioavailable or potentially available" Natural attenuation processes are becoming more popular than previously standard and expensive excavation/landfill procedures. So environmental clean-up companies are having a bit of a rough time whereas environmental risk assessment companies are having a better time of it. Rufus Chaney with the USDA out of Beltsville, MD has a project at the zinc smelter site in Palmerton, PA. They're working on ways to reclaim zinc from the ground surrounding the smelter stacks. High levels of zinc deposition from the stack dust has decimated the landscape along parts of the Appalachian Trail that skirt the smelter. Chaney is also involved in using crops for reclamation of metals from sludge. Treated sludge is land applied and planted with a metal-accumulating crop. After harvesting, the plant material can either be landfilled as hazardous waste or burned for metal reclamation. Biovolatilization is another active area of research in phytoremediation. The Kesterton Reservoir group was formed after ducks with 3 legs or crossed bills started appearing at the Kesterton Reservoir. The mutations were attributed to high selenium levels in the reservoir as a consequence of high levels of naturally occurring selenium in



the surrounding agricultural region. Irrigation drainage concentrated the selenium in run-off which was then pumped into the reservoir. Efforts to remove the selenium by using plants for selenium uptake followed by reduction and methylation of the selenium have been successful. After uptake, plants are harvested and incinerated with the selenium being volatilized during the process. This same concept for volatilizing selenium has also been applied in some marsh studies - using marshland as a type of 'biofilter'. I believe Gary Van Wellis of the USDA and Norman Terry at UC-Berkeley are doing work in this area. Brassicaceous plants - broccoli, cabbage, cauliflower - reduce and methylate selenium naturally. Rich Meagher at Georgia is doing some important work with developing transgenic plants for biovolatilization. He has transformed 3-4 types of trees - sweet gum and poplar are two of them - with a bacterial gene that can extract methylated mercury from the soil and reduce it to elemental mercury. Elemental mercury is volatile and non-toxic and can be off-gassed by the tree. Research needs to continue in developing plants that have more efficient means of metal uptake - greater than 3% by weight would be a significant advance - and increased rates of uptake. Time of remediation is one of our biggest constraints.

EC667: Speaking of constraints, what do you see as the obstacles to the successful use of phytoremediation?

SC: The most notable opposition lies with the legal community. Liability issues are more complicated when a biological system is involved with environmental clean-up. Regulations weren't set up with any consideration towards biological systems in mind. Moving a toxic substance from a contaminated matrix is a regulated activity. Is plant sorption and translocation considered a regulated move? Is a plant that is 2% metal by weight a hazardous waste? Breaking the soil surface with a digging tool - shovel, disk, planter - changes the soil from a hazardous material to a hazardous waste, a much more legally complicated situation. Concern around moving the toxin up the food chain is another constraint. Plant-eating insects would be ingested by birds or fish, toxins would concentrate in tissue and be moved up the food chain. But plants that accumulate metals probably don't taste so good. There is speculation that hyperaccumulators developed their ability for metal uptake as a defense mechanism against predation. In general, too, most metals don't bioaccumulate. Most are excreted as waste. There are exceptions, though, most notably methylated mercury, lead and cadmium. In some cases of heavy metal phytoremediation, chelating agents are used to 'loosen' metals from the soil structure and make them more bioavailable. Metals need to be in the soil solution to be available for plant uptake. Chelating agents increase the concentration of metals in the soil solution without precipitating the metal out of solution, thus enhancing uptake. In areas where groundwater may be in close proximity to a site using chelating agents, concern about groundwater contamination with the more mobile solution-phase metals is a barrier that needs to be addressed. Engineering constraints are another set of obstacles to more widespread use of phytoremediation. Engineers love a defined start and stop to a remediation project. Working with a biological system doesn't allow for defined starts or stops. Phytoremediation also takes too long for most engineers. A field of sunflowers is aesthetically pleasing but for 10-15 years? Isn't it finished already? Here, too, public relations comes into play. People don't necessarily want to see moon suits walking around in the field next door. (ASIDE: Full personal protective clothing, including self-contained breathing apparatus, is typically used for harvesting crops of heavy metal accumulators.) The public likes a sense of finality. Ten years of sunflowers may lead to undue suspicion on the part of the public. And, too, sometimes the odor of harvested metal accumulators, namely the Brassica family of plants, is not very pleasant. You know what old decaying cabbage smells like! Our biggest constraint is that phytoremediation doesn't always work. It is situation-dependent. Root depth may not be sufficient, no known plants survive at pHs below 2 or above 11, roots can't survive in anoxic zones, the soil could have nutrient limitations. Even though phytoremediation is loved conceptually, reduction to practice - the when, where and why - is still confounding.

EC667: What is the future of phytoremediation of heavy metals?

SC: Hmmm, a lot. It would be nice to engineer a tree to take up 25% or more by weight. Presently there are some plants that are very good at accumulating metal, up to 3% by weight, but they are about 2 inches tall. Increasing biomass capable of accumulating metal is critical for more effective remediation. Sludge treatment - land application followed by phytoextraction/remediation of contaminants. This could lead to an effective way of recycling sludge for agronomic purposes. Biomining is another

possible application of heavy metal phytoremediation. Mining companies are looking into using plants to recover valuable metals from areas inaccessible to traditional mining equipment and practices. Some companies are looking at using plants for reclamation of metals from industrial waste streams. An example would be having a green plant biofilter downstream, industrially, from a photo processing plant for silver recovery.

EC667: Do you have one final statement about phytoremediation?

SC: I think the use of plants to accumulate, sequester or detoxify heavy metals will find a place in a hundred different outlets.

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## CONCLUSION

As a group we strongly support the concept of using green plants for remediation of heavy metals. A field of sunflowers is some how more appealing than an excavation site. In addition to being an aesthetically pleasing and non-destructive mode of remediation, the low cost of the technique is an economically appealing attribute. There is a need, however, for critical work in certain areas before the full potential of phytoremediation can be realized. Uptake and sequestration mechanisms need to be clearly elucidated, alternative techniques for processing the metal-filled biomass need to be investigated, uptake rates and efficiencies need to be maximized, alternative uses for metal-accumulating plants need to be explored, regulations need to be re-drafted to incorporate biological systems, and public acceptance needs to be encouraged. In other words, there is unlimited potential for the concept of phytoremediation. Turning the concept into effective practices is a different story and this is where continued and future research should focus.

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## Technology Comparison

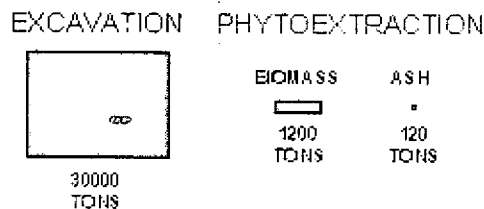
The method traditionally used to clean a site such as the one described below is excavation and landfilling. However, as illustrated in the following example, excavation is both more costly and environmentally damaging than phytoextraction.

Basis:

- 10 acre site
- 1 foot contamination depth
- 500 PPM Pb to be removed.

As shown in the picture below, excavation requires a large amount of mass to be removed from the contaminated area, and merely transfers the problem to another location. **Phytotech technology**, by contrast, does not involve the removal of the contaminated soil, since the soil is all treated **in-situ**.

### COMPARATIVE MASS DISPOSAL (10 ACRES)



This not only reduces the environmental impact of cleaning the soil, but also the remediation cost. Only the plants require disposal, reducing the amount of mass to be disposed of by over **95%**. The result is enormous cost savings.

Finally, Phytotech's technology may allow for the recycling of the remediated metals, which can then be re-used in other applications. Conventional technology merely takes these metals out of circulation through landfilling.

### ECONOMIC COMPARISON OF PHYTOEXTRACTION AND EXCAVATION

	\$000's/10 Acres
Phytoextraction	1,000-1,200
Excavation	3,500-4,500



Have problems viewing these pages? email the webmaster.

# Treatment Technologies Screening Matrix

If you want to see a list of completed projects for any given technology category, click on the appropriate category. For information on a specific technology click on that technology.

Note: Specific site and contaminant characteristics may limit the applicability and effectiveness of any of the technologies and treatments listed below. This matrix is optimistic in nature and should always be used in conjunction with the *referenced text sections*, which contain additional information that can be useful in identifying potentially applicable technologies.

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Rating Codes □ - Better ○ - Average ▲ - Worse I - Inadequate Information NA - Not Applicable	Development Status	Availability	Residuals Produced	Treatment Train (excludes off-gas treatment)	VOCs	SVOCs	Fuels	Inorganic	Explosives	System Reliability/ Maintainability	Cleanup Time	Overall Cost	O&M or Capital Intensive
<b>Soil, Sediment, and Sludge</b>													
4.1 Biodegradation	Full	□	None	No	□	□	□	▲	□	▲	▲	○	O&M
4.2 Bioventing	Full	□	None	No	□	□	□	▲	I	□	○	□	Neither
4.3 White Rot Fungus	Pilot	▲	None	No	▲	▲	▲	▲	□	▲	▲	○	O&M
4.4 Pneumatic Fracturing (enhancement)	Pilot	▲	None	Yes	○	○	○	○	○	□	NA	□	Neither
4.5 Soil Flushing	Pilot	□	Liquid	No	□	○	○	□	▲	○	▲	I	O&M
4.6 Soil Vapor Extraction (In Situ)	Full	□	Liquid	No	□	○	□	▲	▲	□	○	□	O&M
4.7 Solidification/Stabilization	Full	□	Solid	No	▲	○	▲	□	▲	□	□	□	Cap
4.8 Thermally Enhanced SVE	Full	○	Liquid	No	○	□	○	▲	▲	○	□	○	Both
4.9 Vitrification	Pilot	▲	Liquid	No	○	○	○	□	▲	▲	□	▲	Both
4.10 Composting	Full	□	None	No	□	○	□	▲	□	□	○	□	Neither
4.11 Controlled Solid Phase Bio. Treatment	Full	□	None	No	□	○	□	▲	□	□	○	□	Neither
4.12 Landfarming	Full	□	None	No	□	○	□	▲	○	□	▲	□	Neither

4.13 Slurry Phase Bio-Treatment	Full	◊	None	No	◻	◊	◻	▲	◻	◊	◊	◊	Both
4.14 Chemical Reduction/Oxidation	Full	◻	Solid	Yes	◊	◊	◊	◻	▲	◻	◻	◊	Neither
4.15 Dehalogenation (BCD)	Full	▲	Vapor	No	◊	◻	▲	▲	▲	I	I	I	I
4.16 Dehalogenation (Glycolate)	Full	◊	Liquid	No	◊	◻	▲	▲	▲	▲	▲	▲	Both
4.17 Soil Washing	Full	◊	Solid, Liquid	Yes	◊	◻	◻	◻	◻	◊	◻	◊	Both
4.18 Soil Vapor Extraction (Ex Situ)	Full	◻	Liquid	No	◻	◊	◊	▲	▲	◻	◊	◻	Neither
4.19 Solidification/Stabilization	Full	◻	Solid	No	▲	◊	▲	◻	▲	◻	◻	◻	Cap
4.20 Solvent Extraction (chemical extraction)	Full	◊	Liquid	Yes	◊	◻	◊	▲	◻	◊	▲	▲	Both
4.21 High Temperature Thermal Desorption	Full	◻	Liquid	Yes	◊	◻	◊	▲	▲	◊	◻	◊	Both
4.22 Hot Gas Decontamination	Pilot	◊	None	No	▲	▲	▲	▲	◻	◻	◻	◻	Both
4.23 Incineration	Full	◻	Liquid, Solid	No	◊	◻	◻	▲	◻	◊	◻	▲	Both
4.24 Low Temperature Thermal Desorption	Full	◻	Liquid	Yes	◻	◊	◻	▲	◻	◊	◻	◻	Both
4.25 Open Burn/Open Detonation	Full	◻	Solid	No	▲	▲	▲	▲	◻	◻	◻	◻	Both
4.26 Pyrolysis	Full	▲	Liquid, Solid	No	◊	◻	◊	▲	I	I	◻	▲	Both
4.27 Vitrification	Full	◊	Liquid	No	◊	◊	◊	◻	▲	◊	◊	▲	Both
4.28 Excavation, Retrieval, and Off-Site Disposal	NA	◻	NA	No	◊	◊	◊	◊	◊	◻	◻	▲	Neither
4.29 Natural Attenuation	NA	◻	None	No	◻	◻	◻	▲	▲	◻	▲	◻	Neither
Rating Codes ◻ - Better ◊ - Average ▲ - Worse I - Inadequate Information NA - Not Applicable	Development Status	Availability	Residuals Produced	Treatment Train (excludes off-gas treatment)	VOCs	SVOCs	Fuels	Inorganic	Explosives	System Reliability/Maintainability	Cleanup Time	Overall Cost	O&M or Capital Intensive
<b>Groundwater, Surface Water, and Leachate</b>													

4.30 Co-metabolic Treatment	Pilot	▲	None	No	□	□	○	▲	○	▲	○	○	O&M
4.31 Nitrate Enhancement	Pilot	▲	None	No	□	□	□	▲	○	○	○	□	Neither
4.32 Oxygen Enhancement with Air Sparging	Full	□	None	No	□	□	□	▲	○	□	○	□	Neither
4.33 Oxygen Enhancement with H2O2	Full	□	None	No	□	□	□	▲	○	▲	○	○	O&M
4.34 Air Sparging													
4.34 Air Sparging	Full	□	Vapor	Yes	□	▲	□	▲	▲	□	□	□	Neither
4.35 Directional Wells (enhancement)	Full	▲	NA	Yes	○	○	○	○	○	○	□	I	Neither
4.36 Dual Phase Extraction	Full	□	Liquid, Vapor	Yes	□	▲	□	▲	▲	○	○	○	O&M
4.37 Free Product Recovery	Full	□	Liquid	No	▲	□	□	▲	▲	○	□	□	Neither
4.38 Hot Water or Steam Flushing/Stripping	Pilot	○	Liquid, Vapor	Yes	○	□	□	▲	▲	▲	□	○	Cap
4.39 Hydrofracturing (enhancement)	Pilot	I	None	Yes	○	○	○	○	○	□	□	○	Neither
4.40 Passive Treatment Walls	Pilot	▲	Solid	No	□	□	○	□	□	I	▲	I	Cap
4.41 Slurry Walls (containment only)	Full	□	NA	NA	○	○	○	○	○	□	□	□	Cap
4.42 Vacuum Vapor Extraction	Pilot	▲	Liquid, Vapor	No	□	○	□	I	▲	□	○	○	Cap
4.43 Bioreactors													
4.43 Bioreactors	Full	□	Solid	No	□	□	□	▲	○	○	NA	□	Cap
4.44 Air Stripping													
4.44 Air Stripping	Full	□	Liquid, Vapor	No	□	○	○	▲	▲	□	NA	□	O&M
4.45 Filtration	Full	□	Solid	Yes	▲	▲	▲	□	○	□	□	□	Neither
4.46 Ion Exchange	Full	□	Solid	Yes	▲	▲	▲	□	▲	□	○	□	Neither
4.47 Liquid Phase Carbon Adsorption	Full	□	Solid	No	□	□	○	○	□	□	NA	▲	O&M
4.48 Precipitation	Full	□	Solid	Yes	▲	▲	▲	□	I	□	○	□	Neither
4.49 UV Oxidation	Full	□	None	No	□	□	□	▲	□	▲	NA	○	Both
4.50 Natural Attenuation													
4.50 Natural Attenuation	NA	□	None	No	□	□	□	▲	▲	□	▲	□	Neither
Rating Codes □ - Better ○ - Average ▲ - Worse I - Inadequate Information NA - Not Applicable													
	Development Status	Availability	Residuals Produced	Treatment Train (excludes off-gas treatment)	VOCs	SVOCs	Fuels	Inorganic	Explosives	System Reliability/Maintainability	Cleanup Time	Overall Cost	O&M or Capital Intensive

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mobility.

- The potential of washing the contaminant beyond the capture zone and the introduction of surfactants to the subsurface concern regulators. The technology should be used only where flushed contaminants and soil flushing fluid can be contained and recaptured.

#### Data Needs:

Missing PG  
2 of 3 for  
Soil Flushing  
Method.

A detailed discussion of these data elements is provided in Subsection 2.2.1 (Data Requirements for Soil, Sediment, and Sludge). Treatability tests are required to determine the feasibility of the specific soil-flushing process being considered. Physical and chemical soil characterization parameters that should be established include soil permeability, soil structure, soil texture, soil porosity, moisture content, total organic carbon (TOC), cation exchange capacity (CEC), pH, and buffering capacity.

Contaminant characteristics that should be established include concentration, solubility, partition coefficient, solubility products, reduction potential, and complex stability constants. Soil and contaminant characteristics will determine the flushing fluids required, flushing fluid compatibility, and changes in flushing fluids with changes in contaminants.

#### Performance Data:

Soil flushing is a developing technology that has had limited use in the United States. Typically, laboratory and field treatability studies must be performed under site-specific conditions before soil flushing is selected as the remedy of choice. To date, the technology has been selected as part of the source control remedy at 12 Superfund sites. This technology is currently operational at only one Superfund site; a second was scheduled to begin operation in 1991. EPA completed construction of a mobile soil-flushing system, the In Situ Contaminant/Treatment Unit, in 1988. This mobile soil-flushing system is designed for use at spills and uncontrolled hazardous waste sites. There has been very little commercial success with this technology.

#### Cost:

Not available.

#### References:

EPA, 1991. *In Situ Soil Flushing*, Engineering Bulletin, EPA/540/2-91/021.

Nash J., R.P. Traver, and D.C. Downey, 1986. *Surfactant-Enhanced In Situ Soils Washing*, USAF Engineering and Services Laboratory, Florida. ESL-TR-97-18, Available from NTIS, Springfield, VA, Order No. ADA188066.

Sturges, S.G.. Jr., P. McBeth, Jr., R.C. Pratt, 1992. "Performance of Soil Flushing and Groundwater Extraction at the United Chrome Superfund Site," *Journal of Hazardous Materials*, El Savior Science Pub., B.V., Amsterdam, Vol. 29, pp. 59-78.

#### Site Information:

Site Name	Contact	Summary	Beginning Levels	Levels Attained	Costs
Laramie Tie Plant, WY	NA	Primary oil recovery to remove creosote contamination.	Total extractable organics = 93,000 mg/kg	4,000 ppm	NA

Note: NA = Not Available.

