

Technologies for the Restoration of Soils, Waters and Ground waters Contaminated with Hazardous Waste

AEPI-IFP-396

AEPI

Army Environmental Policy Institute

ABSTRACT

The Army Environmental Policy Institute (AEPI) has the mission of remaining abreast of current and emerging technologies in environmental protection and to provide options to Army policy makers initiating, directing, or using new technologies that minimize impacts on the environment. This document is part of an initial phase of study to identify those environmental technologies that will be required to solve future environmental challenges.

The technologies identified and discussed within this document cover established, innovative, and emerging technologies. Not all possible technologies have been addressed in this text. One important aim is a comprehensive review of the applicable literature and the identification of environmental technologies of benefit in the area of remediation. However, many promising technologies have environmental applications beyond the Restoration Pillar area and are potentially applicable to the Compliance and Prevention Pillar areas. As this work continues, technologies in the pilot, bench, or early stages of development, will receive the greatest attention. In this manner, AEPI will attempt to identify promising technologies and promote new and innovative environmental technology development within the US Army.

The technologies identified within this document are a combination of bioremediation, physical, chemical, physico-chemical, thermochemical, and other environmental technologies. The information on each technology has been assembled into Technology Description, Stage of Development, Applications and Effectiveness, Cost Analysis, and References. Where available, case studies, co-technologies /alternative technologies, and personal contacts are provided. AEPI was assisted in the collection of data and information contained in the report by the Stevens Institute of Technology, J.M. Stratta and Associates, and Life Systems, Inc.

The information contained within this summary is available in hard copy as well as on 3.5-inch computer disc. Eventually this information will be available by on-line computer. The intent is to facilitate the availability of this updated information to technology users as well as US Army policy makers.

AEPI-IFP-396

ACKNOWLEDGMENTS

This research was performed for the U.S. Army Environmental Policy Institute under the directorship of Dr. Edward Novak, AEPI contract number DACA88-94-D-0025-1E04 (GIT contract number D-48-x11). The AEPI technical monitors for this program were Dr. Francisco A. Tomei and Dr. Prakash M. Temkar. The data contained in the final report was collected under separate AEPI contracts by the Stevens Institute of Technology, J.M. Stratta and Associates, and Life Systems, Inc. The principal investigator for this research project was Dr. Louis J. Circeo, Director Construction Research Center. He was assisted by two Georgia Tech graduate research assistants, Mr. Ross J. Estabrook and Mr. Andreas Georgiopoulos.

ACRONYMS

acfm	Actual cubic feet per minute
AEC	Army Environmental Center
AEPI	Army Environmental Policy Institute
AFB	(US Air Force) Air Force base
APEG	Alkaline polyethylene glycol
BATS	Biotrol Aqueous Treatment System
BOD	Biological oxygen demand
BTEX	Benzene, toluene, ethylbenzene, xylene
BTU	British thermal unit
CBC	Circulating bed combustor
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFC	Chlorofluorocarbon
COD	Chemical oxygen demand
CPMP	Continuous porous membrane permeator
DAT	2,4-Diaminotoluene
DCA	Dichloroethane
DCB	Dichlorobenzene
DCE	1,1-,cis-1,2-,trans-1,2dichloroethylene
DDT	1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane
DIMP	Diisomethylphosphonate
DNAPL	Dense non-aqueous phase liquid
DNT	2,4-dinitrotoluene
DOE	Department of Energy
DRE	Destruction and removal efficiency
DSM	Deep soil mixing
EBRF	Electron Beam Research Facility
EM	Energetic material
ESV	<i>Ex situ</i> vitrification
FBC	Fluidized bed combustor
FTIR	Fourier Transform Infrared spectroscopy
FY	Fiscal year
GAC	Granulated activated carbon
GC/MS	Gas chromatography/mass spectroscopy
GEMS	Ground elevation measurement system
gpm	Gallons per minute
HCB	Hexachlorobenzene
HDP	High density polyethylene
HE	High explosive
HMX	Cyclotetramethylenetetranitramine
IR	Infrared
IRF	<i>In situ</i> radio frequency (heating)
ISV	<i>In situ</i> vitrification
KPEG	Potassium(K) polyethylene glycol
LLNL	Lawrence Livermore National Laboratory
LUST	Leaking underground storage tank
MIOX	Mixed oxidant (system)

MTBE	Methyl tertiary butyl ether
NC	Nitrocellulose
NO _x	Nitrogen oxides
NPDES	National Pollution Discharge Elimination System
ODC	Ozone depleting chemical
PAH	Polyaromatic hydrocarbons
PC	Personal computer
PCB	Polychlorinated biphenyl
PCE	Tetra(poly)chloroethylene
PCP	Pentachlorophenol
PFE	Pneumatic fracturing extraction
PNA	Polynuclear aromatic compounds
ppb	parts per billion
ppm	parts per million
RBC	Rotating Biological Contactor
RCRA	Resource Conservation and Recovery Act
RDX	Cyclotrimethylenetrinitramine
rpm	revolutions per minute
SAGE	Solvent alternatives guide
SBIR	Small Business Initiative for Research
SBR	Sequencing batch reactors
SBR	Spouted bed reactor
SCR	Selective catalytic reduction
SCWO	Supercritical water oxidation
SITE	Superfund Innovative Technology Evaluation
SIVE	Steam injection vapor extraction
SVE	Soil vapor extraction
SVOC	Semivolatile organic compound
TCA	Trichloroethane
TCDD	Tetrachlorodibenzo-p-dioxin
TCE	Trichloroethylene
TCLP	Toxicity Characteristic Leachate Procedure
TLCC	Total life cycle cost
TNT	Trinitrotoluene
TPH	Total petroleum hydrocarbons
TSCA	Toxic Substances Control Act
TSDF	Treatment, storage, and disposal facility
USAEC	US Army Environmental Center
USATHAMA	US Army Toxic and Hazardous Materials Agency (renamed USAEC)
UIC	Underground injection control
UST	Underground storage tank
UV	Ultraviolet
VC	Vinyl chloride
VIC	Volatile inorganic compound
VOC	Volatile organic compound

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CHAPTER 1. INTRODUCTION

Environmental technologies have evolved rapidly over the last two decades. Demands for secondary, tertiary, and industrial wastewater treatment systems; safer disinfection; new and improved air emission controls; and most recently, the need for more economical and more efficient methods to treat hazardous wastes and clean up our Superfund sites, have all provided the driving force for the development of new and better environmental technologies. "Green engineering" is now offering alternatives to the traditional "end-of-pipe" technologies as pollution prevention has emerged as the current strategy on how to deal with environmental pollution.

This document identifies and discusses emerging, innovative, and established remedial technologies which are the new generation of processes that will be used to remediate our contaminated sites now and in the future. Many of these technologies attempt to optimize natural attenuating factors, such as microbial populations, in dealing with contamination. Others attempt to more efficiently extract and treat contaminants. This trend is expected to continue and future technologies will focus heavily on nonintrusive methods for detecting, identifying, quantifying, and treating the contaminants of concern.

The material within this document will be updated and expanded as new information is obtained about emerging and innovative remedial technologies. The information herein will provide US Army policy makers, as well as environmental technology users, valuable information regarding the direction of new environmental technology.

The EPA has been a valuable source of information. In particular, the EPA Superfund Innovative Technology (SITE) Program has provided information on remedial technologies. Recognition is also appropriate for the US Army Environmental Center (AEC), the Stevens Institute of Technology, J. M. Stratta and Associates, and Life Systems, Inc., for their substantial efforts.

CHAPTER 2. BIOREMEDIATION TECHNOLOGIES

2.1 Introduction

Microorganisms are utilized to dispose of a variety of solid and hazardous materials because they possess the ability to degrade many different compounds and substances. Better understanding of the mechanisms by which microorganisms transform chemical substances is leading to the increased use of bioremediation techniques, particularly in the area of remediating contaminated sites.

Microorganisms are found in a variety of environments. Bacteria in particular are ubiquitous. They can live and proliferate in most unusual places and extreme environments. Some are known to grow in temperatures as high as 105°C, others grow in saturated salt solutions, some will even grow in hot sulfuric acid, and a rich variety of them can be isolated from thousands of feet, deep into the ground.

An examination of the redox chemistry of soil sediments shows redox processes to occur according to thermodynamic predictions, despite kinetic/reaction mechanism constraints. Nitrate will not be reduced to nitrite and N₂ until oxygen disappears almost completely, then ferric iron is reduced to the ferrous form, followed by sulfate to sulfide and CO₂ to methane. All these processes are mediated *in vitro* by bacteria, at rates similar to those observed *in situ*. This finding would suggest that microorganisms are responsible for coupling these reactions in soil sediments.

It is likely then that microorganisms that can mediate the transformation of organic chemicals and metals found in polluted environments are already present at the site. The question is, if they are already there, why do contaminants tend to persist in polluted environments? The question often is not whether microbes could degrade or transform particular contaminants, but how to find the right conditions to promote their growth and thus the transformation and removal of the contaminants in question.

Quite often the problem is one of finding the rate limiting factor—which nutritional, physical or chemical component limits higher rates of growth/substrate consumption for the microorganisms of interest. Lack of a key nutrient such as nitrogen, low temperatures, dry soils or an unfavorable pH can limit faster rates of substrate degradation. Sometimes, pumping air into the ground may suffice to speed up the degradation process and achieve remediation of the site.

Saturated aliphatic hydrocarbons, for example, are known to be degraded only under aerobic conditions. There appears to be a strict requirement for molecular oxygen in the breakdown mechanism. Some polychlorinated hydrocarbons, on the other hand, are degraded at faster rates under anaerobic conditions, although they can also be degraded under aerobic ones. Postulated explanations for these differences are fundamental dissimilarities in reaction mechanisms under aerobic and anaerobic conditions—an oxidation with a monooxygenase in the presence of air and a reductive dehalogenation in its absence.

Heavy metals, while not “degraded” from contaminated soil by bacterial action, owing to their intrinsic nature, can in fact be controlled from spreading by controlling their mobility. Many metals form stable oxyanions which are soluble under aerobic conditions. Under anaerobic conditions the reduced forms of these metals can form insoluble hydroxides. Examples of the latter

are plutonium and uranium salts. Some metals, such as selenium and tellurium, will precipitate as their elemental form. These redox processes can be "manipulated" using microorganisms, as they are known to metabolize these metals.

Other metals exhibit the opposite behavior. Lead and iron, for example, are more soluble under anaerobic conditions, as they form hydroxides, rather than stable oxyanions under aerobic conditions. However, if anaerobic conditions get to the point where sulfate is reduced to sulfide, both will precipitate as lead and iron sulfide, respectively. This differential metal solubility under different redox conditions can be used to mobilize/extract heavy metals in soil and selectively precipitate them in treatment facilities.

The remediation of contaminated sites has often utilized pump and treat technologies. This approach has required that contaminated ground water be brought to the surface in order to be properly treated by physical, chemical, or biological means. Experience has shown that such approaches, while often appropriate and valid, take long periods of time to achieve the desired degree of treatment and are very expensive. Current thinking is oriented more toward bioremediation strategies based on promoting the growth of microorganisms within contaminated sites. Some technologies involve the addition of fertilizer to correct carbon imbalances, others try enriching the development of particular organisms growing in and/or degrading the contaminants of interest, while additional ones try a combination of strategies. Surfactants may sometimes be added to mobilize water-insoluble substances sorbed to soil particles. These bioremediation technologies are at various stages of development. Some are at the research or laboratory level, others have been either pilot-tested or demonstrated in the field, and others are "established" technologies.

2.2 *In Situ* Bioremediation Treatment-General

Technology Description

In situ bioremediation involves stimulating the indigenous (already existing) or introduced aerobic or anaerobic bacteria to biodegrade organic compounds within the soil and/or groundwater. This biological system incorporates naturally occurring microorganisms into the treatment scheme through modifications of the existing soil and groundwater environment to encourage their growth and reproduction. In the process of growth, these microorganisms require a source of energy (electron donor), and a means to extract this energy from the electron donor via an appropriate electron acceptor. The application of biological systems for soil and groundwater treatment uses the contaminants as the electron donors, while supplying electron acceptors and required nutrients to the indigenous microorganisms. Aerobic microorganisms are the most preferred for biological treatment systems due to the more rapid rates of decomposition, inherent stability, and performance characteristics they exhibit. In contrast to many other remedial technologies that simply transfer a waste from one environmental medium to another, *in situ* bioremediation both treats contamination in the soil matrix and offers a partial or complete destruction of the contaminant. The bioremediation of contaminants can take place in the saturated or unsaturated zones. The ultimate goal of the process is to convert hydrocarbons and other organic wastes into biomass and harmless products such as methane, carbon dioxide, and inorganic salts.

Adsorbed and dissolved contaminants are the targets of *in situ* biodegradation. By stimulating the growth of the appropriate bacteria in the subsurface, organic contaminants are reduced by bacterial attack. The bacteria can attach directly onto contaminated liquid films within the porous soils, and onto the surface of the soil particles, thereby being in direct contact with the

polluting chemical. Of the two basic families of microbes that are important to biological treatment, prokaryotes (eubacteria and archaeobacteria) and eukaryotes (fungi, algae, protista, and rotifers), prokaryotes are the ones most important to biological treatment of hazardous waste. By matching microorganisms and conditions with particular contaminants in the soil, treatment objectives can be met with a relatively low potential for failure.

There is a vast array of nutritional requirements for microbial growth, depending on the type of microbe being employed. The source of energy to drive the metabolic process can be light, for phototrophic organisms, or chemical reactions, for chemotrophic organisms. The carbon source from which cell components are synthesized can consist of organic compounds for heterotrophs, or carbon dioxide, for autotrophs. Depending on the type of organism, the metabolic process can be either aerobic, i.e., yielding energy by using oxygen as the final electron acceptor, or anaerobic, that is, yielding energy by using a molecule other than oxygen as the electron acceptor.

Enzymes or protein catalysts are formed during metabolism. Like inorganic catalysts, enzymes work to lower the energy required to allow a reaction to proceed while not altering themselves in the process. It is these enzymes that are responsible for breaking down and thereby treating waste products. It is because enzymes are so specific as to the reactions they catalyze that different microbes, which produce different enzymes, are needed for different types of wastes. Enzyme activity varies greatly with respect to changes in environmental conditions such as pH, temperature, and substrate concentration.

Advantages of In Situ Bioremediation Systems:

- The process can be used to treat a wide variety of organic compounds.
- The process can be utilized to treat large volumes of soil that would be prohibitively expensive to excavate.
- The contaminants in the soil may be transformed into non-toxic compounds, thus reducing future liabilities.
- There is no disposal of contaminated residues; thus the liability associated with a remediation project is limited.
- The technology is not disruptive to ongoing site operations.
- The process can be constructed from standard equipment, labor, and materials.
- The process is highly cost effective.
- The process is effective in cleaning both the soil and groundwater simultaneously without excavation.

Disadvantages of In Situ Bioremediation Systems:

- The process is sensitive to several parameters, including: bacterial population availability, nutrient availability, oxygen supply, temperature, and moisture. Maintaining a stable environment for the bacteria by maintaining the appropriate levels of these factors is one of the most difficult tasks and one of the most important in determining the effectiveness of the degradation process.
- Geologic heterogeneities and soil sorptive capacity can limit achievable target levels.

- *In situ* bioremediation is not applicable for heavy metals, inorganic substances, corrosive wastes, acidic wastes, certain polychlorinated biphenyl (PCBs) and other organic compounds that resist biodegradation, and radioactive wastes.
- Toxicity within the site will limit the applicability and performance of biological systems.
- Soil clogging in the proximity of injection wells has been a recurring problem because of the abundant growth of microbial mass immediately adjacent to the injection point.
- Heavy doses of nutrients such as nitrates can adversely impact groundwater quality.
- Implementation in low-permeability soils is difficult because of the difficulty of transporting the required reactants to the contaminated region.
- Biochemical transformations may produce toxic byproducts.

Stage of Development

In situ bioremediation is a demonstrated, commercially available technology. Current research is conducted on several aspects of the technology, including the following:

- Increasing bioavailability of low solubility compounds.
- Improving oxygen and nutrient delivery systems.
- Introducing and acclimating new and specialized microorganisms into subsurface environments.
- Designing subsurface bioreactors for treatment of contaminated groundwater.

Applications and Effectiveness

The conversion of organic compounds into inorganic end products by microorganisms can occur in a number of ways. Usually the conversion of organic compounds supports the growth of the microorganisms due to the released energy and incorporation into the cell elements (mainly carbon) of the molecule. Factors such as structure of the compound to be degraded, the microbial population, nutrient availability, oxygen supply, temperature, and moisture will determine whether degradation actually occurs and at which rate.

The following is a list of organic contaminant groups that are potential candidates for the bioremediation technology:

- Halogenated volatiles
- Halogenated semivolatiles
- Non-halogenated volatiles
- Non-halogenated semivolatiles
- Polynuclear aromatics (PNAs)
- Benzene, toluene, ethylbenzene, xylene (BTEX)
- Solvents
- Explosives/propellants
- Organic pesticides/herbicides

Field results for biodegradation of polyaromatic hydrocarbons (PAHs) showed removal rates of greater than 97 percent within 91 days. Removal efficiencies for a variety of other organic contaminants in soil are in excess of 90 percent within various time frames.

Case Studies

In situ bioremediation processes, applications, and/or case studies are presented in Table 1. Estimated costs are included where available.

Co-Technologies/Alternative Technologies

Hydraulic fracturing and pneumatic fracturing are being used increasingly to improve the transfer of oxygen and nutrients into the subsurface, thus enhancing bioremediation rates in relatively tight soils. The presence of high concentrations of heavy metals and organic compounds such as non-aqueous phase liquids (NAPLs) limits the applicability of *in situ* bioremediation. Several technologies have been used to reduce the concentration of such compounds to levels that are amenable to bioremediation. Such technologies include water or surfactant enhanced soil flushing, thermal (hot air or steam) stripping, soil vacuum extraction, and air sparging. Bioventing is a combination of vacuum extraction and bioremediation.

Cost Analysis

The largest cost component of an *in situ* bioremediation application is usually associated with the oxygen and nutrient delivery systems. The capital costs range from \$35,000 to \$120,000 while maintenance costs for the systems are fairly high. The peroxide system is the most expensive to operate.

For moderate size remediation programs, i.e., 1,000 tons of soil contaminated with diesel, an *ex situ* bioreactor would cost \$110 to \$145 per ton; *in situ* biological treatment, \$65 to \$120 per ton; and excavation and landfilling would be \$140 to \$180 per ton. The clean-up of JP-4 spill at the Coast Guard facility in Traverse City, Michigan, using nitrate addition cost \$84 per gallon of JP-4 or \$200 per cubic meter of contaminated aquifer. Average costs are in the range of \$40-\$70/ton.

Personal Contacts

For a complete list of personal contacts, refer to Table 1.

Table 1. *In Situ* Bioremediation Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Aerobic and Anaerobic Biotreatment	Reference - Sjef, 1990.	A nitrate-based bio-restoration with interdiction and recirculation wells for nutrient and oxygen injection and circulation.	Soil and groundwater	BTEX, pesticides, JP-4 (aviation fuel)	Field-scale performed at Coast Guard facility.	99.7 percent reduction of BTEX. 36.9 percent reduction of JP-4. See cost analysis section for cost information.
Bioventing	Tech. Contact: Paul McCauley U.S. EPA-RREL 26 W. Martin Luther King Dr. Cincinnati, OH 45268 513-569-7444 EPA Contact: Reinaldo Matias 513-569-7149	System treats contaminated soil <i>in situ</i> by injecting atmospheric air.	Soil and sediments	PCBs and halogenated compounds	EPA SITE demonstration program.	Demonstration implemented at the Reilly Tar site in St. Louis Park, MN.
Augmented <i>in situ</i> Subsurface Bioremediation	Tech. Contact: David Mann Bio-Rem, Inc. P.O. Box 116	Process utilizes a proprietary blend of microaerophilic and micronutrients for	Soil and water	Hydrocarbons, halogenated hydrocarbons, and chlorinated	EPA SITE demonstration program. About 240 compounds	Technology demonstrated at Williams Air Force Base in Phoenix, AZ.

Table 1. *In Situ* Bioremediation Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Wetlands-Based Treatment	Tech. Contact: Rick Brown Colorado Dept. of Health 4210 E. 11th Avenue, Room 252 Denver, CO 80220 303-331-4404 EPA Contact: Edward Bates 513-569-7774	Process utilizes natural geochemical and biological processes inherent in a man-made wetland ecosystem to accumulate and remove metals from influent waters.	Acid mine drainage	Metals	EPA SITE demonstration program.	Drainage study results from the Big Five Tunnel near Idaho Springs, CO, showed that removal efficiency of heavy metals can approach the removal efficiency of chemical precipitation treatment plants. No cost data available.
Fungal Treatment Technology	Tech. Contact: Richard Lamar USDA Forest Products Laboratory One Gifford Pinchot Drive Madison, WI 53705	System utilizes white rot fungi to treat soils. Nutrients may be required, moisture and temperature control is necessary.	Soil	PCPs, PAHs, chlorinated organics	EPA SITE demonstration program.	A treatability study was conducted at the Brookhaven Wood Preserving site in Brookhaven, MS. Study results showed an 89 percent removal of PCP and a 70 percent removal of total PAHs, during a 2-month period.

Table 1. *In Situ* Bioremediation Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Biotreatment	Reference - Semprini, 1990	Utilizes methanotrophic bacteria to biodegrade organic compounds.	Aquifers	Trichloroethylene (TCE), cis-DCE, trans-DCE, and vinyl chloride	Field-scale performed at Moffett Naval Air Station, CA.	90-95 percent reduction of vinyl chloride. 80-90 percent reduction of trans-DCE. 45-55 percent reduction of cis-DCE. 20-30 percent reduction of TCE.
Trench Bio-Sparge	Tech. Contact: George P. Korfiatis Center for Environmental Engineering Stevens Institute of Technology Hoboken, NJ 07030 201-216-5348	A subsurface bioreactor to treat groundwater at the downgradient end of the plume. Packing material is selected to enhance attached microbial growth. Simultaneous sparging of VOCs can be achieved.	Groundwater	All biodegradable organics	Laboratory pilot-scale.	Laboratory scale experiments underway for reactor optimization. No cost data available.
Deep <i>in situ</i> Bioremediation Process	Tech. Contact: Richard Murray <i>In Situ</i> Fixation Co. P.O. Box 516 Chandler, AZ 85244-0516	Process increases the efficiency and rate of biodegradation in deep contaminated soils. System injects site-specific microorganism mixture and	Soil and sludge	Biodegradable organics	EPA SITE demonstration program.	Demonstration program with the U.S. Air Force implemented in 1993. No results or cost data available.

Table 1. *In Situ* Bioremediation Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
<i>In Situ</i> Biological Treatment	Tech. Contact: Linda Yost-Fetui ECOVA Corp. 18640 N.E. 67th Court Redmond, WA 98052 206-883-1900 EPA Contact: Naomi Barkley 513-569-7854	Process biodegrades chlorinated and nonchlorinated organic contaminants by employing aerobic bacteria that use the contaminants as a carbon source.	Water, soil, sludge, and sediment	Biodegradable organics	Laboratory scale treatability studies.	After the completion of treatability studies at the Goose Farm Superfund site in Plumstead Township, NJ, the planned demonstration was canceled. No cost data available.

2.3 *Ex Situ* Bioremediation Treatment-General

Technology Description

Bioremediation processes are used to treat a variety of wastewaters and related contaminated solids which have been extracted from contaminated locations. Many of these technologies have evolved from conventional wastewater treatment technologies. The most commonly used biological processes are:

- Activated sludge (suspended growth)
- Trickling filter (attached growth)
- Rotating biological contactors (attached growth)
- Soil-water slurry reactors (attached/suspended growth)
- Composting
- Aerated lagoons (suspended growth)
- Waste-stabilization ponds (suspended growth)
- Aerobic digestion (suspended growth)
- Anaerobic digestion (suspended growth)
- Immobilized bed systems (attached growth)

Major *ex situ* biological processes are briefly described below.

2.3.1 Activated Sludge

The main units of the process are the aeration basin and the secondary clarifier. The biomass is grown in the aeration basin (suspended growth), which accepts the waste stream with high concentrations of biological oxygen demand (BOD). The BOD is converted to carbon dioxide, water, and cell mass. Air diffusers at the bottom of the aeration basin provide oxygen to the system which is necessary for the proper growth and development of the microorganisms. The effluent from the aeration unit is fed into the clarification tank, where excess biomass is captured and removed from the system.

Activated sludge systems can efficiently and economically treat large volumes of industrial and municipal wastewater, provided that toxic substances, if present, are below the inhibitory levels that cause system instability. Activated sludge can be operated under aerobic or anaerobic environments with mixed or pure bacterial cultures. Aerobic and anaerobic digestion, aerated lagoons, stabilization ponds, and sequencing batch reactors (SBRs) are all examples of different types of activated sludge. Parameters that affect the performance of bioremediation systems include the equalization basin characteristics, nutrients, aeration, oxygen supply, substrate-biomass contact time, microorganism growth phase, temperature, pH, the selection of microorganisms and the biological interactions within the aeration basin. Activated sludge is the most widely used biological process for the treatment of complex wastewater streams as well as of single hazardous substances that may be present in a particular effluent.

2.3.2 Trickling Filter

This attached growth process is easier to operate than suspended growth systems, but difficult to model accurately. This difficulty is primarily due to the large number of variables known to influence the process, including: filter depth, hydraulic flow and organic loading, recirculation ratio, type of filter media, mass transfer of organic material and oxygen from the liquid layer to the attached slime layer, and the metabolism of the attached slime layer. Trickling filters are similar to packed towers. The packing medium which can be random or structured, provides the required surface area where microorganisms can attach and grow.

Trickling filters are designed and classified by their hydraulic or organic loading rate capacities as either low-rate filters, intermediate-rate filters, or high- and super high-rate filters. In a trickling filter, wastewater is flowing over the slime layer, which is attached to the filter media. As the water trickles down the filter, substrate is adsorbed by the microorganisms while at the same time, excess biological material is mechanically removed into the liquid phase and carried out of the filter. Trickling filters are also used to achieve nitrification. The ecosystem in the filter includes aerobic, anaerobic, and facultative bacteria, fungi, algae, and protozoans.

2.3.3 Rotating Biological Contactor

A rotating biological contactor (RBC) operates on a similar principle to a trickling filter, but it has a rotating bed of attached microorganisms which is immersed in a tank of contaminated water. The rotation exposes the surface of the disc to the atmosphere, permitting aeration, and then resubmerges it in the wastewater. The bed comprises a number of circular, closely spaced discs mounted on a rotating drive shaft. The disc rapidly develops a microbial community in the form of a film (up to 3 mm thick) which is responsible for BOD removal. The discs may be made of wood, metal, or polystyrene, in either a flat, corrugated, or honeycombed profile to increase the surface area for film growth. Full-scale RBCs may have discs up to 4 m in diameter mounted on 7 m shafts. Rotation speeds are usually between 1 and 2 revolutions per minute (rpm). Rotation provides mixing of the tank contents and shear forces necessary for sloughing. RBCs can achieve a high degree of carbonaceous and nitrogenous BOD removal. They are easy to operate and have low power and maintenance costs.

2.3.4 Soil-Water Slurry Reactor

Bioslurry reactors have been receiving increased attention for their use in the remediation of soil and groundwater. This is an *ex situ* bioremediation technology where the soil is introduced in a reactor that has been previously inoculated with selected microorganisms suitable for the degradation of the soil contaminants. The soil-water slurry is formed by adding a predetermined amount of water to achieve an optimum soil to solution ratio. The microorganisms are obtained from the soil itself or are cultured in a separate system and transferred to the bioslurry reactor. After start-up the microbial population is maintained by appropriately controlling the reactor parameters, such as retention time, temperature, and pH.

Ellis (1984) demonstrated that some biodegradable surfactants can remove petroleum oil and polychlorobiphenyls by up to 95 percent. The desorption of contaminants makes them available to microorganisms. According to Robichaux and Myrick (1972), one chemical emulsifier increased the biodegradation rate by 18 times. Recently ECOVA Corporation demonstrated the effectiveness of a bioslurry reactor for treatment of polyaromatic hydrocarbons (PAHs) with limited success, less than

90 percent reduction in 2 to 4 weeks (EPA, 1991). BioTrol, Inc., used a slurry reactor for treating PAHs and pentachlorophenol (PCP) as a final polishing step in a chain of processes with 95 percent reduction in 4 weeks (EPA, 1991). Hydrophobicity is the main reason for the observed low removal rates by biodegradation, and research studies are currently being conducted to increase the bioavailability of contaminants in slurry reactors. Recently researchers have shown that biodegradation rates do increase in the presence of surfactants (Aronstein et al., 1991, Ellis et al., 1984, Melissa, 1984).

2.3.5 Composting

Composting is a process in which organic materials undergo microbiological degradation in order to achieve stable end products. The microorganisms involved fall into two major categories: bacteria and fungi. During composting the organic material is destroyed and humic acids are formed. The process proceeds through three distinct stages: the mesophilic, the thermophilic, and the cooling stage.

In the mesophilic stage the temperature is raised to approximately 40°C. As the temperature in the compost pile increases, thermophilic conditions are attained and the temperature reaches approximately 70°C. It is during the thermophilic stage that most of the degradation and stabilization of the organic material occurs.

Composting can be carried out either in aerated static piles or in composting vessels. First dewatered sludge or soil is mixed with an amendment or bulking agent, such as wood chips. Then the pile is aerated by the addition of air or mechanical turning. Materials are typically composted for 21 to 28 days and cured for another 30 days. Composting has a great potential for the treatment of soils contaminated with energetic materials such as nitrocellulose, trinitrotoluene (TNT), and cyclotrimethylenetrinitramine (RDX).

Advantages of Ex Situ Bioremediation Systems:

- Large quantities of wastewater with high organic and nutrient loadings can be handled.
- Easy recovery in case of toxic shocks.
- Less expensive construction and operation costs compared to other physicochemical systems for the same application.
- High destruction capabilities as well as high removal efficiencies.
- Simultaneous carbon and nutrient removal can be achieved by properly controlling the operating parameters of the bioreactor. Single-stage activated sludge and SBRs, for instance, can remove both carbonaceous and nitrogenous BOD in the same unit.
- Years of design experience makes construction and operation of these systems relatively easy.
- Reduced disposal costs.

Disadvantages of Ex Situ Bioremediation Systems:

- Biological processes cannot be applied to highly toxic effluents or soils and groundwater that contain high concentrations of heavy metals and other hazardous substances. However, they can be integrated into a treatment process train where physicochemical pretreatment techniques are used to alleviate the toxic effects of the contaminants on the

microbial population. For instance, when soil is contaminated with mixtures of biodegradable organics and heavy metals, biological treatment may be applied following the removal of heavy metals by soil washing and subsequent precipitation.

- Toxicity usually limits the treatment performance of aqueous streams containing hazardous substances.
- Certain substances that are treated in conventional biological systems may pass through the systems without substantial decomposition. These compounds usually require higher retention times and/or specialized microorganisms in order to be effectively destroyed.
- The effectiveness of microbiological transformations in complex aqueous and soil matrices can be assessed only by appropriate treatability studies.
- Degradation kinetics for many biodegradable organic substances are unknown.

At a recent national workshop (Bury and Miller, 1993; EPA, 1992), the conclusion was reached that the main barriers for implementing biological systems in soil treatment are (a) irreversible adsorption of contaminants, which makes them unavailable to microorganisms; (b) toxicity of the organic compounds to the microbial consortia; (c) unsuitable pH for proper microbial growth; (d) oxygen mass transfer limitations; (e) temperature; and (f) nutrient limitations. To ameliorate these problems, multistage processes have been suggested. These processes include pre-cleaning, washing of soil, thermal desorption to partially remove the organics, and bioremediation as the final polishing step to decontaminate the soil to regulatory levels.

Stage of Development

Conventional biological processes such as activated sludge and trickling filters are established technologies with a wide range of applications. Numerous innovative technologies are currently under development, and the results are very encouraging. Bioslurry reactors, for the decontamination of soils and groundwater, are well on their way to becoming a demonstrated full-scale technology. Immobilized bed reactors for the destruction of hazardous and energetic materials are being developed and tested at the bench scale level. Areas that require further research and development include:

- Reactor type and configuration for the treatment of hazardous materials.
- Kinetics of biodegradation for a large number of energetic and munitions wastes.
- Degradation pathways and enzymatic systems responsible for degradation.
- Isolation and identification of microorganisms that degrade specific substances or groups of hazardous materials.

Some examples of *ex situ* bioremediation are listed in Table 2.

Applications and Effectiveness

Biological processes have been applied to industrial effluents where BOD and/or nitrogen reduction is required, and also toward the remediation of soils, groundwater, and soil slurries. The implementation of biological processes for degradation of contaminants has proven to be effective. Several removal/destruction efficiencies which have been determined for various pollutants are as follows:

Removal/Destruction Efficiency in Aerobic Systems

- Soluble Organics 60-80%
- Phosphorous 25-35%
- Trace Organics 25-35%

Removal/Destruction Efficiency in Anaerobic Systems

- Soluble Organics 40-50%
- Trace Organics 25-35%

Removal/Destruction Efficiency in Nitrification Systems

- Ammonia 75-85%

Removal/Destruction Efficiency in Denitrification Systems

- Nitrate/Nitrite 85-95%

Slurry-phase biological systems are primarily designed to treat non-halogenated volatile compounds and polynuclear aromatic hydrocarbons. Halogenated volatiles, semivolatiles, and pesticides can also be treated but the process is less effective. Aerobic co-metabolism using methanotrophic bacteria can degrade TCE and the lower chlorinated aliphatics, but does not work well with tetrachloroethylene (PCE) and higher chlorinated compounds. The overall costs are highly dependent on the extent of preparation required for the contaminated material prior to slurring, and the need for dewatering and air emission control equipment. Commercial-scale units are in operation.

Composting and land farming have also been applied to soils contaminated with non-halogenated volatile organics and fuel hydrocarbons. Factors that limit the applicability and effectiveness of the process include:

- Large amounts of space are required.
- Excavation of contaminated soil is required.
- Treatability studies must be conducted to determine biodegradability.
- Lengthy time periods are required to achieve the desired reduction.

These treatment processes have been applied to soils contaminated with explosives such as nitrocellulose, TNT, and RDX with limited success. Costs depend on the contaminant, need for additional pre- and post-treatment, and the need for air emission control equipment. However, these processes are relatively simple and require few personnel for operation and maintenance.

Treatability studies performed on contaminated soils indicated that bioremediation is a potentially effective technology that resulted in the following average removal efficiencies (Fox, 1991):

- Non-polar halogenated aromatics - 53%
- PCBs, halogenated dioxins, furans and their precursors - 99%
- Halogenated phenols, cresols, amines, thiols, and other polar aromatics - 74%
- Nitrated compounds - 82%
- Polynuclear aromatics - 87%
- Heterocyclic and simple non-halogenated aromatics - 99%

Case Studies

Ex situ bioremediation technology applications and/or several case studies are presented in Table 2. Estimated costs are included where available.

Co-Technologies/Alternative Technologies

Bioremediation processes include a large number of processes that use active microorganisms for the destruction of organic pollutants in different media. Although modifications of various biological processes are presented by vendors as separate technologies, they all operate on the same principle, which is the use of microorganisms for the oxidation of organic pollutants.

Biological systems can be employed as the sole treatment technology or they can be part of a treatment train that combines physical, chemical, and biological means to achieve the specified treatment objectives.

Biological processes often compete or are sometimes supplemented by other treatment technologies such as incineration, physical separation, carbon adsorption, soil washing, and thermal extraction. However, they are usually the preferred treatment alternative mainly due to low cost, relatively low chemical requirements, ease of operation, and availability of equipment.

Cost Analysis

Bioremediation processes are, in general, more cost effective than physicochemical processes that compete for the same application. Estimated costs for different applications of the technology are given in Table 2.

Personal Contacts

For a complete list of contacts, refer to Table 2.

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- Robichaux, T. J. and H. N. Myrick. 1972. Chemical enhancement of the biodegradation of crude-oil pollution. *Journal of Petroleum Technology* 24: 16-20.

Table 2. Biological Processes - *Ex Situ* Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Biological Treatment (Pump and Treat)	Capt. Catherine M. Vogel HQ AFCESA/RDVW Tyndall AFB, FL 32403-5319 904-283-4628/2942	Aerobic biodegradation using indigenous bacteria. Flow rates 2-3 L/min. Retention time 20-50 min. in reactor.	Groundwater (<i>ex situ</i>)	TCE, and chlorinated aliphatic compounds	Field Scale study implemented February, 1989.	80 percent degradation achieved. Cost data not applicable.
Biological Treatment (Pump and Treat)	Mary K. Stinson U.S. EPA-RREL Woodbridge Avenue Edison, NJ 08837 908-321-6683	Immobilized multiple-cell, submerged fixed film reactor.	Groundwater (<i>ex situ</i>)	PCP, creosote, gasoline, and fuel oil	EPA SITE demonstration program. Field scale study implemented during February, 1989.	96 to 99 percent removal of pentachlorophenol (PCPs) (from 45 to 1 parts per million [ppm] in a single pass). Produced minimal sludge and no air emissions. Cost data not available.
On-Site Bioremediation	Mary Pat Huxley <i>or</i> Carmen Lebron Naval Civil Engineering Laboratory Environmental Restoration Division Port Hueneme, CA 93043-5003	Slurry reactors, indigenous bacteria. Addition of nutrients. Combined aerobic/anaerobic operation.	Groundwater/soil (<i>in situ</i> and <i>ex situ</i>)	Unleaded gasoline and aromatic fuel components	Technical information available. Pilot scale testing in progress.	90 percent removal of aromatics. Inexpensive and non-labor intensive. Excavation not required

Table 2. Biological Processes - *Ex Situ* Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Biological treatment of ordnance contaminated soil	Carmen A. Lebron Naval Civil Engineering Laboratory Environmental Restoration Division Port Hueneme, CA 93043-5003 805-982-1616	Bioreactors mixed with soil nutrients and white rot fungus. Can be applied <i>in situ</i> .	Soil	TNT and RDX	Not available off the shelf but easy to implement.	Cost estimated at \$75/ton of soil.
Bioslurry Reactors with Enhanced Bioavailability	Tech. Contact: Chris Christodoulatos Center for Environmental Engineering, Stevens Institute of Technology Hoboken, NJ 07030 201-216-5675	Simultaneous treatment of soil and groundwater in bioslurry reactors with surfactants used to increase bioavailability	Soils/sludges and groundwater (simultaneously)	Polycyclic aromatics	Laboratory bench-scale.	Laboratory scale studies have shown that bioavailability of higher ring hydrocarbons is increased by up to 2 orders of magnitude.
Biological treatment of soil contaminated with explosives and propellants through composting process	Capt. Kevin Keehan USATHAMA CETHA-TS-D Aberdeen Proving Ground, MD 21010-5401 410-671-2054	Composting - Contaminated soils are excavated and mixed with bulking agents and organic amendments.	Soil, lagoon sediments	TNT, cyclotetramethyl-enetetranitramine (HMX), RDX	All material and equipment commercially available. Treatability protocol under development.	Costs vary with amount of soil to be treated and type of process design employed.
Biological	William Major	Surface pile	Soil	Diesel IP-5 or	Technology is	Field pilot testing

Table 2. Biological Processes - *Ex Situ* Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Biological treatment through enhanced natural biodegradation	Walter Mikucki U.S. Army Corps of Engineers CERL P.O. Box 9005 Champaign, IL 61826 217-352-6511	Soil is disked and covered. The inoculant and nutrients are applied during disking. Aerobic or anaerobic conditions.	Soil	Lube oil such as used motor oil	Aerobic degradation removes 60% of the oil. More work required for the anaerobic part of the process. Commercial systems are available.	Costs are estimated at \$50-150/cubic yard.
Biological treatment of soil contaminated with the pesticide dinoseb	Tech. Contact: Dane Higdem J. R. Simplot Co. Pocatello, ID 208-234-5367 EPA Contact: Wendy Davis-Hoover 513-569-7206	System of slurry bioreactors under anaerobic conditions. Starch is added to enhance biodegradation.	Soil	Dinoseb and TNT (Nitroaromatics)	EPA SITE demonstration program. Bench and pilot scale studies.	No cost data available.
Biological treatment of explosives contaminated soils with slurry bioreactor	Capt. Kevin Keehan USATHAMA CETHA-TS-D Aberdeen Proving Ground, MD 21010-5401 410-671-2054	Soil-water slurry treated in sequencing batch reactor (SBR).	Soil	Explosives: TNT, RDX, HMX	Technology in pilot-scale demonstration phase. However, equipment is	Pilot-scale demonstration at Joliet Army Ammunition Plant,

Table 2. Biological Processes - Ex Situ Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Biological treatment of soil contaminated with propellants through composting process	Capt. Kevin Keehan USATHAMA CETHA-TS-D Aberdeen Proving Ground, MD 21010-5401 410-671-2054	Composting - Contaminated soils are excavated and mixed with bulking agents and organic amendments.	Soil and solids from manufacturing streams	Nitrocellulose (NC)	All material and equipment commercially available. Treatability protocol under development.	Field study conducted at Badger Army Ammunition Plant in Sauk County, WI. Cost data not available and will be site specific. Overall, composting is a low-cost alternative.
Biological treatment of wastewater from munition production	Richard Eichholtz USATHAMA CETHA-TS-D Aberdeen Proving Ground, MD 21010-5401 410-671-2054	SBR	Wastewater	Nitroglycerine, N-nitrosodi-phenylamine, and Dibutyl-phthalate	Demonstration report available. Expected implementation at Badger Army Ammunition Plant.	No cost data available.
ECOVA Corp. - slurry-phase bioremediation	Tech. Contact: William Mahaffey ECOVA Corp. Golden, CO 303-273-7177 EPA Contact: Ronald Lewis 513-569-7865	Utilizes batch and continuous flow bioreactors to process wastes.	Soil, sediments, and sludges	Creosote and petroleum wastes	EPA SITE demonstration program. Bench- and pilot-scale studies completed.	During EPA SITE demonstration program at the Burlington Northern Superfund site in Brainerd, MN, data indicated that almost

Table 2. Biological Processes - *Ex Situ* Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Biological/Chemical Treatment - COGNIS	Tech. Contact: Jonathan Mielenz COGNIS, Inc. Santa Rosa, CA 707-576-6223 EPA Contact: Naomi Barkley 513-569-7854	The COGNIS technology treats soils contaminated with both metals and organics. Two-step process involving chemical leaching of metals followed by slurry bioreactor treatment.	Soil	Heavy metals, PAHs, petroleum hydrocarbons	EPA SITE Emerging Technology Program. Bench scale and pilot-scale testing of the metals extraction and bioremediation process are being conducted.	Experiments with combined pilot-scale process began in 1993. No cost data available.
Biological Sorption - AlgaSORB	Tech. Contact: Tom Powers Bio-Recovery Systems, Inc. Las Cruces, NM 505-523-0405 EPA Contact: Naomi Barkley 513-569-7854	Biological treatment using sorption to remove heavy metal ions from aqueous solutions.	Groundwater, leachate, wastewater	Heavy metals	EPA SITE Emerging Technology Program. Bench- and pilot-scale studies completed.	Effective results for test on mercury-contaminated groundwater at a hazardous waste site in Oakland, CA. No cost data available.
Allied-Signal, Inc. - ICB Biotreatment System	Ralph Nussbaum or Timothy Love Allied-Signal, Inc. P.O. Box 1087 Morristown, NJ 07962 201-455-2122	The immobilized cell bioreactor (ICB) removes organic contaminants through aerobically fixed film biotreatment.	Groundwater and wastewater	Halogenated and non-halogenated VOCs and SVOCs	EPA SITE demonstration program. Full-scale studies completed. Modular units	At the G&H Landfill in Utica, MI, treatability studies show biodegradation of all priority

Table 2. Biological Processes - *Ex Situ* Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Methanotrophic Bioreactor System	<p>Tech. Contact: Durell Dobbins BioTrol, Inc. Chaska, MN 612-448-2515</p> <p>EPA Contact: David Smith 303-293-1475</p>	Degradation through cometabolism of halogenated hydrocarbons.	Water	Halogenated Hydrocarbons	EPA SITE Emerging Technology Program. Bench- and pilot-scale studies completed.	Bench-scale experiments were conducted on a continuous flow, dispersed-growth system. Typical reduction results were from approximately 500 ppb TCE influent to less than 90 ppb effluent. No cost data available.
Biological treatment of hazardous organic emissions using bioscrubbers	<p>Tech. Contact: Paul Liu Aluminum Co. of America Oak Creek, WI 412-826-3711</p> <p>EPA Contact: Naomi Barkley 513-569-7854</p>	Bioscrubber using Alcoa activated carbon medium to support microbial growth.	Soil, water, air	Most organics	EPA SITE Emerging Technology Program. Bench- and pilot-scale studies completed.	No cost data available.
Zimpro/PACT wastewater treatment	<p>Tech. Contact: William Copa Zimpro Treatment Equip</p>	PACT combines powder activated carbon adsorption	Groundwater, industrial	Biodegradable organics	EPA SITE Emerging	Contaminated groundwater from

Table 2. Biological Processes - *Ex Situ* Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Remediation Technologies Inc. - Liquid and solids biological treatment	Tech. Contact: Merv Coover Remediation Technologies, Inc. Seattle, WA 206-624-9349 EPA Contact: Ronald Lewis 513-569-7865	Liquid and solid biological treatment (LST) - similar process to activated sludge treatment of municipal and industrial wastewater.	Soil, sediments and sludges	Biodegradable organics	Over a dozen field applications have been demonstrated. Several bench-and pilot-scale studies completed.	Technology has treated petroleum refinery impoundment sludges in two field-based pilot demonstrations and several laboratory treatability studies. No cost data available.
Biological Aqueous Treatment System (BATS)	Tech. Contact: Dennis Chilcote BioTrol, Inc. Chaska, MN 612-448-2515 EPA Contact: Mary Stinson 908-321-6683	Biological treatment of contaminated groundwater and process water.	Liquid waste, groundwater, lagoons, process water	Nitrates, Chlorinated and Non-chlorinated Hydrocarbons, Pesticides	Technology has been used in over 20 full-scale systems and several pilot-scale studies.	EPA Site demonstration at the MacGillis and Gibbs Superfund site in New Brighton, MN. Resulted in pentachlorophenol concentration reduction from 45 to 1 ppm or less in a single pass. Achieved 96 to 99 percent removal of PCP; unaffected by low concentrations

Table 2. Biological Processes - Ex Situ Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Treatment of Ball Powder Production Wastewater	Tech. Contact: Richard Eicholtz USATHAMA CETHA-TS-D Aberdeen Proving Ground, MD 21010-5401 410-671-2054	Two methods: 1) extended aeration - aerated biological reactor and 2) a sequencing batch reactor - use of single tank process.	Wastewater	A number of contaminants in wastewater, excluding nitroglycerin (NG)	Bench-scale, but commercially available.	Bench-scale testing at Redford Army Ammunition Plant, VA, showed both methods work well in the absence of NG. Up to 1,600 mg/L of NG in feed was tolerable. No cost data available.
Upflow Anaerobic Granular Activated Carbon (GAC) Bioreactors	Tech. Contact: Stephen Maloney U.S. Army Corps of Engineers CERL P.O. Box 9005 Champaign, IL 61826-9005 217-373-3482 800-USA-CERL	The reactor is an upflow expanded reactor containing GAC and anaerobic bacteria acclimated to the contaminant compound.	Wastewater with nitrated toluene	Organics and absorbable and slowly biodegradable dinitrotoluene (DNT)	Bench-scale	100% removal efficiency of DNT from waste stream with no nitrotoluene production. Treats high concentration variations in contaminant stream. No cost data available.

