EPA/Navy CERCLA Remedial Action Technology Guide

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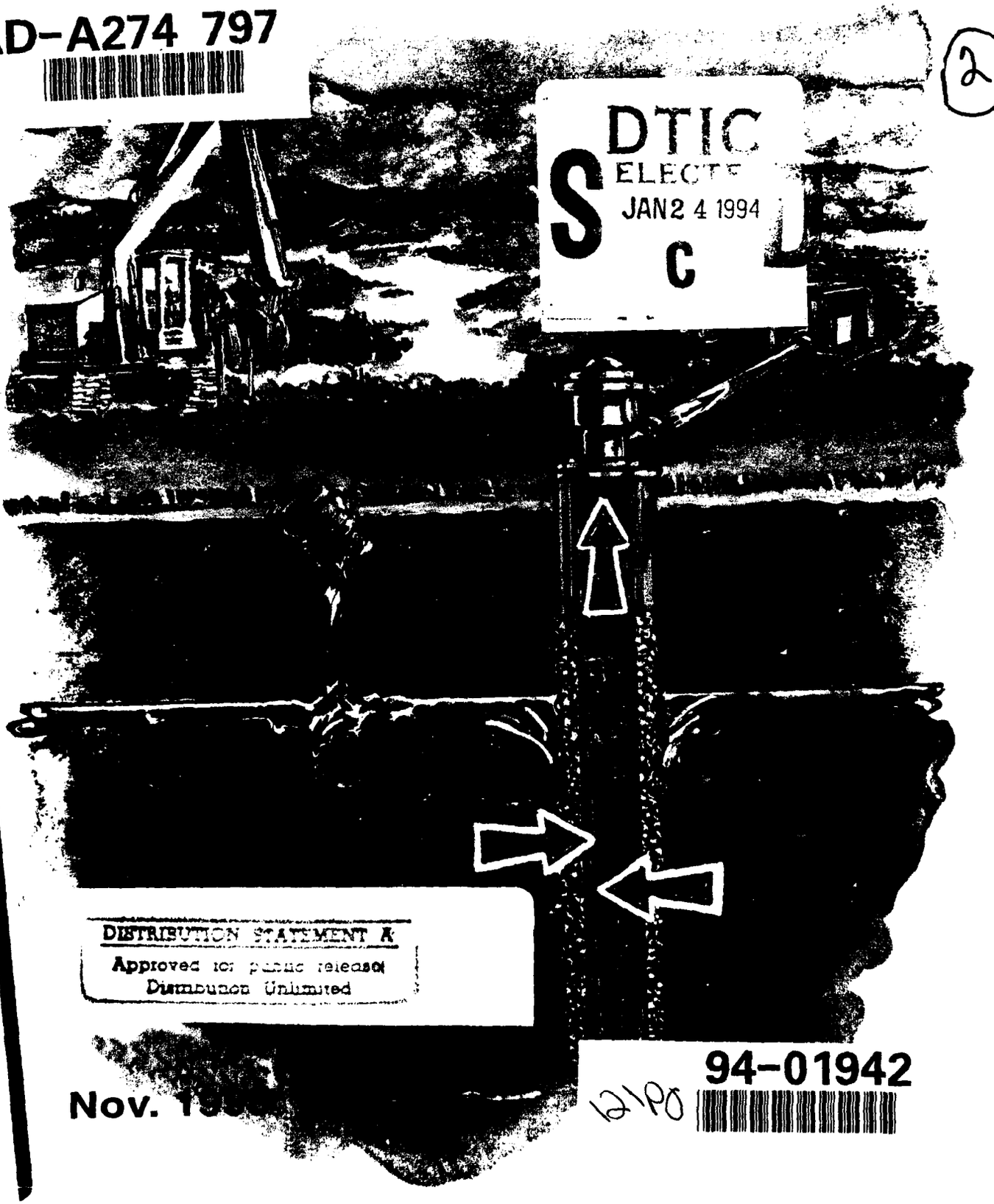

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Prepared by the:

U.S. Environmental Protection Agency
Cincinnati, OH 45268

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Port Hueneme, CA 93043

November 1993

INTRODUCTION

Section 121 (b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the U.S. Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants, and contaminants as a principal element."