**Points of Contact:**

Contact	Government Agency	Phone	Location
Michael Gruenfeld	EPA, Releases Control Branch, RREL	FTS 340-6625 or (908) 321-6625	2890 Woodbridge Avenue Building 10 Edison, NJ 08837
Technology Demonstration and Transfer Branch	USAEC	(410) 671-2054 Fax: (410) 612-6836	SFIM-AEC-ETD APG, MD 21010-5401

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## 4.7 Solidification/Stabilization (In Situ)

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Technology	Description
<b>Soil, Sediment, and Sludge</b>	
<b>3.2 In Situ Physical/Chemical Treatment</b>	
4.7 Solidification/Stabilization (In Situ)	Contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization).

**Description:**

Figure 4-7:

Typical Auger/Caisson and  
Reagent/Injector Head In  
Situ  
Solidification/Stabilization  
Systems

Solidification/stabilization (S/S) reduces the mobility of hazardous substances and contaminants in the environment through both physical and chemical means. Unlike other remedial technologies, S/S seeks to trap or immobilize contaminants within their "host" medium (i.e., the soil, sand, and/or building materials that contain them), instead of removing them through chemical or physical treatment. Leachability testing is typically performed to measure the immobilization of contaminants. In situ S/S techniques use auger/caisson systems and injector head systems to apply S/S agents to in situ soils.

S/S techniques can be used alone or combined with other treatment and disposal methods to yield a product or material suitable for land disposal or, in other cases, that can be applied to beneficial use. These techniques have been used as both final and interim remedial measures.

**Applicability:**

The target contaminant group for in situ S/S is inorganics (including radionuclides). The technology has limited effectiveness against SVOCs and pesticides and no expected effectiveness against VOCs; however, systems designed to be more effective in treating organics are being developed and tested.

**Limitations:**

Factors that may limit the applicability and effectiveness of the process include:

- Depth of contaminants may limit some types of application processes.
- Future usage of the site may "weather" the materials and affect ability to maintain immobilization of contaminants.
- Some processes result in a significant increase in volume (up to double the original volume).
- Certain wastes are incompatible with variations of this process. Treatability studies are generally required.
- Reagent delivery and effective mixing are more difficult than for ex situ applications.
- Like all in situ treatments, confirmatory sampling can be more difficult than for ex situ treatments.

**Data Needs:**

A detailed discussion of these data elements is provided in [Subsection](#)

2.2.1 (Data Requirements for Soil, Sediment, and Sludge). Data needs include particle size, Atterberg limits, moisture content, metal concentrations, sulfate content, organic content, density, permeability, unconfined compressive strength, leachability, pH, and microstructure analysis.

**Performance Data:**

S/S technologies are well demonstrated, can be applied to the most common site and waste types, require conventional materials handling equipment, and are available competitively from a number of vendors. Most reagents and additives are also widely available and relatively inexpensive industrial commodities.

In situ S/S processes have demonstrated the capability to reduce the mobility of contaminated waste by greater than 95%. The effects, over the long term, of weathering (e.g., freeze-thaw cycles, acid precipitation, and wind erosion), groundwater infiltration, and physical disturbance associated with uncontrolled future land use can significantly affect the integrity of the stabilized mass and contaminant mobility in ways that cannot be predicted by laboratory tests.

**Cost:**

Costs for cement-based stabilization techniques vary widely according to materials or reagents used, their availability, project size, and chemical nature of contaminants (e.g., types and concentration levels for shallow applications). The in situ soil mixing/auger techniques average \$50 to \$80 per cubic meter (\$40 to \$60 per cubic yard) for the shallow applications and \$190 to \$330 per cubic meter (\$150 to \$250 per cubic yard) for the deeper applications.

The shallow soil mixing technique processes 36 to 72 metric tons (40 to 80 tons) per hour on average, and the deep soil mixing technique averages 18 to 45 metric tons (20 to 50 tons) per hour.

The major factor driving the selection process beyond basic waste compatibility is the availability of suitable reagents. S/S processes require that potentially large volumes of bulk reagents and additives be transported to project sites. Transportation costs can dominate project economics and can quickly become uneconomical in cases where local or regional material sources are unavailable.

**References:**

EPA, 1989. *Chemfix Technologies, Inc. Chemical Fixation/Stabilization*, EPA RREL, series includes Technology Evaluation, Vol. I, EPA/540/5-89/011a, PB91-127696, and Technology Evaluation, Vol. II, EPA/540/5-89/011b, PB90-274127.

EPA, 1989. *Hazcon Solidification*, EPA RREL, series includes Technology Evaluation, Vol. I, EPA/540/5-89/001a, PB89-158810; Technology Evaluation, Vol. II, EPA/540/5-89/001b, PB89-158828; Applications Analysis, EPA/540/A5-89/001; and Technology Demonstration Summary, EPA/540/S5-89/001.

EPA, 1989. *IWT/GeoCon In-Situ Stabilization*, EPA RREL, series includes Technology Evaluation, Vol. I, EPA/540/5-89/004a; Technology Evaluation, Vol. II, EPA/540/5-89/004b, PB89-194179; Technology Evaluation, Vol. III, EPA/540/5-89/004c, PB90-269069; Technology Evaluation, Vol. IV, EPA/540/5-89/004d, PB90-269077; Applications Analysis, EPA/540/A5-89/004; Technology Demonstration Summary, EPA/540/S5-89/004; Technology Demonstration Summary Update Report, EPA/540/S5-89/004a; and

Demonstration Bulletin, EPA/540/M5-89/004.

EPA, 1989. *SITE Program Demonstration Test International Waste Technologies In Situ Stabilization/Solidification Hialeah, Florida*, Technology Evaluation Report, EPA RREL, Cincinnati, OH, EPA/540/5-89/004a.

EPA, 1989. *Soliditech, Inc. Solidification*, EPA RREL, series includes Technology Evaluation, Vol. I, EPA/540/5-89/005a; Technology Evaluation, Vol. II, EPA/540/5-89/005b, PB90-191768; Applications Analysis, EPA/540/A5-89/005; Technology Demonstration Summary, EPA/540/S5-89/005; and Demonstration Bulletin, EPA/540/M5-89/005.

EPA, 1989. *Stabilization/Solidification of CERCLA and RCRA Wastes: Physical Tests, Chemical Testing Procedures, Technology Screening, and Field Activities*, EPA, CERL, Cincinnati, OH, EPA/625/6-89/022.

EPA, 1990. *International Waste Technologies/Geo-Con In Situ Stabilization/Solidification*, Applications Report, EPA, ORD, Washington, DC, EPA/540/A5-89/004.

EPA, 1993. *Solidification/Stabilization and Its Application to Waste Materials*, Technical Resource Document, EPA, ORD, Washington, DC, EPA/530/R-93/012.

EPA, 1993. *Solidification/Stabilization of Organics and Inorganics*, Engineering Bulletin, EPA, ORD, Cincinnati, OH, EPA/540/S-92/015.

Wiles, C.C., 1991. *Treatment of Hazardous Waste with Solidification/Stabilization*, EPA Report EPA/600/D-91/061.

#### Site Information:

Site Name	Contact	Summary	Beginning Levels	Levels Attained	Costs
Hialeah, FL	Jeff Newton International Waste Technologies 150 North Main Street, Suite 910 Wichita, KS 67202 (316) 269-2660 Geo-Con Dave Miller (817) 383-1400	Deep soil mixing using drive auger to inject additive slurry and water into in-place soil.	NA	NA	\$111-\$194/ton

#### Points of Contact:

Contact	Government Agency	Phone	Location
Mary K. Stinson	EPA RREL	(908) 321-6683 Fax: (908) 321-6640	2890 Woodbridge Avenue (MS-104) Edison, NJ 08837-3679
Patricia M. Erikson	EPA RREL	(513) 569-7884 Fax: (513) 569-7676	26 West M.L. King Drive Cincinnati, OH 45268
Edward R. Bates	EPA RREL	(513) 569-7774 Fax: (513) 569-7676	26 West M.L. King Drive Cincinnati, OH 45268
John Cullinane	USAE-WES	(601) 636-3111	ATTN: LEWES-EE-S 3909 Halls Ferry Road Vicksburg, MS 39180-6199
Technology Demonstration and Transfer Branch	USAEC	(410) 671-2054 Fax: (410) 612-6836	SFIM-AEC-ETD APG, MD 21010-5401

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## 4.9 In Situ Vitrification

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Technology	Description
<b>Soil, Sediment, and Sludge</b>	
<b>3.3 In Situ Thermal Treatment</b>	
4.9 In Situ Vitrification	Electrodes for applying electricity are used to melt contaminated soils and sludges, producing a glass and crystalline structure with very low leaching characteristics.

**Description:**

Figure 4-9:

Typical In Situ Vitrification  
System

In situ vitrification (ISV) uses an electric current to melt soil or other earthen materials at extremely high temperatures (1,600 to 2,000 °C or 2,900 to 3,650 °F) and thereby immobilize most inorganics and destroy organic pollutants by pyrolysis. Inorganic pollutants are incorporated within the vitrified glass and crystalline mass. Water vapor and organic pyrolysis combustion products are captured in a hood, which draws the contaminants into an off-gas treatment system that removes particulates and other pollutants from the gas.

High temperatures are achieved using a square array of four graphite electrodes. To initiate the process, a path of conducting material (graphite) is placed on the surface of the soil so that current can flow in the soil beyond the boiling temperature of water (dry soil is not conductive after the conduction path in soil pore water is boiled off) to the melting point of the soil. The joule heating of the starter path achieves temperatures high enough to melt the soil (value is dependent on the soil's alkali metal oxide content), at which point the soil becomes conductive. The molten soil zone grows downward and outward. New designs incorporate a moving electrode mechanism to achieve a greater process depth. A vacuum pressurized hood is placed over the vitrification zone to contain and process any contaminants emanating from the soil during vitrification. The vitrification product is a chemically stable, leach-resistant, glass and crystalline material similar to obsidian or basalt rock. The process destroys and/or removes organic materials. Radionuclides and heavy metals are retained within the molten soil.

The ISV process was invented by Battelle, Pacific Northwest Laboratory for DOE in 1980. The patent is assigned to DOE, is licensed to Battelle, and is sublicensed to Geosafe Corporation for worldwide rights (Patent No. 4,376,598, issued 15 March 1983).

**Applicability:**

The ISV process can destroy or remove organics and immobilize most inorganics in contaminated soils, sludges, or other earthen materials. The process has been tested on a broad range of VOCs and SVOCs, other organics including dioxins and PCBs, and on most priority pollutant metals and radionuclides.

**Limitations:**

Factors that may limit the applicability and effectiveness of the

process include:

- Rubble exceeding 20% by weight.
- Heating the soil may cause subsurface migration of contaminants into clean areas.
- Combustible organics in the soil or sludge exceeding 5 to 10 weight percent (wt%), depending on the heating value.
- The solidified material may hinder future site use.
- Processing of contamination below the water table may require some means to limit recharge.

**Data Needs:**

A detailed discussion of these data elements is provided in Subsection 2.2.1 (Data Requirements for Soil, Sediment, and Sludge). A minimum alkali content in soil (sodium and potassium oxides) of 1.4 wt% is necessary to form glass. The composition of most soils is well within the range of processability.

**Performance Data:**

There have been few, if any, commercial applications of ISV. The ISV process has been operated for test and demonstration purposes at the pilot scale and at full scale at the following sites: (1) Geosafe Corporation's test site, (2) DOE's Hanford Nuclear Reservation, (3) DOE's Oak Ridge National Laboratory, and (4) DOE's Idaho National Engineering Laboratory. More than 170 tests at various scales have been performed on a broad range of waste types in soils and sludges. A demonstration will take place at the Parsons/ETM site in Grand Ledge, Michigan, where the process is currently operating.

Process depths up to 6 meters (19 ft) have been achieved in relatively homogeneous soils. The achievable depth is limited under certain heterogeneous conditions.

**Cost:**

Average costs for treatability tests (all types) are \$25K plus analytical fees; for PCBs and dioxins, the cost is \$30K plus analytical. Remedial design varies with the design firm. Equipment mobilization and demobilization costs are \$200K to \$300K combined. Vitrification operation cost varies with electricity costs, quantity of water, and depth of process.

**References:**

DOE, 1992. *In Situ Vitrification*, Technology Transfer Bulletin, prepared by Battelle's Pacific Northwest Laboratories for DOE, Richland, WA.

DOE, January 1992. "ISV Planning and Coordination," *FY92 Technical Task Plan and Technical Task Description*, TTP Reference No. RL-8568-PT.

DOE, July 1992. "116-B-6A Crib ISV Demonstration Project," *FY92 Technical Task Plan and Technical Task Description*, TTP Reference No. RL-8160-PT.

EPA, 1994. *In-Situ Vitrification Geosafe Corportion*, EPA RREL, Demonstration Bulletin, EPA/540/MR-94/520.

Kuhn, W.L., May 1992. *Steady State Analysis of the Fate of Volatile Contaminants During In Situ Vitrification*, Battelle, Pacific Northwest Laboratory, Richland, WA, prepared for DOE; PNL-8059, US-602.

Luey, J.S., S. Koegler, W.L. Kuhn, P.S. Lowerey, and R.G.



Winkelman, September 1992. *"In Situ Vitrification of Mixed-Waste Contaminated Soil Site: The 116-B-6A Crib at Hanford,"* CERCLA Treatability Test Report, Battelle, Pacific Northwest Laboratory, Richland, WA, prepared for DOE, Report PNL-8281, UC-602.

Spalding, B.P., G.K. Jacobs, N.W. Dunbar, M.T. Naney, J.S. Tixier, and T.D. Powell, November 1992. *Tracer-Level Radioactive Pilot-Scale Test of In Situ Vitrification for the Stabilization of Contaminated Soil Sites at ORNL*, Martin Marietta Energy Systems, Publication No. 3962, prepared for DOE, Oak Ridge National Laboratory, Oak Ridge, TN, Report ORNL/TM-12201.

#### Site Information:

Site Name	Contact	Summary	Beginning Levels	Levels Attained	Costs
Parson's Chemical Site Grand Ledge, MI	Leonard Zintak, Jr. (517) 627-1311 Fax: (517) 627-1594	Four graphite electrodes and glass frit inserted into soil. Hood and off-gas treatment system placed over soil.	Low levels of pesticides and Hg	Leachable Hg, TCLP, pesticide, non-detect	NA

Note: NA = Not Available.

#### Points of Contact:

Contact	Government Agency	Phone	Location
Jef Walker	DOE Program Manager	(301) 903-7966	EM-551, Trevion II DOE Washington, DC 20585
Teri Richardson	EPA RREL	(513) 569-7949 Fax: (513) 569-7620	26 West M.L. King Drive Cincinnati, OH 45268
Technology Demonstration and Transfer Branch	USAEC	(410) 671-2054 Fax: (410) 612-6836	SFIM-AEC-ETD APG, MD 21010-5401

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## 3.5 Ex Situ Physical/Chemical Treatment for Soil, Sediment, and Sludge

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The main advantage of ex situ treatment is that it generally requires shorter time periods than in situ treatment, and there is more certainty about the uniformity of treatment because of the ability to homogenize, screen, and continuously mix the soil. Ex situ treatment, however, requires excavation of soils, leading to increased costs and engineering for equipment, possible permitting, and material handling.

Physical/chemical treatment uses the physical properties of the contaminants or the contaminated medium to destroy (i.e, chemically convert), separate, or contain the contamination. Chemical reduction/oxidation and dehalogenation (BCD or glycolate) are destruction technologies. Soil washing, SVE, and solvent extraction are separation techniques, and S/S is an immobilization technique.

Physical/chemical treatment is typically cost effective and can be completed in short time periods (in comparison with biological treatment). Equipment is readily available and is not engineering or energy-intensive. Treatment residuals from separation techniques will require treatment or disposal, which will add to the total project costs and may require permits.

Available ex situ physical/chemical treatment technologies include chemical reduction/oxidation, dehalogenation (BCD or glycolate), soil washing, SVE, S/S, and solvent extraction. These technologies are discussed in [Section 4](#) (Treatment Technology Profiles [4.14](#) through [4.20](#)). Completed ex situ physical/chemical treatment projects for soil, sediment, and sludge are shown in [Table 3-8](#).