2.4 Emerging and Innovative Technologies

2.4.1 Composting of Energetic Materials

Technology Description

Composting has been evaluated with regard to its remedial efficacy for soils and sediments which have been contaminated with energetic materials (EM) such as explosives and/or propellants. Microbial populations are able to transform and/or degrade these energetic contaminants. The compost amendments (manure, hay, wood chips, corn cobs, etc.) are often the real targets of the microbial populations; however, the energetic matter is also degraded.

The Army has a number of facilities that have soils and sediments contaminated with various energetic materials. The current method of restoration is incineration. However, composting is viewed as a potential alternative remedial technology. The composting of the explosives TNT, RDX, HMX, and tetryl, as well as the propellant NC, have been studied extensively with very promising results.

The conditions of composting are similar to yard waste composting, except that the amount of amendments to be added are greater when composting contaminated soils. Safety is a major concern when soils contaminated with explosives are being composted. Explosives concentrations below 12 percent is required.

The fate of the energetics remains a matter of debate. Total destruction of the explosives may not be occurring as much as binding with the organic amendments. However, toxicity testing of the final compost has proven negative.

Advantages of Composting Sediments with Energetic Materials:

- Composting of explosive contaminated soils and sediments would enable remediation to take place on site, without the concerns associated with incineration. This technology could be tailor-fit to an installation in combination with other remedial options.
- The toxicity and mutagenicity of the resultant compost products have been demonstrated to be significantly reduced through composting. This information is critical when attempting to demonstrate to regulators that the contaminants and/or their impacts have been mitigated.
- Compost technology has been evaluated as being economically competitive with incineration.
- Composting is viewed much more favorably by the public than is incineration.

Disadvantages of Composting Sediments with Energetic Materials:

- The issues of fate and toxicity of explosives bound to the organic matter during the biotransformation process remains largely unresolved.
- A major risk associated with treating explosives contaminated materials is safety because of their potential reactivity. Explosive concentrations of greater than 12 percent can propagate a detonation.

Stage of Development

Field demonstrations for this technology have been underway for several years. Windrow composting has recently been evaluated for full-scale application. Several in-vessel and aerated static pile field studies have been completed. Additional work is planned to address fate, curing, and maximum content of propellant that can be composted safely.

Applications and Effectiveness

Initial field studies have demonstrated that composting is a feasible alternative treatment technology for explosives contaminated soils and sediments. Composting is viewed as offering effective decontamination at greatly reduced costs relative to alternative treatments such as incineration.

Cost Analysis

Compost technology is competitively priced with incineration. Remedial costs for the incineration of explosives contaminated soils range from \$200 per ton (for amounts exceeding 20,000 tons of soil) up to \$2,000 per ton for only a few thousand tons of soil.

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2.4.2 Lignin Degrading Fungi

Technology Description

This biological technology can apply to the *in situ* treatment of contaminated soils. Organic materials are inoculated with wood rotting fungi, usually the white rot fungus, *Phanerochaete chrysosporium*, and mechanically mixed into the contaminated soil.

The persistence and toxicity of certain chemicals in the environment after their release has raised concerns about the environment's ability to degrade these chemicals.

Several types of fungi have been studied to better determine their abilities to accelerate the pollutant degradation process and generate end products such as carbon dioxide and water. The most promising of these fungi for the mineralization of pollutants has been *Phanerochaete chrysosporium*, which breaks down lignin.

Lignin is the main structural component in wood. Wood rotting fungi have developed enzymes which break apart lignin in order for the fungus to derive energy from the wood. These enzymes are the key to degrading other compounds, such as hazardous pollutants.

In a laboratory environment which is nutrient nitrogen deficient, the fungus goes into secondary metabolism and produces two different types of ligninolytic (lignin-breaking) enzymes. These are ligninases (lignin peroxidases) and manganese-dependent peroxidases.

The unique and desirable feature of the ligninases is their high oxidation potential, which allows them to oxidize compounds such as persistent and recalcitrant pollutants that other peroxidases cannot, thus allowing them to accelerate the biodegradation process.

Advantages of Lignin Degrading Fungi:

- *P. chrysosporium* is desirable because it can metabolize difficult to degrade compounds into carbon dioxide and water.
- This technology is environmentally benign and is not likely to cause public concern.
- This technology is self-regenerating as long as proper environmental conditions are maintained.

Disadvantages of Lignin Degrading Fungi:

- Uniform growth of the fungi is important to its efficiency and efficacy, therefore nutrient and moisture levels must be monitored and maintained.
- *P. chrysosporium* has shown sensitivity to high concentrations of TNT and other explosives. Therefore dilution is required for contaminated materials with high explosive concentrations.

Stage of Development

Laboratory and bench-scale studies have been performed to determine the potential applicability for 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) and PCBs. New Jersey Institute of Technology is investigating white rot fungus as a remedial method for contaminated groundwater.

In 1991, the EPA SITE program accepted this technology for a treatability study into the white rot fungus, *Phanerochaete chrysosporium*'s, efficacy at the Brookhaven Wood Preserving site in Brookhaven, MS. A full-scale study was completed in November 1992.

Bench-scale studies were completed for the remedial properties of white rot fungus on the explosives TNT and RDX at Utah State University in 1992. A pilot field demonstration of the same nature began at Site D, SUBASE Bangor, ME, in 1992.

Applicability

The ligninolytic enzymes of *Phanerochaete chrysosporium* have been shown to degrade paper mill effluents, dyes, polycyclic aromatic hydrocarbons, various insecticides and herbicides, polychlorinated phenols, and PCBs. There has also been success in the degradation of low concentrations of TNT, RDX, and HMX.

Cost Analysis

The cost for the bioremediation of soils contaminated with TNT and RDX and other ordnance is estimated at \$75 per cubic yard.

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2.4.3 Catalytic Hydrodehalogenation

Technology Description

Catalytic hydrodehalogenation is a biologically mediated form of reductive dehalogenation. Microbes serve as catalysts for the process, which removes halogen substituents from contaminant molecules and replaces them with electrons, that is commonly carried out in an anaerobic environment. This is done by two different processes: hydrogenolysis and vicinal reduction (dihaloelimination).

Hydrogenolysis is the replacement of a single halogen component with a hydrogen atom in a contaminant compound. Vicinal reduction is the removal of two halogen substituents from adjacent carbon atoms and formation of an additional bond between the atoms in contaminant compounds. While hydrogenolysis works to transform both alkyl and aryl halides, vicinal reduction works only for alkyl halides.

Both of these processes require a reductant, an electron donor, and are thus called reductive. All examples of reductive dehalogenation which are biologically catalyzed have shown the removed halogen atoms released as halide anions.

Catalytic hydrodehalogenation is an important method of biodegrading hazardous and toxic compounds such as organochlorine pesticides, alkyl solvents, and aryl halides. In addition to biodegrading these compounds, catalytic hydrodehalogenation is the only known method which biodegrades polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), PCP, and TCE.

The conditions under which this form of reductive dehalogenation occurs are mainly anaerobic. This is thought to be due to the fact that many compounds have been known only to degrade in anaerobic microbial communities. However, catalytic reductive dehalogenation has been known to be involved in the aerobic degradation of certain highly halogenated compounds.

Many pure cultures of organisms have been reported to be catalysts for the dehalogenation of alkyl halides, but few pure cultures of organisms have been discovered which can carry out dehalogenation on aryl halides.

Research into aryl halide dehalogenation has uncovered the organism *Desulfomonile tiedjei* DCB-1. It is an unusual specimen since it can gain energy from reductive dechlorination and also enhance the ability of other anaerobes to do so.

Advantages of Catalytic Hydrodehalogenation:

- This is the only technology capable of biodegrading certain xenobiotic and persistent chemical compounds listed above.
- This technology can extend the spectrum of bioremediation-treatable sites, cutting down on the need for incineration or other energy consuming remedial technologies.
- This technology can be used in conjunction with other remedial technologies, allowing site specific flexibility.

Disadvantages of Catalytic Hydrodehalogenation:

- There has been limited field application of this technology.
- If pure microbial cultures have to be introduced, there are greater demands to be met in order to ensure their growth and survival than native microbes generally demand.

Stage of Development

Laboratory, bench, and small pilot-scale tests have been the only documented applications to date.

Applications and Effectiveness

This technology is geared towards the detoxification of certain xenobiotic chemicals to make them more readily degradable. It is of particular interest to those operations involved in the treatment and disposal of pesticides and/or industrial chemical effluents.

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2.4.4 Cometabolism (Methanotrophic Systems)

Technology Description

Cometabolism is the ability of organisms to transform or biodegrade compounds without utilizing these compounds for either an energy source or a carbon source. Bacteria that grow on single carbon compounds such as methane and methanol (methylotrophic or methanotrophic) have been shown to cometabolize short-chain (C₁ and C₂) chlorinated aliphatic hydrocarbons such as TCE.

The enzymatic basis for the process is the presence of a nonspecific oxygenase that metabolizes methane and also transforms TCE. It follows that promoting the growth of these

bacteria, either *in situ*, e.g., by injecting methane into the ground, or in water treatment facilities aboveground, may result in the removal of the contaminants.

This process has been field tested by the Department of Energy (DOE) and the US Air Force. In a separate effort, Princeton University together with the Hazardous Substances Research Centers Program sponsored by the EPA, has reported methylotrophic biodegradation of TCE as being at the research level for the *in situ* bioremediation of TCE-contaminated aquifers. The process being investigated at Princeton involves the injection of methane and oxygen into the aquifer. Plugging of the subsurface due to biomass accumulation has been found to interfere with the process and is yet to be resolved.

Commercial methanotrophic bioreactors are available for aboveground treatment of water contaminated with halogenated volatile organic compounds, such as TCE. A specific microorganism (*Methylosinus trichlosporium* OB3b) is used as an adjunct organism to degrade the target compounds. Methane is used as a carbon source in one stage and TCE is transformed in a separate reaction or stage.

Advantages of Cometabolism:

- Cometabolism provides a treatment alternative for compounds which are not normally susceptible to biodegradation.
- The concentrations treatable by this method are relatively low.

Disadvantages of Cometabolism:

- The volatility of TCE and other halogenated organics may result in stripping during treatment.
- Available data does not conclusively demonstrate that this method of treatment will achieve stringent effluent levels.

Stage of Development

Cometabolism is progressing from laboratory and pilot-scale efforts to commercialization.

Applications and Effectiveness

Cometabolic biological treatment can be applied to the transformation of contaminated groundwater *in situ* and in aboveground treatment systems. Potentially treatable groundwater contaminants include halogenated aliphatic hydrocarbons (including TCE), dichloroethylene isomers, vinyl chloride, dichloroethane isomers, chloroform, dichloromethane, and others. The concentrations at which this process has been demonstrated is about 2,000 ppb.

Tests at the DOE Savannah River site revealed that fluidized expanded bed bioreactors using propane or methane as an energy source were 99% and 50% effective, respectively, in decreasing TCE concentrations in water. Similar performance data from Tinker Air Force Base, OK, showed 80% TCE destruction. Additional destruction can be achieved by increasing the size of the reactor columns or increasing the retention time of the contaminated water.

Cost Analysis

The limited cost data shows only that the cost of methane is \$0.33 per 1,000 gallons of water treated.

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2.4.5 Biofiltration of Gases

Technology Description

Biofiltration is the removal of volatile organic compounds (VOCs) and volatile inorganic compounds (VICs) from contaminated air by soil or compost beds. Under the beds are a series of perforated pipes which run horizontally along the length and width of the bed. The contaminated gases are distributed through the pipes and then adsorbed onto the surfaces of the soil or compost. The treatment and remedial properties which exist in the beds result from the moist-oxygen rich environment within which the native microbes live. The microbes oxidize organic contaminants into carbon dioxide and water. The soil/compost beds are technically mixtures of activated carbon, silica, and lime in combination with native microbes which will catalyze enzymatically the oxidation of the contaminants. Soil is much less permeable than compost and, therefore, needs more area to treat a given flow rate. Compost piles must be checked for compaction, which will inhibit proper flow of gases. Soils are better suited for VICs because their acidity can be neutralized by adding lime to the soil. Lime enhances the compacting of composts, which is undesirable. Sandy, relatively permeable soils are optimum for biofiltration.

Advantages of Biofiltration:

- The oxidation process requires no fuels or chemicals.
- The beds are effective because of their continuous volatile organic compound (VOC) oxidation.
- Low sorption capacity of soils and composts is compensated by the oxidation of the contaminants, thus regenerating their sorption capacities.
- Contaminants in gases are inherently more readily biodegraded than liquids or solids because of their dispersed molecular nature.
- Biofiltration does not contaminate the soil because there is excess oxygen, low loading rates, and rapid gas degradation.

Disadvantages of Biofiltration:

- Biofiltration of contaminated gas has not been tested at full-scale in the United States.
- Biofiltration reaction times are somewhat slow, so larger amounts of space are needed for single layer soil biofilters than other methods.
- The contaminant removal efficiencies of compost and soil biofilters are dependent on proper moisture content levels. Maintaining biofilter moisture content is a problem in some applications.

Stage of Development

Although mostly untested at full-scale in the United States, over 500 biofilters are currently in place in Europe and many are being installed in Japan.

Applications and Effectiveness

This technology is designed for the remediation of VOCs which have been vapor extracted from contaminated soils and groundwater. It is also eligible to be used for industrial stack emissions which contain VOCs and/or VICs that must be decontaminated before release.

Facilities which have VOC or volatile inorganic compound (VIC) contaminated emissions are good candidates for this technology. The facility must have access to several acres of soil or compost which are not encumbered below the surface by pipes, building foundations, or other obstructions.

Cost Analysis

Total cost per ten million cubic feet of contaminated air is \$8 in 1991 dollars. For comparison, incineration total cost for the same amount of air is \$130, and activated carbon with regeneration is \$20.

The costs for natural sorbents are in units of dollars per ton versus the same dollars per pound for synthetic sorbents, such as activated carbon.

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2.4.6 Bioventing

Technology Description

Bioventing is the application and integration of soil vapor extraction (SVE) and bioremediation technologies. The vacuum-enhanced *in situ* bioremediation technology removes volatile organic compounds from the subsurface soils while simultaneously stimulating aerobic biodegradation of the semi-volatile organic hydrocarbons. This combination is extremely beneficial

in allowing lower cleanup standards to be met, and as one of the most positive attributes of bioventing, it has long-term effectiveness and permanence.

The intent of bioventing is to use air movement to provide oxygen for aerobic degradation using either indigenous or introduced microorganisms. While some organic materials are usually brought to the surface for treatment with exhaust air, additional degradation is encouraged *in situ*. This difference in approach renders less volatile materials amenable to the process since volatilization into the air in the soil is not the primary process.

By reducing ambient soil vapor pressure, soil venting can remove hydrocarbons from the soil in the vapor phase. Bioremediation is used to treat adsorbed and dissolved contaminants in the saturated zone. SVE typically provides a rapid recovery of product, as it removes the highly volatile and mobile fractions and leave a less mobile residue. The residue is more responsive to bioremediation, hence the important interaction of these two technologies.

Bioventing uses low flow rates (10 to 50 actual cubic feet per minute [acfm]) versus 100 to 1500 acfm for conventional SVE. The lower flow rate maximizes the residence time of vented gas in the soil and enhances the *in situ* biodegradation and minimizes contaminant volatilization. Biological activity may account for 20% of the remediation during the SVE process.

Advantages of Bioventing:

- The process can be utilized to treat large volumes of soil that would be prohibitively expensive to excavate.
- Bioventing accelerates remediation due to the combination of physical removal and biodegradation.
- The contaminants in the soil will be degraded into non-toxic compounds, as well as being recovered for re-use.
- The technology is not disruptive to ongoing business operations.
- The process can be constructed from standard equipment, labor, and materials.
- Bioventing technology allows lower cleanup standards to be met.

Disadvantages of Bioventing:

- Soil temperature is the major limiting factor in bioventing. Microbes generally prefer a temperature around 90°F rather than the 50°F normally found in the ground.
- Contaminants with a low potential for degradability will not be treated.
- The following factors limit the effectiveness of bioventing: existing bacterial populations, nutrient availability, oxygen supply, temperature, and moisture.
- Soil mineral content, hydraulic conductivity, and soil sorptive capacity can limit achievable target levels.
- The method is not applicable to heavy metals, inorganic substances, corrosive wastes, acidic wastes, certain PCBs, and radioactive wastes.

Stage of Development

Proprietary bioventing systems are available. Bioventing is quickly becoming more commonplace as a part of a remediation treatment train with SVE. Most of the hardware components are readily available. The EPA, however, has not implemented bioventing at any superfund sites. Bioremediation methods, such as biofilters, have been used at Superfund sites along with SVE and other technologies, but bioventing is primarily used on private sites with specific vendors.

Groundwater Technology, Inc., and IT Corporation are the only known U.S. companies applying full-scale operations of bioventing. Groundwater Technology, Inc., has performed 50 bench-scale studies to date and has 18 constructed systems, 20 systems under construction, and 12 systems planned and/or designed. Not as vast in bioventing studies, IT Corp. has 3 bench-scale studies, 5 pilot scale studies, and 2 full-scale systems under construction.

It is quite apparent that more studies need to be performed. Cost data and case studies are difficult to assess with so little information.

Applications and Effectiveness

For bioventing to work, sufficient water must be present in the unsaturated zone to permit the enzyme transfers necessary for biodegradation. The air must diffuse into the soil moisture for use by the microorganisms. This requirement makes the process kinetics more difficult to predict. In addition, nutrients such as orthophosphate and ammonium nitrogen may need to be introduced for optimal degradation rates.

The following is a list of contaminant groups that are potential candidates for the bioventing technology:

- Halogenated volatiles
- Halogenated semivolatiles
- Non-halogenated volatiles
- Non-halogenated semivolatiles
- Polynuclear aromatics (PNAs)
- BTEX
- Solvents
- Explosives/propellants
- Organic pesticides/herbicides
- Diesel fuel, jet fuel, etc.

This technology is most commonly and effectively used to treat halogenated and non-halogenated volatile organics and halogenated semivolatiles. This technology has a consistent removal efficiency in the 76-90% range for selected contaminants.

SVE is not effective for semivolatile fuel oil; however, 90% of the diesel fuel may be responsive to bioremediation. Thus, bioventing is often a preferred method for remediation of semivolatile fuel oil over SVE because it provides a permanent solution. A number of case studies have consistently proven that bioventing achieves a removal efficiency in the 76-90% range for

selected contaminants. The demonstrated effectiveness is in remediating media contaminated to concentration levels in excess of 10,000 ppm. Regardless of concentration levels, soils exhibiting low permeability, a high degree of soil heterogeneity, and/or high organic content will reduce the effectiveness of this technology.

The time required for effective remediation at a site using bioventing is highly dependent upon the specific soil and chemical properties of the contaminated media. Based on representative data from completed and ongoing projects, a reasonable calculation of the time required to clean up a standard site consisting of 20,000 tons of contaminated media is approximately 2 years.

A typical bioventing system requires an operating staff of four. Assuming that a four-person labor force is employed for the duration of the remediation effort, which would be 2 years, then 8 person-years of effort would be required to clean up a 20,000-ton site. This calculation does not include additional labor requirements for start-up, demobilization, or program management.

Case Studies

Bioventing systems are composed of hardware identical to that of conventional soil vacuum systems, with vertical wells and/or lateral trenches, piping networks, and a blower or vacuum pump for gas extraction. They differ significantly from conventional systems, however, in their configuration and philosophy of design and operation. The primary purpose of a bioventing system is to use moving soil gas to transfer oxygen to the subsurface where indigenous organisms can utilize it as an electron acceptor to carry out aerobic metabolism of soil contaminants. As such, bioventing system extraction wells are not placed in the center of the contamination as in conventional SVE systems, but on the periphery of the site, where low flow rates (10 to 50 acfm versus 100 to 1500+ acfm for conventional SVE systems) maximize residence time of vent gas in the soil to enhance *in situ* biodegradation and minimize contaminant volatilization.

Two major design considerations for bioventing systems are: first, whether the contaminants of concern are biodegradable under prevailing site conditions, that is, whether inhibition or toxicity is evident at the site; and second, whether the required terminal electron acceptor, (oxygen) can be effectively transported within the soil to encourage aerobic contaminant biodegradation.

A case study was performed using bioventing and high rate SVE at a site on Hill AFB, Utah. This site was the location of a JP-4 jet fuel spill that occurred in January 1985, after the failure of an automatic shut-off valve. The spill had the following characteristics:

- 27,000 gallons (100,000 L) JP-4 jet fuel spill due to faulty shut-off valve, 2000 gallons (7500 L) of which were recovered as free product.
- Migration of free product laterally, resulting in contamination 50 feet (15 m) deep (approximately 1 acre in extent).
- Soil is the delta outwash of the Weber River, *i.e.*, sand/gravel with clay stringers to confined aquifer at approximately 600 feet (180 m).
- Contamination from hydrocarbons (C-5 to C-15), aromatics, and PAHs (naphthalene, methylnaphthalene, etc.) to concentrations at the site as high as 15,000 mg/kg with average total petroleum hydrocarbons (TPH) levels of 1500 mg/kg.

The actual field bioventing system consisted of:

- Low extraction flow rates of approximately 500 acfm.
- Maximizing the flow path through the contaminated soil by pulling soil from the periphery of the contaminated zone.
- Moisture enhancement by surface spray irrigation (approximately 300 gal/min).
- Nutrient addition of NH_4NO_3 , PO^{a} , and a specific C:N:P ratio.

The final results of this case study revealed the following:

- During bioventing:
 - 11,943 lb (5400 kg) TPH was removed.
 - Removal of 89% of venting residual.
 - Residual TPH soil concentration of approximately 3 mg/kg.
- During venting:
 - 206,424 lb (9400 kg) TPH was removed.
 - Overall 94% removal rate.
 - Residual TPH soil concentration of approximately 80 mg/kg.
- Overall removal:
 - 218,367 lb (99,300 kg) JP-4.
 - Total removal efficiency of >99%.
 - Residual soil concentration of approximately 3 mg/kg in soil.

This case study exemplifies the advantage of implementing both bioventing and SVE at a particular site. While SVE provides cost-effective *in situ* remediation, it is limited to volatile constituents, permeable media, and high residual soil concentrations if semi-volatile constituents exist at the site. In this case, bioventing was a great asset to reaching desired levels of reduction. The application of soil bioventing can broaden the use of SVE greatly, extend the applications of bioremediation, and be complementary to pump and treat processes for residual contamination. In this case it was found to provide *in situ* biodegradation of semi-volatile constituents not amenable to SVE alone.

Co-Technologies/Alternative Technologies

SVE is the primary co-technology which works in conjunction with *in situ* bioremediation to create bioventing. In addition to this *in situ* method, there are other bioremediation methods applied *ex situ*. Pump and treat methods commonly employ bioremediation *ex situ* in the aqueous phase on the surface of the site. Bioslurry systems, landfarming, or other biological treatment systems are among the bioremediation technologies. Landfarming, the disposal and incorporation of wastes on the soil surface and top few inches of subsurface utilizing biological, physical and chemical interactions, is a very common bioremediation method. Applications of landfarming techniques include such industries as petroleum refining, municipal sludge, food processing, pulp and paper, and other industries. Bioslurry or activated sludge treatments are commonly used on wastewater streams and implement the combination of bioremediation with other technologies.

The significant differences between the two vapor-based systems are summarized as:

- SVE systems characteristically are:
 - Utilized for volatile and semivolatile contaminants.
 - Operated at high air flow rates to encourage stripping.
 - Configured to pull from the center of contamination to encourage stripping.
 - Operated at minimum moisture content to maximize air filled pore space.
- Bioventing systems characteristically are:
 - Utilized for biodegradable contaminants whether or not they are volatile.
 - Operated at low flow rates to encourage biodegradation and discourage stripping.
 - Configured to pull from the periphery of contamination to maximize vapor retention time in the contaminated soil.
 - Operated with soil moisture content at 50 to 75% field capacity to optimize for microbial activity.

Cost Analysis

In many cases bioremediation is emerging as the most cost-effective means of controlling toxic wastes. While incineration often costs \$250 to \$500 per ton of waste, biological methods can cost as little as \$40 to \$100 per ton. However, bioremediation remains largely underdeveloped; thus cost-data are difficult to find. As with SVE and other bioremediation technologies, the initial contaminant concentration and depth of contamination are factors which most affect bioremediation costs. This effort is directly related to the type and size of the SVE/bioremediation technology required. The depth to groundwater was reported by many companies to rank high among parameters affecting price. Labor costs, excavation, and site preparation (grading, demolition, etc.) are other important factors that affect the costs of bioventing.

Treatment costs are typically \$100 to \$120 per cubic yard or \$60 to \$90 per ton. Groundwater Technology, Inc., gave a price quote of \$100-\$120 per cubic yard.

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2.5 Case Studies

2.5.1 Bioremediation of Sites Contaminated with Chlorinated Organic Compounds

Carbon compounds that contain halogens as part of their chemical structure are for the most part the result of human activities. Relatively few of the fluorine and chlorine containing compounds found in nature are of biological origin; thus their designation as xenobiotic. Halogenated chemicals have a variety of uses in industry, commerce and agriculture, e.g., industrial solvents, dry-cleaning agents, electrical insulators, and pesticides. These compounds are also generated when elemental chlorine is added to disinfect drinking water and wastewater plant effluents. The compounds are eventually released into the environment. The latter, coupled with the fact that they are poorly degraded by organisms in nature, leads to their accumulation in the environment.

Chlorinated compounds are biodegraded, albeit slowly. Three types of organisms that can break down these contaminants have been identified: a few which appear to use halogenated compounds as growth substrates, e.g., *Desulfomonile tiedjei*, a bacterium that can grow on monohalogenated aromatic compounds; many which use existing metabolic pathways normally used

to catabolize structurally similar compounds; and some that appear to have evolved and developed breakdown mechanisms in response to their exposure to these foreign compounds. Biochemically speaking, two principal breakdown mechanisms have been identified: reductive dehalogenation (usually under anaerobic conditions) and breakdown with oxygenases (thus in the required presence of oxygen). Table 3 provides examples of compounds susceptible to reductive dehalogenation. A profile on catalytic hydrodehalogenation is provided in the preceding section.

Table 3. Examples of Chlorinated Compounds Degraded by Anaerobic Reductive Dehalogenation

Organochlorine Pesticides	Alkyl Solvents	Aryl Halide Compounds
Alachlor DDT Dieldrin Lindane Mirex Toxaphene	Chloromethane Chloroform Tetrachloroethylene, TCE	Chlorobenzoates Chlorobenzene Chlorophenols PCBs

Source: Mohn, W. W. and J. M. Tiedje. 1992. Microbial reductive dehalogenation. *Microbial Reviews* 56: 482-507.

Some of these compounds, e.g., the pesticides, were consciously fashioned to be recalcitrant in nature. Non-biodegradability is a sought for characteristic to achieve long-term biocidal activity. The desirable properties of these pesticides—selective toxicity, persistence, and bioaccumulation in the environment—constitute the root causes of the threat they pose to humans and the environment in general. Chronic exposure to these compounds is thought to increase the incidence of cancer in humans and threaten the existence of many other species in nature.

In situ breakdown of these compounds can be achieved, at least partially. Low molecular weight compounds such as trichloroethylene are easier to degrade than the ones with complex structures such as the polychlorinated biphenyls (PCBs). Often the compound of interest is partially degraded to a still halogenated product which can be equally or more toxic than the parent compound. Thus, it is necessary to monitor the potential appearance of secondary toxic products when the biodegradation of chlorinated compounds in contaminated sites is studied.

An examination of current literature shows this is a very active research area. Investigative efforts focus on understanding the physiology, biochemistry, enzymology, and genetics of the process. The goal is to gain insight into the basic mechanisms that operate in the dehalogenation phenomena. Efforts are also concentrated on understanding microbial processes in sediments, water, and waste.

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Removal of TCE sorbed to soil particles using microbes and surfactants

Unavailability of organic compounds owing to binding to soil particles can be a limiting factor in bioremediation technology. Bioremediation research at Howard University has been directed toward the use of surfactants to increase the availability of contaminants sorbed to soil particles. Surfactants and microbes are applied to contaminated soil either simultaneously or sequentially to help the degradation process. Effective surfactants have been identified and tested for their ability to desorb TCE. A TCE-degrading bacterial consortium also has been isolated. At the time of the report, work was in progress to assess the TCE-degrading ability of the members of the consortium.

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Vegetation-enhanced rhizospheric degradation of TCE

Compounds such as TCE can be removed from surface-contaminated soils by planting vegetation. Establishing stands of vegetation in TCE-contaminated soil promoted oxidation of the contaminant. It is suggested that the microbes found within the rhizosphere are responsible for the degradation of the contaminants. This process was tested at the Savannah River DOE site. It was found that selective vegetation and cultivation techniques could be used to remove this class of contaminants from surface soil in an aesthetic and cost-effective manner.

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Removal of PCP with the BATS

BATS is a patented biological treatment system effective for treating ground water and process water contaminated with PCP, creosote components, gasoline, fuel oil, chlorinated hydrocarbons, phenolics or solvents. Potential target contaminants include organic pesticides and coal tar residues.

An amended microbial mixture (indigenous microbes to which a specific exogenous microbe has been added) is added to the waste stream. This allows the process to degrade the background contaminants as well as the target contaminant. The microbes, nutrients, and contaminated water are combined in a mix tank, where, if necessary, the pH and temperature of the solution are adjusted before entering the reaction vessel.

The reaction vessel is a three-cell, submerged, fixed film system in which the microbes are immobilized in a porous packing material. Air is added for aerobic processes but the system can also be run as an anaerobic system.

Technology performance reported from a Superfund Innovative Technology Evaluation (SITE) program demonstration at the MacGillis and Gibbs Superfund site in New Brighton, Minnesota, which consisted of continuous operation for six weeks at three different flow rates, showed as much as 97% destruction of PCP resulting in effluent PCP concentrations of less than one part per million.

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Biological dechlorination of PCB-contaminated river and lake sediments

This research is being performed at Michigan State University under the Hazardous Substances Research Centers Program. It has been shown that some naturally occurring microorganisms are capable of dechlorinating PCB's in sediments. The intent of this research-level technology is to isolate and propagate those microorganisms found to be capable of dechlorinating PCB's. While some success has been seen, it is reported that isolation and concentration of the microbes of interest has proven difficult. Actual mechanisms for application of this technology once developed were not proposed.

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Use of the white rot fungus for removing chlorinated organic compounds

The lignin-degrading white rot fungus (*Phanerochaete chrysosporium*) has been shown to degrade a wide array of organic contaminants such as lindane, benzo(a)pyrene, DDT, tetrachlorodibenzo-p-dioxin (TCDD), PCBs and chlorinated lignin derived byproducts resulting from the kraft pulping process to harmless metabolites. While this process shows considerable promise, it is reported as having been applied only at the laboratory scale.

The white rot fungus is also being investigated at the New Jersey Institute of Technology as a method for remediating contaminated ground water. The engineering parameters necessary for optimizing the degradation of contaminants are being examined with the intention of upscaling the process.

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2.5.2 Bioremediation Of Sites Contaminated With Crude Oil And Its Derivatives

Oil is of ancient biological and geological origin. Many of its components are refractory; they resist microbial degradation and thus persist in the environment. Other components are biodegradable, but factors such as oxygen availability, water solubility, and nutrient imbalances prevent faster rates of degradation. As mentioned elsewhere, some oil components will be broken down only in the presence of molecular oxygen; their poor water solubility protects them from microbial attack; and lack of nitrogen and phosphorous in the oil act as growth limiting factors for the oil-degrading bacteria.

Technologies developed for the remediation of sites contaminated with oil and its derivatives must overcome the obstacles pointed out above by adding fertilizers, surfactants, and air to such oil-contaminated soils. Other technologies involve the isolation from oil-contaminated sites of microorganisms that can grow on the oil, their enrichment in the laboratory, and their injection in contaminated sites.

One particularly successful technology developed for the remediation of oil-contaminated sites is the use of *Acinetobacter calcoaceticus*. This bacterium, isolated from oil tanks in which nutrients and oxygen have been added, produces an excellent surfactant. The bacterium secretes the surfactant to emulsify the oil, exposing it to enzymatic attack. This product is presently used, among other application, to clean the tanks of oil carriers. It has also been proposed as a gasoline additive to increase burning efficiency.

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Bioremediation/vacuum extraction process for the removal of fuels

This procedure has been applied to soil contaminated by diesel, JP5, and other fuels. Leaking underground storage tanks are the primary cause of this contamination, and excavation of contaminated soil is required.

The excavated soil is placed on a liner with a series of vacuum extraction pipes in the base of the pile. Fertilizer is added to the soil, an irrigation system is installed, and air is drawn into the pile by attachment of a vacuum extraction blower to the vacuum extraction pipes. This process stimulates microbial degradation and draws volatile organics out of the soil.

A pilot project was performed at Bridgeport, California, by the U.S. Navy in 1989. The Navy declared the test site "clean" in a report to the California Regional Water Quality Control Board. After the treatment was in operation for approximately two months, the total petroleum hydrocarbon concentration was 120 ppm.

Cost Analysis

The cost of the pilot project is reported to be around \$80 per ton of soil.

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Nutrient additions for *in situ* bioremediation of soil

Stimulation of bacterial growth by the addition of nutrients to soil contaminated with motor oil has been researched by the U.S. Army Corps of Engineers, Construction Engineering Research Laboratory. In this process inoculant and nutrients are added to the contaminated soils during disking of the soil. The nutrients consist of sodium acetate, minerals (potassium, magnesium, ammonium, phosphate, and sulfate ions) and "Tween 80", a surfactant. The area is then covered with plastic sheeting that has been perforated to allow air to pass through.

This method is applicable to oil spills at maintenance facilities, air strips, and along roadways or streets. Research was focused on used lubrication oil but the process is expected to apply to spills of any aliphatic hydrocarbons with no functional groups. Performance evaluation showed that "noticeable" reductions in contaminant concentrations were evident after four to six weeks.

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Environmental Protection Agency. 1991. Synopses of federal demonstrations of innovative site remediation technologies. Report No. EPA/540/8-91/009.

Bioreclamation of soil and groundwater

This aerobic process can be applied either *in situ* or as an excavation process. Extracted water or leachates are oxygenated, and microbes and nutrients are added. The solution is then pumped back into the soil. This process allows for the degradation of water-borne contaminants and those trapped in the soil matrix. Biodegradable non-halogenated organic contaminants in soil and groundwater have been successfully treated in this manner although data from the demonstration were not included in the technology description.

Restrictions to *in situ* application include site geology and hydrology which could adversely affect the feasibility of extracting and injecting water containing hazardous wastes. Soils for which *in situ* treatment is most applicable include those with neutral pH, high permeability and a moisture content of 50 to 75 percent.

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In-vessel composting of polycyclic aromatic hydrocarbons

Research on in-vessel composting of polycyclic aromatic hydrocarbons (PAHs) is intended to develop a technology that can degrade PAH's with fewer than three rings. The focus of this research is to define the operating conditions for the biological degradation of pyrene. The use of in-vessel composting is being explored for achieving these conditions. Researchers at Howard University together with the Hazardous Substances Research Centers Program, have been performing experiments in which they have varied the initial pH, composting temperature, type of bulking agent, and carbon to nitrogen ratio. Performance of the technology so far has yielded reductions in contaminant concentrations ranging from 10% to 72%. This technology can also be used to treat pesticides.

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Geolock/biodrain treatment

This process is carried out in the soil. An impermeable cylinder of high density polyethylene is installed to prevent the migration of microbes from the treatment area and to prevent clean water from infiltrating the contaminated zone. Wells are installed to remove contaminated soil washing water. Biodrains are installed to allow the addition of bacterial cultures, nutrients, oxygen and proprietary chemicals to the soil column. By controlling the water level within the cylinder, reverse leaching, soil washing and the entry of offsite clean water can be minimized. Controlling water levels within the tank also promotes upward migration of water and contaminants within the water column, which helps treatment.

Reports show this technology's limitations occur when large boulders or rock shelves are present in the treatment area. Extremely dense clay soils may be difficult to treat with this method. There were no technology performance data reported.

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2.5.3 Treatment of Wastes Containing Explosives and Propellants

Anaerobic biotransformation of trinitrotoluene (TNT)

The transformation of TNT by microorganisms isolated from the sheep rumen has been shown to occur at a much higher rate than what is found in TNT-contaminated sediments. Development of this process at Oregon State University is at the research level. Areas of investigation include (1) enrichment of the ruminal microbial flora, (2) degradation of radiolabelled TNT for metabolite identification, and (3) determination of optimal growth and degradation parameters.

The intent of these researchers is to promote commercialization of this process to allow the U.S. Navy and other Department of Defense agencies to use this method in remediation of TNT contaminated sites.

Performance ratings showed that 100 mg/ml of TNT degraded within 96 hours for laboratory studies. Research is continuing in the area of media selection to enhance detoxification.

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Biotransformation of Dinitrotoluene (DNT)

DNT is a waste generated in the facilities that make propellants, unlike its cousin TNT, produced in explosives factories. Conventional wastewater treatment facilities often cannot handle the discharges of DNT and as a result, non-conventional treatment methods must be found. Part of the problem resides in the fact that the aromatic ring will not readily cleave and that fluctuations in

the concentration of the waste make it difficult to maintain a stable population of microorganisms which are capable of degrading it.

Research in progress at the U.S. Army Construction Engineering Research Laboratories addresses the DNT treatment problem by using GAC bioreactors under anaerobic conditions. The GAC acts as a buffer against fluctuations in the concentration of DNT. The latter fact is achieved by adsorption of the DNT to the carbon particles and serving as a growth substrate reservoir until the microbes degrade it. The anaerobic conditions allow for the stoichiometric conversion to diaminotoluene (DAT). Disposal of DAT awaits further developments, as it has not further degraded under present design parameters.

Results of recent research efforts at other laboratories would suggest it may be possible to develop technologies for the complete mineralization of DNT, as a bacterium and a fungus have been shown to completely mineralize the compound.

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2.5.4 Other Technologies

Bioremediation of sites contaminated with uranium

Some bacteria have recently been shown to selectively reduce uranium from the U(VI) to the U(IV) oxidation state. Uranium(VI) is soluble in water, particularly because it forms chemical complexes with carbonates, e.g., uranyl carbonate ($\text{UO}_2(\text{CO}_3)_2$). The reduced form is highly insoluble in water. This fact has been proposed as the basis for removing uranium from soil.

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Mitigation of groundwater and soil contamination using vegetation

Tree planting has been proposed as a remediation technology. The assertion is that the tree roots will draw the organics from the groundwater and soil, thus removing pesticides and other toxic organic chemicals. Plantings in riparian zone buffer strips are expected to prevent the transport of organic compounds present in groundwater into streams. Research has shown that poplars do concentrate organic compounds such as m-xylene, m-dichlorobenzene, toluene and others. In study plots the poplars have also been shown to reduce soil atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine) concentrations.

Vegetation can also be used to control the flow of groundwater into buried wastes. This is particularly true in arid regions, where the rate of evapotranspiration can exceed the rate of water intrusion into the ground.