The EPA/Navy CERCLA Remedial Action Technology Guide is a collection of (1) Engineering Bulletins produced by the EPA's Technical Support Branch in Cincinnati, OH and (2) Remedial Action Tech Data Sheets produced by the Naval Energy and Environmental Support Activity (NEESA) in Port Hueneme, CA. These documents comprehensively summarize the latest information obtainable on many of the best available remedial technologies. The intent is to convey information (based on previous applications) to help remedial project managers, engineers in charge, on-scene coordinators, Navy resident officers in charge of construction, and contractors decide if a technology should be used at a hazardous waste site and if so, what are the relevant design, implementation, and cost considerations. Addenda will be issued periodically to update the original bulletins and tech data sheets, and other technologies may be added.

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* An updated version is planned for these Bulletins/Tech Data Sheets.

United States Environmental Protection Agency | Office of Emergency and Remedial Response Washington, DC 20460 | Office of Research and Development Cincinnati, OH 45268

Superfund | EPA/540/S-93/500 | February 1993

EPA

Engineering Bulletin
Landfill Covers

Purpose

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

Abstract

Landfill covers are used at Superfund sites to minimize surface water infiltration and to prevent exposure to the waste. In many cases, covers are used in conjunction with other waste treatment technologies, such as slurry walls, groundwater pump- and-treat systems, and in situ treatment.

This bulletin discusses various aspects of landfill covers, their applicability, and limitations on their use and describes innovative techniques, site requirements, performance data, current status, and sources of further information regarding the technology.

Technology Applicability

Covers may be applied at Superfund sites where contaminant source control is required. They can sense one or more of the following functions:

- Isolate untreated wastes and treated hazardous wastes to prevent human or animal exposure
- Prevent vertical infiltration of water into wastes that would create contaminated leachate
- Contain waste while treatment is being applied
- Control gas emissions from underlying waste
- Create a land surface that can support vegetation and/or be used for other purposes

Covers may be interim (temporary) or final. Interim covers can be installed before final closure to minimize generation of leachate until a better remedy is selected. They are usually used to minimize infiltration when the underlying waste mass is undergoing most of its settlement. A more stable base will thus be provided for the final cover, reducing the cost of post-closure maintenance.

Covers also may be applied to waste masses that are so large that other treatment is impractical. At mining sites for example, covers can be used to minimize the entrance of water to contaminated tailings plies and to provide a suitable base for the establishment of vegetation. In conjunction with water diversion and detention structures, covers may be designed to route surface water away from the waste area while minimizing erosion.

The effectiveness of covers on underlying soils and groundwater containing contaminants is shown in Table 1. Effectiveness is defined as the ability of the cover to perform its function over the long term without being damaged by the chemical characteristics of the underlying waste. Examples of constituents within contaminant groups are provided in the "Technology Screening Guide for Treatment of CERCLA Soils and Sludges" [1, p. 10].

The degree of effectiveness shown in Table 1 is based on currently available information or on professional judgment when no information was available. The effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites. Demonstrated effectiveness means that, at some scale, chemical resistance tests showed that landfill covers were resistant to that particular contaminant in a soil or groundwater matrix. The ratings of potential effectiveness and no expected effectiveness are based on expert judgment. Where potential effectiveness is indicated, the technology is

* [reference number, page number]

believed capable of successfully containing the contaminant groups so indicated in a soil or groundwater matrix. If the technology were not applicable or probably would not work for a particular combination of contaminant group and matrix, a no expected effectiveness rating is given. Note that this rating does not occur in Table 1 for any of the contaminant groups.

Limitations

Landfill covers are part of landfilling technology, which is generally considered a technology of last resort in remediating hazardous waste sites. Landfilling of hazardous waste is not permitted without first applying the best available treatment. Landfilling technology does not lessen toxicity, mobility, or volume of hazardous wastes. However, when properly designed and maintained, landfills can isolate the wastes from human and environmental exposure for very long periods of time.

Covers are most effective where most of the underlying waste is above the water table. A cover, by itself, cannot prevent the horizontal flow of groundwater through the waste, only the vertical entry of water into the waste. Other procedures (e.g., landfill liners, slurry walls, extraction wells) may be needed to exclude, contain, or treat contaminated groundwater.

It is generally conceded that landfill components (liners and covers) will fail eventually, even though failure may occur after many tens or hundreds of years. Their effective life can be extended by long-term (30 years or more) inspection and maintenance [20]. Vegetation control and repairs associated with construction errors, cover erosion, settlement and subsidence are likely to be required. The need for cover repairs can be lessened considerably by adherence to a rigorous quality assurance program during construction.