**TABLE 3-8 COMPLETED PROJECTS: EX SITU PHYSICAL/CHEMICAL TREATMENT FOR SOIL, SEDIMENT, AND SLUDGE**

Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
EPA Remedial Action Upjohn Manufacturing Company, PR  1/83 to 3/88  Alison Hess (212) 264-6040	SVE/Terra Vac, Inc., Costa Mesa, CA	Soil	Criteria:  Initial concentrations - 70 ppm (carbon tetrachloride to air)  Final concentrations - nondetect (<0.002 ppm)	Ambient conditions	Ex
EPA Remedial Action Palmetto Wood Preserving, SC	Chemical treatment and soil washing; reduction of hexavalent chromium to trivalent	Soil (13,000 yd <sup>3</sup> )	Input:  Arsenic - 2 to 6,200 ppm	Soil - Batch process  Treatment for aqueous waste from soil	(1) m lo an

9/28/88 to 2/8/89	chromium/En-site (ERCS contractor) Atlanta, GA		Chromium - 4 to 6,200 ppm	washing - 25 gpm pH - 2 to 9	ch th se an sol soi us io re pr ch sol tri
McKenzie Mallary (404) 347-7791			Output:  Arsenic - less than 1 ppm  Chromium - 627 ppm		
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
EPA Remedial Action Wide Beach Development, NY  9/90 to 9/91  Herb King (212) 264-1129	APEG dechlorination/Soil Tech Denver, CO	Soil (40,000 yd <sup>3</sup> )	Criteria: PCB - <10 ppm (1 composite sample/day)  Input:  10 to 100 ppm PCB  Output:  2 ppm PCB	Continuous process  8 tons/hour 200 to 580 °C (450 to 1,100 °F) Ambient pH and moisture  Additives - Alkaline polyethylene glycol (APEG)	Ex Sc St
EPA Removal Action Traband Warehouse PCBs, OK  2/90 to 9/90  Pat Hammack (214) 655-2270	Solvent extraction/Terra-Clean	Solids	PCBs Initial: 7,500 ppm	Solvent addition	Ex
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
EPA Removal Action PBM Enterprises, MI  3/25/85 to 10/28/85  Ross Powers (312) 378-7661	Neutralization with hypochlorite process/Mid-American Environmental Service Riverdale, IL	Film chips (464 tons or 1,280 yd <sup>3</sup> )	Cyanide  Input: 200 ppm  Output: 20 ppm	Time: 2 to 3 hours  Additives: sodium hydroxide	A
EPA Removal Action Stanford Pesticide Site No. 1, AZ	Chemical treatment -alkaline hydrolysis/EPA removal contractor	Soil (200 yd <sup>3</sup> )	Methyl parathion  Input: 24.2 ppm  Output: 0.05 ppm	pH: 9.0 Moisture: wet Additives to soil: soda ash, water, activated carbon	Til (in pe

3/20/87 to 11/4/87					
Dan Shane (415) 744-2286					
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
EPA Removal Action General Refining Company, GA  8/86 to 10/86 and 1/87 to 2/87  Shane Hitchcock (404) 347-3136	Solvent extraction/Resource Conservation Technology Company Bellevue, WA	Sludge (3,448 tons)	Input:  PCB - 5.0 ppm  Lead - 10,000 ppm  Output:  PCB - insignificant  Lead - concentrated in solids	Continuous operation  Time: 2 hours pH: 10 Temp: 20 °C Rate: 27 tons/day Moisture content: 60%  Additives:  Sodium hydroxide Triethylamine	Ex Sc Ne Si Mi
EPA Removal Action Basket Creek Surface Impoundment, GA  11/92 to 2/93  Don Rigger (404) 347-3931	Vacuum extraction of soil pile with horizontal wells (ex situ)/OHM	Soil (2,000 yd <sup>3</sup> )	VOCs TCE, PCE, MEK, MIBK, BTEX High 33% VOCs Average 1 to 5%  Criteria: TCE - 0.5 mg/L TCLP  PCE - 0.7 mg/L TCLP All VOCs met TCLP limits	Vacuum pressure monitored. 1,300-CFM/manifold. 3 manifolds 6 to 7 wells/manifold	Su im us of Bu en th Ex soi it scr on ex Re wi an in
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
EPA Removal Action Zbiegner Refining Company	Chemical treatment/ENSCO	Solid (100 lb)	Mercury initial concentration >10% mercury  Final concentration of	Added salt to precipitate the mercury	M pr pr m m so

2/93 to 6/93 Dilshad Perera (908) 321-4356			mercury in recyclable precipitate was >80%.  Less than 260 ppm if mercury in tank nonrecycled salt.		m re re
EPA Removal Action Vineland Chemical Company, NJ  12/92  Don Graham (908) 321-4345	Chemical treatment/ENSCO	Solid (100 lb)	Mercury initial concentration >10% mercury  Final concentration of mercury in recyclable precipitate was >80%.  Less than 260 ppm of mercury in nonrecycled salt.	Added salt to precipitate the mercury	M pr pr m m so m re re
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
EPA Removal Action Signo Trading International, Inc., NY  10/20/87 to 10/21/87  Charles Fitzsimmons (201) 321-6608	KPEG dechlorination/Galson Remediation, Syracuse, NY	Sludge (15 gallons)	Dioxin  Input: 135 ppm  Output: 1 ppb	Temperature: 150 °C  Time: Overnight	Ex
EPA Removal Action Avtex Fibers, VA  4/90 to 8/91  Vincent Zenone (215) 597-3038	Chemical treatment (oxidation using NaClO)/OH Materials, Findlay, OH (ERCS contractor)	Sludge/water from storage unit (2 million gallons)	Carbon disulfide  Criteria: =< 10 ppm -carbon disulfide in the effluent  Input: 50 to 200,000 ppm carbon disulfide  Output: =< 10 ppm -carbon disulfide	Batch operation average retention time - 1 hour pH - 10  Additives: sodium hypochloride  The retention time and reagent feed rates increased with increasing concentration of sludge in the contaminated water.	Pu
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	

Army Saginaw Bay Confined Disposal Facility, MI 10/91 to 6/4/92 Jim Galloway (313) 226-6760	Soil washing; water with flocculent and surfactant as an additive/Bermann USA, Stafford Springs, CT	Sediment (150 yd <sup>3</sup> )	PCBS	30 yd <sup>3</sup> of sediment treated per day	Dr Sc Si
<b>EPA &amp; Navy Demo</b> EPA Lab, NJ Deh Bin Chan (805) 982-4191	Chemical detoxification of chlorinated aromatic compounds	Soil	Dioxin, herbicides, chlorinated aromatic compounds. 99.9% decontamination achieved	Soil heated to 100-150 °C if dehydrated	Ex W as
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
<b>EPA Demo</b> Douglassville, PA 10/87 Paul R. DePercin (513) 569-7797	Chemical treatment & immobilization	Soil, sediments, & sludge	Organic compounds, heavy metals, oil, & grease	In/ex situ. Sediments - underwater. Batch process at 120 tons/hour.	Bl
<b>DOE Demo</b> INEL, ID 1992 Robert Montgomery (208) 525-3937	Physical separation/chemical extraction	Sediments	Radionuclides & metals	Contaminants removed from leachate by ion exchange, reverse osmosis, precipitation, or evaporation	Sc se lea nit
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
<b>EPA Demo</b> Midwest, California, Australia 1987 S. Jackson Hubbard (513) 569-7507	SAREX chemical fixation process	Soil & sludge	Low level metals & organics	Catalyzed by lime and proprietary reagents	Bl re he
<b>EPA Demo</b> Grand Calumet River Site, IL 1992	BEST <sup>TM</sup> solvent extraction process	Oily sludges & soil	PCBs, PAHs, pesticides	pH >10	H hy cy co te

Mark Meckes (513) 569-7348					
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
<b>EPA Demo</b> Santa Maria, CA  5/92  Annette Gatchett (513) 569-7697	Biogenesis <sup>SM</sup> soil washing process	Soil	Organics - oil, fuel, PCBs, PAHs 99% hydrocarbon removal with initial concentration up to 15,000 ppm	30-65 tons/hour	A wi
<b>DOE Demo</b> Clemson Technical Center, SC  Doug Mackensie  (208) 526-6265	Enhanced Soil Washing with Soil*EX <sup>SM</sup>	Soil & debris	Heavy metals, radionuclides, and organics	Particles smaller than 2 inches	Sc dis su ad
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
<b>EPA Demo</b>  1992  Michelle Simon (513) 569-7469	RENEU <sup>TM</sup> extraction technology	Soil	Organics up to 325,000 ppm	Operated under vacuum - 5-45 tons/hour	Sa soi di
<b>EPA &amp; DOE Demo</b> Montclair, West Orange & Glen Ridge Sites, NJ  Mike Eagle (202) 233-9376	Soil washer for radioactive soil	Soils	Radionuclides - 56% volume reduction 40 pCu/g to 11 pCu/g	1 ton/hour	At an hy
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
<b>Army Demo</b> Sacramento Army Depot, CA  1992  Marlin Mezquita (415) 744-2393	Soil washing	Oxidation lagoon soils (12,000 yd <sup>3</sup> )	Cd, Ni, Pb, Cu	Soil treated with wash reagent to extract contaminants	W ne ca pr
<b>DOE Demo</b>	Soil washing	Soil	Uranium	Soil and leachant	At

Fernald Site, OH				attrition scrubbed for 1 minute to solubilize uranium	scr gr se scr
Kimberly Nonfer (513) 648-6556					
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
<b>EPA Demo</b> Coleman-Evans Site, FL  Norma Lewis (513) 569-7665	Soil washing/catalytic ozone oxidation	Soil, sludge, & groundwater	Organics - up to 20,000 ppm	Soil washing enhanced by ultrasound	So gr in
<b>EPA Demo</b> Alaska Battery Enterprises Superfund Site, AK  1992  Hugh Masters (908) 321-6678	Soil washing plant	Soil	Heavy metals, radionuclides	Rate dependent on percentage of soil fines - up to 20 tons/hour	De de se m
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
<b>EPA Demo</b> MacGillis & Gibbs Superfund Site, MN  1989  Mary Stinson (908) 321-6683	Soil washing system	Soil	Removal:  89% PCP 88% PAHs	500 lb/hour 24 hour/day	De pr mi wa (o si pr op
<b>EPA Demo</b> New Bedford Harbor, MA & O'Connor Site, ME  3/91 to 3/92  Laurel Staley (513) 569-7863	Solvent extraction	Soil, sludge, and wastewater	PCB 300-2,500 ppm 90-98% removal	Tray tower for water; extractor/decantors for solids and semi-solids	Ph wi sol
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
<b>EPA Demo</b> Pensacola, FL  11/92  Teri	Volume reduction unit	Soils	Organics - creosote PCP, pesticides, PAHs, VOCs, SVOCs, metals	Up to 100 lb/hour	Pa se sol



Richardson (513) 569-7949					
<b>EPA Demo</b> Iron Mountain Mine Site, CA  1990 to 1991  S. Jackson Hubbard (513) 569-7507	Precipitation, microfiltration & sludge dewatering	Sludge & leachable soil	Heavy metals, non-volatile organics & solvents, oil, grease, pesticides, bacteria, solids	Up to 5% solids, 30 lb/hour of solids, 10 gpm of wastewater	He pr filt co str de
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
<b>EPA SITE Demo</b> Portable Equip. Salvage Co. Clackamas, OR  9/89  Edwin Barth (513) 569-7669	Chemfix process - solidification/stabilization	Soil & Sludge	Solid waste	Uses soluble silicates and silicate-settling agents	Bl dr cal sil re
<b>Navy Demo</b> Naval Const. Battalion Ctr. Port Hueneme, CA  2/91 to 2/92  Jeff Heath (805) 982-1657	Solidification of Spent blasting	Blasting wastes containing abrasives, grit, sands	Lead, copper, and heavy metals	About 2 months required for design	Mi an ag
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
<b>EPA SITE Demo</b> Robins AFB Macon, GA  8/91  Terry Lyons (513) 569-7589	Solidification/stabilization	Soil, sludge, liquid	Organics and inorganics	Uses proprietary bonding agents	La m pr
<b>EPA SITE Demo</b> Selma Pressure Treating Selma, CA  11/90  Edward Bates (513) 569-7774	Solidification/stabilization with silicate compounds	Groundwater, soil, sludge	Organics and inorganics	Silicate compounds	Pr se co m

Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	
Imperial Oil Co./Champion Chemical Co. Superfund Site Morganville, NJ  12/88  S. Jackson Hubbard (513) 569-7507	Soliditech solidification/stabilization process	Soil, sludge	Inorganics and organics, metals, ore, grease	Add water, Urrichem (proprietary additives), and pozzolanic material (fly ash or kiln dust)	Scintaba
Small Arms Range, Naval Air Station Mayport, FL  1990  Barbara Nelson (805) 982-1668	Stabilization of small arms range	Soil	Lead and other heavy metals	Soil is mixed with sodium silicate, portland cement, and water	Scintaba (to an la)

Sources: *Innovative Treatment Technologies: Annual Status Report (EPA, 1993)*. *Synopses of Federal Demonstrations of Innovative Site Remediation Technologies (FRTR, 1993)*.

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## 3.4 Ex Situ Biological Treatment for Soil, Sediment, and Sludge

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The main advantage of ex situ treatment is that it generally requires shorter time periods than in situ treatment, and there is more certainty about the uniformity of treatment because of the ability to homogenize, screen, and continuously mix the soil. However, ex situ treatment requires excavation of soils, leading to increased costs and engineering for equipment, possible permitting, and material handling/worker exposure considerations.

Bioremediation techniques are destruction or transformation techniques directed toward stimulating the microorganisms to grow and use the contaminants as a food and energy source by creating a favorable environmental for the microorganisms. Generally, this means providing some combination of oxygen, nutrients, and moisture, and controlling the temperature and pH. Sometimes, microorganisms adapted for degradation of the specific contaminants are applied to enhance the process.

Biological processes are typically easily implemented at low cost. Contaminants can be destroyed or transformed, and little to no residual treatment is required; however, the process requires more time and difficult to determine whether contaminants have been destroyed. Biological treatment of PAHs leaves less degradable PAHs (cPAHs) behind. These higher molecular cPAHs are classified as carcinogens. Also, an increase in chlorine concentration leads to a decrease in biodegradability. Some compounds, however, may be broken down into more toxic by-products during the bioremediation process (e.g., TCE to vinyl chloride). An advantage over the in situ applications is that in ex situ applications, these by-products are contained in the treatment unit until nonhazardous end-products are produced.

Although not all organic compounds are amenable to biodegradation, bioremediation techniques have been successfully used to remediate soils, sludges, and groundwater contaminated by petroleum hydrocarbons, solvents, pesticides, wood preservatives, and other organic chemicals. Bioremediation is not generally applicable for treatment of inorganic contaminants.

The rate at which microorganisms degrade contaminants is influenced by the specific contaminants present; oxygen supply; moisture; nutrient supply; pH; temperature; the availability of the contaminant to the microorganism (clay soils can adsorb contaminants making them unavailable to the microorganisms); the concentration of the contaminants (high concentrations may be toxic to the microorganism); the presence of substances toxic to the microorganism, e.g., mercury; or inhibitors to the metabolism of the contaminant. These parameters are discussed briefly in the following paragraphs.

**Oxygen** level in ex situ applications is easier to control than in in situ applications and is typically maintained by mechanical tilling, venting, or sparging.

**Anaerobic conditions** may be used to degrade highly chlorinated contaminants. This can be followed by aerobic treatment to complete biodegradation of the partially dechlorinated compounds as well as the other contaminants.

**Water** serves as the transport medium through which nutrients and organic constituents pass into the microbial cell and metabolic waste products pass out of the cell. Moisture levels in the range of 20% to 80% generally allow suitable biodegradation in soils.

**Nutrients** required for cell growth are nitrogen, phosphorous, potassium, sulfur, magnesium, calcium, manganese, iron, zinc, and copper. If nutrients are not available in sufficient amounts, microbial activity will stop. Nitrogen and phosphorous are the nutrients most likely to be deficient in the contaminated environment and thus are usually added to the bioremediation system in a useable form (e.g., as ammonium for nitrogen and as phosphate for phosphorous).

**pH** affects the solubility, and consequently the availability, of many constituents of soil, which can affect biological activity. Many metals that are potentially toxic to microorganisms are insoluble at elevated pH; therefore, elevating the pH of the treatment system can reduce the risk of poisoning the microorganisms.

**Temperature** affects microbial activity in the treatment unit. The biodegradation rate will slow with decreasing temperature; thus, in northern climates bioremediation may be ineffective during part of the year unless it is carried out in a climate-controlled facility. The microorganisms remain viable at temperatures below freezing and will resume activity when the temperature rises. Too high a temperature can be detrimental to some microorganisms, essentially sterilizing the soil. Compost piles require periodic tilling to release self-generated heat.

Temperature also affects nonbiological losses of contaminants mainly through the volatilization of contaminants at high temperatures. The solubility of contaminants typically increases with increasing temperature; however, some hydrocarbons are more soluble at low temperatures than at high temperatures. Additionally, oxygen solubility decreases with increasing temperature. Temperature is more easily controlled ex situ than in situ.

**Bioaugmentation** involves the use of cultures that have been specially bred for degradation of a variety of contaminants and sometimes for survival under unusually severe environmental conditions. Sometimes microorganisms from the remediation site are collected, separately cultured, and returned to the site as a means of rapidly increasing the microorganism population at the site. Usually an attempt is made to isolate and accelerate the growth of the population of natural microorganisms that preferentially feed on the contaminants at the site. In some situations different microorganisms may be added at different stages of the remediation process because the contaminants in abundance change as the degradation proceeds. USAF research, however, has found no evidence that the use of non-native microorganisms is beneficial in the situations tested.

**Cometabolism**, in which microorganisms growing on one compound produce an enzyme that chemically transforms another compound on which they cannot grow, has been observed to be useful. In particular, microorganisms that degrade methane (methanotrophic bacteria) have been found to produce enzymes that can initiate the oxidation of a variety of carbon compounds.

**Treatability or feasibility studies** are used to determine whether bioremediation would be effective in a given situation. The extent of the study can vary depending on the nature of the contaminants and the characteristics of the site. For sites contaminated with common petroleum hydrocarbons (e.g., gasoline and/or other readily degradable compounds), it is usually sufficient to examine representative samples for the presence and level of an indigenous population of microbes, nutrient levels, presence of microbial toxicants, and soil characteristics such as pH, porosity, and moisture.

Available ex situ biological treatment technologies include composting, controlled solid phase biological treatment, landfarming, and slurry phase biological treatment. These technologies are discussed in [Section 4](#) (Treatment Technology Profiles 4.10 through 4.13). Completed ex situ biological treatment projects for soil, sediment, and sludge are shown in [Table 3-7](#).