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Degradation of mixtures of toxic chemicals

The feasibility of *in situ* anaerobic biodegradation of mixtures of toxic chemicals is being investigated at the University of Iowa together with the Hazardous Substances Research Centers Program. This research is intended to examine the effect of complex mixtures on the degradation rate of individual contaminants when subjected to anaerobic degradation. Degradation of individual contaminants has been studied under optimum conditions, and further work with mixtures is expected to show the effects of the complex mixtures.

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Removal of selenium

Selenium represents a major problem in some parts of the Western United States. There, geological strata rich in selenium are presently under cultivation. The selenium is brought into solution by the irrigation waters and transported as agricultural runoff. The latter can eventually end up in wetlands. Places like the Kesterson Reservoir in California are already showing adverse effects, e.g., a high incidence of birth defects in birds, from the accumulation of selenium in the food chain.

Several strategies have been proposed to remove the contaminant from soils and surface waters. Plants known to accumulate selenium in excess of their nutritional needs have been proposed

for removing the element from soil before it goes into solution in the irrigation water. Several strategies have been proposed using algae and bacteria.

Selenium is mostly found in oxic waters as selenate (SeO_4^{2-}). This oxyanion is known to be reduced to water-insoluble elemental selenium (Se^0) by bacteria and fungi. Some bacteria are known to reduce the selenate to Se^0 as part of their energy conservation strategies. Other bacteria and fungi are known to reduce it via non-specific pathways, i.e., cometabolism. Several strategies using bacterial mats, selenate-respiring bacteria, and non-growing cultures adapted to grow in the presence of SeO_4^{2-} have been proposed to remove the metal from solution.

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CHAPTER 3. CHEMICAL TECHNOLOGIES

3.1 Introduction

Chemical technologies continue to be developed for the treatment of various waste streams and are commonly used in site remediation. They involve the promotion of chemical reactions which alter the chemical composition of the waste. These reactions are frequently combined with physical or biological processes. Chemical treatment systems frequently involve neutralization, precipitation, and oxidation.

Dechlorination, for example, is a chemical transformation process which entails chemical reactions for the removal of chlorine atoms in chlorinated compounds. The transformation results in byproducts which exhibit lower toxicity and higher water solubility. Researchers have identified various agents, such as alkali polyethylene glyconate (APEG), which can dechlorinate various organics, including dioxins, furans, and polychlorinated biphenyls (PCBs). The process is usually executed in reactors where the waste soil is slurried to maximize the contact of the dechlorination agents with the waste molecules. The dechlorination of aliphatic compounds is achieved by elimination reactions which result in double or triple carbon-carbon bonds (EPA, 1990). Halogenated aromatic compounds are dechlorinated by substituting a chlorine atom with a hydroxyl group.

Dechlorination has been found effective in treating PCBs, dioxins, and furans with removal efficiencies up to 95 percent. Dechlorination of halogenated aliphatics and nonpolar halogenated organic compounds is possible but has not yet been fully explored. The major advantage of dechlorination processes is the permanent nature of the treatment. The process has substantial limitations in mixed organic-metal wastes. In addition, byproducts of the transformation process may be unstable and toxic.

A technology matrix for selected chemical process technologies is presented in Table 4—Chemical Process Technologies. Those chemical reactions involving elevated temperatures are more fully covered in the Thermochemical Chapter, while those chemical reactions involving physical interactions are contained within the Physico-Chemical Chapter.

3.1.1 Dehalogenation of Aromatic Compounds

The alkaline metal hydroxide/polyethylene glycol (APEG) dehalogenation technology uses a glycolate reagent generated from an alkaline metal hydroxide and a glycol to remove halogens, e.g., chlorine, bromine, and fluorine, from halogenated aromatic organic compounds in a batch reactor. APEG processes involve heating and physical mixing of contaminated soils, sludges, or liquids with the chemical reagents. Water vapor and volatile organics are removed and condensed during the reaction. Carbon filters are used to trap volatile organic compounds that are not condensed in the vapor. The treated residue is rinsed to remove reactor byproducts and unspent reagent and then dewatered before disposal. Treated soil and wash water are end products.

Successful destruction of PCP, chlorinated dioxins, and furans were found at Montana Pole Wood Preserving in Butte, Montana (EPA, 1991c). Also, successful destruction of the pesticide phosphate esters and TCDD were found at Western Processing in Kent, Washington. This process was used in Guam to decontaminate soil polluted with Arochlor 1260.

3.1.2 Chemical Treatment of DNT

DNT, used as a propellant rather than an explosive like its cousin TNT, is a major waste product in Army munitions plants. Chemical methods have been proposed to destroy it or to reduce it to a form, e.g., diaminotoluene, more amenable to conventional wastewater treatment.

3.1.3 Low Temperature Catalytic (Zeolite) Oxidation

The EPA is sponsoring research examining the oxidation of organics at relatively low temperatures (175 to 400°C) mediated by cobalt-zeolite exchange resins. Initial studies have shown complete oxidation of methylene chloride, TCE, and carbon tetrachloride. This result shows promise in destroying VOC emissions from industrial processes and off-gases in restoration activities. The low temperatures offer reduced costs in terms of reduced gas volumes relative to high temperature oxidation.

Advantages of Chemical Process Technologies:

- Treatment of concentrated waste streams where other technologies are not effective.
- Total destruction of the contaminants may be achieved.
- Treatment of a wide variety of waste streams.

Disadvantages of Chemical Process Technologies:

- Co-contaminants may cause problems resulting in incomplete transformations or production of toxic end products.
- *In situ* applications are very limited.
- Some specialized reaction vessels may be required.
- Some processes may be energy intensive, resulting in increased costs.

Table 4. Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Chemical Oxidation - (Exxon Chemical Company and Rio Linda Chemical Company)	Tech. Contact: Brent Bourland Exxon Chemical Co. P.O. Box 4321 Houston, TX 77210-4321 713-460-6822 EPA Contact: Teri Richardson 513-569-7949	Process utilizes chlorine dioxide generated on-site to oxidize contaminants.	Aqueous waste streams, liquid storage vessels, soils, contaminated groundwater, or any leachable solid matrix	Cyanides, sulfides, organosulfur compounds, phenols, aniline, and secondary and tertiary amines	EPA SITE demonstration proposal was accepted and the site is to be chosen.	No case studies or cost data available.
Base-Catalyzed Dechlorination Process - (Risk Reduction Engineering Laboratory)	Tech. Contact: Charles Rogers U.S. EPA Risk Reduction Engineering Laboratory 26 W. Martin Luther King Dr. Cincinnati, OH 45268 513-569-7626 EPA Contact: Laurel Staley 513-569-7863	Process mixes chemicals with contaminated matrix, such as excavated soil or sediment or liquids containing toxic compounds. Mixture is then heated at 340°C for 1 to 3 hours and off-gases are treated. Treated waste is non-hazardous.	Soils and Sediments	Halogenated volatiles and semivolatiles, PCBs, PCPs, herbicides, pesticides, and dioxins/furans	EPA SITE demonstration program completed.	Complete destruction of PCBs (25-6,500 ppm) in 5,000 tons of soil was estimated to be \$245 per ton.

Table 4. Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
DeChlor/KGM E Process (<i>Chemical Waste Management, Inc.</i>)	Tech Contact: Arthur Friedman Chemical Waste Management, Inc. Geneva Research Center 1950 So. Batavia Ave. Geneva, IL 60134-3310 708-513-4332 EPA Contact: Reinaldo Matias 513-569-7149	Dechlorination of liquid-phase halogenated compounds.	Liquid-phase compounds	Halogenated aromatic compounds including PCBs, chloro-benzenes, poly-chlorinated dibenzo-dioxins (PCDDs), and poly-chlorinated dibenzofurans (PCDFs)	EPA SITE demonstration program.	Numerous bench-scale demonstrations have been conducted on a variety of halogenated wastes including PCBs, dioxins, and PCDFs. PCBs have been treated in both liquid and solid matrices with removal efficiencies of up to 99.99 percent. No cost data available.
MAECTITE™ Treatment Process - (<i>MAECORP Inc.</i>)	Tech. Contact: Karl Yost MAECORP, Inc. 155 No. Wacker Dr., Suite 400 Chicago, IL 60606 312-372-3300 EPA Contact:	Mobile two-step process: blending lead-contaminated material with proprietary powder and then blending mixture with proprietary reagent solution.	Lead-contaminated wastes and soils from manufacture and use of storage batteries	Lead	EPA SITE demonstration program acceptance and successfully applied in both bench-and pilot-scale	Full-scale process is cost-effective and has been demonstrated at seven full-scale sites in WI, MI, IN, OH, and VA.

Table 4. Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
<p><i>In Situ</i> Remediation of Chromium in Groundwater - (<i>GEOCHEM, A Division of Terra Vac</i>)</p>	<p>Tech. Contact: Jim Rouse GEOCHEM 12265 W. Bayaud, Suite 140 Lakewood, CO 80228 303-988-8902</p> <p>EPA Contact: Douglas Grose 513-569-7844</p>	<p>Process removes chromium from contaminated groundwater using a variation of traditional pump and treat methods.</p>	<p>Groundwater</p>	<p>Hexavalent chromium, uranium, selenium, and arsenic</p>	<p>EPA SITE demonstration program acceptance and testing site was chosen.</p>	<p>No results or cost data available.</p>
<p>Electrochemical <i>In Situ</i> Chromate and Heavy Metal Immobilization - (<i>Andco Environmental Processes, Inc.</i>)</p>	<p>Tech. Contact: Michael Brewster Andco Environmental Processes, Inc. 595 Commerce Drive Amherst, NY 14228-2380 716-691-2100</p> <p>EPA Contact: Douglas Grosse 513-569-7844</p>	<p>Process utilizes electrochemical reactions to generate ions for removal of hexavalent chromium and other metals.</p>	<p>Groundwater</p>	<p>Hexavalent chromium and other heavy metals</p>	<p>EPA SITE demonstration program. Process can be used for remediation of both confined and unconfined aquifers.</p>	<p>Applied at the Kerr McGee Chemical Corporation site contaminated with hexavalent chromium. Groundwater is treated at a rate of 50 to 120 gallons per minute. Removal efficiencies and cost data not available.</p>

Table 4. Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Soil Treatment with Elektrasol™ - (CET Environmental Services-Sanivan Group)	Tech. Contact: Pierre Fauteux CET Environmental Services-Sanivan Group 1705 Third Avenue P.A.T. Montreal, Quebec HIB 5M Canada 514-645-1621 EPA Contact: Mark Meckes 513-569-7348	Batch process to extract organic contaminants from soil using proprietary, nonchlorinated organic solvents.	Soil	PCBs, PCPs, PAHs, MAHs, pesticides, oils and hydrocarbons	EPA SITE demonstration program.	Project scheduled in Washburn, ME, was canceled by developer and project is on temporary hold. No cost data available.
Solvent Extraction - (CF Systems Corporation)	Tech. Contact: Chris Shallice CF Systems Corporation 3D Gill Street Woburn, MA 01801 617-937-0800 EPA Contact: Laurel Staley 513-569-7863	Process utilizes liquefied gases as a solvent to extract organics.	Soils and sludges	VOCs, SVOCs, PCBs, PAHs, PCPs	The system is available as a continuous flow unit for wastes that can be pumped or a batch system for soils and sludges that cannot be pumped.	Mobile demonstration unit was tested on PCB-laden sediments from the New Bedford Harbor Superfund site in Massachusetts. Extraction efficiencies of PCB of 90 to 98 percent. Projected

Table 4. Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
FORAGER© Sponge (<i>Dynaphore, Inc.</i>)	Tech. Contact: Norman Rainer Dynaphore, Inc. 2709 Willard Road Richmond, VA 23294 804-288-7109 EPA Contact: Carolyn Esposito 908-906-6895	The sponge is an open-celled cellulose sponge incorporating an amine-containing polymer that has a selective affinity for aqueous heavy metals in both cationic and anionic states.	Industrial discharges, municipal sewage, process streams and acid mine drainage waters	Heavy metals	EPA SITE demonstration program bench-scale testing and field-scale installation completed.	In bench-scale testing, mercury, lead, nickel, cadmium, and chromium have been reduced below detectable levels. In field-scale application of aqueous effluent with 6 lbs. of chromate and 0.8 lbs. of silver per day, a 75 percent reduction was achieved. Cost estimate for this site was \$1,100 per month.
Precipitation, Microfiltration and Sludge Dewatering (<i>EPOC Water, Inc.</i>)	Tech. Contact: Ray Groves EPOC Water, Inc. 3065 Sunnyside, Suite 101 Fresno, CA 93727	Three-step process: chemical precipitation of heavy metals, microfiltration of particles larger than 0.2 to 0.1 micron and dewatering of	Wastewater, soil, and sludge	Heavy metals, pesticides, oil and grease, bacteria, suspended solids	EPA SITE demonstration program completed with successful results.	Applied to over 45 sites worldwide with sufficient removal of contaminants. Applications include the following:

Table 4. Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Heavy Metals and Radionuclide Sorption Method (<i>Filter Flow Technology, Inc.</i>)	Tech. Contact: Tod Johnson Filter Flow Technology, Inc. 3027 Marina Bay Dr., Suite 110 League City, TX 77573 713-334-6080 EPA Contact: Annette Gatchett 513-569-7697	Polishing filter process that removes ionic colloidal, complexed, and chelated heavy metal radionuclides via surface sorption and chemical complexing.	Water	Heavy metals and radionuclides	EPA SITE demonstration program acceptance. Bench-scale tests have been conducted.	Testing at the DOE Rocky Flats facility in Golden, CO, using groundwater contaminated with heavy metals and radioactive materials. No results or cost data available.
BEST Solvent Extraction (<i>Resources Conservation Company</i>)	Tech. Contact: Lanny Weimer Resources Conservation Co. 3630 Cornus Lane Ellicott City, MD 21403 301-596-6066 EPA Contact: Mark Meckes 513-569-7348	Process separates sludge into three fractions: oil, water and solids. The solvent extraction system is mobile and uses one or more secondary or tertiary amines to separate organics from soils and sludges.	Sediments, sludges and soils	PCBs, PAHs, and pesticides	EPA SITE demonstration program completed.	Process implemented and completed at the Grand Calumet River and results are available in Applications Analysis Report, 1993. No cost data available.
Propellant Recovery and	Tech. Contact: Richard Eicholtz	Propellants are resolvated in an ether/ethanol or	Propellants	Single (with nitrocellulose)	Bench-scale phase	Bench-scale study performed at Radford

Table 4. Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Hydrolytic Terrestrial Dissipation, HTD (<i>ASI Environmental Technologies, Inc./Dames & Moore</i>)	Tech Contact: Stoddard Pickrell ASI Environmental Technologies, Inc. 3904 Corporex Park Drive Tampa, FL 33619 813-626-6207 EPA Contact: Ronald Lewis 513-569-7856	Process utilizes the metal-catalyzed alkaline hydrolysis reactions to liberate chlorine ions that form various metal salts, depending on the characteristics of the contaminated media.	Soil	Toxaphene or other pesticides	EPA SITE demonstration program.	Treatability studies show that under simulated conditions, HTD methods reduce organochlorine pesticide concentrations in soils. No removal efficiency or cost data available.
RENEU™ Extraction Technology (<i>Terrasys, Inc.</i>)	Tech. Contact: James Mier Terrasys, Inc. 912-D Pancho Road Camarillo, CA 93102 805-389-6766 EPA Contact: Michelle Simon 513-569-7676	Process utilizes proprietary, azeotropic fluid that works in both liquid and gaseous phases for extraction.	Soil	Gasoline, diesel, jet fuels, waste oils, oil processing sludges and hydrocarbon-based contaminants	EPA SITE demonstration program acceptance and is field-scale.	No results or cost data available.

Table 4. Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Carver-Greenfield Process© for extraction of oily waste (Dehydro-Tech Corporation)	Tech Contact: Thomas Holcombe Dehydro-Tech Corp. 6 Great Meadow Lane East Hanover, NJ 07936 201-887-2182 EPA Contact: Laurel Staley 513-569-7863	Process separates materials into their constituent solid, oil, and water phases through the use of carrier oil, an evaporation system, and extraction techniques.	Soils and sludges	Oil-soluble hazardous compounds	EPA SITE demonstration program completed.	At the PAB oil site in Abbeville, LA, the process successfully separated a petroleum-oil contaminated sludge into its solid, indigenous, oil and water phases. Site specific costs range from \$10-\$300 per ton, and technology-specific costs are \$100-\$220 per ton of wet feed.

GENERAL REFERENCES

- Chatterjee, S. and H. Greene. 1991. Oxidative catalysis of chlorinated hydrocarbons by metal-loaded acid catalysts. *Journal of Catalysis* 130: 76-85.
- Chatterjee, S., H. Greene and Y. Park. 1992. Deactivation of metal exchanged zeolite catalysts during exposure to chlorinated hydrocarbons under oxidizing conditions. *Catalysis Today* 11: 569-596.
- Environmental Protection Agency. 1990. Summary of treatment technology effectiveness for contaminated soil. Report No. OSWER-9355.4-06.
- Environmental Protection Agency. 1991. Chemical oxidation treatment, engineering bulletin. Report No. EPA/540/2-91/025.
- Environmental Protection Agency. 1992. Superfund innovative technology evaluation program technology profiles, 5th edition. Report No. EPA/540/R-92/077.
- Nunez, C. M. *et al.* 1993. Corona destruction: an innovative control technology for VOCs and air toxics. Environmental Protection Agency. Report No. EPA/600/J-93/080.
- Nunez, C. M., G. H. Ramsey, W. H. Ponder, J. H. Abbott, and L. E. Hamel. 1992. Corona destruction: an innovative control technology for VOCs and air toxics. Environmental Protection Agency. Report No. EPA/600/A-92/162.
- United States Air Force & Environmental Protection Agency. 1993. Remediation technologies screening matrix and reference guide, version 1. Report No. EPA 542-B-93-005.

CHAPTER 4. PHYSICO-CHEMICAL TECHNOLOGIES

4.1 Introduction

Most of these technologies rely on the generation of free radicals, such as hydroxyl, atomic hydrogen; aqueous electrons (e_{-aq}); and/or oxidants, such as hydrogen peroxide (H_2O_2), ozone (O_3), chlorine (Cl_2), and hypochlorous acid (HOCL) for the destruction of organic compounds. All chemical species, except atomic hydrogen and the aqueous electrons, act as oxidizing agents. The atomic hydrogen and the electrons act as reducing agents. Electron beam irradiation, for example, generates hydroxyl and hydrogen radicals, aqueous electrons, and some hydrogen peroxide. The mixed-oxidant technology developed by Los Alamos Technical Associates generates chlorine, hydrogen peroxide, ozone and, potentially, free radicals, but no free electrons.

Gamma irradiation shares many similarities with electron beam irradiation, to the point that the former is used to model the action of the latter. However, they are not exactly the same; when calibrated to treat wastes at equivalent doses, gamma irradiation seems to be ten times more effective than electron beam irradiation in disinfecting wastes, i.e., selectively killing certain pathogens. The main disadvantage of gamma irradiation is its very nature—it relies on a gamma emitter element, e.g., cobalt, as the tool for generating the reactive species. The latter fact raises issues that go beyond the technical merits of the technology. Despite apprehension about the latter, a Canadian company has developed a process for treating wastes using gamma radiation.

These technologies are pump and treat methods. One must first extract the water from the sediments before treatment can be effected. Furthermore, since these technologies mainly rely on the generation of free radicals, they are limited to the treatment of water-soluble organic contaminants.

Given the underlying similarities between several remediation technologies and the wide ranging costs associated with each, selecting a particular one over the other should be based on cost concerns and its actual applicability to the particular problem. This brings us to considering the issue of lab bench results versus actual conditions in the field (see below).

Free radicals are highly reactive chemical species, a desirable property if one wants to destroy or at least transform hazardous wastes. Similarly, free radicals could react with many other things that may be present in the waste, effectively reducing their ability to destroy the substances of interest. In natural waters the principal scavenger of free radicals is the carbonate-bicarbonate system. It is not surprising to see many of these technologies include an acidification step, to drive off the carbonates as CO_2 , before treatment is carried out. If the latter step is not implemented, performance of the technology will likely be diminished relative to what might be observed in the laboratory.

Besides the carbonates, another potential major problem in the use of these oxidation technologies is the presence of iron (Fe^{2+}) and manganese (Mn^{2+}). Groundwaters contaminated with organic material are likely to have large amounts of dissolved ferrous and manganous cations. These two metals come into solution when their insoluble oxidized forms, naturally present in the sediments, become reduced as the groundwater turns anoxic. The latter phenomenon is caused by the oxygen demand exerted by the organic contaminants. When the two metals come into contact with free radicals they reoxidize and reprecipitate, threatening to clog the conduits through which the groundwater is passed.

A third major concern with these technologies is the fate of the organic carbon in the treated waters. While the technologies that rely on the generation of free radicals and associated substances are quite effective in removing certain contaminants of interest, the overall destruction of organic compounds can be poor. Most of the total organic carbon can in fact remain in solution. This shortcoming raises the question as to what is the nature of the compounds left behind and their potential effects on human health and the environment. Further research on the subject is warranted.

Further information on physico-chemical technologies is available in Table 5.

4.2 Technologies that Rely on the Production of Aqueous Free Radicals

4.2.1 Electron Beam Irradiation

Technology Description

Wastewater streams are irradiated with high energy electron beams. The radicals created oxidize contaminants in the stream. This technology is most effective on non-biodegradable organics in aqueous systems.

The streams, which contain hazardous and other polluting substances, are passed through the electron beam via a weir delivery system. The high energy electrons create free radicals which transform the organic contaminants into nontoxic byproducts.

In the electron beam irradiation treatment process, electricity is used to generate a high voltage (1.5 megavolts) and electrons. The electrons are accelerated by the voltage to approximately 95 percent of the speed of light and then shot into a thin stream of water or sludge as it falls through the beam. The beam photolyses the water, producing chemical species which destroy, or at least transform, organic contaminants. The reactive chemical species include hydroxyl radicals, aqueous electrons (e^-_{aq}), hydrogen radicals, and hydrogen peroxide (H_2O_2). The most important oxidants are the hydroxyl radicals. The e^-_{aq} plays an important role in the transformation (reduction) of halogen-containing compounds.

All reactions are completed in less than 1/10 of a second. Although this technology is a form of ionizing radiation, there is no residual radioactivity. A full-scale operation in the Miami facility can treat more than 170,000 gallons per day.

Electron beam irradiation can be combined with the addition of ozone to the waste stream. The addition of the ozone will cause a reaction with the reducing species (atomic hydrogen and aqueous electrons), increasing the formation of hydroxyl radicals.

Electron beam technology has been in use for decades as industrial technology to accelerate chemical reactions, secure adhesives, sterilize medical instruments, shrink wrap materials, and most recently to irradiate food.

The electron beam technology is not sensitive to wastewater quality and is able to have effective removal in relatively clean water as well as raw sewage.

Advantages of Electron Beam Irradiation:

- This technology can treat a wide range of waste streams, making it flexible in treating different types of wastes at the same location.
- Organic contaminants are converted into carbon dioxide, water, salts, or other biodegradable end products.

Disadvantages of Electron Beam Irradiation:

- The costs of operating transportable units will be significantly higher than those of permanent facilities due to transportation expenses, maintenance requirements, and shorter useful lives.
- Treatment costs are highly dependent on dose requirements and allowable flow rates, which are contaminant dependent.

Stage of Development

There is a full-scale electron beam accelerator in place at the Virginia Key Wastewater Treatment Plant in Miami, Florida. The Electron Beam Research Facility (ERBF), which has done large-scale research for electron beam treatment of wastewaters for several years, is located at the Central District Wastewater Treatment Plant also in Miami, Florida.

Applications and Effectiveness

This technology has been shown to be effective on waste streams containing trihalomethanes, chlorinated solvents, gasoline aromatics including BTEX, phenols, certain pesticides, and others. Military wastewater streams containing these contaminants which are not completely eliminated with conventional wastewater treatment are excellent candidates for this technology.

Cost Analysis

A 160 gallons per minute (gpm) flow has operating costs of approximately \$2.5/1000gal, while a 2100 gpm flow is approximately \$.25/1000 gal. This cost is lower than the costs for comparable flows in ultraviolet (UV) peroxidation and mobile wet air oxidation, and much lower than incineration.

REFERENCES

- Environmental Protection Agency. 1992. Superfund innovative technology evaluation program technology profiles, 5th edition. Report No. EPA/540/R-92/077.
- Farooq, S., C. N. Kurucz, T. D. Waite, W. J. Cooper, S. R. Mane, and J. H. Greenfield. 1992. Treatment of wastewater with high energy electron beam irradiation. *Water Science and Technology* 26: 1265-1274.
- Kurucz, C. N., T. D. Waite, W. J. Cooper, and M. G. Nickelsen. 1991. Full-scale electron beam treatment of hazardous wastes - effectiveness and costs, p. 539-545. *In: Proceedings of the 45th Annual Purdue University Industrial Waste Conference.*, West Lafayette, Indiana.

Waite, D. T., C. N. Kurucz and W. J. Cooper. 1990. Utilizing high energy electrons for treatment of industrial wastes containing non-biodegradable organic compounds, p. 95-99. *In: Proceedings of the Mid-Atlantic Industrial Waste Conference*. Philadelphia, PA.

4.2.2 Ultraviolet Detoxification

Technology Description

UV detoxification, or UV oxidation, has long been recognized as a feasible treatment alternative for contaminated wastewater. In recent years, it has received renewed scrutiny for the treatment of wastewaters containing organics. In this process, strong oxidizers, such as ozone and hydrogen peroxide, are complemented with intense UV radiation for the destruction of refractory toxic compounds (especially chlorinated hydrocarbons) in the parts per million and parts per billion range.

Ultrax International has a commercial system which utilizes a wastewater feed system, a reactor module, an air compressor-ozone generator, a hydrogen peroxide feed system and an off-gas treatment system.

Advantages of Ultraviolet Detoxification:

- A high degree of treatment is possible, especially for refractory compounds.
- Complete oxidation results in little to no contaminant release in treated water.
- Process can be configured to operate in a batch or continuous mode.

Disadvantages of Ultraviolet Detoxification:

- Process can generate potentially hazardous contaminants if not operated properly.
- Cost of the process may be relatively high.
- Potential air emissions have to be treated.

Stage of Development

This technology has undergone a number of treatability studies, to include organics and explosives. Systems are commercially available with treatment capacities of up to approximately 1000 gpm. The technology continues to be evaluated.

Applications and Effectiveness

This technology is applicable to contaminated groundwater, industrial wastewaters, and leachates containing halogenated solvents, phenol, PCP, and pesticides; PCBs; explosives; BTEX; methyl tertiary butyl ether (MTBE); and other organics.

Cost Analysis

Cost estimates vary \$0.10 to \$10.00 per 1,000 gallons.

REFERENCES

- Environmental Protection Agency. 1993. Superfund innovative technology evaluation program technology profiles, 6th edition. Report No. EPA/540/R-93/526.
- Lewis, N. *et al.* 1990. A field demonstration of the UV/oxidation technology to treat groundwater contaminated with VOCs. *Journal of the Air & Waste Management Association* 40: 540-547.
- National Institute for Petroleum and Energy Research. 1992. Installation restoration and hazardous waste control technologies. U. S. Army Corps of Engineers Toxic and Hazardous Materials Agency. Technical Report No. CETHA-TS-CR-92053.
- Topudurti, K. V., N. Lewis and S. R. Hirsh. 1993. The applicability of UV/oxidation technologies to treat contaminated groundwater. *Environmental Progress* 12: 54-60.

4.2.3 Solar Detoxification

Technology Description

A combination of sunlight and light activated catalyst is utilized to destroy a variety of organic compounds in a relatively short time. The catalyst absorbs the sunlight, and the ultraviolet radiation reacts to break down the contaminants into carbon dioxide, water and acids. The acids are neutralized before discharge. One catalyst used in this application is titanium dioxide (TiO₂), which must be removed from the water before discharge. A commercial application which incorporates the catalyst in a solid mesh structure has already been developed, eliminating the need for post treatment filtration. Use of large focusing mirrors is being evaluated to utilize solar energy to enhance this process. Initial studies have been successful at destroying an array of volatile and semi-volatile organics to include TCE, PCE, and BTEX.

Advantages of Solar Detoxification:

- Applicable to a wide range of organic contaminants to include TCE, PCE, and other organics.
- Applicable to contaminated water and air.
- System is mobile for field application.
- Use of solar energy is environmentally attractive.

Disadvantages of Solar Detoxification:

- Not applicable to highly turbid waters without pretreatment.
- System has limited field testing.
- Economics may favor other treatment systems.
- Use of solar energy may present unacceptable level of interruption.

Stage of Development

The technology is undergoing research and development while being made available commercially for select applications. Use of large focusing mirrors are being evaluated by DOE in an attempt to utilize solar energy more efficiently.

Applications and Effectiveness

Solar detoxification can be utilized to destroy an array of organic compounds in wastewater or in conjunction with soil vapor extraction systems in treating contaminated groundwater from contaminated sites. Upon the development of efficient solar systems, the technology will have application to remote site, field deployment, and third world applications.

Cost Analysis

Not available.

REFERENCES

- Anderson, J. V. and R. J. Clyne. 1991. Solar detoxification technology: using energy from the sun to destroy hazardous waste, p. 18. *In: Conference on the challenge of the environment-new technologies*. Reston, Virginia. Technical Report No. SERI/TP-250-4474.
- Environmental Protection Agency. 1993. Superfund innovative technology evaluation program technology profiles, 6th edition. Report No. EPA/540/R-93/526.
- Hasbach, A. 1992. Emerging technologies. *Pollution Engineering* 24: 38-42.
- Sutton, M. M. and E. N. Hunter. 1989. Solar destruction of hazardous organic wastes. *Pollution Engineering* 21: 86-90.

4.2.4 Advanced Ultraviolet (UV) Flashlamps

Technology Description

An advanced pulsed xenon flashlamp is utilized as a source of low-wavelength (200 nm) emission for the direct photolysis of VOCs, particularly chlorinated compounds and freons.

The flashlamp is a pulse-mode arc lamp. It alternately stores electricity in a capacitor and discharges it through a gas within a UV transmissive quartz chamber.

The discharge quickly heats the gas to temperatures at, or above, 14,000°K and high pressures, which causes ionization and creates a plasma which emits light. The plasma has the properties of a black-box radiator with spectral characteristics defined by its temperature. As the energy discharged into the plasma increases, the temperature increases, and the maximum wavelength of emission is reduced.

This process offers a new method for the photo-oxidation of VOCs in air using an advanced UV source. The flashlamps provide a greater output in the 200 - 250 nm range than current lamps of the same power and therefore provide more rapid direct photolysis of select VOCs.

The most promising VOC applications include TCE, perchloroethene (PCE), 1,1-dichloroethene (DCE), chloroform, and methylene chloride.

Current work performed by Lawrence Livermore National Laboratory (LLNL) has been directed toward the study of TCE destruction due to the large number of contaminated sites in the country in need of TCE removal and destruction.

Advantages of Advanced UV Flashlamps:

- The pulsed xenon lamps provides a low-wavelength emission alternative not currently possible with present mercury discharge lamps.
- Technology is uniquely applicable to destruction of TCE, for which there are many potential applications.
- Technology does not suffer from breakthrough potential as is likely with commonly used VOC removal technology.
- Operation at ambient temperatures and pressures results in reduced operating and maintenance costs.

Disadvantages of Advanced UV Flashlamps:

- Current data demonstrates that the state of technology is best suited for only a limited range of organics.
- The generation of intermediate breakdown products results in other potentially toxic materials that must be characterized and eliminated.
- Technology may have to be followed by a wet scrubber collector to remove acidic photo-oxidation products.

Stage of Development

This technology is currently in the pilot stage with full-scale reactor testing.

Applications and Effectiveness

This technology is suitable for direct application to industrial gas streams which require VOC removal in accordance with increasingly stringent permit-related emission requirements of the 1990 Clean Air Act Amendments.

This technology is also well suited to treat the off-gases generated from soil venting and air stripping associated with contaminated site cleanup.

Cost Analysis

Not available.

REFERENCES

Johnson, M., W. Haag and P. Blystone. 1993. Emerging technology report: destruction of organic contaminants in air using advanced ultraviolet flashlamps. Environmental Protection Agency. Report No. EPA/540/R-93/516.

4.2.5 Mixed Oxidants

Technology Description

The patented mixed oxidant system (MIOX) process utilizes a proprietary membrane-less electrolytic cell to produce a liquid mixture of oxidants such as ozone, hydrogen peroxide, and hypochlorite from a brine (salt and water) solution. The process utilizes relatively small amounts of direct current to produce a disinfecting capability for drinking water and organics destruction in contaminated water.

This new system utilizes a patented electrolytic cell which operates off a variety of low-energy, direct current power sources. These sources include both solar or battery operation. Salt water (10 percent salt) is fed to the MIOX cell, which generates 6 gallons per hour of mixed oxidants. For applications requiring greater volumes of oxidant, modules can be installed in addition to a liquid oxidant holding tank.

The disinfecting power of the mixed oxidants is greater than that of chlorine due to the method of pathogen destruction. The mixed oxidants are a strong and short-lived combination which enters and destroys the microbial cell walls. The chlorine that is also generated provides a residual disinfecting capability as well as an indicator of disinfection. Tests on the destruction of BTEX organics in water have reportedly resulted in reduction to below detection levels.

The process was initially developed for the Army as an Small Business Initiative for Research (SBIR) project at Fort Belvoir. The initial objective was to devise a field disinfection technique that would replace calcium hypochlorite and the associated need to send chemicals to troops in the field.

Advantages of Mixed Oxidants:

- Mixed oxidants work synergistically to destroy pathogens.
- Low energy requirements and its light weight allow utilization under field, or remote, conditions.
- Chlorine residual is maintained while reducing the generation of chloro-organic compounds associated with more common chlorination.
- Adverse taste and odor potential is reduced when treating high-organic containing waters.

Disadvantages of Mixed Oxidants:

- Small size requires modules to be added when treating large volumes of water. Economies of scale have not yet been introduced into the current system design.
- The storage of mixed oxidants to handle peak, or periodic, large volumes may reduce the strength of the stored oxidants with time.

Stage of Development

Mixed oxidants technology is in the early stages of commercialization.

Applications and Effectiveness

This system can be used to provide drinking water disinfection capability in remote locations where large and continuous power supplies are not available. Current applications include disinfecting remote drinking water supplies for third world locations. The system can also be used for the destruction of organics in contaminated groundwater for site remediation where the location is particularly remote and the duration of the treatment may be relatively short.

Cost Analysis

Operating costs for the MIOX system are approximately \$0.04 per 1,000 gallons treated.

REFERENCES

- Los Alamos Technical Associates, Inc. Undated. MIOX (Mixed Oxidants) Technical Note.
- Robson, William M. 1994. Method and apparatus for removing organic contaminants. Patent No. 5308507.
- Stratta, J. M. and M. Robson. December 15, 1993. Los Alamos Technical Associates, Inc., personal communications.

4.2.6 Gamma Irradiation of Water Solutions and Sludges

While electron beam irradiation relies on a particle beam to photolyze water, gamma irradiation relies on purely electromagnetic radiation to accomplish the same process. Gamma rays penetrate deeper into the waste, a fact that may explain why it appears to be more effective than electron beam irradiation in disinfecting water. At a given comparable dose, however, the technique is as effective as electron beam irradiation in destroying organic contaminants.

Gamma irradiation technology is already in use in the United States, in the food industry, where it is employed as a replacement for heat treatment. Its use as a waste treatment technology is hampered by the use of a radioactive element, usually cobalt, as the source of electromagnetic radiation. Spent reactor fuel can also serve as the source of gamma radiation.

REFERENCES

- Farooq, S., C. N. Kurucz, T. D. Waite, and W. J. Cooper. 1993. Disinfection of wastewaters: high energy electron vs. gamma irradiation. *Water Research* 27: 1177-1184.
- Mincher, B. J., D. H. Meikrantz, R. I. Murphy, G. L. Gresham, and M. J. Connolly. 1991. Gamma-ray induced degradation of PCBs and pesticides using spent reactor fuel. *Applied Radiation and International Journal of Radiation Application and Instrumentation* 42A: 1061-1066.
- Swinwood, J. F. and F. M. Fraser. 1993. Environmental application of gamma technology—update on the Canadian sludge irradiator. *Radiation Physics and Chemistry* 42: 683-687.

4.2.7 Chemical Oxidation of Contaminants with Ozone and/or Hydrogen Peroxide in the Presence of UV Light

Ozone and hydrogen peroxide are two well-known oxidants of organic matter. They are known to react directly or via the formation of hydroxyl free radicals, with organic contaminants. Free radicals are significantly more reactive chemical species, making them particularly suited for the destruction of chlorinated compounds. Production of free radicals from both oxidants is readily achieved by exposing them to ultraviolet light. UV light also shows oxidizing properties. Thus, several technologies have been developed in which a combination of the two oxidants and UV light are employed to destroy organic contaminants.

The processes act synergistically, their combined destructive capacity being greater than the sum of their individual oxidizing ones. The organics are destroyed by the treatment process without releases to the air or the creation of residual wastes. This treatment process has been used on organic compounds such as trichloroethene, tetrachloroethene, 1,2-dichloroethane, 1,2-dichloroethene, diisomethylphosphonate (DIMP), DBCP, benzene, chloroform, and hydrazine. Good destruction of organics using this process was achieved at Rocky Mountain Arsenal, Commerce City, Colorado (USATHAMA, 1990, p. 601) and at a hazardous waste site in San Jose, California (EPA, 1991; p. 10-13). The results from a full-scale test at a DOE Kansas City plant (EPA, 1991; p. 107) were mostly inconclusive.

REFERENCES

- Environmental Protection Agency. 1991. Innovative treatment technologies overview and guide to information sources. Report No. EPA/540/9-91/002.
- Environmental Protection Agency. 1991. Synopses of federal demonstrations of innovative site remediation technologies. Report No. EPA/540/8-91/009.
- Governal, R. A. and F. Shadman. 1992. Oxidation and removal of organic particles in high-purity water systems using ozone and UV. *Ultrapure Water* 9: 44.
- Lewis, N., K. Topudurti, G. Welshans, and R. Foster. 1990. A field demonstration of the UV/oxidation technology to treat groundwater contaminated with VOCs. *Journal of the Air & Waste Management Association* 40: 540-54.
- Sundstrom, D. W., B. A. Weir and H. E. Klei. 1989. Destruction of aromatic pollutants by UV light catalyzed oxidation with hydrogen peroxide. *Environmental Progress* 8: 6-11.
- Topudurti, K. V. 1992. A UV/oxidation technology demonstration to treat groundwater contaminated with VOCs. *Water Science and Technology* 25: 347-354.
- Topudurti, K. V., N. M. Lewis and S. R. Hirsh. 1993. The applicability of UV/oxidation technologies to treat contaminated groundwater. *Environmental Progress* 12: 54-60.
- U.S. Army Toxic and Hazardous Materials Agency. 1990. Proceedings for the 14th Annual Army Environmental R&D Symposium. Technical Report No. CETHA-TE-TR-90055.

Table 5. Physico-Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
PO*WW*ER™ <i>-(Chemical Waste Management, Inc.)</i>	Tech Contact: Erik Neuman Chemical Waste Management, Inc. Geneva Research Center 1950 So. Batavia Ave. Geneva, IL 60134-3310 708-513-4500 EPA Contact: Randy Parker 513-569-7271	Combination of evaporation with catalytic oxidation to concentrate and destroy contaminants, producing high quality water.	Landfill leachates, groundwater, process wastewater, and low-level radioactive mixed wastes	Organic, inorganic and radioactive compounds	EPA SITE demonstration program.	Tested on landfill leachate at developer's pilot plant in Lake Charles, LA. Removal efficiencies and cost data are not available.
Chemical Oxidation - <i>(Utrox System)</i>	Utrox International David Fletcher 2435 South Anne St. Santa Ana, CA 92704 714-545-5557	Ozone and H ₂ O ₂ with UV radiation destroy toxic compounds. During testing, reaction time, ozone dose, H ₂ O ₂ dose, UV intensity, and pH were varied.	Surface water and groundwater	1,1,1-trichloroethane (TCA), TCE, 1,1-dichloroethane (DCA) and BTEX	Field-scale EPA SITE demonstration program completed.	76-99 percent removal of TCE in the 32-60 percent removal of 1,1-DCA. 37-87 percent removal of 1,1,1-TCA. Costs are \$0.15 to \$90 per 1,000 gallons treated.
Perox-Pure™ Chemical	Tech. Contact: Chris Gigv	Process utilizes UV radiation and hydrogen	Groundwater and	Chlorinated solvents	EPA SITE demonstration	A demonstration to measure how well the

Table 5. Physico-Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Chemical Oxidation - (<i>Peroxidation Systems' Perox-Pure</i>)	Norma Lewis U.S. EPA-RREL 26 W. Martin Luther King Dr. Cincinnati, OH 45268 513-569-7665	Organic destruction process uses H ₂ O ₂ and UV.	Surface water and groundwater	Chlorinated solvents, pesticides, phenolics, PCBs, BTEXs, etc.	Full-scale EPA SITE demonstration program commercial applicability.	32-90 percent removal of contaminants listed. Costs are \$70-150 per 1,000 gallons treated. Electricity is the greatest expense.
Ultraviolet Radiation and Oxidation - (<i>Ultrax Resources Conservation Co.</i>)	Tech. Contact: David Fletcher Ultrax Resources Conservation Co. 2435 So. Anne Street Santa Ana, CA 92704 714-545-5557 EPA Contact: Norma Lewis 513-569-7665	Process uses UV radiation, ozone, and hydrogen peroxide to destroy toxic contaminants.	Groundwater, industrial wastewater and leachate	Halogenated solvents, phenol, PCPs, pesticides, PCBs, explosives, BTEXs, and other organic compounds	Field-scale EPA SITE demonstration completed. Fully commercial.	Treatment of contaminated groundwater at a hazardous waste site in San Jose, CA. VOCs in the wastewater exhibited relatively refractory behavior to conventional oxidation (based on three indicative VOCs). Reduction efficiencies of ozone greater than 99.99 percent. No cost data available.

Table 5. Physico-Chemical Process Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Mobile Environmental Treatment System - (<i>Ensotech, Inc.</i>)	Tech. Contact: Inderjit Sabjerwal Ensotech, Inc. 7949 Ajay Drive Sun Valley, CA 91352 818-767-2222 EPA Contact: Naomi Barkley 513-569-7854	Multipurpose transportable treatment unit can process up to 35 tons of soil per hour. Unit is fitted with an ultraviolet radiation source and a vacuum suction system that uses GAC.	Soil, lagoons, wastewater, ponds and groundwater	Hydrocarbons, chlorinated organics, heavy metals, and mixed wastes	EPA SITE demonstration program acceptance. Over 300 sites have been remediated using this technology.	Sites remediated include gasoline stations; oil refineries; plating shops; chemical manufacturing plants; abandoned hazardous waste dumps; and lead acid battery plants.