Table 1
Effectiveness of Covers on General Contaminant Groups for Soil and Groundwater

	Contaminant Groups	*Effectiveness of Covers*
Organi	Halogenated volatiles	▼
	Halogenated semivolatiles	■
	Nonhalogenated volatiles	▼
	Nonhalogenated semivolatiles	■
	PCBs	■
	Pesticides (halogenated)	■
	Dioxins/Furans	■
	Organic cyanides	■
	Organic corrosives	■
Inorgani	Volatile metals	■
	Nonvolatile metals	■
	Asbestos	■
	Radioactive materials	■
	Inorganic corrosives	■
	Inorganic cyanides	■
Reactiv	Oxidizers	■
	Reducers	■

■ Demonstrated Effectiveness: Short-term effectiveness demonstrated at field-scale.

▼ Potential Effectiveness: Expert opinion that technology will work.

□ No Expected Effectiveness: Expert opinion that technology will not work.

Technology Description

The U.S. Environmental Protection Agency (EPA) has published several documents that provide guidance on the technology of cover construction at land disposal facilities [2] [3] [4] [5] [6] [7]. Other documents specifically address remediation of radiologically-contaminated Superfund sites, including the use of covers [8] [9]. Design and construction of clay liners (not covers specifically), properties of clay, testing methods, soil permeabilities, liner performance, and failure mechanisms are discussed at length in Reference 10.

The design of covers is site-specific and depends on the intended functions of the system. Many natural, synthetic, and composite materials and construction techniques are available. The effectiveness of covers (and other structural components of engineered landfills) has been shown to be primarily a function of the attention given to quality in choosing, installing, and inspecting those materials and techniques [24].

Covers can range from a one-layer system of vegetated soil to a complex multi-layer system of soils and geosynthetics. In general, less complex systems are required in dry climates and more complex systems are required in wet climates. The most complex systems are usually found on engineered landfills in the humid eastern United States, where the cover must meet the erosion and moisture requirements of the associated liner designed to contain the waste. Figure 1 depicts a vertical section of such a cover. Table 2 summarizes the function, materials of construction, and purpose of each of the components. Covers on Superfund sites usually contain some, but not necessarily all, of these components.

The materials used in the construction of covers include low-permeability and high-permeability soils and geosynthetic products. The low-permeability materials (geomembrane/soil layer) divert water and prevent its passage into the waste. The high-permeability materials (drainage layer) carry water away that percolates into the cover. Other materials may be used to increase slope stability.

The most critical components of a cover in respect to selection of materials are the barrier layer and the drainage layer. The barrier layer can be a geomembrane or low- permeability soil (clay), or both (composite).

Geomembranes are supplied in large rolls and are available in several thicknesses (20 to 140 mil), widths (15 to 100 ft), and