**TABLE 3-7 COMPLETED PROJECTS: EX SITU BIOLOGICAL TREATMENT FOR SOIL, SEDIMENT, AND SLUDGE**

Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	Materials Handling
EPA Remedial Action Brown Wood Preserving, FL  10/88 to 12/91  Martha Berry (404) 347-2643	Land treatment/Remediation Technologies, Seattle, WA	Soil/pond sediment (7,500 yd <sup>3</sup> )	Criteria: 100 ppm total carcinogenic PAHs as sampled on 8 subplots on each lift  Input: 800 to 2,000 ppm total creosote contaminants  Output: 10 to 80 ppm total carcinogenic indicators	Retention time - 3 to 6 months  Additives - water and nutrients	Excavation Screening Tilling
EPA Removal Action Poly-Carb, Inc., NV  7/22/87 to 8/16/88  Bob Mandel (415) 744-2290	Land treatment and soil washing/EPA removal contractor	Soil (1,500 yd <sup>3</sup> )	Input:  Phenol - 1,020 ppm  o-creosol - 100 ppm  m- and p-creosol - 409 ppm  Output:  Phenol - 1 ppm  o-creosol - 1 ppm  m- and p-creosol - 0.92 ppm	Additives: water	Excavation  Placement in double-lined pit  Irrigation  Tilling
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	Materials Handling
EPA Removal Action Scott Lumber, MO  8/87 to Fall 1991  Bruce Morrison (913) 551-5014	Land treatment/RETEC Chapel Hill, NC	Soil (16,000 yd <sup>3</sup> )	Criteria:  500 ppm - Total PAH  14 ppm - Benzo(a)pyrene	Additives:  Water Phosphates	Tilling
Matagorda	Ex situ bioremediation;	Soil (500	PAHs	Batch process	Excavated

Island Af Range, TX  10/92 to 2/28/93  Vic Heister (918) 669-7222	solid phase. All constructed on abandoned runway. Bacteria added and mechanically mixed.	yd <sup>3</sup> )	TPH - 3,400 ppm BTEX - 41.3 ppm  Criteria: Texas Water Commission standards 100 ppm for TPH 30 ppm for BTEX	retention time: 3 months  9-inch layers treated  Ambient temperature bacteria added to waste	approximate 40 by 60 ft area. Constructed on poly barr and clean sa base. Did some mixin
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	Materials Handling
Navy Marine Corps Mountain Warfare Center Bridgeport, CA  8/89 to 11/89  Diane Soderland (907) 753-3425 Bill Major (DOD) (805) 982-1808	Bioremediation (ex situ); heap pile bioreactor.	Soil (7,000 yd <sup>3</sup> )	PAHs (petroleum hydrocarbons, diesel), metals (lead)	Temperature, pressure, and moisture content are monitored.	Excavation
Army Ft. Ord Marina, Fritzche AAF Fire Drill Area, CA  Winter 1991  Gail Youngblood (408) 242-8017	Land treatment	Soil (4,000 yd <sup>3</sup> )	TCE, MEK, TPH, BTEX	Initial concentration >1,000 ppm  End concentration <200 ppm	Ex situ
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	Materials Handling
Army Demo Louisiana Army Ammunition Plant, LA  12/87 to 4/88  Peter Marks (610) 701-3039 Capt. Kevin Keehan (410) 671-2054	Aerated static pile composting	Lagoon sediments	TNT, HMX, RDX Initial concentrations: 17000 mg/kg.	Thermophilic (55 °C) and mesophilic (35 °C). Add bulking agents: horse manure, alfalfa, straw, fertilizer, horse feed	Mixing
Army Demo	Aerated static pile	Soil &	Nitrocellulose	Thermophilic	Mixing

Badger Army Ammunition Plant, WI  4/88 to 1/89  Peter Marks (610) 701-3039 Capt. Kevin Keehan (410) 671-2054	composting	sediments	reduction > 99.5%	(55 °C) and mesophilic (35 °C)	
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	Materials Handling
Army Demo Umatilla Depot Activity, OR  Harry Craig (503) 326-3689	Aerobic composting optimization	Soil & sediment (4,800 yd <sup>3</sup> )	TNT, HMX, RDX	Maintain pH, temperature, moisture content, oxygen content	Mix with bulking age & organic amendments
Navy Demo Naval Weapons Station Seal Beach, CA  Steve McDonald (310) 594-7273 Carmen Lebron (805) 982-1615	Bioremediation of aromatic hydrocarbons unleaded gasoline spill	Soil & groundwater	1 ppb to 4 ppm of BTEX	3 80-litre bioreactors at 72 L/day	Site soil placed in reactor - groundwater pumped through
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	Materials Handling
EPA SITE Demo  Ronald Lewis (513) 569-7856 Merv Cooper (206) 624-9349	Liquids & solids biological treatment (LST)	Soils, sediments, & sludge	Biodegradable organics	Suspended solids up to 20%	Mixing & aeration
EPA SITE Demo EPA Test & Evaluation Facility, OH  5/91 to 9/91  Ronald Lewis (513) 569-7856	Bioslurry reactor	Soils, sediments, & sludge	97% reduction in PAHs	Degradation enhanced by control of pH, temperature, oxygen, nutrients, and enriched indigenous microorganisms	Excavation, mixing, additives, sparging
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	Materials Handling
Navy Demo Camp Pendleton, CA	Enzyme catalyzed, accelerated biodegradation	Soil	TPH reduced from 29,000 ppm to 88 ppm (well below 100	50 yd <sup>3</sup> /month capacity	Soil tilled w a garden tractor after each produc.

1991			ppm goal)		application and once ea week
William Sancet (619) 725-3868					
<b>Army Demo</b> Joliet Army Ammunition Plant, IL	Soil slurry-sequencing batch bioreactor	Soil	TNT, RDX, HMX  TNT reduced from 1,300 to 10 ppm	In tank or reactor	Excavation and pre-screenin (to remove large debris)
1992					
Kevin Keehan (410) 671-2054					
Site Name/Contact	Technology/ Vendor	Media Treated	Contaminants Treated	Operating Parameters	Materials Handling
<b>EPA Demo</b> Santa Maria, CA  5/92  Annette Gatchett (513) 569-7697	Biogenesis <sup>SM</sup> soil washing process	Soil	Organics - oils, fuels, PCBs, PAHs 85-99% removal of hydrocarbons with initial concentration up to 15,000 ppm	30-65 tons/hour	Agitation in unit with surfactant

Sources: *Innovative Treatment Technologies: Annual Status Report (EPA, 1993). Synopses of Federal Demonstrations of Innovative Site Remediation Technologies (FRTR, 1993).*

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## 4.14 Chemical Reduction/oxidation

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Technology	Description
<b>Soil, Sediment, and Sludge</b>	
<b>3.5 Ex Situ Physical/Chemical Treatment (assuming excavation)</b>	
4.14 Chemical Reduction/Oxidation	Reduction/oxidation chemically converts hazardous contaminants to non-hazardous or less toxic compounds that are more stable, less mobile, and/or inert. The oxidizing agents most commonly used are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide.

**Description:**

Figure 4-14:

Typical Chemical Reduction/Oxidation Process

Reduction/oxidation (Redox) reactions chemically convert hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. Redox reactions involve the transfer of electrons from one compound to another. Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons). The oxidizing agents most commonly used for treatment of hazardous contaminants are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Chemical redox is a full-scale, well-established technology used for disinfection of drinking water and wastewater, and it is a common treatment for cyanide wastes. Enhanced systems are now being used more frequently to treat contaminants in soils.

**Applicability:**

The target contaminant group for chemical redox is inorganics. The technology can be used but may be less effective against nonhalogenated VOCs and SVOCs, fuel hydrocarbons, and pesticides.

**Limitations:**

Factors that may limit the applicability and effectiveness of the process include:

- Incomplete oxidation or formation of intermediate contaminants may occur depending upon the contaminants and oxidizing agents used.
- The process is not cost-effective for high contaminant concentrations because of the large amounts of oxidizing agent required.
- Oil and grease in the media should be minimized to optimize process efficiency.

**Data Needs:**

A detailed discussion of these data elements is provided in Subsection 2.2.1 (Data Requirements for Soil, Sediment,

and Sludge). Treatability tests should be conducted to identify parameters such as water, alkaline metals, and humus content in the soils; the presence of multiple phases; and total organic halides that could affect processing time and cost.

**Performance Data:**

Chemical redox is a full-scale, well-established technology used for disinfection of drinking water and wastewater, and it is a common treatment for cyanide and chromium wastes. Enhanced systems are now being used more frequently to treat hazardous wastes in soils.

**Cost:**

Estimated costs range from \$190 to \$660 per cubic meter (\$150 to \$500 per cubic yard).

**References:**

EPA, Undated. *Lawrence Livermore National Laboratory Superfund Site*, Project Summary, EPA/540/SR-93/516.

EPA, 1991. *Chemical Oxidation Treatment*, Engineering Bulletin, EPA, OERR and ORD, Washington, DC, EPA/530/2-91/025.

Mayer, G., W. Bellamy, N. Ziemba, and L.A. Otis, 15-17 May 1990. "Conceptual Cost Evaluation of Volatile Organic Compound Treatment by Advanced Ozone Oxidation," *Second Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International*, Philadelphia, PA, EPA, Washington, DC, EPA Report EPA/2-90/010.

**Site Information:**

Site Name	Contact	Summary	Beginning Levels	Levels Attained	Costs
Excalibur Technology	Norma Lewis EPA RREL 26 West M.L. King Dr. Cincinnati, OH 45268 (513) 569-7665	Bench scale - Soil washing and catalytic ozone oxidation  Site demo scheduled for Coleman Evans, Florida	20,000 ppm	NA	\$92 to \$170/m <sup>3</sup> (\$70-\$130/yd <sup>3</sup> )

Note: NA = Not Available.

**Points of Contact:**

Contact	Government Agency	Phone	Location
Naomi Barkley	EPA RREL	(513) 569-7854 Fax: (513) 569-7620	26 West M.L. King Dr. Cincinnati, OH 45268
Technology Demonstration and Transfer Branch	USAEC	(410) 671-2054 Fax: (410) 612-6836	SFIM-AEC-ETD APG, MD 21010-5401

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## 4.17 Soil Washing

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Technology	Description
<b>Soil, Sediment, and Sludge</b>	
<b>3.5 Ex Situ Physical/Chemical Treatment (assuming excavation)</b>	
4.17 Soil Washing	Contaminants sorbed onto fine soil particles are separated from bulk soil in an aqueous-based system on the basis of particle size. The wash water may be augmented with a basic leaching agent, surfactant, pH adjustment, or chelating agent to help remove organics and heavy metals.

### Description:

[Figure 4-17:  
Typical Soil Washing  
Process](#)

Soil washing is a water-based process for scrubbing soils ex situ to remove contaminants. The process removes contaminants from soils in one of two ways:

- By dissolving or suspending them in the wash solution (which is later treated by conventional wastewater treatment methods).
- By concentrating them into a smaller volume of soil through particle size separation, gravity separation, and attrition scrubbing (similar to those techniques used in sand and gravel operations).

Soil washing systems incorporating most of the removal techniques offer the greatest promise for application to soils contaminated with a wide variety of heavy metal, radionuclides, and organic contaminants. Commercialization of the process, however, is not yet extensive.

The concept of reducing soil contamination through the use of particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically, to clay, silt, and organic soil particles. The silt and clay, in turn, are attached to sand and gravel particles by physical processes, primarily compaction and adhesion. Washing processes that separate the fine (small) clay and silt particles from the coarser sand and gravel soil particles effectively separate and concentrate the contaminants into a smaller volume of soil that can be further treated or disposed of. Gravity separation is effective for removing high or low specific gravity particles such as heavy metal-containing compounds (lead, radium oxide, etc.). Attrition scrubbing removes adherent contaminant films from coarser particles. The clean, larger fraction can be returned to the site for continued use.

### Applicability:

The target contaminant groups for soil washing are SVOCs, fuels, and inorganics. The technology can be used on selected VOCs and pesticides. The technology offers the potential for recovery of metals and can clean a wide range of organic and inorganic contaminants from

coarse-grained soils.

**Limitations:**

Factors that may limit the applicability and effectiveness of the process include:

- Fine soil particles (e.g., silt, clays) may require the addition of a polymer to remove them from the washing fluid.
- Complex waste mixtures (e.g., metals with organics) make formulating washing fluid difficult.
- High humic content in soil may require pretreatment.
- The aqueous stream will require treatment.

**Data Needs:**

A detailed discussion of these data elements is provided in Subsection 2.2.1 (Data Requirements for Soil, Sediment, and Sludge). Particle size distribution (0.24 to 2 mm optimum range); soil type, physical form, handling properties, and moisture content; contaminant type and concentration; texture; organic content; cation exchange capacity; pH and buffering capacity.

**Performance Data:**

At the present time, soil washing is used extensively in Europe but has had limited use in the United States. During 1986-1989, the technology was one of the selected source control remedies at eight Superfund sites.

Soil washing is most commonly used in combination with the following technologies: bioremediation, incineration, and solidification/stabilization. Depending on the process used, the washing agent and soil fines are residuals that require further treatment. When contaminated fines have been separated, coarse-grain soil can usually be returned clean to the site. The time to complete cleanup of the "standard" 18,200-metric-ton (20,000-ton) site using soil washing would be less than 3 months.

**Cost:**

The average cost for use of this technology, including excavation, is approximately \$130 to \$220 per metric ton (\$120 to \$200 per ton), depending on the target waste quantity and concentration.

**References:**

EPA, 1989. *Innovative Technology: Soil Washing*, OSWER Directive 9200.5-250FS.

EPA, 1989. *Soils Washing Technologies for: Comprehensive Environmental Response, Compensation, and Liability Act, Resource Conservation and Recovery Act, Leaking Underground Storage Tanks, Site Remediation*. EPA, 1990. *Soil Washing Treatment*, Engineering Bulletin, EPA, OERR, Washington, DC, EPA/540/2-90/017. Available from NTIS, Springfield, VA, Order No. PB91-228056.

EPA, 1991. *Biotrol Soil Washing System*, EPA RREL, series includes Technology Evaluation Vol. I, EPA/540/5-91/003a, PB92-115310; Technology Evaluation Vol. II, Part A, EPA/540/5-91/003b, PB92-115328; Technology Evaluation Vol. II, Part B, EPA/540/5-91/003c, PB92-115336; Applications Analysis, EPA/540/A5-91/003; Technology Demonstration Summary, EPA/540/S5-91/003; and Demonstration Bulletin,

EPA/540/M5-91/003.

EPA, 1992. *A Citizen's Guide to Soil Washing*, EPA, OSWER, Washington, DC, EPA/542/F-92/003.

EPA, 1992. *Bergmann USA Soil/Sediment Washing System*, EPA RREL, Demonstration Bulletin, EPA/540/MR-92/075.

EPA, 1993. *Bescorp Soil Washing System Battery Enterprises Site Brice Environmental Services, Inc.*, EPA RREL, Demonstration Bulletin, EPA/540/MR-93/503.

EPA, 1993. *Biogenesis Soil Washing Technology*, EPA RREL, series includes Demonstration Bulletin, EPA/540/MR-93/510; Innovative Technology Evaluation Report, EPA/540/R-93/510; and Site Technology Capsule, EPA/540/SR-93/510.

Raghavan, R., D.H. Dietz, and E. Coles, 1988. *Cleaning Excavated Soil Using Extraction Agents: A State-of-the-Art Review*, EPA Report EPA 600/2-89/034.

#### Site Information:

Site Name	Contact	Summary	Beginning Levels	Levels Attained	Costs
Toronto Port Industrial Dist. Ontario, Canada	Dennis Lang Toronto Harbor Comm. 60 Harbour St. Toronto, CA M5J 1B7 (416) 863-2047 Fax: (416) 863-4830	Soil washing (volume reduction), metal dissolution, and chemical hydrolysis with biodegradation (organics)	52 ppm Naphthalene; 10 ppm benzo(a)-pyrene	<5; 2.6	NA
Montclair Superfund Site Montclair, NJ	Mike Eagle EPA, Office of Radiation Programs 401 M St., SW, ANR-461 Washington, DC 20460 (202) 233-9376	Attrition mills, classifiers, and filter press to reduce the amount of low-level radioactive waste to be disposed of, 56% volume reduction	NA	11 pCi/g	\$300/hour

Excalibur Technology	Norma Lewis EPA RREL 26 West M.L. King Dr. Cincinnati, OH 45268 (513) 569-7665	Bench scale - Soil washing and catalytic ozone oxidation  Site demo scheduled for Coleman Evans, Florida	20,000 ppm total capacity	NA	\$92 to \$170/m <sup>3</sup> (\$70-\$130/yd <sup>3</sup> )
Alaskan Battery Enterprises Superfund Site, Fairbanks, AK	Hugh Masters EPA RREL 2890 Woodbridge Ave. Building 10 Edison, NJ	Pilot scale, featuring gravity separation and particle size classification	2,280-10,374 ppm lead	15-2,541 ppm	
Twin Cities AAP New Brighton, MN	Michael D. Royer EPA RREL 2890 Woodbridge Ave. Building 10 Edison, NJ (908) 321-6633	Full scale, featuring gravity separation, particle size classification, metal leaching, and lead recovery	Demonstration is in progress. Field work completed but laboratory work not complete.	Targets for background remediation: Cr, Cu, Hg, and Ni. Some batches reached state remediation goals.	NA
Escambia Wood Treating Company Superfund Site, Pensacola, FL	Terri Richardson EPA RREL 26 West M.L. King Dr. Cincinnati, OH	Pilot scale, featuring particle size classification and surfactant addition	550-1,700 ppm PAHs 48-210 ppm PCP	45 ppm PAHs 3 ppm PCPs	\$151/metric ton (\$137/ton) (projected)
Macgill & Gibbs New Brighton, MN BioTrol	Dennis Chilcote BioTrol, Inc. 10300 Valley View Rd. Eden Prairie, MN 55344-3456 (612) 942-8032	Soil washing (volume reduction), process water treated in a bio-reactor, fines treated in a slurry bioreactor.	130 ppm PCP, 247 ppm PAHs	98.88% removal	\$168/ton

Note: NA = Not Available.

#### Points of Contact:

Contact	Government Agency	Phone	Location
Michael Gruenfeld	EPA RREL Technical Support	(908) 321-6625	2890 Woodbridge Ave. MS-104 Edison, NJ 08837-3679
S. Jackson Hubbard	EPA RREL	(513) 569-7507	26 West M.L. King Dr. Cincinnati, OH 45268
Jim Galloway Frank Snite	USAED	(313) 226-6760	Detroit, MI 48231-1027
Technology Demonstration and Transfer Branch	USAEC	(410) 671-2054 Fax: (410) 612-6836	SFIM-AEC-ETD APG, MD 21010-5401
Mary K. Stinson	EPA RREL	(908) 321-6683	2890 Woodbridge Ave. MS-104 Edison, NJ 08837-3679

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## 4.19 Solidification/Stabilization (Ex Situ)

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Technology	Description
<b>Soil, Sediment, and Sludge</b>	
<b>3.5 Ex Situ Physical/Chemical Treatment (assuming excavation)</b>	
4.19 Solidification/Stabilization (Ex Situ)	Contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization).

**Description:**

Figure 4-19:

[Typical Ex Situ Solidification/stabilization  
Process Flow Diagram](#)

As for in situ solidification/stabilization (S/S) (see Technology Profile No. 4.7), ex situ S/S contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization). Ex situ S/S, however, typically requires disposal of the resultant materials.

**Applicability:**

The target contaminant group for ex situ S/S is inorganics, including radionuclides. The technology has limited effectiveness against SVOCs and pesticides; however, systems designed to be more effective against organic contaminants are being developed and tested.

**Limitations:**

Factors that may limit the applicability and effectiveness of the process include:

- Environmental conditions may affect the long-term immobilization of contaminants.
- Some processes result in a significant increase in volume (up to double the original volume).
- Certain wastes are incompatible with different processes. Treatability studies are generally required.
- VOCs are generally not immobilized.
- Long-term effectiveness has not been demonstrated for many contaminant/process combinations.

**Data Needs:**

A detailed discussion of these data elements is provided in [Subsection 2.2.1](#) (Data Requirements for Soil, Sediment, and Sludge). Soil parameters that must

be determined include particle size, Atterberg limits, moisture content, metal concentrations, sulfate content, organic content, density, permeability, unconfined compressive strength, leachability, microstructure analysis, and physical and chemical durability.