GENERAL REFERENCES

- Environmental Protection Agency. 1992. Superfund innovative technology evaluation program technology profiles, 5th edition. Report No. EPA/540/R-92/077.
- Environmental Protection Agency. 1993. Technology demonstration summary: Peroxidation Systems, Inc. Perox-Pure (trade name) chemical oxidation technology. Report No. EPA/540/SR-93/501.
- Farooq, S., C. N. Kurucz, T. D. Waite, W. J. Cooper, S. R. Mane, and J. H. Greenfield. 1992. Treatment of wastewater with high energy electron beam irradiation. *Water Science and Technology* 26: 1265-1274.
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4.3 Selective Extraction

4.3.1 Electrokinetics

Technology Description

Electrokinetics is an *in situ*, *ex situ*, or on-site remediation process in which contaminants are forced to migrate through soils by the application of an electric current. The technology involves the installation of electrodes into the soil to be treated. The application of a low-level direct electric current across these electrodes has several effects on the soil pore fluids, including: (1) the generation of an electric potential which causes electroosmotic flow of the pore fluid from the anode to the cathode, (2) production of acidic conditions in the anode, and (3) movement of the acid front, resulting in desorption of contaminants from the soil surfaces.

Two major effects are achieved during electrokinetic remediation. The first is electromigration, which is when the ions in the soil-water solution begin to migrate toward the oppositely charged electrode. At the same time, electroosmosis takes place. Electroosmosis is the phenomenon at which soil-water begins to flow toward the cathode.

Electrokinetic remediation is based on the coupling of electrical potentials with hydraulic and chemical potentials in soils together with electrolysis reactions. The four electrokinetic phenomena include:

- Migration potential,
- Sedimentation potential,
- Electrophoresis, and
- Electroosmosis.

Migration and sedimentation potentials are the terms used for the generation of an electrical current due to the flow of fluids and the sedimentation of particles, respectively. Electrophoresis and electroosmosis define particle and pore-fluid movement, respectively, under an electrical potential difference.

The contaminants are actually removed by one of several methods. These methods include electroplating at the electrode, precipitation or co-precipitation at the electrode, and either the pumping or ion exchange of water near the electrode.

Chemistry and flow in electrokinetic soil processing are dependent upon the electrolytes generated at the electrodes and the initial chemistry in the specimen.

The end result of the process is that ionic constituents of contaminants are transported toward the electrodes, where they can be recovered for above ground treatment. The attractiveness of this technology is that much higher flow rates can be achieved in fine grained soils by electrical gradients than can be achieved by hydraulic gradients. In addition, various flushing agents can be used to enhance contaminant removal.

The electrokinetic phenomena that occur when the soil is electrically charged can also be used to fence off hazardous waste sites or hazardous industrial sites. Electrodes can be installed horizontally and vertically in deep, directionally drilled tunnels or in trenches around sites polluted by leaking storage tanks and other sources.

Sandia National Labs is evaluating which types of contaminants and soil conditions are appropriate for electrokinetic remediation. Their evaluation includes:

- Evaluation of the process for heavy metals with complete redox chemistry;
- Evaluation of the process in partially saturated soils;
- Evaluation of the effects of mixed soil types in the process; and
- Scaling the process up to field scale.

The results of one study (Acar, 1992) indicate that decontamination will be achieved in shorter periods of time than using the technique of flushing the soil with water. In addition, fine-grained soils have electrical potentials and electroosmotic flows which constitute a more efficient pumping mechanism than the flow generated by hydraulic potentials.

Advantages of Electrokinetics:

- Electrodes placed in soil masses or in pore fluids can create:
 - Electrokinetic barriers that retard contaminant migration across the earthen barriers used in waste containment facilities;
 - Leak detection systems for earthen barriers;
 - Diversion and fencing schemes for migrating contaminant plumes;
 - Injection of grouts or nutrients for growth of microorganisms essential for biodegradation;
 - *In situ* decontamination of soils through the separation of species by migration, diffusion, and electroosmosis.
- Soil and groundwater are treated simultaneously.
- Can be applied *in situ* and *ex situ*.
- Treats low permeability soils.
- Not energy intensive.
- Potentially cost effective.
- Electrokinetic fencing combines contaminant treatment, containment, and prevention.

Disadvantages of Electrokinetics:

- There have been few efforts to move the contaminant removal process up to a larger scale, particularly in the case of partially saturated soils.
- Limited data exists on removal of organic compounds from soils. Organics often have low polarities, and the migration component from electrical currents is not expected to contribute to their removal.
- Precipitation of metals and other inorganics may clog soil pores, limiting transport.
- A conducting pore fluid is required for the process to be successful.
- Potential regulatory limitations in introducing pore fluid conduction/washing agents.
- The process leads to a temporary acidification of the treated soil.
- The efficiency of removal of a contaminant is directly related to its ionic mobility and concentration.
- Electrokinetics can be applied only to soils with a hydraulic conductivity of less than 1×10^{-5} cm/s.

Stage of Development

Electrokinetic technology is an emerging technology. Field pilot-scale studies have been reported in Europe and several large *ex situ* pilot-scale studies are currently being conducted in Baton Rouge, Louisiana, by the EPA Risk Reduction Engineering Laboratory and Electrokinetics, Inc. (Acar, 1993). The first pilot-test of the electroreclamation process was conducted in 1987 in The Netherlands. At least two other successful pilot-scale tests were performed and two cleanup projects were conducted. An additional cleanup project is currently in operation at an air base in The Netherlands.

This technology has recently made significant strides in development. During the past five years, electroreclamation technology has been developed and applied by the Geokinetics Company in Rijssen, The Netherlands (Acar, 1993). Some field trials and actual cleanup projects using this new

technology have removed a number of contaminants successfully. The Russians are using this technology to move radioactive species downward into clay lenses as a means of eliminating mobility. To date they reportedly have remediated several thousand square kilometers using electrokinetics. The technology is commercially available on a limited scale in the United States; the European community has more established vendors.

Applications and Effectiveness

Large-scale electrokinetic techniques have historically been used to densify and solidify slurries and to extract water from liquefied soils, paper mats, and concretes. Electroosmosis has been used more recently to remove heavy metals and soluble organics from saturated clays in laboratory experiments.

Pilot-scale studies in the United States and field-pilot studies in Europe have shown that electrokinetics can be an effective contaminant recovery where radionuclides, explosives, heavy metals, certain organic compounds, and mixed organic-inorganic wastes are found. Most studies have shown cadmium, chromium, lead, and copper to have the highest removal efficiencies at 80 to 99.99 percent.

Electrokinetic remediation is potentially useful in fine-grained soils and sludges where electrical conductivity is not too high. High conductivity, usually caused by inorganics, results in high power demands and higher costs. There is not enough information to assess how low a contaminant concentration can be for treatment to be effective.

Case Studies

Several case studies and/or technology applications are provided in Table 6. Cost data has been provided when available.

Co-Technologies/Alternative Technologies

Recent laboratory experiments show that the electrokinetic technique can be used in combination with other remediation techniques such as pumping, biodegradation, vacuum extraction, and thermal technologies. When combined with electrical heating, the electrokinetic technique can be used to remove polar and nonpolar organic chemicals from soil and groundwater. Electrokinetics may be combined with *in situ* bioremediation as a means of introducing additives required for establishing biologically active zones in relatively tight soils.

Electrokinetics can also potentially be combined with conventional enhanced soil flushing techniques to treat highly heterogeneous soils. Since this is a contaminant removal technology, the recovered contaminated fluid must be treated for disposal. Several other technologies or technology trains may be potentially adopted for this purpose, depending on the contaminants recovered.

Cost Analysis

Treatment costs have not yet been developed for electrokinetic applications. Cost will mainly depend on the type of electrodes, spacing of electrodes, and power requirements. Cost-effective electrode design and manufacturing are currently under progress.

The only cost estimation found was approximately \$45 per cubic yard. Bench scale studies have shown that typical power consumption may be in the order of 60 to 200 kilowatt hours per cubic meter (Acar, 1993).

Table 6. Electrokinetic Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
<i>In Situ</i> Electroacoustic Soil Decontamination (ESD) - (<i>Battelle Memorial Institute</i>)	Tech. Contact: Satya Chauhan Battelle Memorial Institute 505 King Avenue Columbus, OH 43201 614-424-4812 EPA Contact: Jonathan Herrmann 513-569-7839	Process consists of electrodes and an acoustic source. The direct current facilitates the transport of liquids through soils.	Fine-grained soils	NAPLs and heavy metals	Phase I studies completed.	Results indicate that ESD is technically feasible for removal of inorganic species, i.e. metals, and only marginally effective for hydrocarbon removal.
Electrokinetic Remediation - (<i>Electrokinetics, Inc.</i>)	Tech. Contact: Yalcin Acar Electrokinetics, Inc. Louisiana Business and Technology Center Louisiana State Univ. South Stadium Drive Baton Rouge, LA 70803 504-388-3992 EPA Contact:	Process uses direct currents across electrodes and conditioning pore fluids circulating at the electrodes to remove the contaminants.	Saturated and partially saturated soils	Heavy metals, radionuclides, and other inorganic contaminants	EPA SITE demonstration bench-scale and pilot-scale laboratory studies completed and field-scale testing in progress. Full-scale	A pilot-scale laboratory study investigated removal of 2,000 g/g lead loaded onto kaolinite; no results available. Also, a field-scale study investigated at a site with lead concentrations in soil up to 75,000 g/g; no results available. No

Table 6. Electrokinetic Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Electrokinetics (also known as Electroreclamation) - <i>In Situ</i>	Reinout Lageman Geokinetics Rijssen, The Netherlands (also, Baton Rouge, LA)	Electrical currents are applied across electrodes inserted in a soil mass or a pore fluid.	Peat soil	Heavy metals, mostly lead and copper	Pilot-scale testing.	Paint factory in Groninger, The Netherlands. Initial lead concentrations of 300-500 ppm were reduced by up to 70 percent. Initial copper concentrations of 500-1000 ppm were reduced by 80 percent. No cost data available.
Electrokinetics - <i>In Situ</i>	Reinout Lageman Geokinetics Rijssen, The Netherlands (also, Baton Rouge, LA)	Electrical currents are applied across electrodes inserted in a soil mass or a pore fluid.	Clay soil	Zinc	Pilot-scale testing.	Galvanizing plant in Delft, The Netherlands. Average zinc concentration was reduced from 2410 ppm to 1620 ppm. No cost data available.
Electrokinetics - <i>In Situ</i>	Reinout Lageman Geokinetics Rijssen, The Netherlands (also, Baton Rouge, LA)	Electrical currents are applied across electrodes inserted in a soil mass or a pore fluid.	Heavy clay	Arsenic	Pilot-scale testing.	Timber Impregnation Plant in Loppersum, The Netherlands. Arsenic concentrations

Table 6. Electrokinetic Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Electrokinetics - <i>In Situ</i>	Reinout Lageman Geokinetics Rijssen, The Netherlands <i>or</i> Yalcin Acar Electrokinetics, Inc. Louisiana Business and Technology Center Louisiana State Univ. South Stadium Drive Baton Rouge, LA 70803 504-388-3992	Electrical currents are applied across electrodes inserted in a soil mass or a pore fluid.	Soil	Lead	Pilot test under EPA SITE demonstration program.	Former refinery site in Baton Rouge, LA. Testing in progress. No cost data available.

Personal Contacts

Refer to Table 6 for a complete list of personal contacts relative to specific case studies/applications. For further information, the following individual may be contacted:

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4.3.2 Adsorption on Metal Oxides and Hydroxides

Kansas State University is evaluating new materials such as synthesized ultra high surface area metal oxides and hydroxides, for their effectiveness at adsorbing toxic chemicals and destroying them during the adsorption process. Adsorbates being studied are organophosphorus compounds and organohalogen compounds.

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CHAPTER 5. PHYSICAL TECHNOLOGIES

5.1 Introduction

Physical treatment technologies are those which utilize basic physical forces to bring about a desired change or result. These basic processes include extraction, separation, heating, cooling, stripping, vacuuming, washing, and venting. In most cases physical treatment must be followed by, or used in conjunction with, a biological, thermochemical, physical-chemical, or other treatment technology in order to achieve complete treatment of the contaminated media.

The environmental technologies identified and described within this section are technologies that primarily provide a means by which contaminants or contaminated materials are separated or concentrated so that treatment can be made easier, more cost effective, or more efficient.

5.2 Selective Extraction

5.2.1 Soil Vapor Extraction

Technology Description

Soil Vapor Extraction (SVE), also known by various names such as vacuum extraction, *in situ* vaporization, or soil venting, is a remediation technology utilized for the removal of VOCs, and in some cases, SVOCs with vapor pressures greater than 0.5 mm Hg from the unsaturated soil zone.

The principle behind *in situ* SVE is that the mass transfer of contaminants from the liquid to vapor phase. The ambient air necessary for SVE enters the subsurface either passively, through leaky boundaries, or is actively injected into the ground through injection wells. Usually the liquid and vapor phases of a contaminant in the subsurface environment are in equilibrium. The air supplied by the SVE system disturbs this vapor-liquid equilibrium condition and causes contaminant mass to be transferred to the air phase.

Pneumatic pressure gradients created by the injection/extraction wells transport the contaminants by advection. The contaminant rich vapors are then recovered and treated on the surface by such technologies as carbon adsorption, thermal destruction, or condensation. The treatment type is dependent upon the composition and concentration of the contaminant(s) being removed. The injection/extraction wells continue to exchange the air until all of the condensed-phase organics are removed from the higher permeability soils.

Advantages of in situ SVE:

- SVE has great flexibility, causing minimum site disturbance; that is, it may be used to remediate soils underneath buildings and other structures.
- SVE is easily installed and uses standard, readily-available equipment, which allows for rapid mobilization and implementation of remedial activities. Therefore, this process can treat large volumes of soil at reasonable costs.
- SVE treatment is permanent; thus it reduces the potential for further migration by removing VOCs from the vadose zone.

- SVE can be easily integrated with other technologies such as bioremediation, soil flushing, and air sparging.
- Reagents do not need to be added in order to enhance treatment.
- SVE can be applied to soil-gas as well as groundwater.

Disadvantages of in situ SVE:

- Contaminants with low vapor pressures have poor removal efficiencies.
- Partial cleanup is achieved in sites containing mixtures of organics and heavy metals.
- The resulting vapors are hazardous, requiring additional treatment.
- Vapor transport is impeded by fine-grained, low permeability soils.
- Cleanup times may be unpredictable due to site complexity.
- SVE is effective over a relatively small area.

Stage of Development

SVE is commercially available and has been successfully implemented in numerous field-scale applications. A large body of performance and cost data on the bench-, pilot- and field-scale applications has been generated.

The EPA has effectively demonstrated *in situ* SVE at over 9 Superfund sites and at more than 400 other waste sites throughout the United States. The process was demonstrated under the SITE Demonstration Program at Groveland Wells Superfund site in Groveland, Massachusetts, from December 1987 through April 1988.

In situ SVE on sites with complex geology and contaminant distributions may not be effective. Pilot-scale studies are necessary to establish the applicability in such sites.

Applications and Effectiveness

Vacuum extraction technology effectively treats soils containing virtually any VOC and has successfully removed over 40 types of chemicals from soils, including gasoline- and diesel-type hydrocarbons. *In situ* SVE is best employed when any or all of the following situations apply: 1) soil excavation is impossible, 2) the soil contaminants have vapor pressures greater than 0.5 mm Hg, 3) large volumes of contaminated soil need treatment, 4) soils have intrinsic air permeabilities of 10^{-2} to 10^{-5} cm/sec, and/or 5) if biological degradation of the contaminant may need enhancement.

According to Kemblowski et al. (1990), vapor flow rate, contaminant vapor concentration, and the vapor flow path relative to the contaminant location are the critical factors which will determine the effectiveness of an SVE system. In addition, a number of soil factors (such as water content, soil porosity, clay content, absorption site density, organic matter content, pH, temperature, and most importantly soil permeability for air flow) affect the movement of the contaminants in the vadose zone during the implementation of the SVE process.

In situ SVE has been used extensively for the remediation of Leaking Underground Storage Tanks (LUST). The reason for this extensive use is that LUSTs have a well-defined source, with well characterized chemical compositions. The specific contaminants most effectively treated are VOCs

and SVOCs such as halogenated volatiles and semivolatiles, non-halogenated volatiles and semivolatiles, polynuclear aromatics (PNAs), BTEX, and solvents. Hydrocarbons such as jet fuel, diesel fuel, gasoline, and heavy naphthas are also effectively removed by SVE. The contaminants most commonly treated effectively by SVE at Superfund sites, in decreasing order, are BTEX, PCE, TCE, DCE, vinyl chloride, DCA, TCA, and carbon tetrachloride. Through field pilot-scale tests, it has been shown that VOCs can be reduced to non-detectable levels.

Case Studies

Several successful SVE systems are operated throughout the United States. Selected case studies and/or technology applications are presented in Table 7. Cost data are included where available.

Co-Technologies/Alternative Technologies

Air Sparging, the *in situ* removal of volatile organics from saturated soils and/or groundwater by injecting air under pressure below the saturated zone, is closely related to SVE. This combination is particularly effective in the removal of DNAPLs and residual contaminants from the saturated zone.

Integrated Vapor Extraction and Steam Vacuum Stripping (a thermally enhanced SVE system) simultaneously treat groundwater and soil contaminated with organics. The hot steam injection causes a rise in temperature which aids in volatilization of the contaminants, thus providing more effective removal of the SVOCs.

Bioremediation-Bioventing is the integration of soil vapor extraction and bioremediation technologies. The vacuum enhanced *in situ* bioremediation technology removes VOCs from subsurface soils while simultaneously stimulating aerobic biodegradation of SVOCs. This combination can be beneficial in allowing lower cleanup standards to be met and provides permanent degradation.

Cost Analysis

The factors which most affect remediation costs are the initial contaminant concentration in the soil and the regulatory cleanup standard to which the soil must be remediated. Treatment costs are typically \$40 per ton but can range from \$10 to \$150 per ton of soil, depending on the number of extraction/injection wells and type of treatment processes necessary for air and water treatment. These prices do not include indirect costs such as permits and treatment of residuals. Other factors increasing costs include the depth to groundwater, depth of contamination, and the amount of contamination at the site.

Table 7. Air/Vacuum/Steam Extraction Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
<i>In Situ</i> Steam and Air Stripping Treatment System	Novaterra, Inc. Phillip LaMori 373 VanNess Avenue Suite 210 Torrance, CA 90501 310-328-9433	Utilizes steam and air to heat soil and volatilize contaminants. Separation of contaminants accomplished through distillation and carbon beds.	Soil	VOCs and SVOCs	Commercially available. EPA applications analysis report published June, 1991.	September, 1989, SITE demonstration in San Pedro, CA. Overall efficiencies of 85 percent for VOCs and 55 percent for SVOCs. Process treatment rate of 3 cubic yards of soil per hour.
<i>In Situ</i> Steam Enhanced Extraction	Udell Technologies Lloyd Stewart 4701 Doyle St. Suite 5 Emeryville, CA 94608 510-653-9477	Steam is forced through soil by injection wells to thermally enhance the vapor and liquid extraction processes.	Groundwater and soil	VOCs and SVOCs	Commercially available.	August, 1988 - successful pilot-scale demonstration. Also, case study at Lawrence Livermore National Laboratory.
<i>Ex Situ</i> Air Stripping	Dr. James Heidman U.S. EPA-RREL 26 W. Martin Luther King Drive	Five parallel towers each 12 ft in diameter handling 700 gpm. Air-to-water ratio of 2:1.	Groundwater and soil	Primarily chlorinated hydrocarbons	Commercial-scale. Installation in Tacoma, WA, 1988.	Average removal efficiency of 95.5 percent for TCE. 98

Table 7. Air/Vacuum/Steam Extraction Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
<i>Ex Situ</i> Air Stripping	Dr. James Heidman U.S. EPA-RREL 26 W. Martin Luther King Drive Cincinnati, OH 45268 513-569-7632	Air stripping tower, 4 ft. in diameter, with serial carbon adsorption unit. Tower contained 24 ft. bed with polyethylene packing.	Groundwater and soil	Primarily VOCs, iron, pesticides, extractable organics	Commercial-scale. Installation at Sydney Mine Site, Valrico, FL. Operational water flow at 150 gal/min and hydraulic loading rate 12 gpm/ft ² .	90 to 99.9+ percent reduction of VOCs.
<i>In Situ</i> SVE	Capt. Edward G. Marchand HQ AFCEA/RAV Tyndall AFB, FL 32403-5319 504-283-4628	Venting wells in unsaturated zone. Gases are fed to the treatment system.	Soil	VOCs	Commercially available.	Study at Hill AFB found 80 percent removal of VOCs. With catalytic incineration, costs are \$10/yd ³ . Without air treatment, costs are \$15-20/yd ³ . With activated carbon emission treatment, costs are \$15-85/ton.
HRUBOUT [®]	Tech. Contact:	<i>In situ</i> process that uses	Soil	Organic	EPA SITE	Pilot-scale testing was

Table 7. Air/Vacuum/Steam Extraction Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Subsurface Volatilization and Ventilation System (SVVS) - (Billings and Associates, Inc.)	<p>Tech. Contact: Gale Billings Billings and Assoc., Inc. 3816 Academy Parkway North, N.E. Albuquerque, NM 87109 505-345-1116</p> <p>EPA Contact: Kim Lisa Kreiton 513-569-7328</p>	Process uses a network of injection and extraction wells in conjunction with <i>in situ</i> biodegradation.	Soil, sludges, free-phase hydrocarbon product and groundwater	Gasoline and/or diesel fuels, other hydrocarbons	EPA SITE demonstration acceptance. Implemented at 30 underground storage tank (UST) sites in New Mexico and Texas.	Field-study in progress at a site in Buchanan, MI. No cost data available.
Integrated Vapor Extraction and Steam Vacuum Stripping - (AWD Technologies, Inc.)	<p>Tech. Contact: David Bluestein AWD Technologies, Inc. 49 Stevenson Street, Suite 600 San Francisco, CA 94105 415-227-0822</p> <p>EPA Contact: Norma Lewis 513-569-7665</p>	Integrated system consists of an AquaDetox moderate vacuum stripping tower that uses low-pressure steam and an SVE process.	Groundwater and soil	VOCs	EPA SITE demonstration completed.	At the San Fernando Valley Superfund Site, groundwater and soil gas contaminated with VOCs were removed at a percent range of 99.92 to 99.99. Costs are approx. \$3.2, \$4.3, and \$5.8 million for

Table 7. Air/Vacuum/Steam Extraction Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
<i>In Situ</i> SVE at a Superfund Site	Terra Vac, Inc. Jams Malot 356 Fortaleza St. P.O. Box 1591 San Juan, PR 00903 809-723-9171	Utilizes dual vacuum extraction - a vapor and liquid separator and emission control device.	Soil	VOCs, gasoline, diesel range hydrocarbons, and compounds with Henry's constant equal to 0.001 or higher.	Commercially available	At the EPA-Groveland Wells site, an average VOC reduction of 92 percent for sandy soils to 90 percent for clays was determined. Average cost of \$40/ton with a range of \$10-150/ton.
<i>In Situ</i> AquaDetox/SVE System	AWD Technologies David Bluestein 49 Stevenson St. Suite 600 San Francisco, CA 94105 415-227-0822	Vacuum stripping tower using low pressure steam to treat contaminated groundwater and a SVE system to treat contaminated soil simultaneously.	Groundwater and soil	VOCs	Commercially available	99.92-99.99 percent removal of VOCs from groundwater. Estimated cost of \$4.3 and \$5.8 million for 1000 and 3000 gpm systems.
<i>In Situ</i> SVE	OHM Corp. Robert Cox 2950 Buskirk Ave., Suite 315 Walnut Creek, CA 92596 510-256-7187	Utilizes dual vacuum extraction - a vapor and liquid separator and emission control device.	Soil	VOCs	Commercially available	At a field demonstration, 50,000 pounds of gasoline were recovered in six months.

Personal Contacts

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Stinson, M. K. 1989. EPA site demonstration of the Terra Vac *in situ* vacuum extraction process in Groveland, Massachusetts. *Journal of the Air Pollution Control Association* 39: 1054-1062.

5.2.2 Air Sparging

Technology Description

Air Sparging is a remediation technology integrated with *in situ* soil vapor extraction (SVE) for simultaneous treatment of contaminated soils and groundwater. This variation of SVE technology is a physical process for in-place treatment of contaminated soils and groundwater. It is used in cases where drawdown of the water table is not particularly cost-effective due to the volume and duration of pumping that may be required.

Air sparging utilizes the injection of air below the groundwater table to induce the volatilization and stripping of volatile contaminants from the groundwater into the unsaturated zone. The contaminants, volatilized by the air, may then be degraded within the unsaturated zone, essentially utilizing the unsaturated zone as a biofilter. Alternatively, a conventional SVE system may be utilized to extract the vapors as they are emitted. This process is most efficiently used for the removal of volatile organic compounds (VOCs), and in some cases semi-volatile organic compounds (SVOCs), with vapor pressure greater than 0.5 mm Hg from the unsaturated soil zone as well as the saturated zone.

The integration of air sparging with the SVE system creates a unique method of removing volatile and semi-volatile organic compounds from both the unsaturated and saturated zones simultaneously.

The air/steam stripping/SVE system proceeds by disturbing the vapor-liquid equilibrium condition in the soil pores, causing an induced pneumatic pressure gradient in the subsurface environment. This pressure gradient subsequently creates an air flow field around the extraction well, thus transporting the contaminants by advection into the air flow.

The turbulence and increased mixing in the saturated zones created by air sparging increases the contact between groundwater and soil. This process will result in higher concentrations of the VOCs dissolving in the groundwater, which can be recovered by pumping, or by the air sparging itself with the soil vapor extraction system.

Whether air or another gas is injected as the carrier gas depends on the volatilization temperature of the contaminant. When the air is the carrier gas, the process is called air sparging or

air stripping. When steam is the carrier gas, the process is called steam stripping. (This technology will be discussed further in another summary.)

Since air sparging is an integrated technology with SVE systems, its applicability, advantages, and disadvantages are similar to those of SVE systems.

Advantages of Air Sparging:

- Sparging extends the effective volatilization principles applied to SVE to high zones of contaminant concentration-adsorbed chemicals in the saturated zone or below the water table. The contaminants were previously inaccessible to venting.
- Lower equipment maintenance than pump and treat systems - fewer mechanical parts.
- The process is much more rapid than conventional SVE systems: By stripping the groundwater, the treatment can take place without groundwater recovery or treatment.
- The treatment provided is permanent.
- The technology is not disruptive to ongoing business operations.
- The process can be constructed from standard equipment, labor, and materials. However, the evaluation criteria, design tolerances, and systems engineering are far more exacting.
- Reagents are not required to be injected into the groundwater in order to enhance treatment.
- Turbulence caused by air sparging enhances the dissolution and distribution of oxygen in the water phase.
- The process is not limited to the depth of the groundwater.

Disadvantages of Air Sparging:

- *In situ* air sparging is energy intensive due to the larger depth of the inlet system and the required energy to pump air through the pipe.
- Interactions in the subsurface may decrease the effectiveness of the process.
- If soil permeabilities are too low (as fine-grained soils) or the soils are highly layered, air sparging may not be as effective due to the hindering of the escape of air travel. Soil conditions such as high moisture content, large soil aggregates, and stratification affect technology success.
- Care must be taken not to spread the contamination. Lateral spreading of the contaminants is a threat if proper precautions are not taken.
- Contaminants with low vapor pressures (<0.5 mm Hg) have poor removal efficiencies.
- The contaminant toxicity is not always altered if only air stripping is used, thus additional treatment technologies may be needed.
- Dead zones may be created. Dead zones are areas where the pneumatic pressure gradient is zero.
- The process has limited field scale data.
- At sites where dense non-aqueous phase liquids (DNAPLs) are present, air sparging has been observed to spread the immiscible phase and increase the size and concentrations of the contaminant plume.

- Contaminated water with VOC or semi-volatile concentrations greater than 0.01 percent generally cannot be treated by air stripping. Even at lower influent concentrations, air stripping may not be able to achieve cleanup levels required at certain sites.

Stage of Development

Air sparging/stripping is considered an innovative technology in terms of its applications. Like *in situ* soil vapor extraction, it is considered innovative applied technology which is beyond the developing stage of pilot-scale testing and bench-scale studies. It is a well developed technology with wide application.

The process was first utilized as a remediation technology in Germany in 1985, mostly to enhance the cleanup of chlorinated solvent contaminated groundwater. More recently, the technology was used in New Mexico for the enhanced remediation of gasoline contaminated soils and groundwater and in Pawtucket, Rhode Island, for decontamination of a gasoline spill site to remove contaminants from the saturated zone (EPA, 1990).

During 1988, air stripping was part of the selected remedy at 30 Superfund sites. In 1989, air stripping was a part of the selected remedy at 38 Superfund sites, and in 1990, it was selected to remedy over 40 sites. More than 1,000 air stripping units are in operation in the United States.

Applications and Effectiveness

Air stripping/sparging is best applied when any or all of the following conditions apply: 1) soil excavation is impossible, 2) the soil or groundwater contains contaminants with vapor pressures greater than 0.5 mm Hg, 3) the saturated zone needs to be treated, 4) large volumes of contaminated soil and groundwater need treatment, 5) site stratigraphy has relative intrinsic air permeabilities of 10⁻² to 10⁻⁵ cm/sec, and/or 6) when biological degradation of the contaminants may need enhancement.

Site geology is the most important design parameter. Air stripping/sparging is generally most effective in coarse-grained homogeneous soils which have lower air entry pressure requirements and provide a medium for more even air distribution. The fine-grained soils require higher air entry pressures and are more likely to cause the formation of significant gas pockets which, in turn, can cause lateral contaminant displacement and spreading.

As with SVE, the vapor pressure of the contaminants determines the "extractability" of the compound. The following contaminant groups are potential candidates for SVE-air sparging technology:

- Halogenated volatiles
- Halogenated semivolatiles
- Non-halogenated volatiles
- Non-halogenated semivolatiles
- BTEX compounds

A well-designed air stripper can remove more than 99.9% of the volatile petroleum hydrocarbons but cannot attain the 99.99% destruction and removal efficiency (DRE) requirement. Efficiencies tend to be highest for the most highly volatile compounds. Removal efficiencies for

BTEX can exceed 99% for a single pass system. Removal efficiencies under good conditions are generally 95-99% for trichloroethylene, tetrachloroethylene, and methylethylketone; however, higher efficiencies can be obtained by adding a second air stripper in series with the first.

Effective removals have been reported for contaminants at concentrations as high as 250,000 ppb. Typically, BTEX levels in petroleum-contaminated groundwater range from 1000-15,000 ppb, and these levels are readily removed by air stripping. The U.S. Air Force has effectively removed groundwater contaminants in the 63-19,000 ppb range.

Care should be taken in site evaluation to predict potential inhibitory chemical reactions that may occur in the aquifer as a result of the sparging process. An obvious example is compound sorption on soil organic material. Less obvious are the potential geochemical changes that may occur in the subsurface due to the introduction of the air or other gaseous medium. Another feasible interaction is the precipitation of dissolved minerals through changes in reduction-oxidation potential. The compounds most amenable to air sparging are the lighter petroleum compounds (C₃-C₁₀) and chlorinated solvents.

Case Studies

Air sparging is proving to be an effective treatment process. It removes a significant mass of contaminants and reduces dissolved concentrations in a relatively short period of time. Table 8 contains generalized information for the removal of three commonly encountered contaminants. Actual case studies and technology applications of air sparging are in Table 7. Cost data are included where available.

Contaminant	Treatment Time	Pounds Removed	% Reduction in Groundwater
PCE	8 months	1,100	97%
TCE	6 months	11,000	88%
BTEX	11 months	300	82%

The Novaterra, Inc., *in situ* steam and air stripping system uses a transportable treatment unit called the Detoxifier. The two main components of the treatment unit are the process tower and process train. The process tower contains two counter-rotating hollow-stem drills, each with a modified cutting bit 5 feet in diameter, capable of operating to a 27-foot depth. Each drill contains two concentric pipes. The inner pipe conveys steam to the rotating cutting blades. The steam is supplied by an oil-fired boiler at 450 degrees Fahrenheit and 450 pounds per square inch. The outer pipe conveys air at about 300 degrees Fahrenheit and 250 psi.

The steam heats the soil, increasing the vapor pressure of the volatile contaminants, and thereby increasing the rate at which they can be stripped. Both the air and steam convey these contaminants to the surface. The process area above ground is sealed from the outside environment, collects the volatile contaminants, and ducts them to the process train.

In the process train, the condensed water is separated from the contaminants by distillation, then filtered through activated carbon beds. The recovered concentrated organic liquid can be recycled or used as fuel in an incinerator.

The Detoxifier is also used to treat contaminated soil by injecting a wide range of reactive chemicals. Chemical injection processes include stabilization/solidification plus neutralization, oxidation, and bioremediation.

The vital factors of this process are as follows:

- The technology can treat volatile organic compounds (VOCs), such as hydrocarbons and solvents, and semi-volatiles, with sufficient vapor pressure in the soil.
- The technology is not limited by soil particle size, initial porosity, chemical concentration, or viscosity.
- In regard to stabilization and solidification, this technology also treats inorganics, heavy metals, and mixed wastes.

A site demonstration was performed the week of September 18, 1989, at the Annex Terminal, San Pedro, California. The results were as follows:

- Twelve soil blocks were treated for VOCs and SVOCs.
- More than 85% of the VOCs in the soil were removed.
- Up to 55% of the SVOCs in the soil were removed.
- Fugitive air emissions from the process were very low.
- No downward migration of contaminants resulted from the soil treatment.
- The process treated 3 cubic yards of soil per hour.

An air stripping system (EPA, 1987) which employed liquid phase GAC to polish the effluent, was installed at the Sydney Mine site in Valrico, Florida. The vital factors at this operation were the following:

- Consisted of an air stripping tower 4 feet in diameter and 42 feet tall, and contained a 24-foot bed of 3.5-inch diameter polyethylene packing.
- The average design water flow was 150 gallons per minute.
- Effluent water from the air stripper was polished in a carbon adsorption unit.

Co-Technologies/Alternative Technologies

Steam stripping is the most obvious co-technology to air stripping. In this case, the gaseous medium is steam as opposed to ambient air. Similar to this process is the injection of hot, moderately dry air. Both of these methods are thermally enhanced and tend to be more effective because they can volatilize contaminants that are not easily volatilized at ambient room temperatures.

Bioventing is another co-technology. The application of soil vapor extraction and bioremediation technologies with air sparging is an extraordinarily effective method of remediation. The addition of bioremediation allows for complete and permanent destruction of the contaminants.

Soil vapor extraction and bioventing are two co-technologies of air sparging. The application of soil vapor extraction and bioremediation technologies with air sparging may be an effective method for various sites. Enhancing degradation allows for the complete and permanent destruction of the contaminants. Refer to Table 7 for descriptions of co-technology applications with air sparging.

Cost Analysis

The costs for air sparging/stripping systems are similar to those of SVE systems. These costs include:

- Site assessment costs—associated with soil, soil gas, and groundwater sampling. These costs vary dramatically based on the characteristics of the site, depth to groundwater, soil texture, surface textures, etc., and would be expected to range from \$5,000 to \$25,000 per typical site.
- System construction costs—associated with the physical makeup of the SVE/air sparging systems. These costs, again, can vary dramatically based on the extent of the contamination, etc., and would be expected to range from \$20,000 to \$75,000 per typical site.
- System operation and maintenance costs—associated with blower, compressor, and piping system operation and maintenance, recovered liquid handling and disposal, and off-gas treatment. Operating costs for small blower/compressor systems are modest, ranging from \$20 to \$50 per month. Off-gas treatment, when required, represents approximately 50% of total system costs, etc. These costs may range from \$1,000 to \$2,000 per month.
- Overall system costs would be expected to range from \$35 to \$75 per cubic yard of contaminated soil in the unsaturated/saturated zones from petroleum-related site cleanups.
- Overall costs reported by the EPA, U.S. Air Force, and U.S. Army are consistent. In general, it was found that a total life cycle cost (TLCC), including \$8 million in capital costs for a 2900 gpm air stripper operating over 30 years, to be approximately \$0.27/1000 gallons when carbon adsorption is not required.
- Groundwater Technology, Inc., provided an approximate price range per unit waste treated. Their price of \$40 to \$70 per cubic yard does not include indirect costs such as excavation (if necessary), permits, and treatment of residuals.
- Adams and Clark (1991; p. 52) made cost estimates based on flows from 0.1 to 10 mgd assuming a removal efficiency of 99%. Within the range of Henry's Law coefficients of 0.1 to 1.0, the cost ranged from \$0.07/1000 gallons to \$0.70/1000 gallons. As the Henry's Law coefficient approached 0.005, the costs rapidly rose to \$7.00/1000 gallons.
- Hydro Group, Inc., gave an approximate range from \$0.04 to \$0.17 per 1000 gallons (Lenzo, 1985; p. C-6).

The unit cost to clean up the Superfund site in Des Moines, Iowa, for groundwater treatment is estimated to be about \$0.45/1000 gallons based on the 1250 gpm treatment rate and an average operating and maintenance cost of \$2,000,000 per year for ten years at 10% interest (Young et al., 1990.) The site consisted of primary VOCs; TCE-2800 ppb which declined to the 800 to 1000 ppb range after 5 months; and vinyl chloride-38 ppb which declined to undetectable levels. Overall the site had 85 to 96% removal efficiencies and averaged approximately 1300 gpm water flow rate for the air stripper.

The factors which most affect remediation costs are the extent of the contamination, as well as the depth of contamination below the soil subsurface. In addition, site preparation costs may cause the effectiveness of this treatment technology to diminish. Items such as site grading, soil compaction, etc., and necessary site modifications needed prior to the installation of the system, are a large portion of the total remediation costs.

An interesting note on factors affecting price: the firms questioned stated that the initial contaminant concentration is not a large issue in cost analysis because the technology has such low maintenance that the additional time would not appear to appreciably increase the overall cost.

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5.2.3 Steam Stripping

Technology Description

Steam stripping is an *in situ* physical process in which contaminants are stripped from the soil and/or groundwater. The use of steam enhances the stripping of volatile contaminants from the soil and can be used to displace contaminated groundwater under some conditions. Steam is injected into soils contaminated with VOCs or SVOCs via injection wells. Extraction wells transport the steam and contaminants from the unsaturated zone to the surface for treatment. The extracted nonaqueous liquids are separated by gravitational forces or a liquid/gas separator.

Mobile *in situ* steam extraction systems treat blocks of soil. Typical soil blocks measure seven feet by four feet and up to thirty feet deep. A complete site cleanup is performed block by block. The system consists of a process tower that supports and controls a pair of cutter blades which bore vertically through the soil. The cutter blades are rotated synchronously in opposite directions during the treatment process to break up the soil and ensure flow of the gases (blade movements also allow treatment of low-permeability soils). Steam (400°F) and compressed air (275°F) are piped to nozzles located on the cutter blades. Heat from the injected steam and hot air then volatilizes the organics. A vacuum/blower system pulls the gases from the soil to the area covered by a steel shroud to protect against leakage to the outside environment. Once the gases reach the treatment train, water and organics are removed by condensation in coolers. The air-steam is then treated by carbon adsorption, compressed, and returned to the soil being treated. The water is removed from the liquid stream in a gravity separator, followed by batch distillation and carbon adsorption, and is then recycled to a cooling tower. Finally, the condensed organics are collected and held for removal and transportation.

A stationary *in situ* steam extraction system performs primarily the same function as a mobile system. High-quality steam is delivered through injection wells from the manifold. Gases and liquids are removed by the recovery wells. The gases then flow through a condenser and into a separation tank where water and condensed gases are separated from the contaminant phase. The liquid organics and water are pumped separately into holding tanks for treatment and disposal. The non-condensable gases are passed through activated carbon tanks where contaminants are adsorbed before the clean air is vented to the atmosphere.

Steam flushing is a technology which introduces not only water vapor, but also heat. The heat from the steam enhances the volatilization of the contaminants and accelerates the rate of reaction. In conjunction with a vacuum technology, such as SVE, steam flushing can be an effective tool to quicker clean up actions and reduced remedial costs.

Advantages of Steam Stripping:

- It can treat zones of high contaminant concentration in the unsaturated zone or below the water table.
- Simultaneous treatment of groundwater and soil provides more rapid remediation.
- Reagents are not required to be injected into the ground in order to enhance treatment.
- The stationary process is not limited to the depth of the groundwater.

- The technology uses readily available components such as injection and extraction wells, liquid/vapor separators, and emission control equipment.
- Soils which are contaminated with VOCs and SVOCs can be treated without excavation.

Disadvantages of Steam Stripping:

- It is energy intensive.
- Interactions in the subsurface may decrease the effectiveness of the process.
- Soil conditions such as high moisture content, large soil aggregates, and stratification affect technology success.
- Technology may not achieve regulatory cleanup levels, thus additional treatment technologies may be needed.
- The contaminant toxicity is not always altered if only steam stripping is used, thus additional treatment technologies may be needed.
- Limited field-scale performance data are currently available.
- Requires a site with predominantly medium- to high-permeability soil.
- Mobile treatment systems are limited by depth and are mechanically complex.
- It may not remove SVOCs effectively; additional treatment may be necessary.
- Increased soil temperatures may adversely affect other soil properties.
- This technology cannot be performed on soils near the surface unless a cap is put into place.
- This technology is applicable to contaminants which are lighter than water, and should not be performed on denser than water contaminants due to percolation concerns.

Stage of Development

In situ steam extraction is an emerging technology. In conjunction with air stripping, it is currently being performed on at least two sites in the EPA Superfund SITE program. There are at least four vendors promoting *in situ* steam extraction, usually in conjunction with air stripping and/or air sparging. Solvent Service, Inc., is using and testing its first full-scale stationary Steam Injection Vapor Extraction (SIVE) system at its San Jose, California, facility for remediation to a depth of twenty feet of up to 41,000 cubic yards of soil contaminated with numerous organic solvents (Dorrlar and Green, 1993).

SITE demonstrations of this type of technology were performed at the Annex Terminal in San Pedro, California, and at a site in Huntington Beach, California. This technology is currently commercially available.

Applications and Effectiveness

The process is more effective in extracting less volatile compounds than ambient vacuum extraction systems, and has a wide range of applications. Steam extraction has larger applications in reference to a variety of contaminants. Steam extraction has been shown to be effective in treating and/or removing contaminants in soil and groundwater such as VOCs, SVOCs, select fuel

hydrocarbons, PCBs, pesticides, dioxins/furans, cyanides, and some inorganics. It is particularly effective at extracting alkanes and alkane-based alcohols such as octanol and butanol. Hydrocarbons which are suitable for this treatment include gasoline, diesel, jet fuel, TCE, TCA, and dichlorobenzene (DCB).

In general, there may be residual soil contamination after application of steam extraction. Studies of mobile systems show the average removal efficiencies for volatile contaminants to be 85 percent (15 percent of the volatile compounds remained in the soil). The minimum contaminant concentration achievable with steam extraction is usually 5-50 mg/kg in soil and 5-100 ug/L in groundwater.

Case Studies

A number of case studies and/or applications of steam extraction are presented in Table 7.

Co-Technologies/Alternative Technologies

Integrated vapor extraction and steam vacuum stripping (a thermally enhanced SVE system) simultaneously treat groundwater and soil contaminated with VOCs much like the air sparging system. A vacuum stripping tower that uses low-pressure steam to treat contaminated groundwater, and the SVE process to treat the contaminated soil, form a closed-loop system that remediates contaminated groundwater and soil *in situ*.