Figure 1
Cross-section of Multi-layer Landfill Cover

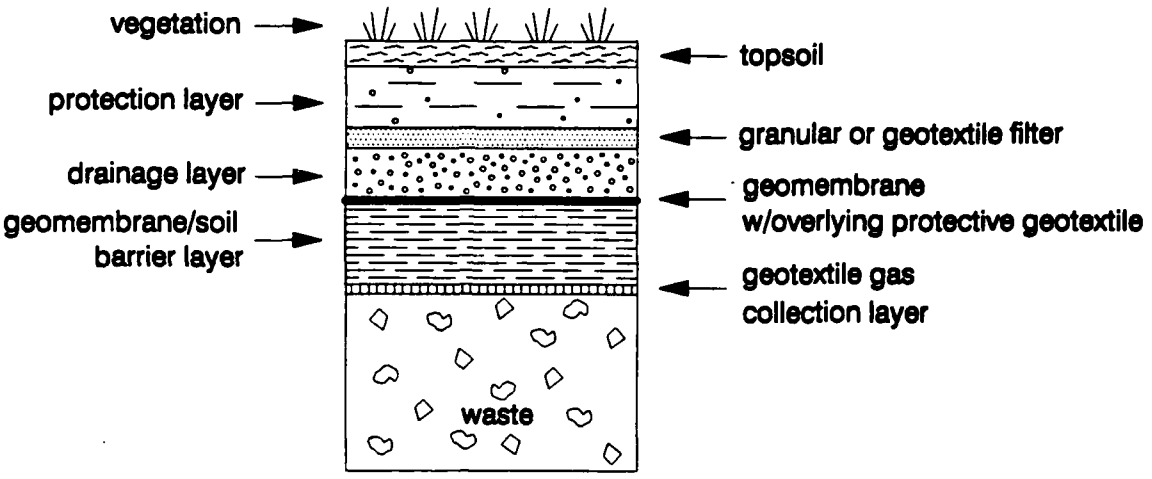

Table 2
Configuration of Cover Systems

Layer	*Primary Function*	*Usual Materials*	*General Considerations*
1. Surface Layer	Promotes vegetative growth (Most covers); Decrease erosion; Promote evapotranspiration.	Topsoil (humid site); Cobbles (arid Site); Geosynthetic erosion control systems	Usually required for control of water and/or wind erosion
2. Protection Layer	Protect underlying layers from intrusion and barrier layer from desiccation and freeze/thaw damage; Maintain stability; storage of water	Mixed soils; Cobbles	Usually required; May be combined with the protective layer into a single "cover soil" layer
3. Drainage Layer	Drain away infiltrating water to dissipate seepage forces	Sands; gravels; geotextiles; geonets; geocomposites	Optional; Necessary where excessive water passes through protection layer or seepage forces are excessive
4. Barrier Layer	Reduce further leaching of waste by minimizing infiltration of water into waste; Aid in directing gas to the emissions control system by reducing the amount leaving through the top of the cover	Compacted clay liners; Geomembranes; Geosynthetic clay liners; Composites	Usually required; May not be needed at extremely arid sites
5. Gas Collection Layer	Transmit gas to collection points for removal and/or cogeneration	Sand; geotextiles; geonets	Usually required if waste produces excessive quantities of gas

lengths (180 to 840 ft). The polymers currently used include polyvinyl chloride (PVC) and polyethylenes of various densities. Geomembranes are much less permeable than clays; measurable leakage generally occurs because of imperfections created during their installation; however, the imperfections can be minimized [15].

Soils used as barrier materials generally are clays that are compacted to a hydraulic conductivity (usually referred to as permeability) no greater than 1×10^{-6} cm/sec or a combination of bentonite and other soil that will achieve a comparable or even lower permeability. Compacted soil barriers are generally installed in 6-inch minimum lifts to achieve a thickness of 2 feet or more.

A composite barrier uses both soil and a geomembrane, taking advantage of the properties of each. The geomembrane is essentially impermeable, but, if it develops a leak, the soil component prevents significant leakage into the underlying waste. A composite liner has proven to be the most effective in decreasing hydraulic conductivity [2, p. A-2].

Geosynthetic clay barriers are beginning to be used in place of both the geomembrane and clay components. The geosynthetic clay barriers are constructed of a thin layer of bentonite sandwiched between two geosynthetic materials. In use, the bentonite expands to create a low-permeability, resealable ("self-healing") barrier. It is supplied in rolls, but does not require seaming as geomembranes do [21].

Other identified alternative barrier materials are flyash-bentonite-soil mixtures; super absorbent geotextiles; sprayed-on geomembranes and soil-particle binders; and custom-made bentonite composites with geomembranes or geotextiles [11, p. 63] [12, p. 6]. Potential advantages of alternative barriers include quick and easy installation, better quality control, cost savings potentially greater than use of compacted soil or standard soil/geomembrane composite, reduction in volume of material, lighter construction equipment required, and some self-healing capabilities [11, p. 65] [12, p. 6] [13, p. 225].

The following discussion briefly describes the construction of a multi-layer cover. It does not attempt to describe all of the possible configurations and materials.

Covers are usually constructed in a crowned or domed shape with side slopes as low as is consistent with good runoff characteristics. The bottom layer, which may be a granular gas collection layer, forms the base on top the waste mass for the remainder of the cover. The clay component of the barrier layer is constructed on this base layer. The clay is spread and compacted in "lifts" a few inches thick until the desired barrier thickness is reached (usually 24 inches or more).

Each lift is scarified (roughed up) after compaction so there will be no discernible surface between it and the next higher lift when the latter is compacted. The top lift is compacted and rolled smooth so the geomembrane may be laid on it in direct and uniform contact. During the entire process the clay must be maintained at a near-optimum moisture content in order to attain the necessary low permeability upon compaction.

Low hydraulic conductivity is the most important property of the clay/soil barrier. Hydraulic conductivity is significantly influenced by the method of compaction, moisture content during compaction, compactive energy, clod size, and the degree of bonding between lifts [11, p. 6].

Geomembranes require a great deal of skill in their installation. They must be laid down without wrinkles or tension. Their seams must be fully and continuously welded or cemented and they must be installed before the underlying clay surface can desiccate and crack. If vent pipes protrude through the cover, boots must be carefully attached to the membrane to prevent tearing if the cover subsides later. Care must be taken that the membrane is not accidentally punctured by workers or tools.