**Performance Data:**

Depending upon the original contaminants and the chemical reactions that take place in the ex situ S/S process, the resultant stabilized mass may have to be handled as a hazardous waste. For certain types of radioactive waste, the stabilized product must be capable of meeting stringent waste form requirements for disposal (e.g., Class B or Class C low level materials). Remediation of a site consisting of 18,200 metric tons (20,000 tons) could require less than 1 month, depending on equipment size and type and soil properties (e.g., percent solids and particle size).

DOE has demonstrated the Polyethylene Encapsulation of Radionuclides and Heavy Metals (PERM) process at the bench scale. The process is a waste treatment and stabilization technology for high-level mixed waste. Specific targeted contaminants include radionuclides (e.g., cesium, strontium, and cobalt), and toxic metals (e.g., chromium, lead, and cadmium). The process should be ready for implementation in FY95.

**Cost:**

Ex situ solidification/stabilization processes are among the most mature remediation technologies. Representative overall costs from more than a dozen vendors indicate an approximate cost of under \$110 per metric ton (\$100 per ton), including excavation.

**References:**

Bricka, R.M., et al., 1988. *An Evaluation of Stabilization/Solidification of Fluidized Bed Incineration Ash (K048 and K051)*, USAE-WES Technical Report EL-88-24.

EPA, 1989. *Chemfix Technologies, Inc. Chemical Fixation/Stabilization*, EPA RREL, Technology Evaluation Vol. I, EPA/540/5-89/011a, PB91-127696; and Technology Evaluation Vol. II, EPA/540/5-89/011b, PB90-274127.

EPA, 1989. *Harcon Solidification*, EPA RREL, series includes Technology Evaluation Vol. I, EPA/540/5-89/001a, PB89-158810; Technology Evaluation Vol. II, EPA/540/5-89/001b, PB89-158828; Applications Analysis, EPA/540/A5-89/001; and Technology Demonstration Summary, EPA/540/S5-89/001.

EPA, 1989. *Solidtech, Inc. Solidification*. EPA RREL, series includes Technology Evaluation Vol. I, EPA/540/5S-89/005a; Technology Evaluation Vol. II, EPA/540/5S-89/005b, PB90-191768; Applications Analysis, EPA/540/A5-89/005; Technology Demonstration Summary, EPA/540/S5-89/005; and Demonstration Bulletin, EPA/540/M5-89/005.

EPA, 1989. *Stabilization/Solidification of CERCLA and RCRA Wastes - Physical Tests, Chemical Testing Procedures, Technology Screening and Field Activities*, EPA, ORD, Washington, DC, EPA/625/6-89/022.

EPA, 1992. *Silicate Technology Corporation Solidification/Stabilization of Organic/Inorganic Contaminants*, EPA RREL, Demonstration Bulletin, EPA/540/MR-92/010; Applications Analysis, EPA/540/AR-92/010, PB93-172948.

EPA, 1993. *Solidification/Stabilization and Its Application to Waste Materials*, Technical Resource Document, EPA, ORD, Washington, DC, EPA/530/R-93/012.

EPA, 1993. *Solidification/Stabilization of Organics and Inorganics*, Engineering Bulletin, EPA, ORD, Cincinnati, OH, EPA/540/S-92/015.

DOE, 1993. *Technology Name: Polyethylene Encapsulation*, Technology Information Profile (Rev. 2) for ProTech, DOE ProTech Database, TTP Reference No. BH-321201.

#### Site Information:

Site Name	Contact	Summary	Beginning Levels	Levels Attained	Costs
Portable Equipment Salvage Clackamas, OK	Edwin Barth - EPA CERI	Dry alumina, calcium, and silica blended in reaction vessel.	NA	93.2 to >99.9% reduction of Cu, Pb, and Zn TCLP levels	\$80/metric ton (\$73/ton)
Naval Construction Battalion Center Port Hueneme, CA	NFESC Code 411  Port Hueneme, CA 93043 (614) 424-5442	Spent blasting abrasives screened and mixed with portland cement and soluble silicates.	NA	<5 ppm TCLP	\$94/metric ton (\$85/ton)
Robins AFB Macon, GA	Terry Lyons EPA RREL 26 West M.L. King Dr. Cincinnati, OH 45268 (513) 569-7589	Addition of pozzolonic cementitious materials.	NA	NA	NA

Note: NA = Not Available.

#### Points of Contact:

Contact	Government Agency	Phone	Location
Edwin Barth	EPA CERI	(513) 569-7669 Fax: (513) 569-7585	26 West M.L. King Dr. Cincinnati, OH 45268
Mark Bricka	USAE-WES	(601) 634-3700	CEWES-EE-S 3909 Halls Ferry Road Vicksburg, MS 39180-6199
Patricia M. Erikson	EPA RREL	(513) 569-7884 Fax: (513) 569-7676	26 West M.L. King Dr. Cincinnati, OH 45268
Technology Demonstration and Transfer Branch	USAEC	(410) 671-2054 Fax: (410) 612-6836	SFIM-AEC-ETD APG, MD 21010-5401
Sherry Gibson	DOE	(301) 903-7258	EM-552, Trevion II Washington, DC 20585

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## 4.27 Vitrification (Ex Situ)

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Technology	Description
<b>Soil, Sediment, and Sludge</b>	
<b>3.6 Ex Situ Thermal Treatment (assuming excavation)</b>	
4.27 Vitrification (Ex Situ)	Contaminated soils and sludges are melted at high temperature to form a glass and crystalline structure with very low leaching characteristics.

**Description:**

Figure 4-27:  
[Typical Ex Situ Vitrification  
Process Block Flow](#)

Ex situ vitrification is designed to encapsulate inorganic contaminants, rather than reduce contaminant concentrations. Destruction of the organic contaminants present in the treated media, however, does occur because of temperatures achieved in the process.

Ex situ vitrification is effective in reducing the mobility of the contaminated wastes within the media. The vitrified mass has high strength and resistance to leaching. The strength properties of material vitrified by different systems can vary widely. Systems in which the vitrified mass is quench-cooled may produce a more easily fractured mass than systems in which the mass is allowed to air cool. Systems in which fluxing agents are used will also have different strength properties. The composition of the soil that is vitrified may also affect the strength properties of the vitrified material.

Ex situ vitrification is normally considered a standalone technology; however, its potential for use in treating the solid residuals from other technologies, such as incinerator ash, is receiving increasing attention.

**Applicability:**

Ex situ vitrification is applicable to the full range of contaminant groups, but inorganics is the target contaminant group. Metals, radionuclides, etc. are encapsulated in the vitrified mass, resisting leaching for geologic time periods.

**Limitations:**

Factors that may limit the applicability and effectiveness of the process include:

- Organic off-gases need to be controlled. Some volatile heavy metal and radioactive contaminants may volatilize and require treatment in the off-gas system.
- Use or disposal of the resultant vitrified slag is required.

**Data Needs:**

A detailed discussion of these data elements is provided in

Subsection 2.2.1 (Data Requirements for Soil, Sediment, and Sludge). In addition to identifying soil contaminants and their concentrations, information necessary for engineering thermal systems to specific applications include soil moisture content and classification (no sieve analysis is necessary), and the soil fusion temperature.

**Performance Data:**

An EPA SITE program demonstration of plasma arc vitrification was conducted in 1991 at DOE's Component Development and Integration facility in Butte, Montana. During the demonstration, the furnace processed approximately 1,820 kilograms (4,000 pounds) of waste. The waste consisted of soil with heavy metals from the Silver Bow Creek Superfund site, spiked with 28,000-ppm zinc oxide and 1,000-ppm hexachlorobenzene and mixed in a 90-to-10 weight ratio with No. 2 diesel oil.

DOE is currently developing a full-scale prototype of a fixed hearth DC plasma torch process that will convert full drums of waste materials directly to an enhanced waste form in a one step process. An arc melter vitrification process exists but requires engineering development.

**Cost:**

Approximate overall cost is \$770 per metric ton (\$700 per ton). Ex situ vitrification is a relatively complex, high-energy technology requiring a high degree of specialized skill and training.

**References:**

Circeo, Louis J., Ph.D., 1991. *Destruction and Vitrification of Asbestos Using Plasma Arc Technology*, Georgia Institute of Technology for USACERL, Champaign, IL.

DOE, undated. *Technology Name: Arc Melter Vitrification*, Technology Information Profile (Rev. 2) for ProTech, DOE ProTech Database, TTP Reference No.: ID-132011.

DOE, 1993. *Technology Name: Arc Melter Vitrification*, Technology Information Profile (Rev. 2) for ProTech, DOE ProTech Database, TTP Reference No.: ID-132010.

DOE, 1993. *Technology Name: Fixed Hearth Plasma Torch Process*, Technology Information Profile (Rev. 2) for ProTech, DOE ProTech Database, TTP Reference No.: PE-021202.

EPA, 1992. *Babcock and Wilcox Cyclone Furnace Vitrification*, EPA RREL, series includes Technology Evaluation Vol. I, EPA/540/R-92/017A, PB92-222215; Technology Evaluation Vol. II, EPA/540/R-92/017B, PB92-222223; Applications Analysis, EPA/540/AR-92/017, PB93-122315; Technology Demonstration Summary, EPA/540/SR-92/017; and Demonstration Bulletin, EPA/540/MR-92/011.

EPA, 1993. *Babcock and Wilcox Cyclone Furnace Vitrification*, EPA RREL, Emerging Tech., Bulletin, EPA/540/P-92/010;

Emerging Tech. Report. EPA/540/R-93/507, PB93-163038;  
Emerging Tech. Summary, EPA/540/SR-93/507.

**Site Information:**

Site Name	Contact	Summary	Beginning Levels	Levels Attained	Costs
DOE Butte, MT	Laurel Staley EPA RREL 26 West M.L. King Dr. Cincinnati, OH 45268 (513) 569-7863 Fax: (513) 569-7620	Heavy metal waste fed into plasma arc centrifugal treatment unit.	28,000 ppm zinc oxide 1,000 ppm hexachlorobenzene	Meets TCLP	\$2,000/metric ton (\$1,816/ton)
Babcock & Wilcox, Alliance Research Center Alliance, OH	Laurel Staley EPA RREL 26 West M.L. King Dr. Cincinnati, OH 45268 (513) 569-7863 Fax: (513) 569-7620	Wastes containing heavy metals and organic compounds fed into a cyclone furnace. Pilot scale.	TCLP 49.9 ppm Cd 2.67 ppm Cr 97.1 ppm Pb	TCLP <0.12 ppm Cd 0.22 ppm Cr <0.31 ppm Pb >99.99% DRE for anthracene and dimethylphthalate	\$495 to \$605/ton (\$450 to \$550/ton)
HRD Facility Monaca, PA	Marta Richards EPA RREL 26 West M.L. King Dr. Cincinnati, OH 45268	Wastes containing heavy metals and organic compounds fed into a hot reducing atmosphere.	54,000 ppm Pb 410 ppm Cd 5,200 ppm As 860 ppm Ba 88 ppm Cr	TCLP 0.474 ppm As 0.175 ppm Ba <0.05 ppm Cd <0.06 ppm Cr <0.33 ppm Pb	\$220 to \$1,020/metric ton (\$200 to \$930/ton)

Note: NA = Not Available.

**Points of Contact:**



Contact	Government Agency	Phone	Location
Jaffer Mohiuddin	DOE	(301) 903-7965	EM-552, Trevion II Washington, DC 20585
Randy Parker	EPA RREL	(513) 569-7271 Fax: (513) 569-7620	26 West M.L. King Dr. Cincinnati, OH 45268
Hany H. Zaghloul, P.E.	USACE CERL	(217) 373-7249 (217) 352-6511 (800) USA-CERL	P.O. Box 9005 Champaign, IL 61826-9005
Technology Demonstration and Transfer Branch	USAEC	(410) 671-2054 Fax: (410) 612-6836	SFIM-AEC-ETD APG, MD 21010-5401

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## 4.28 Excavation, Retrieval, and Off-Site Disposal

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Technology	Description
<b>Soil, Sediment, and Sludge</b>	
<b>3.7 Other Treatment</b>	
4.28 Excavation, Retrieval, and Off-Site Disposal	Contaminated material is removed and transported to permitted off-site treatment and disposal facilities. Pretreatment may be required.

**Description:**

Figure 4-28:

[Typical Contaminated Soil  
Excavation Diagram](#)

Contaminated material is removed and transported to permitted off-site treatment and/or disposal facilities. Some pretreatment of the contaminated media usually is required in order to meet land disposal restrictions.

**Applicability:**

Excavation and off-site disposal is applicable to the complete range of contaminant groups with no particular target group. Although excavation and off-site disposal alleviates the contaminant problem at the site, it does not treat the contaminants.

**Limitations:**

Factors that may limit the applicability and effectiveness of the process include:

- Generation of fugitive emissions may be a problem during operations.
- The distance from the contaminated site to the nearest disposal facility will affect cost.
- Depth and composition of the media requiring excavation must be considered.
- Transportation of the soil through populated areas may affect community acceptability.
- Disposal options for certain waste (e.g., mixed waste or transuranic waste) may be limited. There is currently only one licensed disposal facility for radioactive and mixed waste in the United States.

**Data Needs:**

A detailed discussion of these data elements is provided in [Subsection 2.2.1](#) (Data Requirements for Soil, Sediment, and Sludge).

The type of contaminant and its concentration will impact off-site disposal requirements. Soil characterization as dictated by land disposal restrictions (LDRs) are required. Most hazardous wastes must be treated to meet either RCRA or .

non-RCRA treatment standards prior to land disposal. Radioactive wastes would have to meet disposal facility waste form requirements based on waste classification.

**Performance Data:**

Excavation and off-site disposal is a well proven and readily implementable technology. Prior to 1984, excavation and off-site disposal was the most common method for cleaning up hazardous waste sites. Excavation is the initial component in all ex situ treatments. As a consequence, the remediation consulting community is very familiar with this option.

The excavation of 18,200 metric tons (20,000 tons) of contaminated soil would require about 2 months. Disposal of the contaminated media is dependent upon the availability of adequate containers to transport the hazardous waste to a RCRA-permitted facility.

CERCLA includes a statutory preference for treatment of contaminants, and excavation and off-site disposal is now less acceptable than in the past. The disposal of hazardous wastes is governed by RCRA (40 CFR Parts 261-265), and the U.S. Department of Transportation (DOT) regulates the transport of hazardous materials (49 CFR Parts 172-179, 49 CFR Part 1387, and DOT-E 8876).

DOE has demonstrated a cryogenic retrieval of buried waste system, which uses liquid nitrogen (LN<sub>2</sub>) to freeze soil and buried waste to reduce the spread of contamination while the buried material is retrieved with a series of remotely operated tools. Other excavation/retrieval systems that DOE is currently developing include a remote excavation system, a hydraulic impact end effector, and a high pressure waterjet dislodging and conveyance end effector using confined sluicing.

**Cost:**

Cost estimates for excavation and disposal range from \$300 to \$510 per metric ton (\$270 to \$460 per ton) depending on the nature of hazardous materials and methods of excavation. These estimates include excavation/removal, transportation, and disposal at a RCRA permitted facility. Excavation and off-site disposal is a relatively simple process, with proven procedures. It is a labor-intensive practice with little potential for further automation. Additional costs may include soil characterization and treatment to meet land ban requirements.

**References:**

Church, H.K., 1981. *Excavation Handbook*, McGraw Hill Book Co., New York, NY.

EPA, 1991. *Survey of Materials-Handling Technologies Used at Hazardous Waste Sites*, EPA, ORD, Washington, DC, EPA/540/2-91/010.

EPA, 1992. *McColl Superfund Site Demonstration of a Trial Excavation*, EPA RREL, series include Technology Evaluation

EPA/S40/R-92/015, PB92-226448; Applications Analysis,  
EPA/540/AR-92/015; and Technology Demonstration.  
Summary, EPA/540/SR/-92/015.

**Points of Contact:**

Contact	Government Agency	Phone	Location
Jaffer Mohiuddin	DOE Program Manager	(301) 903-7965	EM-552, Trevion II Washington, DC 20585
Technology Demonstration and Transfer Branch	USAEC	(410) 671-2054 Fax: (410) 612-6836	SFIM-AEC-ETD APG, MD 21010-5401

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# Techknow

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0.45 Coating Removal and Decontamination from Metal, Concrete, and Composite Surfaces Using Lasers

Lasertronics has built a hand-held and a robotically applied laser coating removal system that uses high power laser pulses to remove a variety of coatings and contaminations from almost any surface. This Laser coating removal system is applicable for the removal of radiation decontamination, lead paint, biological contamination, rust, all types of paints, chemicals, heavy metals, and organics and for a variety of surface cleaning requirements. LASER COATING REMOVAL & DECON The operational ...

0.44 Battery Waste Treatment Process (BWTP)

The technology uses washing, liberation and gravity separation techniques to treat waste from battery wrecking operations and produce recyclable products. Typically, the technology will treat mixed and/or landfilled battery wastes, and produce clean hard rubber, clean plastic, and lead concentrate products. The lead concentrate products contain chemical lead compounds in a cake or metallic form.

0.43 TerraMet TM Heavy Metal Removal Technology

TerraMet heavy metal removal technology is an extractive process which leaches heavy metals from contaminated soil, dust, sludge, or sediment with a proprietary aqueous leaching solution. After dissolution of the metal compounds, the metal ion is removed and recovered from the aqueous leachate by one of three metal recovery steps (liquid ion exchange, resin ion exchange, or reduction). The aqueous leaching solution is thereby freed of metal and is reused to leach more metal from ...

0.43 Field Operation Lead Testing Laboratory

On-site laboratory grade analytical analysis of lead in paint, dust, air, soil, drinking water, wastewater and all solid waste materials. Status: Intellectual Property  
Status: Patent Licensing Available No Cost: Cost per analysis is btw. \$4.50 and \$7.00 depending on matrice to be analyzed.

0.42 Portable Lead Analyzer- Pb Analyzer

Updated: 8/27/97 Source: Phoenix D&D Technology Module 1.0 Media Applicable  
Contaminants: PENTACHLOROPHENOLS, HYDROCARBONS, OILS, PHENOLS, HALOGENATED COMPOUNDS, NON-HALOGENATED COMPOUNDS, PAHS, SOLVENTS, POLYNUCLEAR AROMATICS, DNAPLS, PCBS, VOCs, BTEX (BENZENE, TOLUENE, ETHYLENE, XYLENE),

CHLORINATED ORGANIC COMPOUNDS, MERCURY, VAPORS, ORGANICS, LNAPLS, TCE, KETONES, PETROLEUM, NOT DEFINED Status: Intellectual Property Status: Patent Licensing Available No Cost: Capital Cost: \$49,500.00 Operating Cost: ...