Steam extraction may also be used in conjunction with a number of other technologies such as pneumatic fracturing and hydraulic fracturing, which both enhance removal efficiency. In addition, air stripping, chemical processes, and biological processes may be applied after steam extraction to treat the resulting contaminated stream.

Cost Analysis

The most significant factor affecting cost is the time of treatment or treatment rate. With the mobile system, treatment rate is influenced primarily by the soil type, waste type, and on-line efficiency. Cost estimates for this technology are strongly dependent on the treatment rate and range. On average, the cost ranges from \$100 to \$300 per cubic yard based on a 70 percent on-line efficiency.

In stationary *in situ* systems, the most significant factor influencing cost is the number of wells required per unit area, which is related to the depth of contamination and permeability. Shallow contamination requires lower operating pressures to prevent soil fracturing and closer well placement. Deeper contamination requires higher operating pressures and greater well spacing, therefore fewer wells and lower capital costs. Cost estimates for this technology range from about \$50 to \$300 per cubic yard, depending on the site characteristics.

Costs for specific site remediations can be found in Table 7.

Personal Contacts

Refer to Table 7 for a complete list of personal contacts relative to specific case studies/applications. For further information, the following individuals may be contacted:

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5.2.4 Air Stripping (*ex situ*)

Technology Description

Air stripping *ex situ* is an established technology for removing volatile organic compounds from contaminated wastewater. A physical separation process, air stripping volatilizes organic compounds by transferring them from a liquid to a gaseous phase. Several designs have been used over the years, but the packed-tower design is the most common in environmental engineering applications.

Packed towers are continuous-contact equipment that bring two phases in close contact with each other and allow mass to be transported across the boundaries. They usually operate in a

countercurrent mode with the water trickling down the packing by gravity and the air being forced upward through the bed.

Important parameters for the design of air strippers are:

- Contaminant type and levels of contamination: the higher the volatility of the compound, the easier stripped by aeration.
- Type of packing and packing height: packing should provide large wetted surface, should be inert, and should have a large void volume to minimize serious pressure drop.
- Air to water ratio, which is a function of contaminant type and temperature. Typical values are 30:1 for volatile compounds and 200:1 for compounds with high aqueous solubility.
- Liquid loading, which is typically 25 to 30 gpm per square foot.
- Water temperature.

Pilot studies may be necessary to obtain mass transfer coefficients and Henry's law constants if data are not available.

Air stripping towers can efficiently and economically remove VOCs such as:

- Vinyl chloride,
- Trichloroethane (TCA),
- Trichloroethylene (TCE), and
- Tetrachloroethylene (PCE);

and pesticides such as:

- Chlordane,
- Dibromochloropropane, and
- Aldicarb;

and halogenated aromatics such as dibromobenzene. Removal efficiencies of 99.99 percent have been achieved in many cases.

Advantages of Air Stripping:

- Effective at removing a wide array of VOC contaminants.
- Systems are well established due to long history of air pollution control applications.

Disadvantages of Air Stripping:

- May require local air pollution control permit.

Stage of Development

Ex situ air stripping of contaminated groundwater is a well developed, commercially available technology. During 1988, air stripping was used as a partial remediation step in conjunction with other remedial technologies at 30 Superfund sites. Air stripping was used in conjunction with other technologies to remediate 38 Superfund sites in 1989 and over 40 sites in 1990. More than 1,000 air stripping units are estimated to be in operation in the United States.

Applications/Effectiveness

Air strippers can provide very efficient treatment. A well designed air stripper can remove more than 99.9 percent of volatile petroleum hydrocarbons. Efficiencies are greatest for the most highly volatile compounds. Removal efficiencies for benzene, toluene, ethylbenzene, and xylene can exceed 99 percent. Removal efficiencies under standard operating conditions are generally 95 to 99 percent for trichloroethylene, tetrachloroethylene, and methylethylketone. However, higher efficiencies can be obtained by adding a second air stripper in series.

Effective removals have been reported for contaminants at concentrations as high as 250,000 ppb. Typically, BTEX levels in petroleum-contaminated groundwater range from 1,000 to 15,000 ppb, and these levels are readily removed by air stripping. The U.S. Air Force has effectively removed groundwater contaminants in the 63 to 19,000 ppb range.

Case Studies

An EPA study (EPA, 1987) analyzed the performance of 177 air-stripping systems in the United States. The study presented data on system design, contaminant types, loading rates, and removal efficiencies for 52 sites. Table 9 summarizes data from 46 of those sites, illustrating experience with a wide range of contaminants.

Several technology applications and/or case studies of air sparging are presented in Table 7. Cost data are included where available.

Co-Technologies/Alternative Technologies

Treatment of the off-gases generated during air stripping operations may be required. Activated carbon is the most frequently used technology for air emissions control.

Cost Analysis

The cost of air stripping can vary widely depending on the design and types of contaminants to be treated. The following outlines several reported costs:

- Overall costs reported by the EPA, U.S. Air force, and U.S. Army are consistent. In general, it was found that a TLCC, including \$8 million in capital costs for a 2,900 gpm air stripper operating over 30 years, to be approximately \$0.27/1,000 gallons when carbon absorption is not required.
- Adams and Clark (1991) made cost estimates based on flows from 0.1 to 10 mgd assuming a removal efficiency of 99 percent. Within the range of Henry's Law Coefficients of 0.1 to 1.0, the cost ranged from \$0.07/1,000 gallons to \$0.70/1,000 gallons. As the Henry's Law Coefficient approached 0.005, the costs rapidly rose to \$7.00/1,000 gallons.
- Hydro Group, Inc., gave an approximate range from \$0.04 to \$0.17 per 1,000 gallons (Lenzo, 1985).
- The unit cost to air strip groundwater at a Superfund site in Des Moines, Iowa, was estimated to be about \$0.45/1,000 gallons based on a 1,250 gpm treatment rate and an average operating and maintenance cost of \$200,000 per year for 10 years at 10 percent interest (Young *et al.*, 1990). The site consisted of primary VOCs; TCE-2,800 ppb which

declined to 800 to 1,000 ppb range after 5 months; and vinyl chloride-38 ppb which declined to undetectable levels. Overall the site had 85 to 96 percent removal efficiencies and averaged approximately 1,300 gpm water flow rate for the air stripper.

Table 9. Reported Air-Stripper Removal Efficiencies from 46 Sites

Contaminant	No. of Data Points	Influent Concentration (g/L) Average	Reported Removal Efficiency (%) Average
Aniline	1	226	58
Benzene	3	3,730	99.6
Bromodichloromethane	1	36	81
Bromoform	1	8	44
Chloroform	1	530	48
Chlorobenzene	0	95	ND*
Dibromochloromethane	1	34	60
Dichloroethylene	7	409	98.6
Diisopropyl ether	2	35	97.0
Ethylbenzene	1	6,370	99.8
Ethylene dichloride	7	173	99.3
Methylene chloride	1	15	100
Methyl ethyl ketone	1	100	99
2-Methylphenol	1	160	70
2-Methyl tertiary butylether	2	90	97.0
Perchloroethylene	17	355	96.5
Phenol	1	198	74
1,1,2,2-Tetrachloroethane	1	300	95
Trichloroethane	8	81	95.4
Trichloroethylene	34	7,660	98.3
1,2,3-Trichloropropane	1	29,000	99
Toluene	2	6,710	98
Xylene	4	14,823	98.4
Volatile Organic Compounds	3	44,000	98.8
Total Volatile Organics	46	11,120	97.5

* It is important to note that, because different system designs were used for these sites, the results are not directly comparable from site to site.

Source: EPA, Air Stripping of Contaminated Water Sources - Air Emissions and Controls, EPA/450/3-87/017, 1987.

Personal Contacts

Refer to Table 7 for a complete list of personal contacts relative to specific case studies/applications. For further information, the following individuals may be contacted:

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5.2.5 Soil Washing

Technology Description

Soil washing is an *ex situ* physical/chemical separation technology in which excavated soil is pretreated to remove large objects and soil clots and then washed with fluids (water, water/chelating agents, water/surfactants, acids, or bases) to remove contaminants. Soil washing is used in conjunction with other treatment technologies in order to reach the regulatory levels; thus it is

considered a waste reduction, not a contaminant destruction, technology. To be effective, soil washing must either transfer the contaminants to the wash fluid and/or concentrate the contaminants in a fraction of the original soil volume. The contaminated fraction is removed by using size and/or density separation techniques. Ultimately, either the washing fluid or the fraction of soil containing most of the contaminant, or both, must be further treated.

This technology works on the premise that many soil contaminants, both organic and inorganic, tend to chemically and physically bind to the silt or clay fractions of the soil. The silt and clay, in turn, tend to attach to coarser sand and gravel particles. The soil washing process separates the silt and clay away from the coarser fractions. The coarse soil may either be re-deposited on site or otherwise be used in a beneficial way, such as backfill. The contaminated residual generated (usually 10 to 30 percent of the original volume) can be subsequently treated by appropriate destruction or immobilization techniques such as bioremediation or incineration.

The techniques and unit operations employed in soil washing are largely transferred from the minerals processing field. The overall principle of the technique is to agitate the soil in a solution that tends to enhance desorption of the contaminants. Various chemical agents may be used to enhance this process. Typically, the soil is processed through a shearing device and vibratory screen. The screen has a spray system which cleans large rocks and other debris and separates the debris by size. Material passing through the screen is scrubbed by the use of Venturi jets. The solution utilized may contain surfactants and chelants which displace hydrocarbons, metals, and other inorganic and organic substances from the soil particles. In some cases, the soil wash solution can then pass through a column containing metal adsorbent materials. The metal ion free chelating agent is then reused for soil washing. There may be a pH adjustment required prior to the column in order to optimize adsorption. Separation of fines from the coarse fraction is performed by a variety of methods including gravitation, centrifuge, and others.

Advantages of Soil Washing:

- A wide variety of chemical contaminants can be removed; soil washing provides treatment of soils containing both organic and inorganic contaminants.
- Remediation can be performed on-site.

Disadvantages of Soil Washing:

- Not a one-step technique. Residuals must be further treated or disposed.
- Soils with a high affinity for a specific contaminant, or containing low concentrations (less than 0.5 ppm), may not be viable for washing.
- Complex mixtures of contaminants and frequent changes in contaminant composition may require sequential washing steps.
- The contaminant toxicity is not altered or destroyed.
- To operate economically, the contaminated material should not contain more than 20 to 30 percent fines.
- Heavy water usage is required with the estimated amount for 1,000 cubic yards of soil at 130,000 to 800,000 gallons of water.
- The excavated and treated soil will need to be contained and covered.

Stage of Development

Soil washing is considered an innovative technology which has been demonstrated in several pilot- and full-scale operations. However, it lacks well documented cost and performance data under a variety of operating conditions. Extensive research at different operating conditions is required to establish soil washing as an effective full-scale remediation technology.

At the present time, soil washing is used extensively in Europe and has had limited use in the United States. Bergmann USA has constructed over 20 full-scale commercial installations ranging from 5 to 350 tons per hour.

During 1986-1989, the technology was one of the selected source control remedial technologies at eight Superfund sites. As of February 1992, the Superfund program uses soil washing in at least 14 sites.

Applications and Effectiveness

The primary factor limiting the effectiveness of soil washing technology is the soil particle size. Soils must have low clay, silt, and organic content in order to attain the most effective performance. The contaminant is concentrated in the clay portion and removed from the coarse fraction.

In Europe, soil washing has been used in numerous full-scale and commercial operations. In soils consisting mostly of sand, it has been found to effectively remove cyanide, heavy metals, and halogenated and non-halogenated hydrocarbons. For these reasons, soil washing works well with sandy soils.

The following is a list of the particular contaminant groups that are potential candidates for the soil washing technology:

- Halogenated volatiles,
- Halogenated semi-volatiles,
- Non-halogenated volatiles,
- Non-halogenated semi-volatiles,
- Polynuclear aromatics (PNAs),
- Polychlorinated biphenyls (PCBs),
- BTEX,
- Solvents,
- Organic/inorganic cyanides,
- Organic/inorganic corrosives,
- Heavy/radioactive metals,
- Arsenic, selenium, and
- Organometallic pesticides/herbicides.

Vendors promoting the technology claim that it can operate effectively on concentrations in the 15,000-20,000 ppm range, which is considered quite good in comparison to most other innovative technologies.

Washing solutions vary, depending primarily on the pollutants being removed. Water is most effective in removing any water soluble or water-mobile constituents, while surfactants are best for PCBs (particularly anionic surfactants which are ones that contain a negative charge and will not bind with the soil, which is predominantly negatively charged). Acidic aqueous solutions (sulfuric, hydrochloric, nitric, phosphoric, and carbonic acid) are effective for recovering metals and basic organic constituents (amines, ethers, anilines).

Soil washing rates are relatively high. Assuming an average processing capacity of 15 tons/hour (within the range of demonstrated capabilities for soil washing), a standard site containing 20,000 tons of contaminated media, and 24-hour per day operation, the time to complete cleanup is approximately 19 weeks (including two months for start-up and demobilization).

Case Studies

Several case studies and/or technology applications are presented in Table 10.

Table 10. Soil Washing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Biogenesis Soil Cleaning Process	Tech. Contact: Charles Wilde Biogenesis Enterprises, Inc. 10626 Beechnut Ct. Fairfax Station, VA 22309-1926 703-250-3442 EPA Contact: Annette Gatchett 513-569-7620	Integrated soil washing and biodegradation technologies.	Soil (oversized particles removed prior to treatment)	Volatile and non-volatile hydrocarbons, pesticides, and other organics	Full-scale operation began 1989. Commercially available.	No results available. Cost data estimated at \$80-210/ton.
Soil Washing - High Pressure Water Jet-Modified	Klockner Umweltechnik. Reference - Raghavan <i>et al.</i> , 1988.	Physical extraction to remove contaminants. Soil blasted with a water jet at 5,075 psig.	Soil no more than 20% of particles <63 m.	Aliphatics and aromatics with densities <water, volatile organics, some other hydrocarbons	Pilot-scale	96.3 percent removal of HC (82.05 ppm residual). Greater than 75 percent removal of chlorin-HC (<0.01 ppm residual). 99.8 percent removal of aromatics (<0.02% residual). 99.8 percent removal of phenol

Table 10. Soil Washing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
BioTrol Soil Washing System (BSWS)	Tech. Contact: Pamela Sheehan BioTrol, Inc. 210 Carnegie Center Suite 101 Princeton, NJ 08540 609-952-0316 EPA Contact: Mary Stinson 908-321-6683	Water based volume reduction process. Extraction agent-hot water with surfactant. Multi-stage separation and washing. Process water treated biologically.	Bulk soil	Oil & grease	Full-scale application of 20 tons/hr began in 1988. Commercially available. EPA SITE demonstration program.	90-95% removal for PCP (<115 ppm residual). 85-95% removal for most other organics (<1 ppm residual). Cost estimate of \$168/ton.
Soil Washing	MTA Remedial Resources Reference - Trost and Rickard, 1987	Extraction agents are surfactants and alkaline chemicals. Removes inorganics using counter-current decantation with leaking.	Soil (oversized particles removed prior to treatment)	Organics (oil), heavy metals (inorganics) removed using countercurrent decantation with leaking	Bench-scale.	98-99+ percent removal of VOCs (<50 ppm residual). 98-99+ percent removal of SVOCs (<250 ppm residual) and 98-99+ percent removal for most fuel products (<2200 ppm residual).
Soil Washing	Ecotechniek BV Reference - Raghavan <i>et al.</i>	Utilizes no extraction agents. Uses a water-sand	Sandy soil	Crude oil	Commercial scale of 100	About 90 percent

Table 10. Soil Washing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Soil Washing	Harbauer of America Reference - Raghavan <i>et al.</i> , 1988 and Nunno <i>et al.</i> , 1988.	Multi-stage processes. Pre-treatment screens and electromagnetic washers. Utilizes hydraulically produced oscillation/vibration. Surfactants are used for extraction and acids and bases for pH.	Soil particles 15mm - 5mm. Process removes larger particles.	Mostly organics & limited heavy metals	Commercial scale of 15-20 tons/hr.	96 percent removal of total organics (159-201 ppm residual). 86-94 percent total phenol removal (7-22.5 ppm residual). 86-90 percent polyaromatic hydrocarbons (PAH) removal (91.4-97.5 ppm residual). 84-88 percent PCB removal (0.5-1.3 ppm residual).
EPA's First Generation Pilot Drum Screen Washer	Annette Gatchett U.S. EPA-RREL 26 W. Martin Luther King Drive Cincinnati, OH 45268 513-569-7620	Biodegradable surfactant (aqueous slurry) used as extraction agent. Utilizes drum-screen washer.	Soil >2 mm	Petroleum hydrocarbons	Pilot-scale operation began 1988.	99% oil removal (<5 ppm residual). 90% grease removal (2400 ppm residual).

Table 10. Soil Washing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Soil Washing	HWZ Bodemsanering BV. Reference - Raghavan <i>et al.</i> , 1988.	Utilizes NaOH to adjust pH and various surfactants for extraction.	Soil particles <10 mm & >63 mm.	Cyanide, chlorinated HC, some heavy, metals, polynuclear aromatic compounds (PNAs)	Commercial scale of 20-25 tons/hr. Operation began 1984.	95 percent removal of cyanide (5-15 ppm residual). 98 percent removal of PNAs (15- 20 ppm residual). 98 percent of Chlorin-HC (1 ppm residual). 75 percent removal of heavy metals (75-125 ppm residual).
Soil and Sediment Washing (Bergmann USA)	Tech. Contact: Richard Traver Bergmann USA 1550 Airport Road Gallatin, TN 37066-3739 615-452-5500 EPA Contact: S. Jackson Hubbard 513-569-7507	Water and chemical additive based volume reduction process.	Sediment and soils	Heavy metals and organics	EPA SITE demonstration program acceptance and field-scale study evaluated at two sites.	Results and cost data not available.
Soil Washing	Soil Cleaning Company of America Reference - Smarkel 1988	Implements three screw conveyors operated in series. Hot water with	Bulk soil	Oil & grease	Bench-scale.	50-83 percent oil & grease removal (250-

Table 10. Soil Washing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
EPA's Mobile Counter-Current Extractor	Annette Gatchett U.S. EPA-RREL 26 W. Martin Luther King Drive Cincinnati, OH 45268 513-569-7620	Four-stage counter-current chemical extractor. Various extraction agents, solvent additives, surfactants, redox acids and bases, and chelating agent, EDTA. Uses drum-screen.	Soil 2-25 mm in particles in drum washer and <2 mm in 4 stage extractor	Soluble organics (phenol, etc.) and heavy metals (Pb, etc.)	Full-scale application of 4.1 tons/hr. Operation began in 1982.	80-90 percent removal of phenol (1-96 ppm residual) and 50-80 percent removal of As ₂ O ₃ (0.5-1.3 ppm residual).
Soil Washing Plant (<i>Brice Environmental Services Corporation</i>)	Tech. Contact: Craig Jones BESCORP P.O. Box 73520 Fairbanks, AK 99707 907-452-2512 EPA Contact: Hugh Masters 908-321-6678	Highly portable above ground process for overall volume reduction.	Soil	Heavy and radioactive metals	EPA SITE demonstration completed.	Remediation of lead-contaminated soil at the Alaskan Battery Enterprises. Publication scheduled for 1993. No cost data available.
Soil Washing and Catalytic Ozone	Tech. Contact: Lucas Boeve Excalibur Enterprises, Inc. 2111 E. 1st St., Suite 412 Anchorage, AK 99503 907-561-1111	Two-stage process including extraction of contaminants from soil and the oxidation of	Soil, solids, sludge, leachates, and	PCBs, PCPs, pesticides, herbicides,	EPA SITE demonstration acceptance.	No results or cost data available.

Table 10. Soil Washing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Volume Reduction Unit <i>(Risk Reduction Engineering Laboratory)</i>	Tech. Contact: Patrick Augustin U.S. EPA Risk Reduction Engineering Laboratory 2890 Woodbridge Ave. Edison, NJ 08837 908-906-6992 EPA Contact: Teri Richardson 513-569-7949	Mobile volume reduction system designed to remove organic contaminants from soil through particle size separation and solubilization.	Soil	Organics and metals	EPA SITE demonstration program acceptance. Demonstration scheduled.	No results or cost data available.
Debris Washing System <i>(Risk Reduction Engineering Laboratory and IT Corporation)</i>	Tech. Contact: Michael Taylor IT Corporation 11499 Chester Road Cincinnati, OH 45246 513-782-4700 EPA Contact: Naomi Barkley 513-569-7854	Debris washing system includes 300 gallon spray and wash tanks, surfactant and rinse water holding tanks, and an oil-water slurry separator.	Metallics, masonry, or other solid debris	Pesticides, PCBs, lead, and other metals	Pilot-scale EPA SITE demonstration. Full-scale planned.	At the Carter Industrial Superfund site in Detroit, MI, PCB reductions averaged 58 percent in batch 1 and 81 percent in batch 2. No cost data available.

Co-Technologies/Alternative Technologies

Since soil washing is producing concentrated waste streams, it can be integrated with many other technologies. Examples of pre-treatment and post-treatment co-technologies include:

Debris Washing: This technology takes advantage of the relative ease with which contaminants can be removed from large pieces of debris. The debris washing system is a mobile unit on a 48-foot semi trailer and is assembled at the site on a 25- by 24-foot concrete pad. A basket of debris is sprayed with a high pressure stream of detergent solution from a tank. The solution is recycled after purification and the contaminant is collected in filters and activated carbon canisters.

Catalytic Ozone Oxidation: This system is designed to treat residuals with organic and inorganic contaminants. It is similar in design to the generic system; contaminants, once removed from the soil, are destroyed by oxidation using ozone and UV radiation. The decontaminated water is recycled through the system, reducing the need to dispose of large quantities of contaminated water.

Solvent Extraction: This design uses liquefied gas solvent to remove organics from the residuals. Carbon dioxide is used for aqueous solutions, while propane or butane is used for sludges and soils. A separator is used to vaporize the solvent and segregate it from the organic contaminants, which are collected in a carbon packed absorber and disposed.

In addition to these technologies, bioremediation, incineration, and other techniques are being used to treat the process residuals.

Cost Analysis

Average cost for use of this technology, including excavation, is approximately \$120-\$200/ton, depending on the target waste quantity and concentration. The upper end of this range would include costs for residual disposal, which is the primary cost consideration. The U.S. Air Force and Environmental Protection Agency rated the cost outstanding (less than \$275/ton) based upon one of six possible ratings against 42 other remediation technologies. However, potential sites should have a minimum of 5,000 tons of material in order to justify mobilization costs required to perform soil washing.

The relatively low cost of this technology can be attributed to several factors. Readily available mining equipment are utilized, resulting in a simpler operation, and operation requires a staff of only 5-12 persons. Assuming cleanup duration of 19 weeks, operations would require less than 5 person-years.

Another factor to consider is that contaminants are removed from coarse soil fractions (greater than U.S. standard 200-mesh sieve) with relatively high removal efficiencies (95-99.99 percent) at low to moderate costs. On the other hand, fine soils, silts, and clays (less than 200-mesh) achieve only moderate contaminant removal efficiencies (50-90 percent) at a moderate to high cost. Thus, the site soils must be carefully characterized before soil washing is chosen as the technology for remediation. For large soil volumes (greater than 100,000 to 250,000 tons), costs will be substantially reduced, particularly for a fixed facility with an operating life of five years or more. Larger capacity and longer periods of capital recovery would lower total treatment costs to approximately \$25 to \$40 per ton.

Various vendors of soil washing technologies have provided an approximate price range per unit waste treated. These prices do not include indirect costs such as excavation (if necessary), permits, and treatment of residuals, which are given in Table 11.

Table 11. Soil Washing Vendors and Typical Cost Ranges	
Vendor	Cost (\$/ton)
Bergmann, USA	75-125
BioTrol	100-200
Canonie Environmental	50-100
Northwest Environmental	50-150
OHM	50-150
On-site Technology	60-120
Waste Technology Services	70-150
A more realistic estimate of the total soil washing costs would include items such as the permits and feasibility studies and would be in the range of \$165 to \$250 per ton. Table 10 includes cost data from specific case studies.	

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- Pflug, A. D. (no date). Abstract of treatment technologies. BioTrol, Inc., Chaska, Minnesota.
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Stinson, M. K. *et al.* 1988. Workshop on the extractive treatment of excavated soil. Environmental Protection Agency.

Traver, R. P. 1987. Interim report investigation of feedstock preparation and handling for mobile on-site treatment technologies. Environmental Protection Agency. Contract No. 68-03-3450.

Trost, P. B. and R. S. Rickard. 1987. On-site soil washing - a low cost alternative. Presented at ADPA.

United States Air Force and Environmental Protection Agency. 1993. Remediation technologies screening matrix and reference guide, version 1. Report No. EPA 542-B-93-005.

Williams, D. and C. Gutterman. 1991. Soil washing technologies for soils contaminated with heavy metals. Environmental Protection Agency.

5.2.6 Soil Flushing

Technology Description

Soil flushing is an *in situ* process used to remove organic and/or inorganic contaminants from soils. *In situ* soil flushing consists of injecting a solvent or surfactant solution (or water) to enhance the contaminant solubility, which results in increased recovery of contaminants. Flushing fluid is applied to the contaminated soil *in situ* by above-ground sprayers, surface flooding, or subsurface injection wells. These fluids then percolate through the soil to remove contaminants on their way to the ground water. The system is similar to pump and treat technology which includes extraction wells drilled in the contaminated soils zone, reinjection wells upgradient of the contaminated area, and a wastewater treatment system. The contaminants are separated from the elutriate, and the extracting agents are recycled back to the process. Recovery of the elutriate is required to prevent uncontrolled contaminant migration to uncontaminated areas. Hydraulic gradients, slurry walls, or other engineering designs are utilized to ensure that none of the contaminants escape without treatment.

Removal of contaminants from the soil can take place via three mechanisms: displacement, solubilization, and dispersion. Displacement occurs when the contaminants are carried through the soil pores. This mechanism is dependent on the ratio of the viscous pressure drop across the contaminant/flushing solution interface. Solubilization occurs when the contaminant solubility in the flushing solution is increased. Dispersion occurs when reduced surface tension between the flushing solution and the contaminant cause the contaminant to disperse and become trapped within the flushing solution.

Contaminated flushing fluids are considered hazardous, thus their handling requires special safety precautions. Appropriate personnel protection and handling requirements should be included in the site safety plan.

If underground injection wells are to be used, an underground injection control (UIC) permit may be required. If the groundwater is not recycled after treatment, a National Pollution Discharge Elimination System (NPDES) permit or comparable state permit will be required.

Climatic conditions should be considered when designing a soil flushing site. Precipitation may cause surface runoff which must be captured to ensure contamination does not spread if the site

becomes saturated. Freezing conditions may pose problems for above ground sprayers and other shallow fluid dispersal mechanisms.

Advantages of Soil Flushing:

- Removal of contaminants is long term; no additional treatments are necessary if the soil flushing process is successful.
- Technology is easily applied to homogeneous permeable soils.
- Costs are moderate, depending on the flushing solution chosen, particularly due to the *in situ* capability.
- Soil flushing can be integrated with a number of other technologies, such as bioremediation.
- Mixtures of organic and inorganic contaminants can be removed.

Disadvantages of Soil Flushing:

- Technology introduces potential toxins (the flushing solution) into the soil system.
- Physical/chemical properties of the soil system may be altered because of the introduction of the flushing solution.
- Potential exists for solvents to transport contaminants away from the site into uncontaminated areas.
- Potential exists for incomplete removal of contaminants due to soil heterogeneities.
- Further treatment of the recovered contaminants is required.

Stage of Development

Soil flushing is an emerging technology and has been applied in both pilot-and full-scale systems. All equipment and materials required for installation of soil flushing systems are commercially available. As of September 1991, the EPA (1991) has reported 12 applications of soil flushing at various Superfund sites for a variety of contaminants. Most of the available data are from bench- and pilot-scale studies. Several researchers are exploring the potential of surfactants to remove or make available for bioremediating contaminants of low aqueous solubility.

Applications and Effectiveness

The level of treatment achieved by soil flushing will vary, depending on the contact of the flushing solution with waste constituents, the effectiveness of the surfactants solutions, the soil adsorption properties, and the hydraulic conductivity of the soil. This technology should produce the best treatment results in homogenous, highly permeable soils having low organic content. If the surfactant application rate is carefully controlled, permeation and washing of the intended zone can be successfully accomplished without significant lateral spread of the surfactant and leachate. Furthermore, careful control of the rate of recovery of the leachate at the water table can lead to the complete recovery of the leachate.

Surfactants used in flushing fluids or precipitates formed as byproducts to soil flushing additive chemical reactions may block the small passageways between the soil particles. This blockage may form a "mat" which impedes fluid flow and will halt flushing in that area of soil.

Field data on the effectiveness of this technology are not widely available in the United States. Bench- and pilot-scale results have been reported by Nash (1988), Dworkin *et al.* (1988), Kuhn and Piontek (1989), EPA (1984), and Dermatas and Korfiatis (1993).

Case Studies

Several case studies and technology applications are provided in Table 12.

Co-Technologies/Alternative Technologies

Several physico-chemical and biological processes may be integrated with soil flushing to achieve complete site remediation. Such technologies must be used to treat the recovered contaminated fluid matrix.

Soil flushing can be used as a pretreatment in sites containing Non-Aqueous Phase Liquids (NAPLs), followed by bioremediation or soil vapor extraction.

Cost Analysis

Since soil flushing is used in conjunction with other technologies, overall costs can be very high. The system may be economically viable for a variety of organic compounds including PCP, creosote, and heavy metals. The cost of soil flushing depends greatly on the type and concentration of surfactants used, and the recycle and recovery of surfactants. Rough estimates ranging from \$25 to \$250 per cubic yard have been reported in the literature.

Table 12. Soil Flushing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Application/Case Studies
Soil Flushing	United Chrome Products Michael Gruenfeld U.S. EPA-RREL 2890 Woodbridge Ave., Bldg. 10 Edison, NJ 08837 908-321-6625	Two percolation basins installed to flush soil.	Soil	TCE and chromium	Developing stage with limited application. Currently, being tested at over 12 Superfund sites.	Average removal of 80 percent for hexavalent chromium. No cost data available.
Soil Flushing	PRP Lead Tech. contact: Eduardo Gonzales New York, NY 212-264-5714	Flushing being performed on an uncontrolled dump site and landfill at Byron Barrel & Drum, NY.	Soil (5,200 cubic yards)	VOCs (PCE, TCE, DCE, and DCA)	Developing stages.	No results or cost data available.
Soil Flushing	Fund Lead; Bechtel Environmental, Inc. Fred Cataneo New York, NY 212-264-9542	Flushing being performed at a commercial dump site, Lipari Landfill, NJ.	Soil (650,000 cubic yards)	VOCs (benzene, DCA, dichloro-methane, and toluene), phenol, and metals	Developing stages.	No results or cost data available.
Soil Flushing	Fund Lead; Crosby & Overton, EMI (subcontractors to Reidel Env. Services)	Flushing performed at a commercial waste management site, Poly-Carb. NV.	Soil (1,500 cubic yards)	Phenols and cresol	Process completed, operational 7/87-8/88	No results or cost data available.

Table 12. Soil Flushing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Application/Case Studies
Soil Flushing	Waste Tech. Services, Inc. Michael Gruenfeld U.S. EPA-RREL 2890 Woodbridge Ave, Bldg. 10 Edison, NJ 08837 908-321-6625	Consists of slowly flooding soil surface with water. Then utilizing alkaline agents, polymers and surfactants.	Soil	Creosote (TEO)	Developing stage with limited application. Currently, being tested at over 12 Superfund sites.	84 to 96 percent reduction of TEO. No cost data available.
Soil Flushing	Tech. Contact: Michael Gruenfeld U.S. EPA-RREL 2890 Woodbridge Ave. Bldg. 10 Edison, NJ 08837 908-321-6625	Infiltrated water into the ground by ditches. Leaching liquid and polluted groundwater were pumped out and treated with activated carbon.	Soil	TCE and other chlorinated hydrocarbons	Developing stage at a site in Sindelfingen, Germany.	Within 18 months, 17 metric tons of chlorinated hydrocarbons were removed. No cost data available.
Soil Flushing	Fund Lead Tech. contact: Robert Whippo 312-886-4759	Flushing performed at chemical packaging facility. Site at U.S. Aviex, MI.	Soil (11,500 cubic yards)	VOCs (carbon tetrachloride, DCA, BTEX, PCE, TCE, TCA, freon, & chloroform)	Developing stages.	No results or cost data available.

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5.2.7 In Situ Radio Frequency (IRF) Heating

Technology Description

The IRF heating process uses electromagnetic energy in the range of 2 to 45 Megahertz to heat large volumes of soil. The principles of IRF are very similar to those of a microwave oven. The system removes volatile and semivolatile contaminants from the soil through the primary mechanisms of vaporization, distillation, and steam stripping. The gases and vapor formed in the soil matrix can be recovered at the surface or through vented electrodes used for the heating process. The process does not depend on heat transfer fluids or *in situ* combustion of fuels; thus, a concentrated gas stream can be recovered. The bulk of the contaminants can be recovered as a liquid by permitting condensation, with only a minor portion adsorbing on an activated carbon bed for treatment.

The system is made up of four components: (1) radio frequency (RF) energy deposition electrode array; (2) RF power generation, transmission, monitoring, and control system; (3) vapor barrier and containment system; and (4) gas and liquid condensate handling and treatment system. The radio frequency electromagnetic energy is applied to soil formations by a system of exciter and ground electrodes. These electrodes may be placed over the surface of the contaminated site, or in vertical or horizontal boreholes drilled through the contaminated zone. When the electrode array is supplied with electromagnetic energy, an electromagnetic wave is launched by the exciter electrodes into the target volume of soil. The energy in the electromagnetic wave is attenuated due to absorption by the molecules present in the heated volume. The electromagnetic energy appears as heat, as a result of induced dipole rotation and molecular vibration. Since heating is not dependent on the slow process of thermal conduction, rapid heating of the soil is accomplished. Heating occurs throughout the volume of the target material. Soil is heated to between 200°F and 1000°F. A vapor containment cover is placed over the treatment zone to capture the vaporized VOCs. A vacuum can also be applied to the hollow electrodes and the vapor containment zone, further enhancing collection of organics. The collected vapors are treated by thermal treatment or carbon adsorption.

Advantages of in situ radio frequency:

- Contaminants recovered in a relatively concentrated form without dilution from large volumes of air or combustion gases.
- Soil does not have to be excavated.
- All equipment is portable.

Disadvantages of in situ radio frequency:

- Currently limited to the removal of VOCs, such as chlorinated solvents, petroleum hydrocarbons, and other organics with boiling points of approximately 500°F.
- Not effective for wastes requiring metals removal, and cannot be used if large buried metal objects are in the treatment zone.
- High moisture or presence of groundwater in the treatment zone results in high power requirements to heat the soil.

Stage of Development

Laboratory and pilot-scale studies have been conducted. Field tests have also been performed to assess the feasibility of the process on soils contaminated with jet fuel and VOCs.

A bench-scale pilot test (volume < 20 drums) has been conducted at IIT Research Institute Facilities. A larger field-pilot was completed at an Air Force site in November, 1987. A full-scale demonstration was completed at Volk Field ANGB, Wisconsin, during October 1989. Full-scale implementation will begin during the Fall of 1990 at Kelly AFB, San Antonio, Texas.

Applications and Effectiveness

Observed efficiencies in pilot and field studies vary from 70 percent to 99 percent, depending on the soil and contaminant types.

Case Studies

An abandoned fire training area located at Volk Air National Guard Base, Camp Douglas, Wisconsin, was selected for the field demonstration. It was estimated that approximately 50,000 gallons of jet fuel soaked into the sandy soil of the fire training area. The feasibility of IRF decontamination was demonstrated by heating a block of soil of dimensions 6 ft x 12 ft x 7 ft to a temperature range of 150-170°C. Analysis of numerous pre- and post-tests on soil samples showed that on average, 99 percent of the volatile aromatics and aliphatics had been removed from the treated volume. On average, 94 percent of the semi-volatile aliphatics and 99 percent of the aromatics were also removed.

Co-Technologies/Alternative Technologies

Technologies that are used in conjunction with IRF are mainly gas and vapor collection systems and treatment units. Alternative technologies include:

- Bioremediation (*in situ* or *ex situ*)
- Soil washing (*ex situ*)
- Soil vapor extraction (*in situ*)
- Low temperature thermal desorption
- Incineration

Cost Analysis

The treatment of a 3-acre site to a depth of 8 feet containing 12% moisture raised to a temperature of 170°C could cost \$80/ton of treated soil. The treatment of such a site would require about 1 year. The initial equipment investment for full-scale projects is estimated to be about \$2.5 million. Power requirements for the pilot-scale field demonstration totaled approximately 800 kW-hr/m³. Use of the state-of-the-art RF generator for full-scale application could reduce the power input to less than 650 kW-hr/m³. The treatment cost varied between \$34 to \$65 per ton of treated soil from the field demonstration at Camp Douglas, Wisconsin.

Personal Contacts

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REFERENCES

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5.2.8 Thermal Desorption

Technology Description

Thermal desorption technology is an *ex situ* process used to physically separate volatiles and semi-volatile contaminants from sludges, sediment, soil, and filter cakes. It is applicable to organic wastes and generally is not used for treating metals and other inorganics. Thermal desorption can be used to treat wastes containing 10 percent organics or less.

A physical separation process, thermal desorption, uses either indirect or direct heat exchange to vaporize the contaminants. Air, combustion gas, or inert gas is used as the transfer medium for the vaporized components. Depending on the specific thermal desorption vendor selected, the technology heats contaminated media between 200-1000°F, driving off water and volatile contaminants.

The process consists of:

- Excavation of the contaminated matrix.
- Removal of large objects (greater than 1.5 inches) through screening.
- Delivering the medium by gravity to the desorber inlet or conveying by augers to a feed hopper.
- Desorption occurring at specified temperature and residence time.
- After desorption occurs, off-gases may be burned in an afterburner, condensed to reduce the volume to be disposed, or captured by carbon adsorption beds. The selection of the gas treatment system will depend on the concentration of the contaminants, cleanup standards, and the economics of the off-gas treatment system(s) employed.

Significant system variations exist in the desorption step. The treatment bed may be heated directly or indirectly. Direct heating devices consist of firing fuel oil, natural gas, or propane in a burner primarily to heat the soil by radiant energy from the flame and convective heat from the combustion gas. This method is utilized by rotary dryers, asphalt plant aggregate dryers, and conveyor furnaces. Indirect heating is accomplished by transferring heat across a physical barrier to the soil. No combustion gases from the heat source are in contact with the soil. Thermal screws utilize indirect heating by using a hot transfer fluid that circulates through a shell and transfers heat to the soil. The off-gas volume from an indirectly heated device is 2 to 10 times less than the off-gas volume from a directly heated device with an equivalent throughput capacity.

The thermal desorption alternatives discussed above—rotary dryers, asphalt plant aggregate dryers, conveyor furnaces, and thermal screws—are key design features in the different types of thermal desorption systems. Rotary dryer systems use a cylindrical metal reactor (drum) that is inclined slightly to the horizontal. The flow of the solids may be either concurrent or countercurrent to the direction of purge gas flow. A series of lifters inside the rotary drum pick up the soil, carry it to the top of the drum, and drop it through the hot combustion gases from the burner. The direct heat and intense mixing in the drum allow soils to heat very rapidly in rotary dryer systems. Temperatures range from 300 - 1,200°F, and treatment capacities range from 5 to 15 tons per hour for small systems and up to 30 to 100 tons per hour for large systems.

Asphalt plant aggregate dryers are rotary dryers that exclusively use a countercurrent rotary dryer followed by a cyclone, fan, and stack. The treated soil may then be incorporated into the asphalt as an aggregate. The temperatures range from 300 to 600°F, and treatment capacities range from 25 up to 150 tons of soil per hour.

Conveyor furnaces use a flexible metal belt to convey soil through the primary heating chamber. As the belt moves through the system, soil agitators lift the belt and turn the soil over exposing it to a series of burners (direct heating) firing into a chamber above the belt. The temperatures range from 300 to 800°F, and treatment capacities range from 5 to 10 tons of soil per hour.

Thermal screw processes consist of 1 to 4 screw augers arranged in a series to increase the solids residence time or parallel to increase throughput capacity. The auger system conveys, mixes, and heats contaminated soils to volatilize moisture and organic compounds into a purge gas stream. Most thermal screw systems circulate a hot-heat transfer oil through the hollow flights of the auger and return the hot oil through the shaft to the heat transfer fluid heating system (fired with propane, natural gas, or No. 2 fuel oil). Approximately 75 to 90 percent of the combustion gas does not contact the waste material and can be discharged directly to the atmosphere without emission controls. Using hot oil as the transfer medium can bring soil temperatures up to 500°F and steam-heated systems can heat soil up to 350°F. Treatment capacities range from 3 to 15 tons of soil per hour.

Advantages of Thermal Desorption:

- Separation of the contaminants from the waste media occurs as opposed to burning off the contaminants.
- Thermal desorption costs less than incineration due to lower permitting costs.
- Can reduce the mass to be taken off-site for treatment by as much as 50 percent.

Disadvantages of Thermal Desorption:

- The bed temperature of the reactor directly determines which organic will be removed.
- Contaminants must contain at least 20 percent solids to facilitate placement of waste into desorption equipment.
- Energy losses result in higher treatment costs due to heating moisture contained in contaminated soil. A high moisture content can result in low contaminant volatilization or the need to recycle the soil through the desorber.
- A high fraction of fine silt or clay in the soil generates fugitive dusts and a greater dust loading rate will be placed on the downstream air pollution control equipment.
- Tightly aggregated or soils with high clay concentrations can result in poor processing performance due to caking.
- A medium exhibiting very high pH (greater than 11) or very low pH (less than 5) may corrode the system components.
- Polymers may foul and/or plug heat transfer surfaces.
- High concentrations of inorganic constituents and/or metals probably will not be effectively treated by thermal desorption. However, the maximum bed temperature and the presence of chlorine can result in volatilization of some inorganic constituents in the waste.

Stage of Development

An innovative technology, thermal desorption, is the selected remedy for one or more operable units at 14 Superfund sites with the EPA. Successful bench- and pilot-scale studies are numerous, and full-scale studies have begun recently. Direct demonstration of thermal desorption through both treatability testing and full-scale cleanups is continuously being performed.

Commercial-scale thermal desorption units exist and are in operation. Most of the hardware components of thermal desorption are available off the shelf and represent no significant problem of availability.

A successful pilot-scale demonstration of Japanese soils "roasting" was conducted in 1980 for the recovery of mercury from highly contaminated (up to 15.6 percent) soils at a plant site in Tokyo. The high concentration of mercury made recovery and refinement to commercial grade (less than 99.99 percent purity) economically feasible.

Applications and Effectiveness

Thermal desorption has been proven effective in treating contaminated soils, sludges, and various filter cakes. Chemical contaminants for which bench-scale through full-scale treatment data exist include primary volatile organic compounds (VOCs), semivolatiles (SVOCs), and even higher boiling point compounds, such as PCBs. In general, the process is applicable for the separation of organics from refinery wastes, coal tar wastes, wood-treating wastes, creosote-contaminated soils, hydrocarbon-contaminated soils, mixed (radioactive and hazardous) wastes, synthetic rubber processing wastes, and paint wastes.