0.41 Electro-Klean (TM)

Electrokinetic soil processing system is powered by direct current (DC) and generates both electrokinetic and electrochemical (EK/EC) functions which jointly remove or capture the contaminants from the soil. The EK/EC process is an in situ continuous process which can be applied to removal or or capture of: heavy metals, radionuclides, and selected organic pollutants from sands, silts, fine-grained clays, and sediments. The acid front chemically extracts the organic compounds and heavy ...

0.41 Macroencapsulation of Mixed Waste

Macroencapsulation is a process in which larger pieces of waste not suitable for extrusion processing (e.g. lead, debris) are surrounded by a layer of clean polyethylene to isolate the contaminants from the environment. Polyethylene is an inert, low permeability, thermoplastic material that is highly resistant to chemical attack, microbial degradation and radiation damage. The polyethylene macroencapsulation process utilizes a single-screw plastics extruder to melt, convey, and pump molten ...

0.41 High-Temperature Vacuum Distillation Separation of Plutonium Waste Salts

A high-temperature vacuum distillation separation process is being developed for residue sodium chloride-potassium chloride salts resulting from past pyrochemical processing of plutonium. Separation of the plutonium from the waste salts will lead to a large reduction in the cost of disposal even if the salts do not meet low-level waste disposal criteria. This process has the potential of providing clean separation of salt from the actinide content with minimal amounts of secondary waste ...

0.41 Phosphate Induced Metal Stabilization

Metals readily leach from contaminated soils and sediments and serve as a constant source of metal contamination to groundwater. This proposal seeks to stabilize lead, zinc, cadmium and other metals of concern in various industries, especially DOE waste streams, the mining industry, and industrial wastes, by chemically binding them into new stable phosphate phases (apatite minerals) and other relatively insoluble solids in permeable groundwater barriers or in above-ground treatment systems. ...

The problem of contaminant metals in soils and groundwater is presently identified by the United States Environmental Protection Agency (EPA) as one of the most

- 0.41 Phosphate Induced Metal stabilization
- critical environmental risks. Metals readily leach from contaminated soils and sediments and serve as a constant source of metal contamination to groundwater. This proposal seeks to stabilize lead, zinc, cadmium and other metals of concern in the Coeur d'Alene district in Idaho, by chemically binding them into new stable phosphate ...
- 0.41 Crystalline Silicotitanates for Removal of Acidic Strontium, Anionic Radionuclides, Actinides, Lead and Cadmium
- THIS TECHNOLOGY PROFILE IS BEING UPDATED/COMPLETED BY THE DEPARTMENT OF ENERGY. Real time information on this technology can be found at the DOE OST web site as it becomes available. The web site address is listed in the related sites section below.
- 0.41 Laser Surface Cleaning
- The objectives of the laser cleaning project are to develop, demonstrate and commercialize laser ablation technology systems for lead-based paint abatement and radiological surface decontamination on concrete and metal surfaces. Pulsed-repetition CO2 laser systems are able to effectively clean coatings from a variety of substrates including metals, composite materials, wood and concrete. Laser-based systems are well suited for the removal of many DOE complex coatings including lead-based ...
- 0.40 Prompt Fission Neutron Logging
- A pulsed source of MeV neutrons in a logging tool provides neutrons which lead to slow-neutron-induced fission of U235 in the formation. Epithermal neutrons and thermal neutrons returning from the formation following fission are counted separately in detectors in the logging tool. Technique measures both epithermal and thermal neutrons.
- 0.40 Electrically-Charged Fog for Dust Control
- Devices have been used in a laboratory and have been successfully demonstrated in one or more lead, copper, steel foundries, in ore milling, battery building companies, several sections of a steel mill including: ore recovery, coke ovens, rough and fine grinding areas. Use in a copper mine has covered the drilling, milling, casting areas and disposal of wastes. It requires 110 volts at 3 amps, 1 CFM of compressed air at 80 psi and a supply of water, 1 gallon per minute.
- 0.40 MAECTITE Chemical Treatment Process
- Lead & heavy metal treatment process for soil and waste. Reagents simulate the nucleation of crystals by chemical bonding to yield mineral compounds in molecular forms. Process readily liberates water in waste prior to treatment.
- We would like to propose the use of Bac-Terra Remedial Technology as a method of treatment for (1) metals in soil and combinations of metals and organics in soil, (2) in situ

0.40 Bac-Terra Remedial Technology

ground water treatment technologies, (3) in situ and on site treatment processes for large volume of soil, and sediment with below free product level of contaminant concentration. Listed below is a PARTIAL LIST of compounds readily biodegradable with the use of Bac-Terra Remedial Technology... Bac-Terra, marketed by ...

0.40 Earth Technologies

Earth Technologies metal recovery system recovers heavy metals such as lead from soils, sludges and sediments. Earth Technologies metal recovery system is mobile and self contained. Earth Technologies, Inc. has developed a mobile machine that uses a rotary riffle concentrator to separate metal particulate from the soil or sludge.

0.40 Terra-Vit

Terra-Vit can process waste containing nearly the entire periodic table of elements with the exceptions of gases, iodine, and mercury. The process' ability to thermally destroy organic materials and chemically bind waste metals into a chemically durable solid is broad. Terra-Vit is a continuous, above ground melting technology that oxidizes, melts, and transforms a broad spectrum of wastes into a glass or rock like material.

0.40 In Situ Gaseous Reduction System

The major effort of this project is currently directed toward testing the feasibility of treating unsaturated soils by injection of reactive gases. Using in situ immobilization of contaminants avoids the costs and risks to public health and worker safety associated with excavation, surface treatment, transportation, and disposal. To avoid the excessive costs and risks to public health and worker safety associated with excavation, treatment, transportation, and disposal, The In Situ Gaseous ...

0.40 On-site leaching of low level radioactive soils

On-site leaching of low level radioactive soils using lixivants, the O3LRS technology, combines lixivants, excursion containment, in-situ or ex-situ lixiviant delivery, leachate solution collection, and leachate solution processing to mobilize and recover low level radionuclides from soil. The process consists of applying a solution to an in-situ contaminant soil plume or intact pile of excavated contaminated particulate matter. On site remediation of low level radioactive soils and non-...

0.40 Polymer Microencapsulation

The process operates at a low temperature, requires no offgas treatment, and generates no secondary waste. The U.S. Department of Energy has supported over the past 12 years the development of polymer encapsulation technologies for treatment of low-level radioactive, hazardous, and mixed wastes. Mixed waste stabilization using polymers is adopted from existing processes widely



used in the polymer industry.

0.40     Chemcloud

The technology is targeted for battery waste sites. The batteries or the broken parts of batteries will be treated mechanically to separate the lead, plastic, and battery paste. The technology is limited to wastes existing on waste battery sites or similar situations.

0.39     Ultra-High Pressure (UHP)  
Water Jet

A fully integrated radon and thoron working-level measurement system using alpha spectroscopic analysis to discriminate between Radon and Thoron. The UHP is one of the leading systems for nuclear plant services and for the decontamination and decommissioning applications. Over 15 years of system development and field service work.

0.39     Remotely Operated Scabbler  
MOOSE

Best application of MOOSE technology is to floor areas greater than 200 sq. Automatic removal of contaminated surfaces of concrete floors and slabs. Chief advantage is completely dustless operation, minimized waste generation, and automatic packaging of completely dry concrete waste for further disposal.

0.39     Acid Extraction

The Acid Extraction Treatment System (AETS) removes heavy metal contamination from soil. AETS includes a regeneration system to remove metals from the spent extractant and reclaim the acid for continuous reuse, thereby eliminating waste extractant treatment systems or effluent discharge. The soil is rinsed and further dewatered, while the extractants are pumped to a proprietary regeneration system which removes the metals and regenerates the acid solution.

More ...

<b>Terra-Vit</b>		<b>Updated:</b> 8/13/98
<b>Terra-Vit</b>		
<b>Source:</b>		<b>Media</b> Soil Sludge
<b>Applicable Contaminants:</b> ASBESTOS, BTEX (BENZENE,TOLUENE,ETHYLENE,XYLENE), CYANIDES, DIOXINS/FURANS, EXPLOSIVES/PROPELLENTS, HALOGENATED COMPOUNDS, NON-HALOGENATED COMPOUNDS, OTHER, PCBS, PESTICIDES & HERBICIDES, SOLVENTS		
<b>Summary:</b>  Terra-Vit can process waste containing nearly the entire periodic table of elements with the exceptions of gases, iodine, and mercury. The process can be considered for almost any waste stream. The process' ability to thermally destroy organic materials and chemically bind waste metals into a chemically durable solid is broad. This makes it well suited to wastes containing both organic materials and heavy metals or to those containing radioactive constituents.		
<b>Long Description</b>  Terra-Vit is a continuous, above ground melting technology that oxidizes, melts, and transforms a broad spectrum of wastes into a glass or rock like material. The melting energy is derived from the feed and from direct electrical heating of the molten material, similar to the process of the commercial glass industry. The process is typically operated continuously, 24 hours per day, particularly for large-scale operations (5 to hundreds of tons per day). The process can accommodate a broad range of chemical and physical compositions.		
<b>Related Information</b>  Description:		
<b>Status:</b> Available for Use		<b>Intellectual Property Status:</b> Patent
<b>Licensing Available:</b> Yes		<b>Cost:</b>
<b>Capital Cost:</b>		<b>Operating Cost:</b> \$50 to \$300 per wet ton
<b>Limitations:</b>  Water content in the waste in excess of 85 percent increases energy costs of the process. Solubility or inorganic materials in the final waste form is sometimes limited. Frequently, higher concentrations can be incorporated, but phase separation can occur. This can lead to lower waste concentration in the final glass, which may lead to higher costs. The separated phase may become encased in the glass matrix without degradation or release of the second phase. For specific wastes, special glass formulations can be developed that allow for higher concentrations. This must be done on a case by case basis. For example, some phosphate glasses can incorporate much higher concentrations of metal oxides such as chromium, arsenic, sulfur, and chlorine salts, and mercury. For silicate glasses the concentration limits for the metal oxides and other elements in the periodic table is approximated as follows: Appropriate		

concentration limits for elements in final waste form: less than 0.1 percent by weight: H, He, N, Ne, Ar, Br, Kr, Ru, Rh, Pd, Ag, I, Xe, Pt, Au, Hg, Rn; between 1 and 3 percent by weight: C, S, Cl, Cr, As, Se, Tc, Sn, Sb, Te; between 3 and 5 percent by weight: Ti, Mn, Cu, Co, Ni, Mo, Bi; between 5 and 15 percent by weight: F, La, Ce, Pr, Nd, Gd, Th, rare earths; between 15 and 25 percent by weight: Li, B, Na, Mg, Al, K, Ca, Fe, Zn, Rb, Sr, Cs, Fr, Ra, U; greater than 25 percent by weight: Si, P, Pb

The technology cannot treat gases or iodine. Mercury is difficult to incorporate. Chlorides and sulfates have a practical limit of about 1 weight percent in the final glass.

**Secondary Waste:**

**D&D:**

**Other Applications:**

**Tech Need:**

**Tech Sponsor:**

**DOE:**

Subsurface Contaminants

**External Database Source:**

VISITT

**Contacts:**

Name: Joe Perez

Title: Technical Group Manager

Phone: (509)37-5982

Email: [jm\\_perez@pnl.gov](mailto:jm_perez@pnl.gov)

**Comments:**

<b>Earth Technologies</b>		<b>Updated:</b> 8/11/98
<b>Envo-Tec</b>		
<b>Source:</b>		<b>Media</b> Soil Sludge
<b>Applicable Contaminants:</b> EXPLOSIVES/PROPELLENTS, HALOGENATED COMPOUNDS, HEAVY METALS, NON-HALOGENATED COMPOUNDS, RADIOACTIVE METALS		
<b>Summary:</b>  <p>Earth Technologies metal recovery system recovers heavy metals such as lead from soils, sludges and sediments. Earth Technologies metal recovery system is mobile and self contained. It can be set up and operating in under 4 hours. It is self-powered by its diesel generator. It will process 20 to 50 tons per hour on a continuous basis. The wash water is reticulated through the system during operation. A reagent can be added to the wash water and a complete water recovery system used to filter and clean the wash solution. Cleaned solids can be used as backfill on the same site. A smaller version powered by 5 horsepower gasoline engine will process up to 10 tons an hour. This smallest unit is mounted on a trailer and can be towed by a pick up.</p>		
<b>Long Description</b>  <p>Earth Technologies, Inc. has developed a mobile machine that uses a rotary riffle concentrator to separate metal particulate from the soil or sludge. This same equipment has been successfully recovering gold and diamonds for miners around the world for over 15 years. The process starts by screening soil through a grizzly into feed hopper mounted on the machine. The soil is then metered out of the feed hopper via a weight belt conveyor. An optional clay buster is available to pulverize hard clay soil. A screen system can be first used to screen out large pieces of debris or overburden from the soil. The conveyor feeds the soil into the top of the rotary riffle concentrator where wash water is added. The metal particles are separated from the soil by a physical scrubbing action and gravity separation within the rotary riffle concentrator. A triple lead reverse spiral separates and augurs the metal particulates to the recovery chute. The metal particles move counter-current to the water flow and are discharged at the upper end. Coarse aggregate and the water slurry are discharged at the upper end. Coarse aggregate and the water slurry are discharged at the lower end. The metal particles are discharged into containers for disposal. The coarse aggregate is discharged via a conveyor to a stockpile or to a dump truck. The water slurry is discharged into a water recovery pit or tank. The water is recirculated through the machine. This is a continuous system with soil fed into it by a front-end loader. The machine is completely mobile, it is mounted on tires and equipped for highway travel. It can be set up and operating on a site in 4 hours. A suitable reagent can be added to the wash water to recover some metal leachate or VOCs from the soil.</p>		
<b>Related Information</b>		
Description:		
<b>Status:</b> Basic Research	<b>Intellectual Property Status:</b> Patent	
<b>Licensing Available:</b> Yes	<b>Cost:</b>	

<b>Capital Cost:</b>		<b>Operating Cost:</b> \$30.00 to \$50.00 per ton	
<b>Limitations:</b>  Earth Technologies process will not operate in below freezing temperatures, or when the soil is frozen. Sandy or gravel soils are processed faster than clay soils. If the metals have leached into the soils this process may not remove all leached compounds.			
<b>Secondary Waste:</b>			
<b>D&amp;D:</b>			
<b>Other Applications:</b>			
<b>Tech Need:</b>			
<b>Tech Sponsor:</b>			
<b>DOE:</b>  Subsurface Contaminants		<b>External Database Source:</b>  VISITT	
<b>Contacts:</b>  Name: Michael H. Burns  Title: Vice President of Operation  Phone: (612)942-5282  Email: <a href="mailto:tritec@travis.com">tritec@travis.com</a>			
<b>Comments:</b>			

<b>MAECTITE Chemical Treatment Process</b>		<b>Updated:</b> 3/12/97
<b>MAECTITE Chemical Treatment Process</b>		
<b>Source:</b> Vendor Brochure		<b>Media</b> Sludge Soil
<b>Applicable Contaminants:</b> HEAVY METALS		
<b>Summary:</b>  Lead & heavy metal treatment process for soil and waste. Reagents simulate the nucleation of crystals by chemical bonding to yield mineral compounds in molecular forms. Does not use physical binders. Process readily liberates water in waste prior to treatment.		
<b>Long Description</b>  Lead & heavy metal treatment process for soil and waste. Reagents simulate the nucleation of crystals by chemical bonding to yield mineral compounds in molecular forms. Does not use physical binders. Process readily liberates water in waste prior to treatment.		
<b>Related Information</b>		
<b>Status:</b>	<b>Intellectual Property Status:</b> Patent	
<b>Licensing Available:</b> No	<b>Cost:</b> TBD	
<b>Capital Cost:</b>	<b>Operating Cost:</b>	
<b>Limitations:</b>  Does not use binders and results in volume reduction. No material found resistant to treatment. Over 250k tons successfully treated.		
<b>Secondary Waste:</b>		
<b>D&amp;D:</b>		
<b>Other Applications:</b>		
<b>Tech Need:</b>		
<b>Tech Sponsor:</b>		
<b>DOE:</b>	<b>External Database Source:</b>	
<b>Contacts:</b>  Name:  Title:		

Phone: (219) 836-0116

Email:

Comments:

<b>Phosphate Induced Metal Stabilization</b>  <b>PIMS</b>	<b>Updated:</b> 8/6/97
<b>Source:</b>	<b>Media</b> Soil Groundwater Water Wastewater
<b>Applicable Contaminants:</b> RADIOACTIVE METALS, HEAVY METALS	
<p><b>Summary:</b></p> <p>Remediation Of Metals In Groundwater and Leachate Using Phosphate Induced Metal Stabilization</p> <p><b>Long Description</b></p> <p>Metals readily leach from contaminated soils and sediments and serve as a constant source of metal contamination to groundwater. This proposal seeks to stabilize lead, zinc, cadmium and other metals of concern in various industries, especially DOE waste streams, the mining industry, and industrial wastes, by chemically binding them into new stable phosphate phases (apatite minerals) and other relatively insoluble solids in permeable groundwater barriers or in above-ground treatment systems. Specifically, previous work addressed the groundwater associated with mine tailings in the Coeur d'Alene district in Idaho that have high levels of metal contamination and dissolved solids that are amenable to apatite remediation. Three field demonstrations are scheduled for emplacement in the summer of 1998: 1) an in-place permeable reactive downgradient barrier near the mouth of Government Gulch, Idaho, 2) two in-ground barriers to treat seeps at Success Mine in Idaho, and 3) one or more mobile above-ground treatment tanks at Sidney Tunnel that will treat the heavily-contaminated water exiting the adits before it enters the drainage or aquifer system. Metals most affected by this treatment are lead, zinc, copper, cadmium, nickel, uranium, barium, cesium, strontium, plutonium, thorium, neptunium and all other lanthanides and actinides. An important aspect of this treatment is that the metal-stabilization is nearly irreversible. It is not a simple sorption that can later desorb, it is not a reduction that can later oxidize, and it is not a mineral phase that can later leach. Metals sequestered in apatites have great durability and leach resistance that significantly exceed other chemically stabilized waste forms because the apatite mineral structure is very stable over a wide range of environmental conditions, e.g., pH 2.5 to 13.5, to over 1000 degrees C, in the presence of aqueous and non-aqueous phase liquids, in fresh water and in brines, and under disruptions such as earthquakes, ground subsidence or human intrusion, for geologically long time periods, i.e., hundreds of millions of years. Therefore, the metals will no longer be a source for further groundwater contamination. Also, because of this extreme stability, the effects of gravity, soil heterogeneity, hydrology and other properties of the subsurface do not affect the performance, and, themselves, are not affected by this treatment. The bioavailability of ingested metal-apatite is also greatly reduced (Davis et al, 1992; Ruby et al, 1992), making human intrusion less dangerous should the metal-apatite phase be ingested, and making bioremediation more effective in mixed waste environments. The reaction between the apatite and metal is rapid (Ma et al, 1993; Moody and Wright, 1995), and so the treatment is effective immediately, requiring no time for the material to "set up." Previous results indicate that the efficiency is over 20%, i.e., the apatite can sequester over 20% of its weight in metals, and as much as 40% for ideal metals such as lead. Remediation technologies for other contaminants are not inhibited by this treatment, e.g., metal-stabilization by phosphate treatment will not affect vapor stripping or bioremediation of organics from the same soils in a mixed-waste system. While apatite treatment can provide some phosphate nutrients for subsurface microbial populations, the solubilities are so low that eutrophication, and other phosphate-loading</p>	



problems that occur with organophosphates, do not occur with apatite. Apatite treatment is possible using existing technologies for emplacement. Also, performance depends upon the apatite selected; not all apatites are equally reactive or efficient.

## Related Information

[ufa.owt.com/ufo\\_ventures/tech\\_briefs/apatite.html](http://ufa.owt.com/ufo_ventures/tech_briefs/apatite.html)

Description: Phosphate Induced Metal Stabilization (PIMS)

<b>Status:</b>	<b>Intellectual Property Status:</b> Patent Eligible
<b>Licensing Available</b> No	<b>Cost:</b> depends upon site
<b>Capital Cost:</b> none required	<b>Operating Cost:</b> depends upon site

### Limitations:

The present limitations include the difficulties of in-ground emplacement, and the need to obtain a reactive phosphate in large amounts. For some contaminants, immobilization is less effective under alkaline conditions. Residence of the contaminated water in contact with the phosphate must be long enough for reactions to take place. This time varies depending upon contaminant, from minutes to hours.

### Secondary Waste:

none

### D&D:

none

### Other Applications:

### Tech Need:

The problem of contaminant metals and radionuclides in soils and groundwater is presently identified by the United States Environmental Protection Agency (EPA) as one of the most critical environmental risks.

### Tech Sponsor:

### DOE:

### External Database Source:

### Contacts:

Name:

Title:

Phone: 509-375-3268

Email: [nestt@ufa.owt.com](mailto:nestt@ufa.owt.com)



Techknow  
Search Results  
31 Records Found

Score Title

Summary

0.39 HNU SEFA-P Portable XRF for Metals

The SEFA-P Portable XRF is designed for use as a field screening instrument. It meets the requirements for use in the analysis of soil and water for heavy metal contaminants. It has also proven effective in screening mixed waste at radiation contaminated hazardous waste sites.

0.39 Surface Interface Radar- SIR

The SIR System-10A provides a detailed look at what's beneath the surface. Designed to interface with Geophysical Survey Systems Inc.'s entire line of state-of-the-art antennas, it is the first system to offer leading-edge, ground-penetrating radar (GPR). With the capability of performing at depths of more than 30 meters, the portable SIR System-10A is extremely effective in the earth's most critical zone 0-10 meters below the surface.

0.39 ENVEST TM Remedial Action Models

Using ENVEST lets an owner compare more remedial options faster and determine which is most cost effective. ENVEST lets the owner develop a reasonable estimate based on limited information to determine the relative cost of each alternative. This leads to much better cost management and cost control.

0.39 Sponge Jet System

The foam cleaning media removes, captures and contains contaminants for subsequent proper disposal. Uses various grades of patented water-based urethane foam cleaning media, ground to produce fine particles for surface cleaning & preparation. This unit reduces the waste water to a minimum volume disposable residue Using wetted foam cleaning media also provides for dust control.

0.39 Soil Air Circular Flow (BLK)

The BLK is capable of generating a directed circulation through the center of the contamination. No fresh air is added to the circulation system. Air passing through the blower is heated, thereby enhancing desorption of contaminants adsorbed onto soil particles.

A pilot study was undertaken at an industrial facility in the midwest to demonstrate the efficiency of utilizing a

- 0.39 [In Situ Reactive Zones for Microbial Precipitation of Heavy Metals and De-Nitrification](#) microbial induced reduction process to convert hexavalent chromium to the less soluble trivalent chromium. The goal of the reactive zone for metallic ions is to simulate the above-ground precipitation process by injecting fluids into the plume to cause dissolved oxidized metals to precipitate and then rely on aquifer materials to absorb/filter out the solids. The in situ ...
- 0.39 [Westinghouse Soil Washing System](#) Soil is fed into the Westinghouse TDU, in which the soil temperature is raised above the boiling point of the contaminants present, causing the contaminants to volatilize. The Westinghouse thermal desorption unit (TDU) heats the surface of the solid to reverse adsorption. The principle of operation of the Westinghouse TDU is as follows: Soil is fed into the Westinghouse TDU, in which the soil temperature is raised above the boiling point of the contaminants present, causing the contaminants ...
- 0.39 [Liquid FileMaker Testing](#) Trying to add new records and verifying that Liquid FileMaker is running without error. Verifying Liquid FileMaker process is working for the Techknow system. The only limits is the amount of money you want to spend.
- 0.39 [A Combined Zorption/Oxidation Process](#) Geo Resources' "Mobile" Remediation system utilizes a combined Zorption/Oxidation process. The patented process, as a better alternative to carbon processes, offers the following advantages: · Polymer has the capability of treating high concentrations of contamination. Overall process concept: Contaminated water, containing dissolved organic species, is first fed to a pre-filter arrangement to remove traces of suspended solids:
- 0.39 [MicroFluidizer \(TM\)](#) Models are available to function at elevated temperatures (to 400 degrees Celsius), to process streams which are solid or highly viscous at ambient temperatures. Scale-up to any attempted throughput from lab results has been wholly predictable as to size, distribution, extraction and other performance. Air-operated models are available where fire or explosion risks exist.
- 0.39 [Ecology Technologies International, Inc.](#) FyreZyme is effective in accelerating bioremediation of a wide range of organic contaminants in an environmentally friendly, scientifically sound, and cost-effective manner. FyreZyme is a multifactoral liquid (aqueous) agent, combining a rich source of bacterial growth-enhancing agents, extracellular enzymes, and bioemulsifiers. Slurry-phase bioremediation adapts soil washing, utilizing FyreZyme as the washing agent and rapidly cleanses petroleum products.

0.39 Environmental Technology  
Network for Asia

Covers air pollution controls, water liquid pollution, solid waste treatment, containment and disposal, groundwater treatment, environmental services, energy conservation, renewable energy, and waste minimization.  
(Environmental Enterprises Development Initiative (EEDI), Urban Environmental Infrastructure Programme (UE/P), Environmental/Energy Technology Fund).  
Users/Accessibility/Costs - Free through US-AEP offices in Bangkok, Bombay, Hong-Kong, Jakarta, Kuala Lumpur, Manila, Seoul, ...

0.39 BIO-INTEGRATION

APPLICATIONS AND PERFORMANCE DATA SITE IDENTIFICATION: Cellulosic Resin Facility WASTE SOURCE: Phenolic Byproducts Generated During Resin Exudation LOCATION: South-Central U. S. PROJECT TYPE: Environmental Cleanup MEDIA: Lagoonal Process Waters REGULATION/STATUTE/ORGANIZATION: DEM NPDES Permit Violation MEASUREMENTS: Volume/Quantity Treated - 3,000,000 Gallons EQUIPMENT SCALE: Full PROJECT DURATION (interval to closure): 17.5 hours PERFORMANCE DATA: Contaminant -Phenol + Derivatives...

0.39 Ultrasonic Technology As an  
Enhanced Sludge Washing  
Alternative

Advantages of alternative approaches to alkaline sludge washing would be to improve the effectiveness of dissolution, thereby significantly reducing the volume of HLW glass produced. One specific technique for improving overall sludge dissolution is the use of sonication, or ultrasonic technology. Pacific Northwest National Laboratory(PNNL) is evaluating alternative techniques that can be used in conjunction with alkaline sludge washing to enhance dissolution of key waste components.

0.39 Removal and Recovery of Toxic  
Metal Ions from Aqueous Waste  
Sites Using Polymer Pendant  
Ligands

The purpose of this project is to develop polymer pendant ligand technology to remove and recover toxic metal ions from aqueous wastes. The purpose of this project is to develop polymer pendant ligand (group of atoms or molecules anchored to a central atom in a complex) technology to remove and recover toxic metal ions from aqueous wastes. Polymer pendant ligands are organic ligands anchored to crosslinked, modified divinyl benzene-polystyrene beads that can selectively latch onto metals ...

0.39 MAG\*SEP

MAG\*SEP is a technology for the SELECTIVE recovery of radioactive or heavy metal contaminants from environmental waters, effluent water or process water. MAG\*SEP uses composite particles to selectively adsorb contaminants of concern. Under such conditions, the

MAG\*SEP particles are injected into the water, where they selectively adsorb the contaminant(s) of concern, leaving other solids unaffected.

0.39 PSI Hazardous Waste Monitor

The PSI Hazardous Waste Monitor uses selective atomic emission to produce a rugged, reliable, low maintenance, field instrument that is highly sensitive to a wide variety of compounds. The monitor has been designed to be versatile owing to the wide variety of hazardous waste streams present at contaminated sites. The PSI Hazardous Waste Monitor has been developed under contract to the Department of Energy.

0.39 Laser Ablation of Contaminants from Concrete and Metal Surfaces

The laser ablation technology uses the proper combination of wavelength, pulse duration, energy, power densities on target, pulse repetition rate, and scan rate. This not only yields efficient removal of coating material from the surface and surface pores, but also ablates material faster than a thermal wave can propagate into the substrate, preventing entrainment of surface contamination in molten substrate, and leaving behind a cool surface. A gas, vapor, and particulate suction device ...

0.39 In Situ Bioremediation Using Horizontal Wells

In Situ Bioremediation, remediates soils and ground water contaminated with volatile organic compounds (VOCs) both above and below the water table. ISB involves injection of air and nutrients (sparging and biostimulation) into the ground water and vacuum extraction to remove VOCs from the vadose zone concomitant with biodegradation of VOCs. In Situ Bioremediation (ISB), which is the term used in this report for Gaseous Nutrient Injection for In Situ Bioremediation, remediates soils and ...

0.39 Unsaturated Flow Apparatus

The UFA uses open-flow centrifugation to rapidly and directly measure the unsaturated and saturated transport properties on cores of any porous media with aqueous and non-aqueous phase liquids. Most often, the only site specific transport data collected are porosity, saturated hydraulic conductivity, or other easily-measured properties. Fortunately, a new technology, the UFA Method, rapidly and directly measures these properties in any porous media.

0.39 Sodium Bicarbonate Blasting

Soda blasting is an unprecedented decontamination process that quickly removes surface contaminants such as uranium, PCBs, technetium and cadmium from metal and concrete surfaces up to 50% faster than CO<sub>2</sub> blasting. Soda blasting is a process in which compressed air delivers sodium bicarbonate media, under pressure, and impacts

contaminated surfaces at high velocities. Sodium Bicarbonate Media The physical and chemical characteristics (crystalline structure, non-destructive, non-toxic, and ...

0.39 [Geosynthetic Membrane Monitoring System](#) This project, which started in the autumn of 1995, covers the development of a prototype monitoring system, to address the need to monitor barriers used for landfill stabilization. This task includes development of a sensor system, primarily based on optical fibers, and development of the technology used to incorporate the sensors into a geosynthetic membrane. Geosynthetics are used extensively in landfill liners and covers.

0.39 [Mobile Liquid Storage Systems](#) Northeastern states leading tank rental company, Russell Reid Mobile Liquid Storage Systems provide temporary storage of hazardous and non-hazardous bulk liquids. Our new, rodless epoxy coated 10,000 and 21,000 gallon tanks offer safe, economical alternatives to other bulk storage. Russell Reid Mobile Liquid Storage Systems provides turnkey bulk storage solutions to customers including a long list of publicly owned treatment facility managers, industrial pretreatment plant operators, ...

0.39 [Chemical reaction based test paper](#) Gallard-Schlesinger offers a full range of test papers for the semi-quantitative determination of selected cations, anions, and substances. When the test paper is dipped into a solution containing the specific ion or substance, the color change of the test paper is compared to the provided color scale to determine the amount of ion or substance present. One box of any of our test papers usually measures under 4 inches x 2 inches x 1 inch.

0.39 [Transient Infrared Spectroscopy \(TIRS\)](#) TIRS is a noncontact, on-line technique which provides real-time chemical (molecular) analysis of process streams of solid or viscous-liquid material. TIRS uses the infrared spectrum of the process stream captured on the fly to derive the stream composition, or any other property that affects the spectrum. Numerous on-site demonstrations have been performed applying TIRS to monitoring the molten polymer stream during polymer encapsulation of waste.

More ...

<b>In Situ Reactive Zones for Microbial Precipitation of Heavy Metals and De-Nitrification</b>		<b>Updated:</b> 3/13/97
<b>In Situ Reactive Zones for Microbial Precipitation of Heavy Metals and De-Nitrification</b>		
<b>Source:</b> Vendor Brochure		<b>Media</b> Groundwater
<b>Applicable Contaminants:</b> VOCS, HEAVY METALS		
<b>Summary:</b>  A pilot study was undertaken at an industrial facility in the midwest to demonstrate the efficiency of utilizing a microbial induced reduction process to convert hexavalent chromium to the less soluble trivalent chromium. An existing 50 gpm pump and treat system was controlling the plume, but operation and maintenance was costing several hundred thousand dollars annually.		
<b>Long Description</b>  The goal of the reactive zone for metallic ions is to simulate the above-ground precipitation process by injecting fluids into the plume to cause dissolved oxidized metals to precipitate and then rely on aquifer materials to absorb/filter out the solids.		
<b>Related Information</b>		
<b>Status:</b>	<b>Intellectual Property Status:</b> Patent	
<b>Licensing Available:</b> No	<b>Cost:</b> TBD	
<b>Capital Cost:</b>	<b>Operating Cost:</b>	
<b>Limitations:</b>  The in situ precipitation process can be used to achieve precipitation of the the following heavy metals: hexavalent chromium, lead, mercury, nickel, cadmium, silver, and zinc. Excavated soils, Low Concentrations of metals.		
<b>Secondary Waste:</b>		
<b>D&amp;D:</b>		
<b>Other Applications:</b>		
<b>Tech Need:</b>		
<b>Tech Sponsor:</b>		
<b>DOE:</b>	<b>External Database Source:</b>	
<b>Contacts:</b>		



Name:

Title:

Phone: (813) 264-3400

Email:

Comments:

<b>Removal and Recovery of Toxic Metal Ions from Aqueous Waste Sites Using Polymer Pendant Ligands</b>		<b>Updated:</b> 9/15/97
<b>Removal and Recovery of Toxic Metal Ions from Aqueous Waste Sites Using Polymer Pendant Ligands</b>		
<b>Source:</b> US DOE		<b>Media</b> Wastewater
<b>Applicable Contaminants:</b> OTHER, RADIOACTIVE METALS, HEAVY METALS		
<b>Summary:</b>  The purpose of this project is to develop polymer pendant ligand technology to remove and recover toxic metal ions from aqueous wastes. Polymer pendant ligands are organic ligands (group of atoms or molecules anchored to a central atom in a complex) anchored to crosslinked, modified divinyl benzene-polystyrene beads that can selectively latch onto metals ions.		
<b>Long Description</b>  The purpose of this project is to develop polymer pendant ligand (group of atoms or molecules anchored to a central atom in a complex) technology to remove and recover toxic metal ions from aqueous wastes. Polymer pendant ligands are organic ligands anchored to crosslinked, modified divinyl benzene-polystyrene beads that can selectively latch onto metals ions. The objectives include synthesizing selective polymer pendant ligands for removal and recovery of ions, determining the kinetics of the process, and transferring the technology to our industrial partner, AquaEss, San Jose, California, who performs application studies and will eventually implement the technology. Studies in FY94 and FY95 focused on acid mine waste water (e.g., pH 2.5) represented by the Berkeley Pit at Butte, Montana, with emphasis on removing iron(III), aluminum, chromium(III), copper(II), zinc, manganese(II), magnesium, nickel(II), and silver. Because iron is the dominant cation (positive ion) in the Berkeley Pit, we focused on devising iron-selective ligands to remove this species first. AquaEss has developed a strategy for using this kind of ligand for acid waste water. In FY96, we are focusing on removing RCRA metal ions, including silver, mercury(II), lead, cadmium, and copper(II). This application of the technology is opposite to that for acid mine waste water dominated by iron(III). Instead, ligands are needed to remove RCRA metal ions in the presence of modest iron(III) cations. AquaEss has begun devising column processing strategies for using such ligands.		
<b>Related Information</b>  <a href="http://www.gnet.org/basesystem/ias/earthvision/filecomponent/17910-esp3-2.pdf">www.gnet.org/basesystem/ias/earthvision/filecomponent/17910-esp3-2.pdf</a>  Description: Rainbow Book (PDF)  <a href="http://www.pnl.gov/eff_sep/97tasks/97currnt.htm">www.pnl.gov/eff_sep/97tasks/97currnt.htm</a>  Description: DOE-Current Tasks		
<b>Status:</b>		<b>Intellectual Property Status:</b> Don't Know

<b>Licensing Available</b> No	<b>Cost:</b> TBD
<b>Capital Cost:</b> TBD	<b>Operating Cost:</b> TBD
<b>Limitations:</b> TBD	
<b>Secondary Waste:</b> TBD	
<b>D&amp;D:</b> TBD	
<b>Other Applications:</b> TBD	
<b>Tech Need:</b> Efficient removal or recovery of Resource Conservation and Recovery Act (RCRA) metals and radionuclide from aqueous wastes at DOE sites will benefit from improved ion exchange materials. The cost of developing and deploying advanced ion exchange materials	
<b>Tech Sponsor:</b>	
<b>DOE:</b>	<b>External Database Source:</b>
<b>Contacts:</b> Name: Richard H. Fish Title: Phone: (510) 486-4850 Email: Name: Richard Scott Title: Phone: (510) 637-1623 Email:	
<b>Comments:</b>	