The technology is not effective in separating inorganics from the contaminated medium. Volatile metals, however, may be removed by higher temperature thermal desorption systems. The presence of chlorine in the waste can also significantly affect the volatilization of some metals, such as lead.

The actual bed temperature and residence time are the primary factors affecting performance in thermal desorption. These parameters are controlled in the desorption unit by the use of a series of increasing temperature zones, multiple passes of the medium through the desorber where the operating temperature is sequentially increased, separate compartments where the heat transfer fluid temperature is higher, or sequential processing into higher temperature zones. Heat transfer fluids used to date include hot combustion gases, hot oil, steam, and molten salts.

Thermal desorption is not incineration, since the destruction of the organic contaminants is not the desired result. The temperatures achieved and residence times designed into thermal desorption systems will volatilize selected contaminants, but typically not alter or destroy them. System performance is typically measured by comparison of untreated soil/sludge contaminant levels with those of the processed soil/sludge.

Case Studies

Thermal desorption technology application and several case studies are presented in Table 13. Estimated costs are included where available.

Co-Technologies/Alternative Technologies

Technologies which may supplement thermal desorption are usually those dealing with off-gas treatment systems to prevent possible emissions of contaminants. Thermal desorption can be used in conjunction with the following technologies to enhance removal of contaminants:

- Soil washing before or after thermal desorption to remove non-volatile metals.
- Solidification/stabilization after thermal desorption if medium is still contaminated with compounds not treatable with thermal desorption.
- Chemical treatment technologies to remove non-volatile compounds including metals and to prevent possible off-gas treatment.
- Bioremediation for organic compounds which are difficult to volatilize.

Cost Analysis

Treatment costs are highly application-specific and depend on the type and size of the thermal desorption system, quantity of soil to be treated, soil type, type and concentration of contaminants, soil moisture content, operating temperature, and soil cleanup criteria. Thermal desorption can be performed on-site or off-site at a facility; the location greatly impacts the cost of treatment. Mobile, on-site treatment systems require cost analysis based on plant/site design, permitting, site preparation, performance testing, treatment operation, equipment mobilization and erection, and equipment demobilization. Off-site treatment facilities require cost analysis based on soil transportation, soil treatment operations, and treated soil disposal.

Several vendors have documented processing costs per ton of feed soil processed. The overall range for thermal desorption costs vary from \$80 to \$350 per ton of soil processed, with the higher end of the range usually pertaining to on-site treatment facilities. This cost range does not

include costs associated with excavation, remedial investigation, procurement activities, and project management by the site owner.

Additional cost data are provided where available in Table 13.

Personal Contacts

Please refer to Table 13 for a complete list of personal contacts relative to specific case studies/applications. For further information, the following individuals may be contacted:

Chemical Waste Management, Inc.

Daniel Schleck
1950 South Batavia Avenue
Geneva, IL 60134-3310
(708) 218-1785

E M & C Engineering Association

Mohammed Elgafi
1665 Scenic Avenue, Suite 104
Costa Mesa, CA 92626
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Texarome, Inc.

Gueric R. Boucard
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U.S. Environmental Protection Agency (EPA)

Risk Reduction Engineering Laboratory
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(908) 321-6625

Table 13. Thermal Desorption Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
X*TRAX™ - (Chemical Waste Management, Inc.)	Tech. Contact: Carl Swanstrom Chemical Waste Management, Inc. 1950 S. Batavia Geneva, IL 60134 708-513-4578 EPA Contact: Paul dePercin 513-569-7797	Process uses an externally-fired rotary dryer which volatilizes the water and inorganic contaminants into an inert carrier gas stream.	Soil, sludge, and other solid media	VOCs, SVOCs and PCBs	EPA SITE demonstration program.	Full-scale system is being used to remediate 35,000 tons of PCB-contaminated soil at the Re-Solve, Inc., Superfund site in Massachusetts. The unit has treated 158 tons of soil per day to less than 2 ppm PCB with a treatment standard of 25 ppm. No cost data available.
Desorption and Vapor Extraction System - (Recycling Sciences International.	Tech. Contact: Mark Burchett Recycling Sciences International, Inc. 30 South Wacker Drive, Suite 1420 Chicago, IL 60606 312-559-0122	Mobile system that uses a low-temperature fluidized bed reactor.	Soil, sludge, and sediment	PCBs, PAHs, PCPs, volatile inorganics, and some pesticides	EPA is selecting a demonstration site for this process.	No results or cost data available.

Table 13. Thermal Desorption Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
<p>Low Temperature Thermal Aeration - LTTA[®] - (Canonie Environmental Services Corporation)</p>	<p>Tech. Contact: Chetan Trivedi Canonie Environmental Services Corp. 800 Canonie Drive Porter, IN 46304 219-926-7169</p> <p>EPA Contact: Paul dePercin 513-569-7797</p>	<p>Process uses a direct-fired rotary dryer to heat an air stream which desorbs water and organic contaminants from the soil.</p>	<p>Soil, sediment, and some sludges</p>	<p>VOCs, SVOCs, organo-chlorine pesticides (OCP), total petroleum hydrocarbons (THP)</p>	<p>EPA SITE demonstration program. A demonstration was performed on soils contaminated with OCPs at a pesticide site in Arizona in 1992. Results published in Applications Analysis Report and Technology Evaluation Report.</p>	<p>Full-scale systems have remediated contaminated soils at six sites including three Superfund sites. More than 60,000 tons of soil have been treated by the system. No cost data available.</p>
<p>High Temperature Thermal</p>	<p>Tech. Contact: Mark McCabe Remediation Technologies, Inc. 9 Bond Lane</p>	<p>System consists of material feed equipment, a thermal processor, a particulate removal</p>	<p>Soil, sludge, and sediment</p>	<p>VOCs and SVOCs</p>	<p>EPA SITE demonstration program test proposed for the</p>	<p>No results or cost data available.</p>

Table 13. Thermal Desorption Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Solid Waste Desorption - (<i>Texarome, Inc.</i>)	<p>Tech. Contact: Gueric Boucard Texarome, Inc. P.O. Box 157 Leakey, TX 78873 512-232-6079</p> <p>EPA Contact: John Martin 513-569-7758</p>	Process uses superheated steam as a continuous conveying and stripping gas in a pneumatic system to treat contaminated solids. After desorption, the last stage of the system is used for quenching and as a reactor loop to provide a final chemical breakdown of the minute traces of volatiles left in the solid.	Soil, sludges, and sediment	VOCs, SVOCs, pesticides, creosote, PCBs, volatile inorganics, and organic wastes	EPA SITE demonstration program testing site proposed. Private testing on a pilot- and small commercial-scale has been conducted (12 tons per day).	No results or cost data available.
Low Temperature Thermal Treatment (LT ³) System - (<i>Roy F. Weston, Inc.</i>)	<p>Tech. Contact: Mike Cosmos Roy F. Weston, Inc. 1 Weston Way West Chester, PA 19380 215-430-7423</p> <p>EPA Contact: Paul dePercin 513-569-7797</p>	Low temperature, transportable, thermal treatment system that thermally desorbs organic compounds from contaminated soil without heating the soil to combustion temperatures.	Soil	Coal tar, drill cuttings, No. 2 diesel fuel, JP-4 jet fuel, gasoline, petroleum hydrocarbons, VOCs, SVOCs, and PAHs	EPA SITE demonstration program testing completed.	At the Anderson Development Company Superfund site in Adrian, MI, the system was tested on lagoon sludge from the site. The system removed VOCs to below

REFERENCES

Environmental Protection Agency. 1992. Superfund innovative technology evaluation program technology profiles, 5th edition. Report No. EPA/540/R-92/077.

Environmental Protection Agency. 1993. Superfund innovative technology evaluation program technology profiles, 6th edition. Report No. EPA/540/R-93/526.

5.2.9 Permeable Barriers - Passive Treatment Walls

Technology Description

Permeable barriers, or passive walls, are barriers placed in the ground to intercept and treat *in situ* contaminated groundwater flow. Unlike impermeable barriers, permeable barriers do not require that groundwater be pumped out of the ground, treated, and recharged back into the ground downgradient. The permeable barrier has the ability to selectively remove organic as well as inorganic contaminants.

The barrier is installed with traditional excavation and fill means. A trench is installed perpendicular to the groundwater flow and down to a lower confining layer. Based upon the specific contaminant, a fill material is specially selected. For organic contaminants, a mixture of activated carbon, sand, and clay may be selected. For example, a 3 percent mixture of carbon has proven effective in removing benzene.

Biological treatment can occur within the barrier. Oxygen may be a limiting factor. The latter would require oxygen additions or limiting the application to low-level biodegradable organic contamination.

Advantages of Permeable Barriers:

- Permeable barriers would eliminate the significant expense of pump and treat systems.
- Where the contaminant is destroyed, as with biological treatment, there is no residual contaminant remaining in the groundwater or barrier.

Disadvantages of Permeable Barriers:

- The life of the permeable barrier fill material is limited. When the reactant or absorbent is spent, the fill has to be replaced.
- The treatable subsurface formation is limited to relatively shallow depths of less than 50 feet.
- Lower formations can potentially become contaminated because this method is intrusive in nature, requiring periodic excavation.
- Non-homogeneous aquifer flow and contaminant gradients may cause the barrier to reach the end of useful life unevenly along the length of barrier. Determining "breakthrough" and loss of treatment efficiency becomes difficult.
- When the contaminant is concentrated in the barrier, it must eventually be removed from the subsurface.

Stage of Development

The permeable barriers are currently in full-scale development testing and are not commercially available.

Applications and Effectiveness

It is conceived that permeable barriers can have application in the cleanup of groundwater contaminated with BTEX, MTBE, and heavy metals.

Cost Analysis

Not available.

REFERENCES

- Knox, R. C. 1984. Assessment of the effectiveness of barriers for the retardation of pollutant migration. *Ground Water* 22: 279-284.
- Liljestrand, H. M., M. C. Lo and Y. Shimizu. 1992. Sorption of humic materials onto inorganic surfaces for the mitigation of facilitated pollutant transport processes. *Water Science Technology* 26: 1221-1228.
- National Institute for Petroleum and Energy Research. 1992. Installation restoration and hazardous waste control technologies. U. S. Army Corps of Engineers Toxic and Hazardous Materials Agency. Technical Report No. CETHA-TS-CR-92053.
- Rael, J., S.P. Shelton and R. Dayaye. 1995. Permeable barriers to remove benzene - Candidate media evaluation. *Journal of Environmental Engineering - ASCE* 121: 11-415.
- United States Air Force and Environmental Protection Agency. 1993. Remediation technologies screening matrix and reference guide, version 1. Report No. EPA 542-B-93-005. p. 83-84.

5.2.10 Semipermeable Membranes

Technology Description

This technology uses membranes that are exclusively permeable or impermeable to certain gases to screen which gases reach sampling and testing equipment used to evaluate environmental exposure to these gases.

Semipermeable membrane technology has also been used for the separation of organic solvents, such as ethyl alcohol, methyl alcohol, xylene, perchloroethylene, trichloroethane, toluene, and acetone. The solvents are then recycled into the industrial process after separation, an example of pollution prevention applicability.

One of the products which uses this technology is the Continuous Porous Membrane Permeator (CPMP), which uses Vycor glass as its membrane component. The CPMP allowed the condensable vapor in the feed stream to selectively permeate through the membrane under the pressure difference across the membrane. The Vycor glass was used to recover ethanol and acetone vapors from their off-gas mixtures with nitrogen.

Advantages of Semipermeable Membranes:

- There is direct and continuous recovery of the solvent without loss or emission.
- Recovery and recycle of valuable solvents saves money which would otherwise be spent on buying more solvent and off-stack emissions compliance technologies.

Disadvantages of Semipermeable Membranes:

- The complexity of off-gas composition will slow the process because of the time needed for separation.
- Some types of gases do not have membranes developed yet which can separate them effectively on the market.

Stage of Development

This process has been evaluated by the EPA SITE program at the bench- and pilot-scale.

Applications and Effectiveness

Industrial processes that include printing and coating, metal cleaning, dry cleaning, transport and storage of petroleum products, or other highly solvent-dependent processes could use this technology.

Cost Analysis

Not available.

REFERENCES

- Campbell, N. T., G. A. Beres, T. J. Blasko, and R. H. Groth. 1982. Effect of water and carbon dioxide in chemiluminescent measurement of oxides of oxygen. *Air Pollution Control Association Notebook 32*: 533-535.
- Environmental Protection Agency. 1992. Superfund innovative technology evaluation program technology profiles, 5th edition. Report No. EPA/540/R-92/077.
- Qiu, M. M. and S. T. Hwang. 1991. Continuous vapor-gas separation with a porous membrane permeation system. *Journal of Membrane Science 59*: 53-72.

5.2.11 Freeze Crystallization

Technology Description

Freeze crystallization is a change-of-phase contaminant separation process that crystallizes pure water at 20°F, isolating it from the contaminants. The freezing process begins when an aqueous waste stream contaminated with organics and inorganics is fed into a crystallizer. The temperature of the stream is then lowered directly or indirectly with a refrigerant. The waste stream forms an ice crystal slurry that is then fed into a crystal separator where the refrigerant, ice crystals, and hazardous wastes are separated from one another. The refrigerant is recycled in a closed loop system; the water is melted and sent to a wastewater treatment facility; and the concentrated solvent wastes are sent to a treatment, storage, and disposal facility (TSDF).

The recovery of wastewater byproducts can be cost effective if the waste is worth more than one cent a gallon. Wastes with heavy metals require 1000 to 100,000 mg/L (ppm) to be profitably recoverable. Aqueous waste streams require between 3 and 7 percent organics by weight to be economical. A waste stream with both organics and heavy metals, however, needs only 0.5 and 1.5 percent by weight to be cost effective.

Advantages of Freeze Crystallization:

- The concentration of contaminants makes all forms of treatment more cost-effective.
- The elimination of large amounts of water enhances the thermal destruction of these waste streams by reducing the evaporation heating load.
- Freeze crystallization is fairly insensitive to the chemical composition of waste streams, allowing a broad range of waste effluents to be treated by the technology.
- Portable systems, such as the DirCon unit, is designed for easy transport between cleanup sites.
- Freeze crystallization offers opportunities for recycling and reuse.

Disadvantages of Freeze Crystallization:

- Some hazardous chemicals could react with the introduced refrigerant, causing emissions problems in the solvent effluent. Specific refrigerants must sometimes be used.
- The freon commonly used as the refrigerant in freeze crystallization is currently strictly regulated as an ozone depleting chemical (ODC). There are emissions concerns and a requirement for a tightly closed-loop system to ensure zero leaks.

Stage of Development

The Freeze Technologies Corporation has a DirCon freeze crystallization unit commercially available. The Freeze Technologies Corporation unit has been demonstrated by the EPA SITE program at the Stringfellow Superfund site in Riverside, California.

Applications and Effectiveness

The freeze crystallization process has been shown to effectively treat waste streams containing pickling liquor, pharmaceutical and chemical plant wastes, munition plant wastes, heavy metals from metal-finishing operations, and wastewaters containing acetic, formic, and citric acids.

Cost Analysis

The cost is \$.10 per gallon for the DirCon demonstration facility, but is estimated to be only \$.03 per gallon for a 40 gpm facility.

REFERENCES

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- Roy, K. A. 1990. Freeze crystallization leaves contaminants out in the cold. *HazMat World* 3: 56-61.

5.2.12 Cryoprocessing-Cryofracture

Technology Description

Cryofracture is a diminution and desensitization technology which is used for the pretreatment of munitions or transuranic contaminated wastes before they are incinerated. The waste objects are first unpacked or unloaded by robotic arms, which then immerse them in a liquid nitrogen bath. The liquid nitrogen brings the wastes to cryogenic temperatures (-320°F), brittling the steel and making the wastes easier to fracture.

The wastes are sent from the liquid nitrogen bath to a hydraulic press for fracturing. Size reduction takes place when the fractured wastes are placed in shredding machinery. The shredded wastes are then sent to a single rotary kiln for incineration, with the off gases treated by a pollution abatement system.

The cryofracture process was developed by General Atomics for the Department of the Army for the demilitarization of chemical and biological agents. It is a pretreatment process which can render inert and desensitize explosives and pyrophorics.

The Department of Energy's (DOE) weapons mixed wastes, contaminated with transuranic wastes, are also contaminated with volatile organic compounds which pose a threat of fire or explosion during diminution. The cryogenic process eliminates that threat. Freezing time for drums and boxes containing wastes to reach -320°F was estimated to range from 0.2 to 2.7 hours.

The cryofracture method has been successful in size reducing waste materials, including steel plates and tanks. Over 90 percent of the wastes were reduced to less than 6 inches, and >80 percent of the wastes were reduced to less than 3 inches.

Advantages of Cryoprocessing/Cryofracture:

- Cryofracture is deemed safer because it renders sensitive and reactive wastes inert.
- The cooling process solidifies liquids and sludges, and also recondenses most gaseous vapors.
- Cryofracture size reduction affords the opportunity to accomplish several goals: reduction in volume for interim storage until ultimate disposal, homogenization of the waste, and an increase in surface area to better facilitate thermal destruction.

Disadvantages of Cryoprocessing/Cryofracture:

- Cryofracturing cannot be used for bulk chemical agents or chemical rocket destruction. The aluminum found in rockets actually strengthens in cryogenic environments.
- The incineration of the waste materials as the ultimate disposal method remains controversial.
- Composite material containers which may contain aluminum, or other troublesome metals which do not work well in cryoprocessing, may be hard to detect. This difficulty could cause safety problems if not closely monitored.

Stage of Development

Field demonstrations have taken place, testing the cryofracture method on stored transuranic wastes in 1990 and 1991. A small-scale demonstration of solid propellant cryoprocessing for rocket motors took place in 1992.

Applications and Effectiveness

Facilities which manufacture or store chemical weapons agents, chemical munitions, or transuranic wastes would have use for this technology as a pretreatment method.

Cost Analysis

A robotic cryofracture process line facility could cost \$3.6 million. This facility could process up to 43,200 tons/year of 2x2x8 ft metal boxes containing waste, at \$115/ton. The same facility could process up to 2,160 tons per year of 55-gallon paper-containing drums, at \$595/ton.

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5.2.13 Froth Flotation

Mosmans Mineraaltechniek has spent several years developing a froth flotation process for the purification of polluted soils, waste, and waste effluents (EPA, 1989). To achieve a separation between the contaminants and soil in a soil-water mixture, the surfaces of the particles have to be adequately manipulated so that the former will be hydrophobic and the latter hydrophilic. The manipulation is not related to changing the chemical structure of the particles, but to modifying the double layer by selective adsorption. The hydrophobic particles glue themselves to air bubbles produced in the soil-water mixture.

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5.2.14 Liquefied Gas Extraction

CF Systems Corporation uses a liquefied gas extraction system to remove organics from sludges, contaminated soils, and wastewater. Propane is the solvent typically used for sludges and contaminated soils. Carbon dioxide is used for wastewater streams. The solvent is vaporized and recycled as fresh solvent. The organics are drawn off and either reused or treated as a waste stream.

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5.3 Solidification/Stabilization

5.3.1 Introduction

Stabilization and immobilization of hazardous waste and contaminated soils encompasses a wide array of treatment processes. These are technologies designed to improve waste-handling and physical characteristics; decrease surface area through which pollutants can transfer or leach; and/or limit the solubility or mobility of hazardous constituents.

Solidification implies that the physical characteristics of the wastes are improved primarily by production of a monolithic block of treated waste with high structural integrity. Immobilization implies a chemical technique that limits the solubility or mobility of the contaminants with or without changing or improving the physical characteristics of the waste material. The term fixation is used to mean either solidification or stabilization.

These technologies are applicable to wastewater sludges contaminated with heavy metals and certain organics, electroplating wastes, electric arc furnace dusts, and other soil-type matrices contaminated with heavy metals.

Technology Description

The majority of solidification/stabilization technologies currently applied in the United States are based on cement and lime chemistry. Less developed technologies include organic stabilization processes which may become more useful in the future for specialized applications. Solidification/stabilization technologies can be characterized as follows:

Inorganic solidification/stabilization processes:

- Cement based
- Lime based
- Pozzolanic based

Organic solidification/stabilization processes:

- Thermoplastic
- Macroencapsulation
- Organic polymerization

Each of these technologies is discussed below.

5.3.2 Cement-Based Solidification/Stabilization

Cement-based solidification/stabilization is a process in which waste materials are mixed with Portland cement. Water is added to the mixture, if not already present in the waste material, to promote hydration reactions necessary for cement bonding. The wastes are incorporated into the cement and, in some cases, undergo physico-chemical changes that further reduce their mobility in the waste cement mixture. Small amounts of fly ash, sodium silicate, bentonite, or proprietary additives are often added to the cement to enhance processing. The final product may vary from a granular, soil-like material, to a cohesive solid, depending on the reagent added and the types and amounts of wastes solidified/stabilized.

Cement-based solidification/stabilization has been applied to wastes containing various metals such as arsenic, cadmium, chromium, copper, lead, nickel, and zinc. Cement has also been used with some complex wastes containing oils, PCBs, oil sludges; wastes containing vinyl chloride; resins; stabilized/solidified plastics; asbestos; sulfides; and other materials. These technologies, however, cannot be applied to wastes that require longer setting times. Increased setting and curing times result in product performance degradation. The effectiveness of this technique on wastes containing organics has not been well established.

The advantages of cement solidification/stabilization techniques are that low cost additives, common commercial cement processing equipment, and unskilled equipment operators are needed for its application. The disadvantages are that the wastes are not bound and, as such, they may be subject to acid leaching and subsequent resolubilization of the metal hydroxides or carbonates. The volume of the treated product can be as high as twice the original waste product volume.

5.3.3 Lime-Based Solidification/Stabilization

Lime-based solidification/stabilization involves the same mechanisms of cement-based solidification/stabilization. The difference is the generally higher pH resulting from lime treatment. Lime is a broad term applied to a variety of calcium bearing compounds. Various forms of lime have been successfully used as a soil stabilizing agent for many years, including products with various degrees of purity. Commonly used products are hydrated high calcium lime $\text{Ca}(\text{OH})_2$, monohydrated dolomitic lime $\text{Ca}(\text{OH})_2 \cdot \text{MgO}$, calcite quicklime CaO , and dolomitic quicklime $\text{CaO} \cdot \text{MgO}$. However, the most frequently used compound is CaO (quicklime), especially when dealing with high water content wastes, or low temperature regions. For these applications, CaO is a much more effective additive because its heat of hydration can be substantial in accelerating other ongoing reactions and reducing the time required for remediation. In addition, the subsequent drying of the surrounding ground can be a significant outcome.

Lime has been known to be effective in stabilizing both organic and inorganic wastes. It is generally more effective than cement-based solidification/stabilization, because the materials which potentially interfere with setting and hardening are less common with lime than with cement. In addition, the volume increase resulting from treatment generally is less when lime is the additive. Furthermore, lime use allows for better control of pH increases than cement. Finally, when *in situ* pressure injection techniques are used for treatment of deep layers, lime slurry grouts have a similar viscosity with that of water, as lime is readily soluble in water. On the other hand, cement involves particulate grouts that have much less mobility in porous media. Lime is not as widely used as

cement-based solidification/stabilization techniques. Lime techniques have been proven to be very effective in heavy metal wastes. Its effectiveness in high organic content wastes has not been well established.

5.3.4 Pozzolanic Solidification/Stabilization

Pozzolanic solidification/stabilization involves siliceous and aluminosilicate materials. These materials do not display cementing action alone, but form cementitious substances when combined with lime or cement and water at ambient temperatures. The primary containment mechanism is a physical entrapment of the contaminant in the pozzolanic matrix. Examples of common pozzolans are clay, fly ash, pumice, lime kiln dusts, and blast furnace slag. Pozzolanic solidification/stabilization is generally much slower than cement or lime solidification/stabilization, and involves much larger volume increases as compared to the original waste product volume.

5.3.5 Thermoplastic Techniques

Thermoplastic solidification/stabilization is a microencapsulation process in which the waste materials do not react chemically with the encapsulating material. In this technology, a thermoplastic material, such as asphalt (bitumen), polyethylene or paraffin, is used to bind the waste constituents into a solidified/stabilized mass. The asphalt binder may be heated before it is mixed with the dry waste materials, or the asphalt may be applied as a cold mix. In the latter, water is being removed by subsequent compaction of the solidified material. Inclusion of water-bearing soluble salts in the waste can create problems in the final product, as water may diffuse through the matrix and can cause swelling and cracking.

The process requires trained operators and specialized equipment, and is extremely energy intensive. The elevated process temperature also limits the types of materials which can be incorporated into the matrix, citrates and certain plastics being examples. Also, there is a fire risk associated with working on organics at high temperatures. Among the benefits of thermoplastic techniques is the reduction of waste volume due to water being removed from the matrix, associated leach rates that are very low, and satisfactory long-term performance of the stabilized matrix, under water and microbial exposure.

5.3.6 Macroencapsulation

This solidification process involves the encapsulation of waste products by sealing them in an organic resin or binder (overpack drum). The waste is generally thermoplastically solidified prior to macroencapsulation. High density polyethylene (HDP) and polybutadiene are used to perform the encapsulation. The materials are commercially available, and chemically stable, as they show very good resistance to biodegradation. They are also mechanically tough but flexible. The waste product geometry can be optimized during the molding phase to suit transportation, storage disposal, or burial requirements. Skilled labor is required for molding, and the process is again energy intensive.

5.3.7 Organic Polymerization

Organic polymerization solidification/stabilization relies on polymer formation to immobilize the constituents of concern. Urea formaldehyde is the most commonly used organic polymer for this purpose. Organic polymerization has been primarily used to solidify radioactive wastes. This technology, however, as well as other organic polymerization systems, are believed to be obsolete at this point, at least in the United States. This obsolescence is due to their extremely

high costs, their tendency to throw off free water during the condensation reaction, and more importantly due to recent environmental concerns over formaldehyde. However, various nuclear plants that installed such systems in the 1970s may still have them in use.

Advantages of Solidification/Immobilization:

- Chemically and/or physically binds waste materials into a durable solid, making it well suited for wastes containing heavy metals, radioactive constituents, and certain organics.
- The process can treat a diverse range of contaminants simultaneously.
- The final product is durable enough in most cases to reduce weathering, chemical leaching, and biotoxicity.
- The additives are generally very inexpensive and widely available.
- Treated material requires little or no further treatment, and free liquids are eliminated.
- Solidified materials may be re-used.
- Solid and liquid waste sludges contaminated with high organic content, oils and greases, and heavy metals can be effectively treated.
- Low skill level is adequate to effectively apply the technology.

Disadvantages of Solidification/Immobilization:

- The contaminant toxicity is not altered or eliminated.
- The volume increases due to addition of binding agents.
- Uniform mixing for *in situ* treatment may be difficult to achieve.
- Emission of volatiles and particulates may occur during mixing operations and may require costly controls.
- *In situ* solidification/stabilization of sensitive areas, e.g., wetlands, may inhibit restoration or alter future use.
- The immobilization of PCBs has not been confirmed, and therefore wastes which contain them are not encouraged for solidification/stabilization treatment.
- Some of the technologies which are commercially available have had large fluctuations in removal efficiencies during their demonstration phases.
- Toxicity Characteristic Leachate Procedure (TCLP) testing of the treated wastes may be required before disposal.
- Volume increases may be a potential problem.

Stage of Development

Solidification/stabilization technologies are relatively mature. Most have been applied *ex situ* after excavation of contaminated soils and in sludge processing. *In situ* applications have been limited. Solidification/stabilization technologies have been selected as a component of the remedy in approximately 75 Records of Decisions in the EPA. These technologies are actively promoted by over a dozen vendors.

Several versions of this technology are commercially available, including CHEMFIX, International Waste Technology/GeoCon Deep Soil Mixing (IWT/DSM), IMTECH, SOLIDITECH, and Hazcon. All of the above commercial technologies have been demonstrated under the EPAs SITE program.

Applications and Effectiveness

Solidification and stabilization is applicable to sludges contaminated with heavy metals, electroplating wastes, electric arc furnace dusts, and other wastes. Organic containing wastes have been treated with varying degrees of success. However, select solid and liquid waste sludges contaminated with high organic content, oils and greases, and heavy metals can be effectively treated.

Case Studies

Several case studies and technology applications are presented in Table 14.

Co-Technologies/Alternative Technologies

Solidification/stabilization is usually a one-step application. As such, integration with other technologies is limited. The presence of volatile organics in the soil matrix may be due to the exothermic reactions involved in some of the processes. As a result, pretreatment involving extraction of VOCs or VOC control during the process may be required.

Cost Analysis

Representative overall costs of solidification/stabilization cement-based technologies ranges from \$30/ton to \$250/ton. A summary of relative costs for solidification/stabilization, as reported by the EPA (1992), are given in Table 15. In all cases, 500,000 gallons (2850 tons) of waste was treated with 30 percent Portland cement and 2 percent sodium silicate, with on-site disposal. Costs include only those operations necessary for treatment. Final costs are per ton of waste treated. Additional cost data are provided where available in Table 14.

Table 14. Solidification/Stabilization Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Solidification and Stabilization - (WASTECH, Inc.)	Tech. Contact: E. Benjamin Peacock WASTECH, Inc. P.O. Box 4638 114 Tulsa Road Oak Ridge, TN 37830 615-483-6515 EPA Contact: Terry Lyons 513-569-7589	Process applies proprietary bonding agents to contaminated matrices and uses a reagent to chemically immobilize contaminants in waste.	Waste streams consisting of soils, sludges, and raw organic streams	Organic and inorganic compounds	EPA SITE demonstration program bench-scale testing completed.	At the Robins Air Force Base in Warner Robins, GA, a bench-scale study was completed to treat hazardous wastes contaminated with various organics, inorganics, and mixed wastes. No results or cost data available.
Quick Lime Solidification of Heavy Metals	Dimitris Dermatas Center for Environmental Engineering Stevens Institute of Technology Hoboken, NJ 07030 201-216-5326	Treatment of heavy metal contaminated soils by using quicklime and other additives.	Soil	Chromium, lead, mercury, arsenic	Laboratory-scale.	Aggressive lab-scale studies on artificially contaminated soils. Acidic leaching experiments have shown very good long-term behavior of solidified matrices.

Table 14. Solidification/Stabilization Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Solidification and Stabilization - (<i>Chemfix Technologies, Inc.</i>)	Tech. Contact: Sam Pizzitola Chemfix Technologies, Inc. National Technology Marketing Center 161 James Drive West St. Rose, LA 70087 504-461-0466	Pozzolanic materials react with polyvalent metal ions and other waste components to produce a chemically and physically stable solid material.	Soil, sludge, ashes, and other soil wastes	Heavy metals	EPA SITE demonstration program completed.	At the Portable Equipment Salvage Co. site in Clackamas, OR, the technology effectively reduced copper and lead in the wastes to 94 to 99 percent less than the treated waste. The cost of the treatment process was estimated at approx. \$73 per ton, not including excavation, pretreatment, and disposal.
Solidification using Portland cement as binder	U.S. Plating Company Tech. Contact: Edwin R...	<i>In situ</i> treatment of 16,000 cubic yards of sludge	Sludge	Copper, chromium, and	Full-scale operation.	Volume increase was minimal and

Table 14. Solidification/Stabilization Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
<p>SAREX Chemical Fixation Process - <i>(Separation and Recovery Systems, Inc.)</i></p>	<p>Tech. Contact: Joseph DeFranco Separation and Recovery Systems, Inc. 1762 McGaw Avenue Irvine, CA 92714 714-261-8860</p> <p>EPA Contact: S. Jackson Hubbard 513-569-7507</p>	<p>Thermal and chemical reactive process that removes VOCs and SVOCs and the remaining constituents of organic and inorganic sludge materials in a stable matrix.</p>	<p>Organic and inorganic compounds</p>	<p>Soil, sludges, lube oil acid sludges, tars, and large crude oil spills</p>	<p>EPA SITE demonstration program acceptance and testing site to be chosen.</p>	<p>During field demonstration in 1987 at a Midwest refinery, approx. 400 cubic yards of lube oil ace sludges were treated. No results or cost data available.</p>
<p>NOMIX[®] Technology - <i>(Hazardous Waste Control)</i></p>	<p>Tech. Contact: David Babcock Hazardous Waste Control 403 Stillson Road Fairfield, CT 06430 203-366-7020</p> <p>EPA Contact: Teri Richardson 513-569-7949</p>	<p>Technology combines specially formulated cementitious materials with waste media.</p>	<p>Aqueous wastes</p>	<p>Arsenic trioxide, barium bromide, cadmium acetate, mercuric chloride, potassium chromate, selenium dioxide, silver nitrate and zinc sulfate, among others</p>	<p>EPA SITE demonstration program acceptance. Undetermined demonstration site.</p>	<p>Technology has been tested and significantly reduced the leachability of each waste stream and achieved compressive strengths of a few hundred pounds per square inch. No cost data available.</p>

Table 14. Solidification/Stabilization Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
<i>In Situ</i> Solidification and Stabilization - (<i>International Waste Technologies/Geo-Con, Inc.</i>)	Tech. Contact: Chris Ryan Geo-Con, Inc. 4075 Monroeville Boulevard Corporate One, Building II Monroeville, PA 14246 412-856-7700 EPA Contact: Mary Stinson 908-321-6683	Process wastes in wet or dry soils, using reagents to produce a cement-like mass.	Soils, sediments, and sludge-pond bottoms	Organic compounds, PCBs, PCPs, chlorinated and nitrated hydrocarbons and metals	EPA SITE demonstration program testing completed.	At a PCB-contaminated site in Hialeah, FL, the demonstration yielded that immobilization of PCBs appeared likely and bulk density of soil increased 21 percent after treatment. Cost of the process is \$194 per ton for the 1-auger machine used in the demonstration and \$111 per ton for a commercial 4-auger operation.

Table 14. Solidification/Stabilization Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Solidification and Stabilization Treatment Technology - <i>(Silicate Technology Corporation)</i>	Tech. Contact: Stephen Pelger Silicate Technology Corporation 7655 East Gelding Drive Suite B-2 Scottsdale, AZ 85260 602-948-7100 EPA Contact: Edward Bates 513-569-7774	Process uses silicate compounds to solidify and stabilize waste.	Soils, sludges and wastewaters	Metals and organics	EPA SITE demonstration program testing completed.	At the Selma Pressure treating wood preserving site in Selma, CA, the technology reduced up to 97 percent PCP extract and leachate concentrations; arsenic, copper, and chromium can be immobilized; and volume increase was 59 to 75 percent. Cost is estimated at \$200 per cubic yard when used to treat large amounts.

Table 14. Solidification/Stabilization Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Solidification and Stabilization - (<i>Solidtech, Inc.</i>)	Bill Stallworth Solidtech, Inc. 1325 S. Dairy Ashford, Suite 130 Houston, TX 77077 713-497-8558	Process immobilizes contaminants by binding them in a concrete-like, leach-resistant matrix.	Soils and sludges	Organic compounds, metals, inorganic compounds, and oil and grease	EPA SITE demonstration program testing completed.	At the Imperial Oil Company/Champion Chemical Co. Superfund site in Morganville, NJ, the process solidified both solid and liquid wastes with high organic content as well as oil and grease; VOCs were undetected in the treated waste; waste volume increased 22 percent. Cost data not available.

Table 15. Relative Cost Comparison for Solidification/Stabilization

Parameter	In-drum	<i>In Situ</i>	Pumpable plant mixing	Unpumpable plant mixing	Area mixing
Metering and mixing efficiency	Good	Fair	Excellent	Excellent	Good
Processing days required	374	4	10	14	10
Cost/ton	-----	-----	-----	-----	-----
Reagent	\$20.50 (9%)	\$20.50 (63%)	\$20.50 (53%)	\$20.50 (42%)	\$20.50 (49%)
Labor and per diem	51.07 (23%)	1.36 (4%)	3.83 (10%)	6.93 (14%)	6.35 (15%)
Equipment rental	37.14 (17%)	1.38 (4%)	3.93 (10%)	7.54 (16%)	4.07 (10%)
Used drums @\$11/drum	48.18 (21%)	-----	-----	-----	-----
Mobilization/Demonstration	15.68 (7%)	1.58 (5%)	1.43 (4%)	2.26 (5%)	1.20 (3%)
Cost of treatment processes	\$172.57	\$24.83	\$29.69	\$37.23	\$32.11
Profit and overhead (30%)	51.72 (23%)	7.45 (23%)	8.91 (23%)	11.17 (23%)	9.63 (23%)
Total cost/ton	\$224.29	\$32.28	\$38.60	\$48.40	\$41.75

Personal Contacts

Refer to Table 14 for a complete list of personal contacts relative to specific case studies/applications. For further information, the following individuals may be contacted:

Bergmann USA

Richard Traver, P.E.
72-II West Stafford Road
P.O. Box 535
Stafford Springs, CT 06076-0535
(203) 684-6844

Biotrol, Inc.

Dennis D. Chilcote, Ph.D
11 Peavey Road
Chaska, MN 55318
(612) 448-2515

Canonie Environmental Services Corp.

James Murray
84 Inverness Terrace East, Suite 100
Englewood, CO 80112
(303) 790-1747

Northwest Enviroservice, Inc.

Richard Owings
1700 Airportway South
P.O. Box 24443
Seattle, WA 98124
(206) 622-1085

On-Site Technologies, Inc.

Benjamin Roberts, Ph.D
1715 South Bascom Avenue
Campbell, CA 95008
(408) 371-4810

Waste-Tech Services, Inc.

R. Stanley Rickard, Ph.D
800 Jefferson County Parkway
Golden, CO 80401
(303) 279-9712

5.3.8 Vitrification

Technology Description

Vitrification is a high temperature remediation process that immobilizes hazardous substances in a vitreous mass. Electrical energy is used to oxidize, melt, and transform a broad spectrum of wastes and soil into a glass-like residual product form. Organics are destroyed by pyrolysis, while inorganic contaminants are immobilized by incorporation in the melt and resulting residual product.

The *in situ* vitrification (ISV) process involves the following: upon the identification of the boundaries of the contaminated soil, four molybdenum or graphite electrodes are placed in a square for treating individual melts (batches) of up to 1,000 tons. After the moisture has been driven off the contaminated soil to ensure the soil is no longer conductive, a mixture of graphite and glass frit is placed on the soil surface to provide a starter path for the electrical current flow. An electric potential is then applied between electrodes, which begin the moltenization along the starter path, causing a current flow through the contaminated zone and heating the adjacent soil to the melting point. Typical soil melt temperatures achieved range between 1600 to 2000°C.

The soil melts until the entire area between the electrodes is molten. The soil then forms a molten stream that moves downward and outward, forming an electrically conductive pool. As this process happens, the organic waste constituents are pyrolyzed, with the resulting gases migrating to the soil surface. The inorganic constituents remain in the molten soil and are incorporated into the vitrified mass. An off-gas treatment "hood" is employed over the entire treatment zone to collect the vapors emitted from the treatment area. The emissions are directed to a treatment system consisting

of quenching, scrubbing, humidity control, filtration, and carbon adsorption processes. Contaminants collected from these treatment units can then be recycled back to the vitrification process, thus decreasing the amount of wastes requiring disposal or further treatment.

ISV is also a volume reduction technology which has resulted in 20 to 40 percent volume reduction, depending on the type of waste treated. This reduction leaves the area above the ISV at a lower elevation than the surrounding area, so backfilling over the area is required to keep an even surface grade.

ISV destroys organics via pyrolysis due to the strong reducing environment. Commonly 99.995 percent of the organics are destroyed during ISV. ISV has also been shown to have efficient destruction of various mixtures of wastes, including hazardous, inorganic, organic, and radioactive.

In the *ex situ* process (ESV), the resultant waste formed upon cooling is considered permanently leach-proof. Since the ceramic-like material has a high degree of ductility, it can be used for various applications such as aggregate or fill. However, re-use of vitrification end product is not practiced widely because of regulatory limitations. These limitations arise mainly from the fact that the long-term environmental compatibility of these materials has not yet been established.

Advantages of Vitrification:

- Vitrification binds waste materials into a chemically durable solid, making it well suited for wastes containing heavy metals or radioactive constituents.
- The technology can treat wastes with diverse chemical and physical properties.
- The *in situ* application capabilities allow treatment without the costs and hazards associated with excavation, handling, pretreatment, and transportation.
- The resulting vitrified product can be re-used in a variety of applications.
- The process results in a substantial volume decrease of the treated waste.
- Underground storage tank contamination which meet ISV's requirements are treatable with this technology.

Disadvantages of Vitrification:

- Large scale ISV application is limited to total organic concentration in the treated media in the order of a few percent by weight. This limitation is related to the off-gas treatment systems capability to handle the heat and volume of off-gas.
- Volatile metals may vaporize, complicating the treatment of the off-gases.
- ISV requires homogeneity of the media.
- ISV is effective only to a maximum depth of approximately 20 feet (6 meters).
- ISV is limited to operations in the vadose zone.
- The technology has requirements for the area of contaminated media which limit its use. Some areas may not meet these requirements and will have to be treated by some other means.
- Regulations may require TCLP tests be done to ensure the integrity of the monolith.
- ISV has a relatively high energy cost.

Stage of Development

The vitrification technology has been demonstrated both *in situ* and *ex situ* and is commercially available. Its development began in 1980 for the U.S. Department of Energy and is presently a participant in the EPA SITE Program. DOE then licensed the technology to Battelle Memorial Institute's Pacific Northwest Laboratories, who in turn sublicensed it to the Geosafe Corporation for commercialization. A full-scale technology, *ex situ* vitrification is now available by more than five vendors. Numerous field applications have been performed by the DOE and current vendors of ISV.

A pilot-scale technology, ISV has had six full-scale demonstrations of the process conducted on radioactive waste at the Department of Energy's Hanford Nuclear Reservation. More than ninety tests at various scales have been performed on polychlorinated biphenyl wastes, industrial lime sludges, dioxins, metal plating wastes, and other solid combustibles and liquid chemicals.

Research is ongoing for both ESV and ISV, mostly in the area of improving the technology energy efficiency and establishing long-term behavior of the vitrified products. Pacific Northwest Laboratory, the developer of the ISV process, is currently conducting research to extend the technology to buried wastes and underground tanks for the U.S. Department of Energy. Since these types of wastes are anticipated to contain high concentrations of metals, new processing techniques are being developed and tested. In addition, the effects of metals on melt shape and on the solubility of heavy metals are being studied and tested.

An electrode feeding technique has been developed and tested for processing high concentrations of metals. Instead of predrilling casings for electrode installation into the contaminated soil to be vitrified, electrode feeding allows the electrodes to be inserted as the vitrified soil melts downward. The concept has been successfully tested four times on engineering scale equipment.

Applications and Effectiveness

Vitrification can be used to destroy or remove organics and/or immobilize inorganics in contaminated soils or sludges. The process is applicable to VOCs, SVOCs, fuel hydrocarbons, pesticides, and inorganics, with inorganics as the target contaminant group. Most of the organics tend to be destroyed by vitrification through pyrolysis due to the higher temperatures (approx. 3000°F) achieved in the process. Performance data from vitrification tests for a variety of organic compounds reported destruction and removal efficiencies of greater than 99.99 percent.

The vitrification process is most effective in reducing the mobility of the contaminated wastes within the media. Studies indicate that the glass-like product of vitrification permanently immobilizes hazardous inorganics and will retain its physical and chemical integrity for geologic time periods. The vitrified mass has high resistance to leaching and possesses strength properties better than those of concrete. The monolith formed has hydration properties similar to those of obsidian, which hydrates at rates of less than 1 mm/10,000 years. For vitrification to be applied, sludges must contain a sufficient amount of glass-forming material (non-volatile, non-destructible solids) to produce a molten mass that will destroy or remove organic pollutants and immobilize inorganic pollutants.

ISV treats contaminated soil, dewatered sludge, sediments, mine tailings, or asbestos. Contaminants which are effectively destroyed by ISV include: heavy metals, organo-chlorine pesticides, PCBs, hazardous, organic, inorganic, and radioactive wastes.

While *in situ* vitrification is broadly applicable, there are limits to its applications. ISV cannot be applied to the saturated zone or soils of particularly high water content because the soil will not heat to its melting point. In addition, although ISV can accommodate a significant quantity of rubble, debris, and other inclusions within the treatment zone, each application needs to be addressed in detail to determine whether, and under what conditions, it may be suitable for ISV processing. Lastly, the high energy costs associated with this technology has limited its widespread applications.

Case Studies

Madden *et al.* (1992) discussed six full-scale demonstrations of the ISV processes that have been conducted on radioactive waste at the Department of Energy's Hanford Nuclear reservation. More than 90 tests at various scales have been performed on polychlorinated biphenyl wastes, industrial sludge, dioxins, metal plating wastes, and other solid combustibles and liquid chemicals.

Several technology applications and/or case studies are presented in Table 16. Costs are included when available.

Co-Technologies/Alternative Technologies

Vitrification is a one-step process, and integration with other technologies is limited. The need of co-technologies arises in the treatment of off-gases and the re-use of the vitrified products. Conventional gas scrubbing technologies and activated carbon can be used for off-gas treatment.

Various stabilization techniques have been investigated as an alternative for reuse of vitrified end products. These techniques include recycling the end product by incorporating it into cement or other non-leachable structures. In addition, vitrification has been used in tandem with incineration to remove both organic and inorganic contaminants from soil. This technology combines a vortex combustor and a cyclone melter to incinerate organic contaminants and vitrify inorganic materials. Soil vapor extraction, air sparging/stripping, or biochemical processes may be combined with vitrification in order to vitrify soils that have contaminant concentrations in which these technologies were not able to remediate the soil to acceptable levels.

Table 16. Vitrification Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
<i>In Situ</i> Vitrification - (Geosafe Corporation)	Tech. Contact: James Hansen Geosafe Corporation 2950 George Washington Way Richland, WA 99352 509-375-7721 EPA Contact: Teri Richardson 513-569-7949	Process uses and electric current to melt soil or sludge at extremely high temperature (1,600 to 2,000°C), destroying organic pollutants by pyrolysis.	Soil or sludge	Organic and most inorganic compounds	EPA SITE demonstration program acceptance. Has been demonstrated at 22 pilot-scale sites and 10 large-scale sites. More than 130 various scale tests have been performed.	Field studies began in 1993 for Superfund, DOE, DoD, and private facilities. No results or cost data available.
Waste Vitrification Through Electric Melting - (Ferro Corporation)	Tech. Contact: Emilio Spinosa Ferro Corp. Corporate Research 7500 East Pleasant Valley Road Independence, OH 44131 216-641-8580	Process chemically bonds inorganic and toxic species into an oxide glass through an electric melter.	Hazardous waste	Organic and inorganic compounds	EPA SITE emerging technology program acceptance.	Several glass compositions for processing synthetic soil have been subjected to TCLP testing. Results show

Table 16. Vitrification Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Oxidation and Vitrification Process - (<i>Vortec Corporation</i>)	Tech. Contact: James Hnat Vortec Corp. 3770 Ridge Pike Collegeville, PA 19426 215-489-2255 EPA Contact: Teri Richardson 513-569-7949	System oxidizes and vitrifies slurries through a three step process of (1) precombustion, (2) suspension preheat, and (3) melting in a cyclone melt chamber.	Soil, sludge, and mill tailings	Organics, inorganic and heavy metals	EPA SITE emerging technology program acceptance.	A 20-ton-per-day pilot-scale testing facility has been processing non-hazardous industrial waste material since 1988, and results indicate vitrified materials passed EPA standard or the TCLP test.
<i>In Situ</i> Vitrification	Teri Shearer U.S. EPA-RREL 26 West Martin Luther King Drive Cincinnati, OH 45268 513-569-7949	Process uses an electrical network of large electrodes (usually four) in contaminated zones.	Soil and sludge	Organic and inorganic compounds	Commercially available. Full-scale demonstrations have been conducted on radioactive waste at the Dept. of Energy's Hanford Nuclear Reservation.	No results or cost data available.

Cost Analysis

Ex situ vitrification technologies commercially available have been reviewed, each using different processes to achieve the end result of encapsulation hazardous substances in a vitreous mass. Averaging the available cost data across this technology category results an approximate overall cost of \$700/ton. U.S. Department of Energy (DOE) life-cycle cost analysis suggests the overall cost of *in situ* vitrification would be approximately \$790/ton. An approximate price range per unit waste treated provided by different vendors are listed in Table 17 below. These prices do not include indirect costs, such as excavation (if necessary), permits, and treatment of residuals. Cost comparison should be made on comparable remediation activities.

VENDOR	\$/ton
Battelle	60-200
Bio-Electrics	100-400
Contamination Control	425-500
Geosafe	300-500
Glasstech	75-150
Retech	600-1000
Texaco Syngas	200-600
Western Product Rcv.	150-1000

Personal Contacts

Please refer to Table 16 for a complete list of personal contacts relative to specific case studies/applications. For further information, the following individuals may be contacted.

Battelle Pacific Northwest Laboratories

Dan Anderson
Battelle Boulevard, Box 999
Richland, WA 99352
(509) 376-7855

Bio-Electrics, Inc.

1215 West 12th Street
Kansas City, MO 64101
(816) 474-4895

Contamination Control Services, Inc.

P.O. Box 1017
Easley, SC 29641
(803) 859-2048

Geosafe Corporation

2000 Logston Avenue
Richland, WA 99352
(509) 375-3268

Geotech Development Corp.

630 Valley Forge Plaza Building
King of Prussia, PA 19406
(215) 337-8515

Glasstech, Inc.

995 Fourth Street
Perrysburg, OH 43552
(419) 536-8828

Retech, Inc.

100 Henry Station Road
P.O. Box 997
Ukiah, CA 95482
(707) 462-6522

Texaco Syngas, Inc.

2000 Westchester Avenue
White Plains, NY 10650
(914) 253-6019

U.S. Environmental Protection Agency-RREL (EPA-RREL)

Teri Shearer
26 West Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7949

Western Product Recovery Group, Inc.

10690 Shadow Wood, Suite 132
Houston, TX 77043
(505) 672-9444

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- Stinson, M. K. 1990. EPA SITE demonstration of the international waste technologies/geo-con *in situ* stabilization/solidification process. *Journal of the Air & Waste Management Association* 40: 1569-1576.
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- U.S. Army Corps of Engineers Toxic and Hazardous Materials Agency. 1990. p. 650. *In: Proceedings of Annual Army Environmental Research & Development Symposium (14th)*, Williamsburg, Virginia. Technical Report No. CETHA-TE-CR-90067.

CHAPTER 6. THERMOCHEMICAL TECHNOLOGIES

6.1 Introduction

Incineration and other thermochemical technologies have been used for many years to dispose of a variety of solid and hazardous wastes as well as treat residues from contaminated sites requiring remediation. Thermochemical technologies utilize elevated temperatures to oxidize or otherwise convert large, complex molecules to less noxious compounds such as carbon dioxide and water. Unfortunately, the generation of potentially hazardous ash, wastewater, and air pollutants is of concern and has, at least in part, been responsible for the generation of significant public opposition to incineration technologies.

Thermochemical technologies are capable of high degrees of contaminant destruction, pathogen inactivation, and waste volume reduction, and are normally applicable to media having a wide range of physical and chemical properties and contaminant concentrations. Unfortunately uncontrolled air pollution include nitrogen oxides, organics, and metal particulates which require additional treatment. The ash residues often have to be tested to determine compliance with Resource Conservation and Recovery Act (RCRA) hazardous waste regulations.

Established, innovative, and emerging thermochemical technologies are summarized within this chapter.

6.2 Established Thermochemical Technologies

6.2.1 Wet Air Oxidation

Technology Description

In the wet air oxidation process, organic substances are oxidized under high pressures and elevated temperatures. The temperature range is between 350-650°F, and the pressure varies between 300 and 3000 psi. This process was initially developed in Norway for pulp mill wastes and has been modified for untreated wastewater sludges and other wastes. Combustion is incomplete, and typically averages between 80 to 90 percent.

In a typical aqueous waste treatment oxidation process, the pH of the wastewater is first lowered to 4 with acid and then pressurized to 700 psi. The wastes are passed through a heat exchanger that preheats the wastes from the hot oxidized products emerging from the reactor system. The wastes are transferred into the reactor that bombards the waste with oxygenated air from the top and bottom of the reactor.

The hot oxidized products emerge from the reactor after approximately 30 minutes, pass through the heat exchanger to heat the incoming waste, and then pass through a product cooler. These cooled products then go to a gas/liquid separator which extracts the gases, sends them to scrubbers that remove VOCs, and releases the clean gases to the atmosphere.

The effluent liquids from the process are treated separately, for the removal of heavy metals and, more thoroughly, for the biological degradation of organic molecules, before they are discharged to a wastewater treatment plant.

Advantages of Wet Air Oxidation:

- Has been in use for many years as a treatment technology and many are familiar with its general concepts, cutting down on the amount of training time needed.
- Ideal for the treatment of problematic wastewater which is too diluted to incinerate, yet too toxic to treat biologically.
- Small space requirements.
- Low energy requirements.
- Can potentially destroy many organic substances.

Disadvantages of Wet Air Oxidation:

- Not a stand-alone technology and must use additional treatment technologies to treat the waste effluents before they can be released, adding to the cost of the technology.
- Not effective for the oxidation of highly refractory chlorinated organics.
- Incomplete combustion materials generated.
- Odor problems are possible.
- Ammonia has been observed in end products.
- Highly skilled operators needed for process control.

Stage of Development

Commercially available for full-scale use.

Applications and Effectiveness

The wet air oxidation process has been shown to be effective in the treatment of wastes with a very high chemical oxygen demand (COD). The process can reduce the COD of some waste streams by 80 to 90%. Organic waste molecules are oxidized in the process to carbon dioxide and water products.

The wet air oxidation technology is appropriate for the treatment of aqueous effluents from chemical, pharmaceutical, munitions production, and other processes.

Due to the high pressures necessary for wet air oxidation, it is not commonly practiced. However, it is becoming popular to perform wet air oxidation in a deep well reactor. A typical deep well injection system consists of a tube and shell reactor. Concentric tubes in the reactor separate the down-flowing and up-flowing waste streams. Air is pumped into the system and the oxidation reaction occurs at the bottom of the well. Through the use of natural hydrostatic pressures, high pressure pumps and high temperature heat exchanger equipment are eliminated.

Cost Analysis

Not available.

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6.2.2 Fluidized Bed Incinerator (Combustor)

Technology Description

The fluidized bed combustor (FBC) incinerator has five basic system components: fluidized bed reactor, fluidizing air blower, waste feed system, auxiliary fuel feed system, and air pollution control device system. In FBC incineration, coal ash and other inert materials are mixed with waste of other combustible material in the incineration process. The use of inert materials in the combustor more effectively transfers heat to the waste stream.

The incinerator consists of a refractory-lined vessel containing inert granular material. Gases are blown through this material at a rate sufficiently high enough to cause the bed to expand and act as a fluid. The gases are injected through nozzles that permit upward flow into the bed and restrict downward flow of the bed material. Waste feed, which can be in any form, enters the reactor either above or within the bed. Pre-heating of the bed to start-up temperatures is accomplished by a burner located above and impinging down on the bed.

The FBC temperature range is 840-1800°F. Various residence times are required for different materials. Liquids and gases have residence times of a few seconds; whereas hazardous liquids are on the order of 12-14 seconds. Solid wastes require longer residence times. Typical wastes include organic and phenolic wastes, toluene diamine, methyl methacrylate, organic peroxide, and ethylene bromide manufacturing wastes. The feed rate for dry solids is 200 to 5,000 lb/hr and 48 to 55 cu ft/hr for liquids.

Circulating bed combustors (CBCs) are a subset of FBCs. The difference between the two is the configuration of their beds, with FBCs having fixed beds and CBCs having rotating beds which create "hot cyclones." This difference is disadvantageous to FBCs because if their beds go beyond the maximum fluidization velocity, the bed material may become entrained and carry-over out of the combustion chamber. If the FBC bed fluidization velocity is below minimum, the bed may slump.

Advantages of Fluidized Bed Incinerators:

- FBCs have a compact simple design with a large active surface area and are relatively simple to operate.
- FBC incineration combines thermal destruction and pollution control by trapping some gases and particulates in the bed.
- There is excellent gas/solids contact in FBCs, resulting in efficient combustion at lower temperatures than other combustion systems. This attribute reduces the amount of nitrogen oxides (NO_x) produced.
- FBCs have general applicability for the disposal of combustible solids, liquids, and gaseous wastes.
- FBCs have relatively low gas temperatures, excess air requirements, long incinerator life, and low maintenance costs.

Disadvantages of Fluidized Bed Incinerators:

- Erosion of the in-bed heat exchanger tubes is a problem with large particle and corrosive characteristic waste streams.
- FBCs have fixed beds and operate with narrow ranges of gas fluidization velocities.
- Considerable public concern over the incineration of hazardous wastes remains.
- It is difficult to remove residual materials from the bed.
- Operating costs are relatively high, particularly power costs.

Stage of Development

Utilities and industries have used this technology in the past for power generation. Hazardous waste destruction applications are still in the demonstration phase.

Applications and Effectiveness

Fluidized bed combustion has been in use by industry since the 1920s, especially in the petrochemical industry. The first fluidized bed wastewater sludge incinerator was built in 1962. There are now many units operating in the United States. The FBC technology has become more attractive to emerging independent power markets because of its flexibility to burn a variety of low-quality waste fuels.

FBCs are being designed to treat soils, sludges, and other solid waste contaminated with hazardous wastes.

Cost Analysis

Not Available.

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6.2.3 Co-incineration

Co-incineration refers to the joint incineration of hazardous waste with refuse and/or sludge. Co-incineration is not a separate technology, but one used with any of the established incineration technologies. The goals of co-incineration are to obtain better destruction and removal of a particular waste material, and to reduce the combined costs of incinerating sludges and hazardous wastes.

Advantages of Co-incineration:

- Potentially incinerates any thermally destructible hazardous waste
- Incinerates hazardous waste in existing incineration facilities
- Produces necessary heat energy for water evaporation
- Supports the combustion of solid wastes and sludges
- Reduces costs of incinerating sludges and soils
- Provides excess heat for steam generation
- Does not require auxiliary fossil fuels

Disadvantages of Co-incineration:

- Expensive air pollution control equipment
- High water content refuse or sludge cannot be incinerated with this technology

The temperature range for co-incineration is from 300 to 1600°F, and the residence times range from seconds to hours. Disposal ratios of 1 lb of dry wastewater solids to 5 lbs. of solid wastes are found in normal operation. Co-incineration has been successfully used for most hazardous wastes, including sludge, soils, organics, pesticides, and PCBs.

6.2.4 Liquid Injection Incineration

Liquid injection incinerators can be used for most any combustible liquid wastes (liquids, slurries, and sludges). A liquid injection incinerator operates by atomizing the waste and mixing it with air into a suspension. Atomization is provided mechanically using either a rotary cup or gas

fluid nozzles using high pressure air or steam. Thermal destruction of the waste takes place in the combustion chamber.

Advantages of Liquid Injection Incineration:

- Capable of incinerating a wide range of liquid wastes (liquids, slurries, sludges, etc.)
- Continuous ash disposal systems not needed
- Virtually no moving parts
- Low maintenance costs

Disadvantages of Liquid Injection Incineration:

- Burners are susceptible to clogging
- Particle size is a critical parameter
- Supplemental fuels may be necessary for sustained combustion

The most popular liquid injection incinerators are horizontally and vertically fired units. Since the liquid must be converted into a gas before combustion, viscosity and particle size are critical design parameters. The operating temperatures vary from 1200 to 2900°F, and residence times from 0.1 seconds to 2 seconds. In addition, liquid injection incinerators usually require 20 to 60 percent excess air to ensure complete combustion of the waste.

Liquid injection incineration has been effective for most liquid organic wastes and sludges. These include: phenols, thinners, solvents, PCBs, paints, and digester sludges. The utilization of this type of incineration for heavy metals, inorganic salts, inert materials, and high moisture content materials has not shown to be effective.

6.2.5 Multiple Hearth Incineration

The multiple hearth furnace is a widely used wastewater sludge incinerator in the United States. It is simple, durable, and has the flexibility of burning a wide variety of material even with fluctuations in the feed rate.

The multiple hearth furnace design includes a refractory-lined steel shell, a central shaft, a series of solid flat hearths and rabble arms, an air blower, fuel burners, ash removal system, and a waste feeding system. Sludge and/or granulated solid combustible waste is fed through the furnace by a screw feeder or belt and flapgate. The rotating air-cooled central shaft with air-cooled rabble arms and teeth moves the waste material across the top hearth to drop holes. The waste then falls to the lower hearths until it is discharged as ash at the bottom. The waste is agitated as it moves across the hearths to make sure fresh surface is exposed to hot gases.

As the hazardous waste travels across the hearths, it is constantly turned and broken into smaller particles by the rotating rabble arms. This process provides maximum surface exposure to the hot furnace gases for induction of rapid and complete drying as well as burning of the waste. The rabble arms also form spiral ridges of waste on each hearth, and the surface area of these ridges varies with the angle of repose of the sludge. This angle varies with the moisture content of the material. The surface area of waste exposed to the hot gases is considerably greater than the hearth area, by as much as 130 percent.

Advantages of Multiple Hearth Incineration:

- The retention or residence time is high, allowing maximum exposure for destruction.
- Large quantities of water can be evaporated.
- A wide range of wastes with different chemical and physical properties can be handled.

Disadvantages of Multiple Hearth Incineration:

- Difficulty in controlling the firing of supplementary fuels.
- Maintenance costs are high.

The temperature range for multiple hearth incineration is between 1400 and 2000°F, in which the drying zone is between 600 to 1000°F. Residence time varies from 0.25 to 1.5 hours, and the feed rate is typically 200 to 8000 lb/hr (dry sludge basis). Chemical sludges, oil refinery sludges, and solid residues from manufacturing of aromatic amines are typical examples of applicable wastes.

6.2.6 Rotary Kiln Incineration

Rotary kilns (such as used in the cement industry) have been utilized in both industrial and municipal installations burning solid, liquid, and gaseous wastes. Rotary kilns are currently used for Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) site cleanups requiring decontamination of soils, and lagoon sediments. In addition, rotary kilns have also been used to destroy obsolete chemical warfare agents and munitions. Rotary kilns are well suited for waste streams which are highly variable in terms of bulky solids, liquids, and sludges.

The rotary kiln incinerator is a cylindrical refractory metal shell that is mounted at a slight incline from the horizontal plane, sloping from the solids feed end of the kiln to the discharge end. It is used as a primary combustion chamber in incineration applications for hazardous waste destruction and includes five components: waste feed system, rotary kiln, auxiliary fuel feed system, afterburner, and air pollution control device system. Rotation of the shell and the slope provides transportation of the solids through the kiln while enhancing mixing of waste with combustion air. The rotational velocity of the kiln is used to control the retention time of solids within the kiln. The combustible portions of the waste are volatilized into gas as the solids travel the length of the kiln. Enhanced mixing and high retention time of solids in the kiln results in a high degree of burnout and increases the chances of producing non-hazardous ash from the kiln.

Rotary kilns typically have one or two auxiliary burners which can be located at either end of the kiln. These burners are used to pre-heat the kiln to minimum operating temperatures at the introduction of the waste feed and to provide supplemental heat to maintain minimum temperatures during operation. The auxiliary fuel burners can burn natural gas, propane gas, fuel oils, or high British thermal unit (BTU) liquid wastes.

Advantages of Rotary Kiln Incineration:

- Applicability to a wide range of liquid and solid wastes.
- Characterized by high turbulence and air exposure of solid wastes.
- Retention or residence time of the nonvolatile components can be easily controlled.
- Operational temperatures in excess of 2500°F, thus minimizing the amount of heat energy input required.

Disadvantages of Rotary Kiln Incineration:

- High capital costs for installation.
- High particulate loadings.
- Relatively low thermal efficiency.
- Problems in maintaining seals at either end of the kiln are a significant operating difficulty.

The temperature range is 1500 to 2900°F. Liquids and gases have residence times of a few seconds, whereas solid residence times are in hours. Typical wastes include PCBs, obsolete chemical warfare agents, and chlorinated solvents. The feed rate is 1300 to 4400 lb/hr.

6.3 Innovative Thermochemical Technologies

6.3.1 Spouted Bed Reactor

Technology Description

Spouted bed reactor (SBR) technology is a variation of the fluidized bed incinerator. The design is uncomplicated in comparison to other fluidized bed incinerators due to elimination of the fluidized bed bottom plate or structures immersed in the reactor. The SBR is a vertical reactor which provides a zone for volatilization, pyrolysis, and gasification reactions.

Steam, oxygen, and methane gas are introduced at the bottom of the vertical reactor, with superheated steam acting as the spouting fluid. Waste is fed into the spouted reactor via an extrusion feeder which grinds the waste. The shredded waste is introduced about midway up the reactor, well above the injection point for the steam and other gases. A nozzle projecting into the lower region of the bed provides a means by which to pass gas into the bed. The gas enters with sufficient velocity to cause a region of the bed above the nozzle to become fluidized. This process allows for robust circulation, mixing, comminution (particle size reduction through abrasion), and more efficient combustion to take place. The wastes are destroyed by the endothermic pyrolysis reactions, by the steam and by oxidation. Pyrolysis gas from the reactor is sent to an afterburner. Ash is discharged by the pneumatic force of the combustion gas.

Advantages of Spouted Bed Reactors:

- SBRs combine the benefits of fluidized combustion heat transfer rates and comminution.
- The gaseous products from the SBR can be used to power prime movers or to fuel conventional oxidation/incineration technologies.

Disadvantages of Spouted Bed Reactors:

- Technologies which use combustion to destroy toxic wastes are generally of public concern for health reasons. This public concern could delay acceptance of SBR as a full-scale remediation and disposal technology.
- SBR creates significant amounts of particulates in its off-gases, which need scrubbers, baghouses, or other treatments to remove them.

Stage of Development

The EPA SITE program finished a pilot-scale demonstration of the technology in August 1993 with the cooperation of the Energy and Environmental Research Corporation.

Applications and Effectiveness

Wastes which are applicable to the SBR technology include those containing significant heat contents that are contaminated with toxic organics and heavy metals. Soils which are contaminated with coal tar residue, petroleum refinery wastes, and municipal solid wastes are applicable to the SBR process. Munitions, chemical wastes, and propellants are also good candidates for SBR.

Cost Analysis

Not available.

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6.3.2 Infrared Incineration

Technology Description

Infrared (IR) incineration system utilizes heat generated from IR radiation for waste combustion. A high temperature alloy wire mesh conveyor carries waste through a horizontal reactor. Temperatures of up to 1850°F are achieved within a primary combustion chamber (2.5 ft x 9 ft x 3 ft) from IR radiation, which is generated by providing electrical energy to a series of silicon carbide rods mounted horizontally within the chamber. Residence times for the wastes range from 10 minutes to 3 hours. The combustion system can operate in an oxidizing, reducing, or neutral atmosphere.

A secondary chamber of similar size utilizes a propane burner and IR energy to incinerate the gases produced by the waste and raise the temperature to 2300°F, with a residence time of up to 2.2 seconds and 100 percent excess air.

Solids have an 18 to 19 minute residence time within the primary chamber, and the gases have residence times less than 3 seconds in the secondary chamber. The feed rate for a mobile unit is 3.6 to 4 tons/hr.

Air pollution control equipment are located after the secondary chamber. Exhaust gases are passed through a liquid Venturi scrubber for acid and particulate removal and gas cooling to 180°F. Generally, the air pollution equipment can be changed in order to accommodate varying wastes and emission regulations.

Data on this system demonstrates the ability of a portable incineration technology to destroy PCBs with high efficiencies. However, data from early field tests demonstrate there is incomplete combustion occurring for the applications tested. Downwind air samples subjected to Ames testing were found not to be mutagenic.

Advantages of Infrared Incineration:

- Destruction and removal efficiencies of PCBs and dioxin are very high.
- Current configuration of a portable unit can lower capital and transportation costs and allow a single facility to service a number of contaminated sites.
- Control of temperature and conveyor system.
- Control of residence time.

Disadvantages of Infrared Incineration:

- Volatile organic, semivolatile organic, and particulate emissions from this system were noted during SITE testing. This result indicates the system is not well suited for applications involving high efficiency removal of either organics (other than PCBs) or particulates.
- Waste feed materials handling during testing was demonstrated to be a problem. Waste must be fed into incinerator in a uniform manner. Pre-treatment of waste may be required to ensure appropriate solids size.
- Current cost data indicate it to be more expensive than other comparable disposal technologies such as conventional incineration.
- Liquids must be adsorbed to solid matrix to prevent dripping of waste through conveyor.

Stage of Development

A portable system was initially developed in the mid 1980s by Shirco Infrared Systems, Inc. On-site tests were conducted in Times Beach, Missouri, for dioxin removal in contaminated soils. Destruction and removal efficiencies (DREs) of dioxin exceeded 99.9999 percent, with low particulate emissions.

Subsequent tests under the SITE Program at Peak Oil Site in Brandon, Florida, and Rose Township, Michigan, demonstrated PCB DREs of greater than 99.99 percent. Acid gas removal efficiencies were consistently greater than 99 percent.

A commercial system is currently available.

Applications and Effectiveness

This technology is currently applicable to the disposal of PCB contaminated solids. Data supporting a broader application is not available.

Cost Analysis

Cost data for a commercial transportable system that had an "on-stream factor of 19 percent" was \$795 per ton of contaminated soil (in 1990 dollars - approximately). These costs exclude transportation, feed preparation, ash disposal, and other costs not directly related to the operation of the system.

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6.3.3 Pyrolysis

Technology Description

Pyrolysis is the thermal degradation and destruction of materials in an inert atmosphere with little or no oxygen. The contaminated wastes are placed in an incinerator or rotary kiln and heated up to as much as 1,800°F. Since the reaction contains less than the stoichiometric oxygen requirement, the resultant gases can be recycled for fuel.

There are two types of pyrolysis, non-slugging and slugging. Non-slugging pyrolysis is more widely used, and it takes place in conventional incinerators which have been adapted to limit the amount of oxygen entering the combustion chamber. Slugging pyrolysis is a much more specialized form. It requires higher temperatures and heats the waste past the char state to the molten state. This process achieves maximum volume reduction as well as toxicity reduction but it requires additional fuel and specialized facilities.

Advantages of Pyrolysis:

- Pyrolysis is capable of doubling the throughput of conventional combustion incinerators, thus increasing the rate of waste destruction per unit time.
- The solid residues from pyrolysis destruction can be contaminant-free and are capable of being backfilled.
- The relatively slow and even heating of the wastes prevents a "crusting" of the waste which would result in inhibited volatilization of the hazardous constituents.
- Lower heat input is required in pyrolysis than in combustion, resulting in less fuel consumption.

Disadvantages of Pyrolysis:

- This technology is not appropriate for the treatment of aqueous, heavy metal, or inorganic waste streams.
- There is growing public concern over the use of any thermal destruction technology, and approval of this technology may be difficult to obtain.

Stage of Development

The EPA SITE demonstration of the Pyretron Burner at the Stringfellow Acid Pit Superfund site in California was completed in January 1988. This technology is commercially available.

Applications and Effectiveness

The Pyretron Burner treats high and low BTU solid wastes contaminated with rapidly-volatilized hazardous organic compounds.

Cost Analysis

Cost estimates for pyrolysis technology using indirectly heated rotary kilns are between \$65 and \$80 per ton of soil.

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6.4 Emerging Thermochemical Technologies

6.4.1 Plasma arc Technology

Technology Description

Plasma arc technology was developed over 30 years ago by NASA for the U.S. space program to simulate re-entry temperatures on heat shields. Only recently has this technology begun to emerge as a commercial tool in several industries such as steelmaking, metallurgy, precious metal recovery, and waste disposal. Plasma occurs naturally in the form of lightning.

A plasma is a highly ionized gas that is conditioned to respond to electromagnetic forces. The plasma arc is created when a voltage is established in the ionized gas between two points, and the plasma acts as a resistive heating element. This resistive heating element presents a distinct advantage over any solid heating element since it is a gas and cannot melt and fail. A plasma arc torch is capable of generating temperatures of over 7,000°C. Thus, plasma torches operate at much higher temperatures, higher enthalpies, and greatly increased efficiencies than fossil fuel burners. With such high temperatures, hazardous wastes can be efficiently destroyed and residues can be melted and subsequently solidified, or vitrified. In addition, plasma torches require only about 5% of the gas necessary for fossil burners. Therefore, effluent gases are greatly reduced, and waste treatment systems can be built much more compactly than traditional systems, at correspondingly reduced capital costs.

A plasma torch generally consists of a stainless steel cylinder several inches in diameter and several feet in length, the specific dimensions being related to the torch power levels and the planned applications. This cylinder integrates the electrodes, insulators, gas injectors, and water dividers into a functional torch. Cooling water is circulated within the walls of the torch to prevent it from melting.

Advantages of Plasma Arc Technology:

- A large array of difficult to treat hazardous wastes are effectively treated with plasma technology.
- Plasma arc technology generates relatively small volumes of air pollution which have to be captured and treated.
- The system is compact and well-suited to mobile applications.
- The system has the potential to return recoverable energy in the form of heat from its by-products and combustible gases.
- Plasma torches can be operated in subterranean boreholes for *in situ* remediation of contaminated soils and buried hazardous waste deposits.

Disadvantages of Plasma Arc Technology:

- Plasma vitrification must compete with other remediation technologies which may be more cost effective for selected waste streams.
- Significant electrical power capacity must be available on-site.

- High furnace/reactor temperatures may require frequent replacement of refractory materials.
- For *in situ* applications, cased boreholes must be emplaced throughout the zone of contamination prior to treatment.

Stage of Development

Several plasma torch furnace/reactor processes for the destruction of hazardous and toxic wastes have been developed and successfully tested. The very high temperatures and energy densities, in conjunction with an ionized and reactive medium, have fully demonstrated the potential of plasma technology to treat a large variety of hazardous and toxic waste materials in an environmentally safe and cost-effective manner. Some of these processes have been commercialized, while others are still in the development stage. Materials vitrified with plasma arc torches readily pass all standard leaching tests. Plasma arc technology is currently being utilized or planned for a variety of industrial and experimental waste treatment processes. These processes include:

- Pyrolysis of Municipal Solid Waste
- Vitrification of Asbestos-Containing Materials
- Destruction of Medical Waste
- Destruction of Polychlorobiphenols (PCBs)
- *In Situ* Remediation of Contaminated Soils and Buried Deposits
- Incinerator Ash Vitrification
- Stabilization of Radioactive Wastes
- Vitrification of Hazardous/Toxic Wastes

Applications and Effectiveness

Plasma arc technology is applicable to the treatment of municipal and industrial wastes, heavy metals, organic contaminants in soils, sludges, asbestos, low-level radioactive wastes, and other hazardous wastes. In addition, it is anticipated that military hazardous materials such as chemical weapons wastes, explosives, unexploded ordnance, pyrotechnic wastes, etc., may also be treated with plasma technology. It is applicable to both solids and liquids.

Cost Analysis

Based on several years of laboratory studies, the cost of plasma treatment of hazardous/toxic wastes can be estimated. For *ex situ* treatment of wastes in a plasma furnace/reactor, costs will range from \$200 per ton for asbestos-containing materials, up to \$1,200 per ton for highly toxic (non-radioactive) wastes. Utilizing a 5 MW mobile plasma heating system, the estimated costs of *in situ* treatment range from \$50 per ton for a municipal solid waste landfill to \$130 per ton for a hazardous/toxic (non-radioactive) waste burial pit.

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6.4.2 Microwave Incineration

Technology Description

Microwave energy is applied to a discrete amount of contaminated waste. The applied energy heats the soil or waste to well over 100°C and volatilizes the contaminants. Insoluble nonvolatile organics become "fixed" in the soil at a relatively low temperature. Volatilized contaminants are collected for further disposition. The collection medium may be activated carbon, and the ultimate disposal varies according to the waste and other factors.

This technology requires that a vapor barrier be placed over the area that is being remediated. This process will ensure that contaminant vapors are captured and not allowed to escape into the air. The vapors are condensed. Normally this technology is economically applied to only a small area and to shallow depths. Available data shows volatile and semivolatile organic compound removal is 99 percent and 97 percent successful respectively, with contaminant removal to a depth of 2 meters.

The process of microwave incineration is similar to plasma arc incineration in that gas particles are ionized and release ultraviolet radiation through a generated plasma arc. In this case, reactions that occur in the plasma are not always decomposition reactions. Oxygen is maintained at high levels to ensure that most of the reactions occurring are combustion reactions (Kiang, 1982).

The temperature range is variable with a residence time of 0.1 to 3 seconds. Typical wastes include liquids and solids. No full-scale feed rates are available.

Advantages of Microwave Incineration:

- The contaminants are concentrated and not diluted by large volumes of gas.
- This provides a short-term, energy-efficient remediation.
- Microwave systems may not be classified as hazardous waste incinerators, and may not require permits.
- Equipment is relatively small and can be easily adapted to a mobile system.

Disadvantages of Microwave Incineration:

- This technology cannot be used if metal objects are buried in the subsurface.
- High moisture content will result in large power consumption while heating the soil.
- Public concern remains significant for any type of thermal system which has potential air emissions.
- No guarantee of predictable destruction efficiencies.
- Some byproduct recombination's are as toxic as the initial waste.

Stage of Development

The New Jersey Institute of Technology has recently installed a 6-kilowatt microwave pilot-scale plant, and a full-scale implementation of radio frequency is scheduled for Kelly Air Force Base.

Applications and Effectiveness

This methodology is most applicable to the removal of volatile organics from contaminated soils as might be expected from areas in and around leaking USTs or old disposal pits.

Cost Analysis

The initial equipment investment for radio frequency application is estimated at \$2.5 million, with an estimated remediation cost of \$80 per ton of soil. The process is most economical when the area involved is one acre or less.

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- National Institute for Petroleum and Energy Research. 1992. Installation restoration and hazardous waste control technologies. U. S. Army Corps of Engineers Toxic and Hazardous Materials Agency. Technical Report No. CETHA-TS-CR-92053.

6.4.3 Molten Salt Incineration

Technology Description

Molten salt incineration is a method of burning organic material while simultaneously scrubbing the combustion products which might be released in the effluent. A molten salt, such as sodium carbonate, is the base of this technology and serves as a heat transfer and reaction medium. Waste and air are fed under the surface of a molten salt bath. The salt serves as a catalyst as well as a flue gas scrubber. The molten salt also serves as a heat sink, absorbing heat when waste is oxidized and releasing it when cooler waste is added to the salt bath.

Sodium carbonate is generally used because it is compatible with water, carbon dioxide, and combustion products. It is also used for its acid neutralizing capability. Sodium carbonate is also stable, nonvolatile, inexpensive, and nontoxic.

This technology is well suited for highly toxic and/or highly halogenated solid and liquid waste streams. Typical wastes include non-acidic shredded solids, liquids, sludges, and flowing powders. The acidic gases HCl and SO₂, created from the combustion of halogenated and sulfur-containing organic compounds, are absorbed and neutralized in the alkaline molten bed. The combustible waste and air are introduced beneath the surface of the molten pool, which is kept at a temperature on the order of 900°C. This temperature is hot enough to cause the hydrocarbons of the organic matter to immediately oxidize into carbon dioxide and water, but too low to permit significant fixation of oxides to form NO_x emissions.

The combustion byproducts, which may contain phosphorus, sulfur, arsenic, and halogens, react with the sodium carbonate. The byproducts are retained in the melt as inorganic salts rather than being released as volatile gases into the atmosphere.

Ash deriving from the waste must periodically be removed to preserve the fluidity of the melt. Those waste streams which contain large percentages of materials which are non-combustible or will produce large amounts of ash are not well suited to the technology, because they necessitate bed replacement more often. Concentration of ash in the melt should be at 20% by weight to maintain a significant margin of safety.

Result data indicate that for optimum operating conditions, high temperatures and deep beds (30 cm or higher) are required. The temperature range is 1500 to 1800°F, with relatively long

residence time. Pilot-size feed rates have been shown to be 100 kg/hr. The higher temperatures also increase waste throughput significantly.

Advantages of Molten Salt Incineration:

- The sodium carbonate commonly used in molten salt beds is stable, inexpensive, nonvolatile, and nontoxic.
- All of the bench studies indicated destruction efficiencies which were as good as or better than the RCRA restrictions of the time.
- This technology would treat several highly problematic categories of waste for disposal with greatly reduced probability of harmful byproducts than standard methods of thermal destruction.
- Salt acts as a scrubber by removing halogens from flue gas.
- Metals and other materials remain in the salt which is removed and stripped.
- Emissions are minimal compared to other incineration technologies.
- Temperatures in the melt are not high enough to promote the formation of nitrogen oxides.

Disadvantages of Molten Salt Incineration:

- There are safety concerns due to the nature of the molten medium and the toxic nature of the influent wastes. Acidic wastes may react explosively with the salts.
- Little information is available as to the energy requirements of this technology. It is anticipated that a great deal of energy is required to heat up and maintain the temperatures needed for destruction capabilities.
- Salt bath must be disposed or regenerated when the ash and other inerts build up to 20 percent of the melt.

Stage of Development

A pilot-scale facility with a processing capability of 80 to 200 lb/hr was constructed in 1987 by Rockwell International for PCB and other wastes.

The LLNL built a pilot-scale unit for the testing of molten salt incineration of high explosive (HE) and high explosive containing wastes.

Applications and Effectiveness

The molten salt process has been bench tested by Rockwell International, with destruction efficiencies of 99.9990% to 99.9998% on solid wastes impregnated with PCBs. This research indicates that this technology would be suitable for any transformer oil or oils from capacitors.

Explosive and explosive containing wastes were destroyed at the LLNL facility with a high success rate. In 1992, a slurry of >35 percent HMX in mineral oil was safely and successfully destroyed with the molten salt method. This result indicates that other energetic materials could be disposed of in the future with this technology.

Cost Analysis

Not available.

REFERENCES

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6.4.4 Molten Glass Incineration-Vitrification

Technology Description

Electric furnaces commonly used in glass manufacturing can also be used to destroy hazardous wastes. The high temperatures generated in the production of glass are used to convert contaminated soils, sediments, and sludges into glass. The hazardous materials are rendered nontoxic and suitable for disposal as a solid waste.

In this process, an electric furnace has a pool of molten glass in the bottom. Temperatures of about 1500°C are maintained with electrodes within the glass. Liquid or slurry wastes can be introduced at a controlled rate, depending upon the furnace configuration. Wastes are charged from above the molten glass to form a solid cover of feedstock and waste over the molten glass. This process keeps potential emissions largely contained within the molten mass.

Inert material is captured within the molten glass. Included in the system is an assortment of air pollution control devices. Fabric filters capture the particulate emissions. These filters can be fed back into the furnace with the feedstock for disposal. The inert particulate is then retained in the glass. When halogenated organics are fed into the system, liquid scrubbers are required for HCl control.

The use of electrodes for heating, as opposed to fossil fuels, results in significantly reduced off-gas volumes requiring treatment.

The glass solidifies and is sold as a commercial product or is disposed of as a solid waste after passing RCRA testing or delisting as appropriate.

Advantages of Molten Glass Incineration:

- The high temperatures achieved with this process generate a high level of destruction.
- This method of operation allows a wide range of materials to be incinerated within this system.
- Electric heating, which is used to melt the materials, has a much lower volumetric emission rate as compared to fossil fuel heating systems.

Disadvantages of Molten Glass Incineration:

- The increasingly stringent environmental standards for hazardous wastes incinerators require rigorous system testing.
- Electrical costs for the furnace are greater than other sources of thermal treatment energy.
- Incineration systems are currently viewed by the public as not being benign disposal options.

Stage of Development

Reported to be commercially available; however, additional emissions testing is needed to address compliance with air emission standards. The EPA is planning pilot-scale testing on this "electric melter" technology.

Applications and Effectiveness

This system was developed in the mid 1980s and has undergone some changes. Of major concern are the air emissions from the process and the destruction efficiencies achieved for the hazardous wastes incinerated. Characterizing air emissions will be part of future EPA tests. This incineration technology would be applicable to the disposal of most solid and hazardous wastes.

Cost Analysis

Not available.

REFERENCES

- Environmental Protection Agency. 1985. Innovative thermal processes for hazardous waste treatment and destruction. Report No. EPA/600/D-85/169.
- Environmental Protection Agency. 1992. Superfund innovative technology evaluation program technology profile, 5th edition. Report No. EPA/540/R-92/077.
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6.4.5 Supercritical Water Oxidation

Technology Description

Supercritical water oxidation (SCWO) is a process which destroys hazardous wastes above the critical temperature and pressure of water. The reaction is carried out entirely within an enclosed container. The waste is mixed with an oxidant such as oxygen, air, or hydrogen peroxide above the critical point of water (374°C and 218 atm). The supercritical water is a unique solvent medium which allows oxidation to take place at temperatures significantly lower than incineration. The lower temperature of reaction (compared to incineration) also limits the amount of NO_x produced. The time of reaction is typically seconds to minutes, with the resulting end products being water, carbon dioxide, and nitrogen. Destruction efficiency rates for the organics tested have been very high. Inorganics are practically insoluble in supercritical water, rendering them easily removed from the reaction stream.

Organics can be processed utilizing a waste and water slurry with 5 percent by weight organics. The slurry is preheated and injected with air or oxygen into the reactor vessel. Organics are commonly oxidized in less than one minute. At 5 percent organics, the temperature of the reactor increases the effluent stream to approximately 500°C. The effluent is fed to a solids separator, where the inorganic salts are removed. The waste heat can then be used for power generation or other useful purposes.

SCWO has successfully treated a variety of compounds to include simple hydrocarbons and oxygenates, chlorinated organics and aromatics, nitro-organic compounds, pharmaceuticals and biopharmaceuticals, dioxin-contaminated soil, and fermentation wastes, as well as municipal and industrial sludges.

Advantages of Supercritical Water Oxidation:

- Supercritical water oxidation oxidizes organic wastes and entraps inorganic wastes in solid precipitates.
- Air emissions from this operation are minimal.
- NO_x emissions are much less using SCWO than by incineration.
- The reaction vessel operates like a "totally enclosed system."

Disadvantages of Supercritical Water Oxidation:

- The high temperatures and pressures required create safety concerns as well as high operating expenses.
- Destruction of compounds containing chlorine and similar compounds cause the pH to drop within the reactor and create significant corrosion problems.

Stage of Development

This technology has been under commercial development since 1980. Pilot facilities with capacities up to 300 gallons per day have been tested to treat a variety of organic wastes.

The Army is investigating SCWO for the treatment of energetic materials from munitions manufacturing. These studies are still in the pilot stage. The Army is also examining this technology for disposal of chemical agents.