<b>MAG*SEP</b>  <b>MAG*SEP</b>	<b>Updated:</b> 9/15/97
<b>Source:</b> Selentec, Inc.	<b>Media</b> Water Waste
<b>Applicable Contaminants:</b> RADIOACTIVE METALS, OTHER, HEAVY METALS	
<p><b>Summary:</b></p> <p>MAG*SEP is a technology for the <b>SELECTIVE</b> recovery of radioactive or heavy metal contaminants from environmental waters, effluent water or process water.</p> <p><b>Long Description</b></p> <p>MAG*SEP is a technology for the selective recovery of radioactive or heavy metal contaminants from environmental waters, effluent water or process water. The primary benefit of this technology is that it recovers the contaminants from water without removing non-hazardous minerals. This allows the potential to recycle the material recovered, or if it must be disposed of as waste, produces minimal waste volumes. This also has the benefit of not significantly altering the treated water chemistry, which is important in returning treated groundwater to the environment. MAG*SEP uses composite particles to selectively adsorb contaminants of concern. The particles contain a magnetite core, which allows for recovery of the particles (and adsorbed contaminants) by magnetic filtration. The MAG*SEP process is able to <b>SELECTIVELY</b> remove (either ex-situ or in-situ) the following contaminants from aqueous solutions (e.g. water, groundwater, process effluents, etc.): titanium, copper, cadmium, arsenic, cobalt, molybdenum, platinum, selenium, chromium, zinc, gold, iodine, manganese, technetium, mercury, strontium, iron, ruthenium, thallium, cesium, cobalt, palladium lead, radium, nickel, silver, bismuth, antimony, zirconium, palladium, cerium and <b>ALL ACTINIDES</b>. MAG*SEP is especially effective in treating large volumes of water which contain small concentrations of contaminants and large concentrations of non-hazardous solids. Under such conditions, the MAG*SEP particles are injected into the water, where they selectively adsorb the contaminant(s) of concern, leaving other solids unaffected.</p> <p><b>Related Information</b></p> <p><a href="http://www.gnet.org/basesystem/ias/earthvision/filecomponent/17926-magsep.pdf">www.gnet.org/basesystem/ias/earthvision/filecomponent/17926-magsep.pdf</a></p> <p>Description: MAG*SEP Rainbow Book (PDF File)</p> <p><a href="http://www.selentec.com/magsep.html">www.selentec.com/magsep.html</a></p> <p>Description: MAG*SEP at Selentec, Inc.</p> <p><a href="http://em-52.em.doe.gov/ifd/scfa/solutions/pfa05.htm">em-52.em.doe.gov/ifd/scfa/solutions/pfa05.htm</a></p> <p>Description: DOE Technology Card</p> <p><a href="http://www.wpi.org/initiatives/init/jun96/rci.html">www.wpi.org/initiatives/init/jun96/rci.html</a></p>	

Description: RCI Press Release

[www.wpi.org/initiatives/init/aug95/magsep.html](http://www.wpi.org/initiatives/init/aug95/magsep.html)

Description: Initiatives Online

[www.wpi.org/initiatives/init/oct96/whereare.html](http://www.wpi.org/initiatives/init/oct96/whereare.html)

Description: Initiatives Online

<b>Status:</b>	<b>Intellectual Property Status:</b> Patent
<b>Licensing Available</b> Yes	<b>Cost:</b> The cost for utilizing the MAG*SEP system is approximately one-sixth to one-tenth of the cost of competitive technologies such as simple ion exchange, precipitation/filtration, or precipitation/filtration/ion exchange.
<b>Capital Cost:</b> TBD	<b>Operating Cost:</b> \$.0019 - \$.005/gal
<b>Limitations:</b>  TBD	
<b>Secondary Waste:</b>  Recovered materials only	
<b>D&amp;D:</b>  Recovery of radioactive and heavy metal contaminants from liquid decontamination streams.	
<b>Other Applications:</b>  Can be used to remove heavy metals from liquids, such as milk contaminated as a result of environmental causes.	
<b>Tech Need:</b>  With existing technologies, the liquid to be treated may require pH adjustment to precipitate the contaminants, then filtration (to remove suspended solids), followed by ion exchange to reduce contaminant levels to acceptable standards. These processes r	
<b>Tech Sponsor:</b>	
<b>DOE:</b>	<b>External Database Source:</b>
<b>Contacts:</b>  Name: Steve Weldon, Business Development Manager  Title:  Phone: 770-640-7059	

Email: [info@selentec.com](mailto:info@selentec.com)

**Comments:**

# Techknow

## Search Results

### 6 Records Found

Score	Title	Summary
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0.39	<u>NDC Mobile, Self Contained Decontamination Technology</u>	<p>NDC has a successful, safe, cost effective decontamination technology that generates no secondary waste. NDC's technology is the only non destructive decontamination technology that has removed mixed contamination and transuranic contamination. NDC's Decontamination Technology is the only technology that is able to decontaminate mixed contamination, transuranic contamination, and hazardous contamination without generating secondary wastes.</p> <p>The AWJ is one of the leading systems for nuclear plant services and for the decontamination and decommissioning applications. It is very versatile and can cut, clean or scarify a wide variety of materials in air or underwater. Status: Intellectual Property Status: Patent Licensing Available NoCost: TBD Capital Cost: Operating Cost: Limitations:</p> <p>The objective of this project is to develop an operational, commercial system for real-time, multisensor, characterization and mapping of small diameter, contaminated process pipes. The Multisensor Inspection and Characterization Robot for Small Pipes (MICROSPI) is a semi-autonomous device with onboard miniature sensors and a remote operator interface with an integrated data system. MICROSPI is a system for real-time, multisensor, characterization and mapping of small diameter, contaminated ...</p> <p>The Model 4100 Vapor Detector and Analyzer quickly (&lt;30 sec.) captures samples of gas, water, or soil and tests for volatile organic compounds. Model 4100 Vapor Detector and Analyzer consists of a portable gas chromatograph and a Surface Acoustic Wave (SAW) sensor with a dynamic particle/vapor sampling head. This technology can quickly (&lt;30 sec.) identify chemical signatures in well gas, water, and soil samples.</p> <p>CBPCs have the potential for stabilizing several problematic mixed-waste streams that have been identified by DOE. Typical mixed-waste streams</p>
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0.39 Phosphate Bonded Ceramic Final Waste Forms

contain mercury-contaminated aqueous liquids, toxic and heavy-metal-containing materials including ashes. CBPCs have the potential for stabilizing several problematic mixed-waste streams that have been identified by DOE, including mercury-contaminated wastes, salt wastes, transuranics, debris, and ashes.

0.39 Terrazyme

At the present time, NATK is operating a full scale processing unit on a leading waste disposal company's landfill. Terrazyme is a proprietary processing system for separating soil contaminants from reusable earth. Essentially a mechanical process for the extraction of contaminants from soils, sludges, and other solids, the system minimizes the ultimate volume of waste requiring disposal and separates clean materials for beneficial use.



## Remediation Technologies

GWRTAC focuses on innovative ground-water remediation technologies as compared to the standard "pump and treat" approach. Many of the remedial activities summarized within GWRTAC are in situ technologies requiring no ground-water extraction. However, means of enhancing pump and treat, and selected types of ex situ technologies are also addressed. GWRTAC includes those remediation technologies which through design and/or application, improve ground-water quality and are integral to ground-water clean-up.

Following are brief descriptions of technologies that are currently included in GWRTACs list of Technical Documents On-Line:

### GWRTACs Glossary of Hydrogeologic Terms

#### **In Situ Physical/Chemical Treatment**

- Air Sparging
- Horizontal Wells
- Hydraulic and Pneumatic Fracturing
- In-Situ Flushing
- In-Situ Stabilization/Solidification
- In-Well Vapor Stripping
- Surfactants/Cosolvents
- Thermal Enhancements
- Treatment Walls

#### **Ex Situ Physical/Chemical Treatment**

- UV/Oxidation Treatment Processes

#### **Biological Treatment**

- Bioslurping
- Intrinsic Bioremediation
- Phytoremediation

#### **Electrokinetics**

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#### **In Situ Physical/Chemical Treatment**

- Air Sparging - Injection of gas (usually air or oxygen) under pressure into well(s) installed within the saturated zone to volatilize contaminants dissolved in groundwater, present as non-aqueous phase

liquid, or sorbed to the soil matrix. Volatilized contaminants migrate upward and are removed upon reaching the vadose zone, typically through soil vapor extraction. Most applicable for volatile organic contaminants in relatively moderate to high permeability geologic materials.

- **Horizontal Wells** - Also known as directional wells. Trenched or directly drilled wells installed at any non-vertical inclination for purposes of ground-water monitoring or remediation. Especially useful when contaminant plume covers a large area and has linear geometry, or when surface obstructions are present. This technology can be used in the application of various remediation techniques such as ground-water and/or non-aqueous phase liquid extraction, air sparging, soil vapor extraction, in situ bioremediation, in situ flushing, treatment walls, hydraulic and pneumatic fracturing, etc.
- **Hydraulic and Pneumatic Fracturing** - Techniques to create enhanced fracture networks to increase soil permeability to liquids and vapors and accelerate contaminant removal. Especially useful for vapor extraction, biodegradation and thermal treatments. Hydraulic fracturing involves injection of high pressure water into the bottom of a borehole to cut a notch; a slurry of water, sand and thick gel is pumped at high pressure into the borehole to propagate the fracture from the initial notch. The gel biodegrades, leaving a highly permeable sand-filled lens that may be up to 60 feet in diameter. Pneumatic fracturing involves injection of highly pressurized air into consolidated sediments to extend existing fractures and create a secondary fracture network. Most applicable for unconsolidated sediments or bedrock.
- **In Situ Flushing** - Also known as injection/recirculation or in situ soil washing. General injection or infiltration of a solution into a zone of contaminated soil/groundwater, followed by downgradient extraction of groundwater and elutriate (flushing solution mixed with the contaminants) and above ground treatment and/or re-injection. Solutions may consist of surfactants, cosolvents, acids, bases, solvents, or plain water. Any variety of configurations of injection wells, horizontal wells, trenches, infiltration galleries and extraction wells or collection trenches may be used to contact the flushing solution with the contaminated zone. Excellent understanding of the hydrogeologic regime for potential projects is essential; best applied to moderate to high permeability soils. May be used for variety of organic contaminants, including non-aqueous phase liquid; may have application to some inorganic contaminants.
- **In Situ Stabilization/Solidification** - Also known as in situ fixation, or immobilization. Process of alteration of organic or inorganic contaminants to innocuous and/or immobile state by injection or infiltration of stabilizing agents into a zone of contaminated soil/groundwater. Contaminants are physically bound or enclosed within a stabilized mass (solidification), or their mobility is reduced through chemical reaction (stabilization). Excellent understanding of the hydrogeologic regime for potential projects is essential; best applied to moderate to high permeability soils; may be used for variety of organic and inorganic contaminants.
- **In-Well Vapor Stripping** - Also known as in situ vacuum, vapor, or air stripping. Creation of ground-water circulation "cell" through injection of air or inert gas into a zone of contaminated ground-water through center of double cased stripping well which is designed with upper and lower double screened intervals. Injection of air creates "airlift pumping system" due to density gradient, causing ground-water with entrained air bubbles to rise and partition volatile contaminants from dissolved to vapor phase. Water exits upper screen beneath a divider, where vapors are drawn off through annular spaces between well casings by vacuum pump, and ground-water re-enters the contaminated zone, where it is again drawn into the stripping well. In this manner, ground-water is recirculated through the stripping well until remediation goals are met. Several commercial types of in-well vapor stripping exist which strive to make the general process most efficient, or to use the process to enhance bioremediation or metals fixation by taking advantage of the circulation cell development. Most applicable to volatile organic contaminants; modifications of the basic remedial process are proposed for application to semivolatile organic compounds, pesticides and inorganics. May be used in unconfined or confined aquifers; process has been applied to geologic materials of

- wide ranging permeability.
- Surfactants/Cosolvents - Addition of cosolvents, mixtures of surfactants, or surfactant/co-surfactant/cosolvent mixtures to the groundwater system to aid in mobilizing and/or solubilizing non-aqueous phase liquid (NAPL) or contaminants sorbed to the soil matrix. Generally considered an enhancement to conventional pump and treat by increasing contaminant mass removal per pore volume of groundwater flushing through contaminated zone. May be used for variety of organic contaminants and NAPL; may have application to some inorganic contaminants. Best applied to moderate to high permeability geologic materials; excellent understanding of hydrogeologic conditions is essential.
  - Thermal Enhancements - Use of steam, heated water, or radio frequency (RF) or electrical resistance (alternating current or AC) heating to alter temperature-dependent properties of contaminants in situ to facilitate their mobilization, solubilization, and removal. Volatile and semivolatile organic contaminants may be vaporized; vaporized components then rise to the vadose zone where they are removed by vacuum extraction and treated. Steam best applied to moderate to high permeability geologic materials; RF and AC heating may be applied to low permeability, clay-rich geologic materials as the clay will preferentially capture the RF or AC energy. Excellent understanding of hydrogeologic conditions essential for all applications. May be used for variety of organic contaminants and non-aqueous phase liquid; may have application to some inorganic contaminants.
  - Treatment Walls - Also known as passive barriers or passive treatment walls or trenches. An in-ground trench is backfilled with reactive media to provide passive treatment of contaminated ground-water passing through the trench. Treatment wall is placed at strategic location to intercept the contaminant plume and backfilled with media such as zero-valent iron, microorganisms, zeolite, activated carbon, peat, bentonite, limestone, saw dust, or other. The treatment processes which occur within the treatment wall are typically contaminant degradation, sorption or precipitation. Applicable to wide range of organic and inorganic contaminants; choice of media for treatment wall is based on specific contaminant. Hydrogeologic setting is critical to application; geologic materials must be relatively conductive and a relatively shallow aquitard must be present to provide a "basement" to the system. Ground-water flow should have a high degree of preference, and ground-water quality must support the desired reaction without imposing additional loading of the reactive media or creating undesirable by-products.

### Ex Situ Physical/Chemical Treatment

- UV/Oxidation Treatment Processes - Ex situ treatment process combining the use of ultraviolet (UV) light and chemical oxidants such as ozone and hydrogen peroxide to destroy organic and explosive contaminants in ground-water. Typically, high intensity UV radiation reacts with the oxidant through direct photolysis to generate highly reactive hydroxyl radicals which attack the organic molecules and destroy the parent compound, resulting in production of carbon dioxide, water, and an inorganic salt.

### Biological Treatment

- Bioslurping - Use of vacuum-enhanced pumping to recover light, non-aqueous phase liquid and initiate vadose zone remediation through bioventing. In bioventing, air is drawn through the impacted vadose zone via extraction wells equipped with low vacuums to promote biodegradation of organic compounds.
- Intrinsic Bioremediation - Natural, non-enhanced microbial degradation of organic constituents by which complex organic compounds are broken down to simpler, usually less toxic compounds through aerobic or anaerobic processes. For environmental application, documentation that current biodegradation rates are sufficient to control or degrade a contaminant plume or zone without

creation of unacceptable risk to human health or the environment must be demonstrated.

- Phytoremediation - The general use of plants to remediate environmental media in situ. Includes rhizofiltration (absorption, concentration, and precipitation of heavy metals by plant roots), phytoextraction (extraction and accumulation of contaminants in harvestable plant tissues such as roots and shoots), phytotransformation (degradation of complex organic molecules to simple molecules which are incorporated into plant tissues), phytostimulation or plant-assisted bioremediation (stimulation of microbial and fungal degradation by release of exudates/enzymes into the root zone), and phytostabilization (absorption and precipitation of contaminants, principally metals, by plants). May or may not involve periodic harvesting of plants, depending upon method utilized. Applicable to a wide range of organic and inorganic contaminants; most appropriate for sites where large volumes of ground-water with relatively low concentrations of contaminants must be remediated to strict standards. Most effective where ground-water is within ten feet of the ground surface, and soil contamination is within three feet of the ground surface.

## Electrokinetics

- Electrokinetics - An in situ process involving application of low intensity direct electrical current across electrode pairs implanted in the ground on each side of a contaminated area of soil, causing electro-osmosis and ion migration. Contaminants migrate toward respective electrodes depending upon their charge. Process may be enhanced through use of surfactants or reagents to increase contaminant removal rates at the electrodes. Process separates and extracts heavy metals, radionuclides, and organic contaminants from saturated or unsaturated soils, sludges, and sediments. Especially unique due to ability to work in low permeability soils as well as high permeability soils; applicable to a broad range of organic and inorganic contaminants.

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Contact GWRTAC by phone at 1 (800) 373-1973 or (412) 826-5512 ext. 215

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## 4.5 Soil Flushing

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Technology	Description
<b>Soil, Sediment, and Sludge</b>	
<b>3.2 In Situ Physical/Chemical Treatment</b>	
4.5 Soil Flushing	Water, or water containing an additive to enhance contaminant solubility, is applied to the soil or injected into the groundwater to raise the water table into the contaminated soil zone. Contaminants are leached into the groundwater, which is then extracted and treated.

**Description:**

Figure 4-5:  
Typical Soil Flushing  
System

In situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. Soil flushing is accomplished by passing the extraction fluid through in-place soils using an injection or infiltration process. Extraction fluids must be recovered from the underlying aquifer and, when possible, they are recycled.

Recovered groundwater and flushing fluids with the desorbed contaminants may need treatment to meet appropriate discharge standards prior to recycle or release to local, publicly owned wastewater treatment works or receiving streams. To the maximum extent practical, recovered fluids should be reused in the flushing process. The separation of surfactants from recovered flushing fluid, for reuse in the process, is a major factor in the cost of soil flushing. Treatment of the recovered fluids results in process sludges and residual solids, such as spent carbon and spent ion exchange resin, which must be appropriately treated before disposal. Air emissions of volatile contaminants from recovered flushing fluids should be collected and treated, as appropriate, to meet applicable regulatory standards. Residual flushing additives in the soil may be a concern and should be evaluated on a site-specific basis.

**Applicability:**

The target contaminant group for soil flushing is inorganics including radioactive contaminants. The technology can be used to treat VOCs, SVOCs, fuels, and pesticides, but it may be less cost-effective than alternative technologies for these contaminant groups. The addition of compatible surfactants may be used to increase the effective solubility of some organic compounds; however, the flushing solution may alter the physical/chemical properties of the soil system. The technology offers the potential for recovery of metals and can mobilize a wide range of organic and inorganic contaminants from coarse-grained soils.

**Limitations:**

Factors that may limit the applicability and effectiveness of the process include:

- Low permeability soils are difficult to treat.
- Surfactants can adhere to soil and reduce effective soil porosity.
- Reactions of flushing fluids with soil can reduce contaminant