The first supercritical water oxidation facility designed to treat petroleum related wastes is being built by Texaco Chemical Company in Austin, Texas.

Applications and Effectiveness

SCWO is a very promising technology for the destruction of wastes containing a wide variety of organic and inorganic contaminants. Special applications for the Army include destruction of explosive and explosive contaminated wastes, propellants, organics, and chemical warfare agents.

Cost Analysis

Not Available.

REFERENCES

- Beard, J. 1993. Destroying toxic wastes in a pressure cooker. *New Scientist* 139: 19.
- Dyer, R. B. *et al.* 1992. Destruction of explosives and rocket fuels by supercritical water oxidation. Los Alamos Laboratory. Technical Report No. LA-UR-92-2378.
- Freeman, H. M., R. A. Olexsey, D. A. Oberracker, and R. E. Mournigham. 1987. Thermal destruction of hazardous waste - a state-of-the-art review. *Journal of Hazardous Materials* 14: 103-117.
- Sanchez, J. 1993. Super critical water oxidation on energetic materials, p. 13. *In: 1993 MAES national symposium on super critical water oxidation on energetic materials, Long Beach, California.* Los Alamos Laboratory. Technical Report No. LA-UR-93-921.

6.4.6 Selective Catalytic Reduction (SCR)

Technology Description

This flue gas treatment system for nitrogen oxides (NO_x) utilizes an anhydrous or aqueous ammonia (NH_3) injection system and a catalytic reactor to reduce NO_x within a boiler effluent gas stream. An injection grid disperses NH_3 in the flue gas upstream of the catalyst. The NO_x and NH_3 are both reduced to N_2 and water in the catalytic reactor. This technique reduces NO_x generated from the combustion of organic nitrogen in the fuel as well as the NO_x generated from the thermal reaction of the nitrogen in the air that enters the combustion process.

Most SCR installations utilize base-metal catalysts and operate at approximately 260°C-400°C. This temperature requirement limits the use of existing SCR systems to flue gas locations where the gas stream temperature has cooled sufficiently. This requirement accounts for the limited application in the United States for systems which simultaneously cool the gas, such as following other control systems or in conjunction with heat recovery steam generators. However, new high-temperature zeolite catalysts are expanding the use of SCR into the 600°C range.

Application of SCR with the combustion of sulfur-containing oil and coal raises some additional concerns. The sulfur, which is converted to SO₂ during combustion, may convert to SO₃ in the catalytic reactor. Reaction of the SO₃ with the NH₃ results in the formation of an ammonium salt. This salt can result in fouling, corrosion, and back pressure. System operations must be closely controlled, and particulates must be periodically removed.

Advantages of Selective Catalytic Reduction:

- SCR provides a system of NO_x control of up to 90 percent efficiency.
- Retrofit capability is possible with the SCR technology.
- SCR can be used as a "polishing" treatment step following another combustion control process for NO_x reduction.

Disadvantages of Selective Catalytic Reduction:

- The selected catalysts are subject to potential masking agents in the flue gas.
- Ammonia that is injected into the gas stream can "slip" out in the effluent gas in the several ppm range.
- Sulfur-containing fuels can generate an ammonium salt requiring periodic removal.

Stage of Development

SCR technology was first developed in Japan in the late 1970s and expanded to use in Germany in the middle and late 1980s. It is being experimented with in the United States in the 1990s in order to achieve stringent fossil fuel combustion emission limits created by the 1990 Clean Air Amendment acid rain provisions. Nearly all current United States SCR applications are following combustion controls for NO_x reduction or collocated as part of heat recovery systems. EPA is reporting on SCR technology that is being utilized in the pilot plant stage. Virginia and California are starting to permit facilities utilizing SCR technology for varying degrees of NO_x control.

Applications and Effectiveness

SCR technology is applicable to nearly all stationary fuel combustion systems, to include boilers and turbines. Future application will depend upon the degree of NO_x control required. SCR can be used in conjunction with other control systems.

Cost Analysis

Cost data are available for turbine applications and used in conjunction with combustion controls for NO_x removal. Costs reduce exponentially with size and range from \$5,000 to \$25,000 per ton of NO_x removed (1990 dollars).

REFERENCES

[Anonymous]. 1992. Plant must be cleanest yet. *Engineering New Record* 228: 16.

Armor, J. N. 1992. Environmental catalysis. *Applied Catalysis B: Environmental* 1: 221-256.

Kotter, M. and H. G. Lintz. 1991. Selective catalytic reduction of nitrogen oxides-an original concept. *International Chemical Engineering* 31: 685-692.

Princiotta, F. T. 1992. Technologies options for acid rain control. Environmental Protection Agency. Report No. EPA/600/A-92/216.

Scharer, B. 1993. Technologies to clean up power plants. *Staub* 53: 157-160.

Snyder, R. 1993. Alternative control techniques document NO_x emissions from stationary gas turbines. Environmental Protection Agency. Report No. EPA-453/R-93-007.

6.4.7 Circulating Bed Combustor

Technology Description

The CBC is a technology which uses turbulent air at high velocities to create a cyclone inside a CBC chamber. This cyclone uniformly mixes and treats contaminated soils or wastes at temperatures between 1450 and 1600°F.

Wastes and limestone (which neutralizes acid gases) are introduced into the CBC chamber, then the ash and hot gases are conveyed to a cooling chamber. The post CBC products are passed through a convective gas cooler and baghouse before they are released into the ambient air.

For wastes or soils which contain a net heating value of at least 2900 BTU per pound, there is no need for auxiliary fuels to be used to heat the CBC. Auxiliary fuels include: natural gas, fuel oil, or diesel.

Advantages of Circulating Bed Reactor:

- Effective mixing in the CBC and relatively low operating temperatures reduce emissions of nitrogen oxides and carbon monoxide.
- CBC has been permitted under the Toxic Substances Control Act (TSCA) to treat PCBs in all of the EPAs regions.
- Operating temperatures prevent slagging of the treated soils/wastes.

Disadvantages of Circulating Bed Reactor:

- The ash derived from this technology may be hazardous wastes which must be disposed of in hazardous waste landfills or other approved disposal sites. This factor may add significant cost.

Stage of Development

CBC technology was accepted into the EPA SITE program in March 1989. A treatability study was done at the McColl Superfund site in California. A pilot-scale study has been completed at the Ogden Research Facility in San Diego, California.

Applications and Effectiveness

Soils and sludges which are contaminated with halogenated and nonhalogenated hydrocarbons, and soils contaminated with PCBs, are well suited to CBC treatment. Liquids, soils, slurries, and sludges which contain cyanides, dioxins/furans, corrosives, inorganics, oxidizers, and pesticides can be treated with the CBC process.

This process may be applicable to industrial wastes from refineries, chemical plants, manufacturing site cleanups, and contaminated military sites.

Cost Analysis

Not available.

REFERENCES

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6.4.8 Oxygen Incineration

Technology Description

A conventional incinerator design such as a rotary kiln can be modified by replacing the traditional air blower with pressurized oxygen system. The burner in the incinerator must also be modified or replaced in order to use oxygen instead of air.

The temperature range is 1500 to 2000°F, with variable residence time. Typical wastes include sludges, liquids, and solids which are fed at variable flow rates into the oxygen incinerator. These flow rates are higher than conventional systems.

Advantages of Oxygen Incineration:

- Incinerator can be small in size.
- Incinerator uses less additional fuel due to the reduced gas flow.
- Temperatures are easy to control inside the incinerator because the pressurized oxygen can be continuously controlled by monitoring equipment.
- Double waste throughput as compared to some existing incinerators.
- Flue gas pollution control equipment are more effective because there is substantially less gas to treat.

Disadvantages of Oxygen Incineration:

- High oxygen costs.
- Flame temperatures tend to be higher, thereby reducing the life expectancy of the incinerator.
- Some byproducts are as toxic as the initial waste.

6.4.9 High Temperature Fluid Wall Incineration

Technology Description

A cylindrical core made of graphite and carbon felt is heated by resistive carbon rods. An inert gas flows from the outside of the reactor wall to the inside for prevention of the waste coming into contact with the reactor core. The waste is heated as it falls through the center of the graphite tube.

The temperature range is 3500 to 4500°F, with relatively short residence time. Solid wastes are fed at a feed rate of 15 lb/min. Adequate testing on hazardous wastes have not been performed.

Advantages of High Temperature Fluid Wall Incineration:

- High operating temperature is sufficient to destroy almost any chemical bond.
- Minimal tendency for formation of new byproduct recombination's.
- Solid glass-like particles formed as a byproduct have tested to be non-leachable.

Disadvantages of High Temperature Fluid Wall Incineration:

- Solid wastes must be ground to 20-mesh size to assure thorough heating.
- Only solids may be treated.
- Adjustment of residence time is not possible.
- Liquids or gases must be blended with a material to make a suitable treatment matrix.

6.4.10 Catalytic Incineration

Technology Description

A reactor is designed to heat the water to the required activation temperature and to bring the waste into contact with a suitable catalyst. The process is often designed utilizing fluidized bed technology because it allows for significant contact time between reactants and the catalyst. The temperature range is 600 to 1000°F, with variable residence time based upon design.

Advantages of Catalytic Incineration:

- Operational temperatures are about half that of normal incineration.

Disadvantages of Catalytic Incineration:

- System is best suited to gases only; however, there is work underway to make the system compatible for liquids.
- Catalyst tends to be expensive and can easily be fouled.
- Lower reactor temperatures destroy only specific chemicals which take part in the catalyzed reaction.
- Contaminants which do not take part in the catalyzed reaction may go through the reactor unaffected.

6.4.11 Controlled Incineration

Technology Description

Incineration oxidizes organic waste by burning. The Pyretron technology controls the heat input and oxygen level into the incineration process. American Combustion, Inc., successfully demonstrated their Pyretron thermal destruction technology at EPA's Combustion Research Facility in Jefferson, Arkansas, using a mixture of 40 percent contaminated soil from the Stringfellow Acid Pit Superfund site in California and 60 percent decanter tank tar sludge from coking operations.

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- Environmental Protection Agency. 1991. Superfund innovative technology evaluation program technology profiles, 4th edition. Report No. EPA/540/5-91/008.
- Staley, L. J. and R. E. Mournighan. 1989. SITE demonstration of the American Combustion Pyretron oxygen-enhanced burner. *Journal of the Air Pollution Control Association* 39: 149-153.

Table 18. Thermochemical Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
PYRETRON [®] Thermal Destruction - <i>(American Combustion, Inc.)</i>	Tech. Contact: Gregory Gitman American Combustion, Inc. 4476 Park Drive Norcross, GA 30093 770-564-4180 EPA Contact: Laurel Staley 513-569-7863	Computer controlled technology to automatically adjust the temperatures of the primary and secondary combustion chambers and the amount of excess oxygen.	High- and low-BTU solid wastes	VOCs	Technology is commercially available. EPA SITE demonstration conducted at EPA's Combustion Research Facility in Jefferson, AR.	The demonstration program conducted used a mixture of 40 percent contaminated soil and 60 percent decanter tank tar sludge. The technology achieved greater than 99.99 percent destruction and removal efficiencies of six principal polycyclic aromatic hydrocarbons. Cost savings can be achieved when operating. Fuel costs are high, and oxygen costs are relatively low.

Table 18. Thermochemical Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Cyclone Furnace - <i>(Babcock & Wilcox Co.)</i>	Tech. Contact: Lawrence King Babcock & Wilcox Co. 1562 Beeson Street Alliance, OH 44601 216-829-7576 EPA Contact: Laurel Staley 513-569-7863	The furnace is designed for high heat-release rates and high turbulence in cyclones to assure achievement of the high temperatures required for melting high-ash fuels. The inert ash exits the cyclone furnace as a vitrified slag.	Sludge, soil, and highly contaminated inorganic wastes	Heavy metals and organic compounds	EPA SITE demonstration completed.	In the demonstration program, the EPA supplied wet, synthetic soil matrix (SSM) spiked with heavy metals, organics, and simulated radionuclides. Destruction and removal efficiencies for organics were greater than 99.997 percent, and greater than 75 percent of the metals were incorporated in the slag. Cost data not available.
Thermal Gas Phase Reduction Process <i>(ELI)</i>	Tech. Contact: Jim Nash ELI Eco Logic International, Inc.	Reaction takes place within a specially designed reactor that utilizes thermochemical reactions.	Soil, sludge, liquid, and gas	PCBs, PAHs, pesticides, landfill leachates, dioxin	EPA SITE demonstration program testing completed.	At Hamilton Harbour, Ontario, PAH- and PCB-contaminated

Table 18. Thermochemical Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Flame Reactor - <i>(Horsehead Resource Development Co., Inc.)</i>	Tech. Contact: Regis Zagrocki Horsehead Resource Development Co., Inc. 300 Frankfort Road Monaca, PA 15061 412-773-2289 EPA Contact: Donald Oberacker 513-569-7510	System is hydrocarbon-dueled, flash-smelting reactor.	Granular solids, soil, flue dusts, slags, and sludges	Heavy metals	EPA SITE demonstration program testing completed.	At the National Smelting and Refining Company Superfund site in Atlanta, GA, the test was conducted on 72 wet tons of waste material. All effluent slag passed the TCLP limits criteria. No cost data available.
Infrared Thermal Destruction - <i>(Gruppo Italmpresse)</i>	Tech. Contact: Gruppo Italmpresse Rome 011-39-06-8802001 Padova 011-39-049-773490 EPA Contact: Howard Wall 513-569-7691	Mobile thermal processing system that uses electrically-powered silicon carbide rods to heat wastes to combustion temperatures.	Soil or sediment	Organic compounds	EPA SITE demonstration program testing completed.	Full-scale unit treated nearly 7,000 cubic yards of waste oil sludge containing PCBs and lead in one study and organics, PCBs and metals in soil in another study. For both, PCBs were reduced to less than 1

Table 18. Thermochemical Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Circulating Bed Combustor (CBC) - (<i>Ogden Environmental Services</i>)	<p>Tech. Contact: Derrel Young Ogden Environmental Services 12755 Woodforest Blvd. Houston, TX 77015 713-453-8571</p> <p>EPA Contact: Douglas Grosse 513-569-7844</p>	The CBC uses high velocity air to entrain circulating solids and creates a highly turbulent combustion zone that destroys toxic hydrocarbons.	Liquids, slurries, solids, and sludges	Corrosives, cyanides, dioxins/furans, inorganics, metals, organics, oxidizers, pesticides, PCBs, phenols, and volatiles	EPA SITE demonstration program completed.	At the McColl Superfund site in California, a treatability study and demonstration on wastes was conducted. DRE values of 99.99 percent were obtained for principal organic constituents. No cost data available.
Plasma Arc Vitrification - (<i>Retech, Inc.</i>)	<p>Tech. Contact: R.C. Eschenbach Retech, Inc. P.O. Box 997 100 Henry Station Ukiah, CA 95482 707-462-6522</p> <p>EPA Contact: Laurel Staley 513-569-7863</p>	Process occurs in a plasma centrifugal furnace, where heat from a transferred plasma arc torch creates a molten bath that detoxifies the feed material.	Mixed waste, transuranic waste, chemical plant soil, incinerator ash, munitions, sludge, and hospital waste	Organic and inorganic compounds	EPA SITE demonstration program completed.	At the Component Development and Integration Facility of the U.S. DOE in Butte, MT, the furnace processed about 4,000 pounds of waste. The DRE ranged from 99.9968 to 99.9999 percent for

Table 18. Thermochemical Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Entrained-Bed Gasification - <i>(Texaco Syngas, Inc.)</i>	Tech. Contact: Richard Zang Texaco Syngas, Inc. 2000 Westchester Avenue White Plains, NY 10650 914-253-4047 EPA Contact: Marta Richards 513-569-7783	Noncatalytic, partial oxidation process in which carbonaceous substances react at elevated temperatures and pressures, producing a gas containing mainly carbon monoxide and hydrogen.	Soil, sludge, and sediment	Organic and inorganic compounds	EPA SITE demonstration program testing in progress.	A demonstration 40-hour pilot run showed carbon conversion in the waste stream to be over 99 percent. Both wastewater and solid residue were free of trace organics and EPA priority pollutants. No cost data available.
Frequency Tunable Pulse Combustion System - <i>(Sonotech, Inc.)</i>	Tech. Contact: Zin Plavnik Sonotech, Inc. 575 Travis St., NW Atlanta, GA 30318 404-525-8530 EPA Contact: Marta Richards 513-569-7783	System consists of an air inlet, a combustion section and/or a tailpipe, a control panel, and a safety system. The system improves an incinerator's performance by increasing mixing rates between the fuel and air and between reactive gas pockets and ignition sources.	Any material that can be treated in a conventional incinerator	Not specified	EPA SITE demonstration program testing in progress.	No results or cost data available.

Table 18. Thermochemical Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Incineration of Explosives Contaminated Soil	Wayne Sisk USATHAMA CETHA-TS-D Aberdeen Proving Ground, MD 21010 410-671-2054	Rotary kiln incinerator operated at about 1,200 to 1,600°F.	Soils from lagoons used in the past for the disposal of wastewater; munitions load, assemble, and pack operations; and from demilitarization and wash-out operations.	Explosives	Equipment is commercially available. Technology has been implemented at the Cornhusker Army Ammunition Plant, Grand Island, NB, and the Louisiana Army Ammunition Plant, Shreveport, LA.	No results are available. Total project costs for on site incineration with a transportable system range from \$200 to \$400 per cubic yard. These costs include operating and capital costs for excavation, transportation, and processing.
Anaerobic Thermal Processor - <i>(Soiltech ATP Systems, Inc.)</i>	Tech. Contact: Roger Nielson Soiltech ATP Systems, Inc. 6300 South Syracuse Way, Suite 300 Englewood, CO 80111 303 290 8336	Wastes are heated and mixed in a special, indirectly-fired rotary kiln where the unit desorbs, collects, and recondenses hydrocarbons and other pollutants found in the	Soil and sludges	PCBs, chlorinated pesticides, oil, VOCs	EPA SITE demonstration program testing completed.	At the Wide Beach Development Superfund site in Brant, NY, and at the Outboard Marine Corporation site in Washburn, N.J.

Table 18. Thermochemical Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Use of Waste Explosives and Propellants as Supplemental Fuel in Industrial Boilers	Tech. Contact: Capt. Kevin Keehan USATHAMA CETHA-TS-D Aberdeen Proving Ground, MD 21010-5401 410-671-2054	Wastes are dissolved in toluene, fed into blending tank, and combined with fuel oil. The resulting mixture is co-fired into standard industrial boiler.	Explosives	TNT and RDX	Pilot-scale field demonstration phase	Pilot-scale demonstration at Hawthorne Army Ammunition Plant, Hawthorne, NV. Initial tests showed dilute solutions of TNT can be co-fired efficiently and safely. No cost data available.

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CHAPTER 7. ANCILLARY TECHNOLOGIES

7.1 Soil Fracturing

7.1.1 Hydraulic Fracturing

Technology Description

The hydraulic fracturing technique is a mechanical process that consists of creating fractures in rock and low permeability soils by high pressure pumping of a liquid mixture into the ground through a well. The technology, initially developed over a half century ago to increase the yield in the oil industry, can be used to promote *in situ* movement, removal, and treatment of a variety of organic and inorganic compounds. Once the subsurface has been fractured, other technologies are employed to remove and treat the contaminants.

The liquid mixture consists of a granular solid (termed a proppant), which is usually a sand and a viscous fluid, usually a guar gum and water mixture. An enzyme added to the viscous fluid breaks down the gel, leaving the sand to hold the open fracture and enhance permeability. This technology has the potential to significantly improve the performance of *in situ* vapor extraction systems and bioremediation processes in low permeability soils. A recent innovation utilizes slow release oxygen encapsulated solids in conjunction with sand to enhance the *in situ* bioremediation process. Oxygen can also be supplied in the form of hydrogen peroxide or dissolved oxygen.

The technology is applied in the following sequence. A lance is driven to the desired depth and removed, leaving soil exposed at the bottom of the casing. Steel tubing with a narrow orifice at one end is then inserted in the casing. Water is pumped through the steel tubing and into the narrow orifice, forming a jet that cuts laterally into the soil. The jetting device is rotated, producing a disc-shaped notch extending 4 to 6 inches away from the borehole.

Hydraulic fractures are created by injecting the guar gum gel and sand slurry into the casing. Injection rates in the range of 16 to 24 gpm have been used. The lateral pressure of the soil on the outer wall of the casing effectively seals the casing and prevents leakage of the slurry. The fractures nucleate at the notch and grow away from the borehole. These fractures are placed at multiple depths ranging from five to forty feet below the ground surface. The direction and distance of the propagation of the fracture from the wall of the borehole is measured by monitoring the uplift of the ground surface. A leveling telescope is used to measure ground elevation at an array of points before and after each fracture is created to determine the location and net uplift resulting from the fracture. A laser system called Ground Elevation Measurement System (GEMS) was developed by the University of Cincinnati to measure uplift in real time during hydraulic fracturing. The system uses a laser and an array of sensors to track the displacement of each point in the array with time.

Advantages of Hydraulic Fracturing:

- Hydraulic fracturing facilitates the application of *in situ* remediation technologies in soils of low permeability, typically less than 10^{-6} cm/sec. Without fractures, many of these soils would not be considered candidates for *in situ* remediation.
- Wells containing sand-filled fractures have been demonstrated to have a greater area of influence than conventional wells. Drilling and well installation costs are reduced by increasing the spacing of the wells.
- Sand placed in hydraulic fractures allow fractures to remain open at large depths and decrease the time required for remediation.
- Hydraulic fractures can be filled with a variety of compounds to enhance remediation. Hydraulic fractures filled with granular nutrients and time-release oxygen compounds can act as subsurface reservoirs of materials needed for bioremediation. Electrically conductive materials placed in the fractures offer the potential to induce electroosmosis, electrophoresis, or electromigration of contaminants.
- Hydraulic fractures may act as resistive heaters to increase temperatures and volatilize contaminants or to increase bioactivity.
- Hydraulic fracturing is applicable to the vadose zone as well as within the ground water.

Disadvantages of Hydraulic Fracturing:

- Contaminants present in pockets of the formation treated may migrate through pre-existing or newly formed fractures and further spread the contaminants.
- For longer remediation programs, refracturing efforts may be required at six- to twelve-month intervals.
- Hydraulic fracturing should not be used in areas of high seismic activity. The fracturing may cause instability.
- Investigation of possible underground utilities, structures, or trapped free product is required.
- Technology is applicable to contaminated areas of relatively small aerial extent. Large areas require a number of application.

Stage of Development

Hydraulic fracturing is an emerging technology. It has been demonstrated in a field-scale application with soil vapor extraction in the EPA SITE Superfund Program in 1991 and 1992 at the XEROX Oak Brook site. Another pilot-scale demonstration was conducted with bioremediation in 1991 and 1992 at a Dayton site, also as part of the Superfund SITE Program (EPA, 1993). Future feasibility studies are planned for locations in Columbus, Ohio, and southern Michigan.

Applications and Effectiveness

Hydraulic fracturing is an enhancement technology designed to increase the efficiency of other *in situ* technologies in difficult subsurface conditions. The technology can be applied to low permeability silty clays and rock (less than 10^{-6} cm/sec) and is used to improve remedial methods for target organic compounds. Hydraulic fracturing is applicable to VOCs, SVOCs, fuel hydrocarbons, pesticides, and inorganics.

The technology can be used in the vadose zone as well as within the groundwater. Hydraulic fracturing is effective up to the depths of 40 feet, and minimizes the number of wells needed for *in situ* remediation of the site. Potential sites for applying this technology to contaminated soils include Superfund and RCRA corrective action sites where solvents and/or petroleum hydrocarbons have spilled. Lateral compressive stresses that are greater than vertical stresses in over consolidated clays favors the propagation of horizontal fractures. Horizontal fractures are effective in increasing the permeability of the soil over larger radial distances than steeply dipping fractures; hence, over consolidated clays are preferred sites for application of the hydraulic fracturing technology.

Case Studies

The University of Cincinnati and U.S. Environmental Protection Agency Risk Reduction Engineering Laboratory, EPA-RREL, (EPA, 1992; p.150-151) developed the hydraulic fracturing technology to enhance the permeability of silty clays. This technology was evaluated under the EPA Superfund Innovative Technology Evaluation (SITE) program. The hydraulic fracturing technology was developed and tested at the Center Hill Solid and Hazardous Waste Research (Center Hill) Facility. Tests were conducted at the Center Hill Facility to determine factors affecting the performance of the hydraulic fractures. Demonstrations were conducted during 1991 and 1992 at two sites, a Xerox Corporation site in Oak Brook, Illinois, where soil vapor extraction was being conducted, and a site in Dayton, Ohio, where bioremediation was being conducted.

Several hydraulic fracturing case studies and technological applications are presented in Table 19. Cost data are provided when available.

Co-Technologies/Alternative Technologies

An enhancement process, hydraulic fracturing extraction has a number of companion technologies. Once the formation permeability has been improved with hydraulic fracturing, other technologies can be applied to facilitate *in situ* contaminant removal. The companion technologies currently under evaluation for use with hydraulic fracturing are the following:

- Soil vapor extraction is the most directly applicable companion technology. Normally, vapor extraction can be applied only to high-permeability formations; however, with hydraulic fracturing enhancement, vapor extraction may be applied to low-permeability soils.
- Bioremediation combined with hydraulic fracturing consists of injecting gases, microbes, and nutrients immediately after the hydraulic fracturing. This injection can aid in proper oxygen and nutrient distribution.
- Thermal treatment can be combined with hydraulic fracturing in the form of a hot-gas injection system. Hot gases are introduced into the subsurface, usually coupled with soil vapor extraction. The hydraulic fracturing aids in opening flow paths for less permeable soils.
- Soil flushing may be coupled with hydraulic fracturing in order to facilitate contaminant removal. The fracturing facilitates pathways for removal.

Table 19. Hydraulic Fracturing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Hydraulic Fracturing - <i>(Risk Reduction Engineering Laboratory and The University of Cincinnati)</i>	Tech. Contact: Larry Murdoch Univ. of Cincinnati Center Hill Facility Cincinnati, OH 45224 513-569-7897 EPA Contact: Naomi Barkley 513-569-7854	Process places fractures at discrete depths through hydraulic pressurization at the base of a bore-hole.	Soil and groundwater	Contaminants or wastes associated with remediation by soil vapor extraction, bioremediation, or pump and treat systems.	EPA SITE demonstration program pilot-scale feasibility studies conducted.	Dayton, OH, site data indicates the flow of water was about 25 to 40 times greater in the fractured well than in the unfractured well. Permitting and regulatory (one-time) cost is \$5,400. An estimated cost per fracture is \$950-\$1,425 based on 4-6 fractures (daily total = \$5,700).
Hydraulic Fracturing - <i>(Risk Reduction Engineering Laboratory and The University of Cincinnati)</i>	Tech. Contact: Larry Murdoch Univ. of Cincinnati Center Hill Facility Cincinnati, OH 45224 513-569-7897 EPA Contact: Naomi Barkley	Process places fractures at discrete depths through hydraulic pressurization at the base of a bore-hole.	Soil and groundwater	Contaminants or wastes associated with remediation by soil vapor extraction, bioremediation, or pump and treat systems.	EPA SITE demonstration program pilot-scale feasibility studies conducted.	Center Hill Facility in Cincinnati, OH, data indicated vapor yield tests increased by one order of magnitude. The zone of pneumatic control of the fractured wells was more than 10

Table 19. Hydraulic Fracturing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
Hydraulic Fracturing - <i>(Risk Reduction Engineering Laboratory and The University of Cincinnati)</i>	Tech. Contact: Larry Murdoch Univ. of Cincinnati Center Hill Facility Cincinnati, OH 45224 513-569-7897 EPA Contact: Naomi Barkley 513-569-7854	Process places fractures at discrete depths through hydraulic pressurization at the base of a bore-hole.	Soil and groundwater	Contaminants or wastes associated with remediation by soil vapor extraction, bioremediation, or pump and treat systems	EPA SITE demonstration program pilot-scale feasibility studies conducted.	XEROX Oak Brook Site data indicated that fractured wells yielded vapor flow rates 15 to 30 times greater than unfractured wells. The contaminant yields from the fractured well zones were 7 to 14 times greater than from comparable zones in the unfractured wells. Permitting and regulatory (one-time) cost is \$5,400. An estimated cost per fracture is \$950-\$1,425 based of 4-6 fractures (daily total = \$5,700).

Cost Analysis

Costs include those for preparation, permitting, capital equipment, labor, supplies and consumables, analytical and monitoring costs, and demobilization. Hydraulic fracturing equipment, including the cost of the GEMS, is estimated at \$93,000. Based on renting this equipment about 30 times per year, and a depreciation period of 3 years, the rental cost per day is about \$1,000. Costs for site preparation, labor, supplies, and consumables (sand, guar gum gel, enzyme, and diesel fuel), and pneumatic piezometer installation for monitoring the fracture performance are estimated to be \$4,700 per day. Assuming that 4 to 6 fractures are created per day, the cost per fracture is estimated to be \$950 to \$1,425 (Murdoch, 1993).

Personal Contacts

Refer to Table 19 for a complete list of personal contacts relative to specific case studies/applications. For further information, the following individuals may be contacted:

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REFERENCES

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7.1.2 Pneumatic Fracturing Extraction (PFE)

Technology Description

PFE is a mechanical process used to enhance permeability in soils of complex geologic formations. The technology acts to promote removal and/or treatment of volatile organic compounds (VOCs) within the vadose zone *in situ* or *ex situ*. The geologic deposits in the subsurface zone are fractured by the introduction of high pressure air and result in an increase of the permeability. Small fractures can have a significant impact upon subsurface migration because fluid flow through a subsurface fracture is a function of the cube of the aperture opening.

PFE involves the use of an air compressor and expandable packers to seal the borehole or well so that sufficient pressures can be applied to the treatment zone. Most formations, including soil and rock, can be fractured with pressures that do not exceed 100 psi. Compressed air is introduced in short bursts of normally less than one minute and up to 500 psi pressure. The size of the zone to be fractured can be controlled by the depth of placement of the packers, the operating pressures used and the duration of the treatment. In general, the shorter the distance from the borehole or well, the greater the control over the amount and distribution of fracturing. The effective radius of fracturing can range from five to ten feet in soils and from ten to twenty feet in rock. Under favorable subsurface conditions, such as horizontal bedding, the effective radius to develop fractures can extend to 100 feet or more. Finally, clean, fine sand can be injected into the fractures to prevent them from closing. Filling the fractures with a sand allows fractures to remain open at depths and in formations where improper fractures may close (such as fine clay soils). This process is usually not necessary in consolidated rock formations; however, it may be useful in soft clay soils.

Advantages of Pneumatic Fracturing Extraction Technology:

- PFE facilitates the application of *in situ* remediation technology in soils of low permeability or over consolidated sediment. Without fractures, many of these soils would not be considered candidates for *in situ* remediation.
- Wells containing sand-filled fractures have been demonstrated to have a greater area of influence than conventional wells. Drilling and well installation costs are reduced by increasing the space of the wells.
- The increase of subsurface fluid flow associated with sand-filled pneumatic fractures decreases the time required for remediation.
- Pneumatic fractures can be filled with a variety of compounds to enhance remediation. Fractures filled with granular nutrients and time-release oxygen compounds can act as subsurface reservoirs of materials needed for bioremediation. Electrically conductive materials placed in the fractures offer the potential to induce electroosmosis, electrophoresis, or electromigration of contaminants.
- Pneumatic fractures may act as resistive heaters to increase temperatures and volatilize contaminants or to increase bioactivity.

Disadvantages of Pneumatic Fracturing Extraction Technology:

- Contaminants present in pockets of the formation treated may migrate through pre-existing or newly formed fractures and further spread the contaminants.
- For longer remediation programs, refracturing efforts may be required at six- to twelve-month intervals.
- PFE should not be used in areas of high seismic activity. The fracturing may cause instability.
- Investigation of possible underground utilities, structures, or trapped free product is required since subsurface anomalies can contribute to variations in the fracture distribution.
- PFE technology applies to the vadose zone.

Stage of Development

Pneumatic fracturing extraction technology is an emerging technology. Numerous bench-scale and theoretical studies have been conducted, and PFE has been demonstrated at two sites in New Jersey under the Environmental Protection Agency SITE Program.

In 1990, Accutech Remedial Systems, Inc., combined PFE with soil vapor extraction and hot-gas extraction to expedite commercialization and development of the technology. This technology integration was intended for complex geological conditions.

Applications and Effectiveness

The subsurface microfracturing, created by pneumatic fracturing, can be effective in increasing the hydraulic conductivity of fine grained soils. As such, it can be integrated with various *in situ* remedial technologies to treat soils contaminated with various organic compounds. PFE is effective in enhancing the removal of VOCs, SVOCs, fuel hydrocarbons, pesticides, and some inorganics. By increasing the removal rate and quantity of contaminants from the soil, PFE can result in removal efficiencies 2 to 25 times higher than vapor extraction alone.

Normal operation of a PFE system employs a 2-person crew, making twenty-five to forty fractures per day with a fracture radius of 15 to 20 feet and to a depth of 50 to 100 feet.

Case Studies

Pneumatic fracturing was tested with hot gas injection and extraction in the EPA SITE program in August 1992. In addition, numerous bench-scale and theoretical studies have been conducted. Pneumatic fracturing, integrated with dewatering, air injection, and vapor extraction, was applied to remediate the solvents, principally TCE and acetone that had leaked from underground storage tanks into the Brunswick, New Jersey, shale aquifer (EPA, 1993). As a result of the pneumatic fracturing, an increase in the pumping rates of the wells from less than 0.5 gpm to greater than 5 gpm was observed. Pneumatic fracturing developed fracture flow by opening up dead-end fractures and greatly increased the low yield of the weathered Brunswick shale. Prior to treatment, acetone was detected at levels up to 77,000 ppb. After sixty days of treatment, acetone was reduced to trace levels.

Selected case studies and/or application can be found in Table 20.

Co-Technologies/Alternative Technologies

An enhancement process, pneumatic fracturing extraction has a number of companion technologies. Once formation permeability has been improved with PFE, other technologies can be applied to facilitate contaminant removal. The companion technologies currently under evaluation are the following:

- Soil vapor extraction is the most directly applicable companion technology. Normally, vapor extraction can be applied only to high-permeability formations; however, with PFE enhancement, vapor extraction may be applied to low-permeability soils.
- Bioremediation combined with PFE consists of injecting gases, microbes, and nutrients immediately after the pneumatic fracturing. PFE can assure proper oxygen and nutrient distribution. Bench-scale and field tests are underway to investigate the ability of microbes to survive pneumatic injection under high pressures.
- Thermal treatment can be combined with PFE in the form of a hot-gas injection system. Hot gases are introduced into the subsurface, usually coupled with soil vapor extraction. PFE aids in opening flow paths for less permeable soils. This combination was studied in the Hillsborough site pilot test (case study included in Table 20).
- Soil flushing may be coupled with PFE in order to facilitate contaminant removal. Once again, PFE facilitates pathways for contaminant removal.

Cost Analysis

PFE has an average cost of \$5-\$10 per ton (\$5.50-\$11 per metric ton). Based upon a SITE demonstration at Somerville, New Jersey, it is estimated that the cost per pound of TCE removed was from \$140 to \$200.

Table 20. Pneumatic Fracturing Technologies

Technology	Developer/Contact	Technology Description	Waste Media	Applicable Waste	Technology Status	Applications/Case Studies
PFE and Catalytic Oxidation <i>(Accutech Remedial Systems, Inc.)</i>	Tech. Contact: Harry Moscatello Accutech Remedial Systems Cass Street and Highways 35 Keyport, NJ 07735 908-739-6444 EPA Contact: Uwe Frank 908-321-6626	Integrated treatment system incorporating PFE and hot gas injection	Low permeability formations, such as clay and fractured rock	Halogenated and non-halogenated volatile and semi-volatile organic compounds	EPA SITE demonstration program acceptance	Demonstrated at Brunswick Shale aquifer (NJ) in 1992. Demonstration results published. No cost data available.
PFE	Harry Moscatello Accutech Remedial Systems Cass Street and Highways 35 Keyport, NJ 07735 908-739-6444	High pressure air injection to fracture formation. Companion technologies can include vapor extraction, bioremediation, and thermal treatment.	Soil, shale, and bedrock	TCE	EPA SITE demonstration program acceptance	Hillsborough, NJ, demonstration site test held in 1992. Fracturing opened up the formation, creating large surface areas and increased formation permeability, thereby accelerating removal and/or treatment of

Personal Contacts

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REFERENCES

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7.2 Aerial Remote Sensing

7.2.1 Fourier-Transform Infrared Spectroscopy

Technology Description

Fourier Transform Infrared Spectroscopy (FTIR) is a relatively new air monitoring technology. It is based upon the ability of the adsorption spectra of gas molecules to be successfully captured, separated, and identified. The overlapping spectra are separated and characterized by Fourier analysis.

The FTIR operates in either an "active" or a "passive" mode for the identification of trace quantities of organics in ambient air as well as stack gases. The active mode utilizes an IR source for the generation of the molecular spectra while the passive mode utilizes natural IR for the generation of the molecular spectra. In either case the spectra is captured and analyzed by a receiving or detection device.

The increased need to monitor air emissions from contaminated sites, as well as stationary and mobile air pollution resulting from the 1990 Clean Air Act Amendments, has generated an increased awareness of the desirability to measure emissions in an easy, efficient, and cost-effective manner. Based upon work since the late 1970s, it appears that FTIR technology can contribute to accomplishing this objective.

Advantages of Fourier Transform Infrared Spectroscopy:

- FTIR can analyze solid, liquid, and gas phase samples without destroying the sample, allowing samples to be saved for future use.
- FTIR provides near "real-time" analytical results, with the primary emphasis on the detection and measurement of volatile organic compounds.
- The technology is applicable to an indoor, industrial, as well as a general environmental setting.
- This technology is portable for field application.
- A large number of gaseous components can be measured simultaneously without separating the components from the medium being evaluated.
- Technology can be used for fence-line monitoring and perform as a sentinel or leak warning system.
- Technology applications allow analysis to be performed remotely without a sample being physically taken and transported to the measuring device.
- Industrial plumes and accident related toxic chemical plumes can be "tracked" as they move from a stationary location.

Disadvantages of Fourier Transform Infrared Spectroscopy:

- Technology requires high capital and operational costs.
- Interferences have to be considered when deciding upon a specific application.
- Single discrete point-sampling is not yet possible with this technology. Applications are for "line-of-sight" analysis.

Stage of Development

FTIR technology has been developing since the late 1970s. Experimentation and applications have included the detection of organic air emissions at hazardous waste sites, toxic/explosive emissions from mines, exhausts from stationary and moving vehicles, air emissions from industrial operations, and indoor air contaminants. Pilot work has been performed with some commercial application.

Applications and Effectiveness

FTIR can be used to measure VOC emission from point as well as area air pollution sources. This technology can be used to identify fugitive emissions, track industrial plumes, and monitor the movement of accidental releases of toxic chemicals.

Testing of FTIR to detect chemical emissions at the Shaver's Farm Superfund site, Georgia, in 1990 proved to be inconclusive. This result was due to the relatively low concentrations of gas components in the air.

The Army is currently developing a model (XM-21) for the detection of chemical agents in the battlefield.

Cost Analysis

Portable FTIR applications with software cost \$100,000.

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7.3 Software

7.3.1 SAGE-Solvent Alternatives Guide

Technology Description

SAGE is a computer program recently developed and made available through the EPA Control Technology Center. This system is designed to assist in the selection of nonpolluting surface cleaning alternatives. SAGE was developed for use by individuals ranging from shop foremen to regulatory agency personnel, both technical and non-technical.

The program is a personal computer (PC)-based logic tree system that evaluates the user's present operating scenario and then identifies possible surface cleaning alternative solvent chemistries and processes that best suit the requirements of the user. SAGE recommends options and important technical parameters. It also provides information on environmental considerations that must be taken into account, regulations that must be addressed when using the alternatives, safety requirements, and other information that must be considered when implementing the recommended alternatives. In addition, SAGE will provide case studies with similar operating scenarios and requirements.

Advantages of SAGE:

- Allows individuals of varying technical skills to select surface cleaning options by answering questions about their process requirements.
- Is based upon a decision tree format which allows other industrial operations to be effectively added and treated in the same manner as surface cleaning operations.

Disadvantages of SAGE:

- The indiscriminate use of computer based expert systems can sometimes provide misleading information when used by people with only minimal technical skills.

Stage of Development

SAGE is operational. The initial version was released in May, 1993, with an update later in 1993. SAGE is scheduled for continued upgrade through 1995. Future upgrades will expand the operations and alternatives covered.

Future versions of SAGE will include paint stripping, electronic manufacturing, and machinery and printing equipment cleaning. In addition, a process and facility design capability, economic and cost projection capability, and a regulation summation by state will be incorporated into the system.

Applications and Effectiveness

This expert computer system is available for use by both technical and non-technical personnel who must make decisions about pollution prevention alternatives involving surface cleaning operations.

Cost Analysis

Computer discs are free from the EPA.

REFERENCES

Darvin, C. undated. Solvent alternatives guide (SAGE), prepared by the Environmental Protection Agency Control Technology Center.

Darvin, C. and J. M. Stratta. October 15, 1993. Solvent alternatives guide (GUIDE), personal communications.

7.3.2 Immunoassay Testing

Technology Description

Immunoassay testing utilizes an antibody specifically developed for particular compounds. An enzyme conjugate competes with the target analyte for binding with the antibody coated within a test tube. A washing step removes unbound conjugate, and a colorimetric reaction identifies the amount of target compound within the sample. The color intensity, generated by a reaction with the conjugate, is inversely proportional to the amount of target compound present in the sample.

Immunoassay testing is particularly applicable to field testing where BTEX and PCB contamination is suspected and a rapid screening procedure are required to determine if further, more expensive testing and time-consuming sampling and analysis are required. This testing is also applicable to field testing to aid in cleanup actions where segregation of contaminated materials are required, based upon the level of contamination.

Advantages of Immunoassay Testing:

- The relatively rapid test provides real time results.
- The immunoassay test provides a screening tool for detection of pollutants as well as field checks while cleanup actions are progressing.
- The costs per test are low when compared to other currently accepted gas chromatography/mass spectroscopy (GC/MS) techniques.
- Tests can be performed on aqueous as well as soil samples.
- Skill level for the test is relatively low as long as adequate training is initially provided.
- Testing kits can be ordered and kept available for field use when needed.

Disadvantages of Immunoassay Testing:

- The technology does not have the same degree of sensitivity possessed by GC/MS technologies.
- The tests are not currently accepted by the EPA as standard methods. However, the EPA is intently investigating the test reliability.

Stage of Development

The immunoassay testing is being evaluated by the EPA as an emerging technology within the SITE Program.

Applications and Effectiveness

Current immunoassay testing kits are available for a number of compounds, to include benzene, toluene, ethylbenzene, xylene, gasoline, polynuclear aromatics, PCB, and TNT. The test is applicable to contaminant detection in water and soils. Several tests can be performed in a single hour. These tests are considered to be good for screening purposes. The detection levels vary, with PCBs detectable to 0.1 ppb in water and 0.1 ppm in soil and hydrocarbons to about 1 ppm.

Cost Analysis

The cost for the prepackaged tests range from approximately \$20 to \$200 per test, with several tests per kit. An accessory package may be required, depending upon laboratory materials already available, that will range up to about \$2,000.

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