Extremes of temperature can adversely affect geomembrane installation, e.g., stiffness and brittleness are associated with low temperatures and expansion is associated with high temperatures. Thus, air temperature and seasonal variation are important design considerations [15].

A geotextile may be laid on the surface of the geomembrane for the geomembrane's protection, particularly if relatively coarse and sharp granular materials are applied as the drainage layer. Another geotextile can then be put on top of the drainage layer to prevent clogging of the drainage layer by soil from above. Fill soil and topsoil are then applied (compaction is not so critical) and the topsoil seeded with grass or other vegetation adapted to local conditions.

The drainage layer in a cover is designed to carry away water that percolates down to the barrier layer. It may be either a granular soil with high permeability or a geosynthetic drainage grid or geonet sandwiched between two porous geotextile layers. A geotextile may be used as a filter at the top of a granular soil drainage material to separate it from an overlying soil of different characteristics to prevent the drainage layer from becoming plugged with fine soil. A geotextile may also be used at the bottom of a granular drainage layer to protect the underlying geomembrane barrier from abrasion or puncture by sharp particles.

Other component layers may be used in landfill covers. Wider tolerances are generally acceptable in the material and construction requirements for these layers. Topsoil and subsoil from the vicinity are likely to be suitable for the surface and protection layers, respectively. The gas collection layer may be similar to the drainage layer in its characteristics, but it does not need to be. For example, gravel or coarse sand may be appropriate. Geosynthetic drainage materials may be used here too, but the chemical resistance to volatile wastes may be of greater concern due to the proximity of the waste and possibility for contact with it. However, EPA has no data that suggest damage to covers by volatiles.

Many laboratory tests are needed to ensure that the materials being considered for each of the cover components are suitable. Tests to determine the suitability of soil include grain size analysis (ASTM D422), Atterberg limits (ASTM D4318), and compaction characteristics (ASTM D698 or D1557). These tests generally are performed on the source material (called "borrow" material) before and during construction at predetermined intervals. EPA is expected to publish a new manual on construction quality assurance in the spring of 1993 [23].

The major engineering soil properties that must be defined are shear strength and hydraulic conductivity. Shear strength may be determined with the unconfined compression test (ASTM D2166), direct shear test (ASTM D3080), or triaxial compression test (ASTM D2850). Hydraulic conductivity of soils may be measured in the laboratory with either ASTM D2434 or D5083. Field hydraulic conductivity tests are generally recommended and may be performed, prior to actual cover construction on test pads to ensure that the low-permeability requirements can actually be met under construction conditions. EPA strongly encourages the use of test pads [3] [4].

Laboratory tests are also needed to ensure that geosynthetic materials will meet the cover requirements. For example, geosynthetics in covers may be subjected to tensile stresses caused by subsidence and by the gravitational tendency of a geomembrane or material adjacent to it to slide or be pulled

down slopes. Hydraulic conductivity of geomembranes is not defined but leakage should not be significant in undamaged materials. Geosynthetic drainage materials (reinforcement type products such as geonets and geotextiles) can become clogged or compressed under pressure and lose some or all of their drainage capacity.

The geosynthetics in a cover generally are not in direct contact with the underlying waste, so chemical resistance to the waste is not often a limitation [14, p. 79] [3, p. 109]. On the other hand, vapors from volatile contaminants have the potential to degrade cover materials. Note in Table 1 that although the organic volatiles are the only chemical groups with less than demonstrated effectiveness, the opinion of experts is that the use of geosynthetics in cover systems will work. EPA has no evidence to suggest damage to covers by volatile organic compounds.

High-quality seams are essential to geomembrane integrity. Test-strip seaming, in which the actual seaming process is imitated on narrow pieces of excess membrane, can help to ensure high seam quality. The test strips should be prepared and subjected to strength (shear and peel) testing whenever equipment, personnel, or climatic changes are significant [15, p. 14]. Failure to meet specifications with the test strips indicates the necessity for destructive testing of actual field seams and correction of deficiencies in the seaming process.

Although construction quality assurance, including testing, will increase the installation cost about 10 to 15 percent and the time required to complete the project, it has been shown to improve the performance of the installation [22].

Steeply mounded landfills can have a negative effect on the construction and stability of the cover. A steep slope can make it difficult to compact soil properly due to the limited mobility and reduction of compacting effort of some compaction equipment. The rate of erosion is also a function of slope. Difficulty may arise in anchoring a geomembrane to prevent it from sliding along the interfaces of the geomembrane and soils. In some instances, geosynthetic reinforcement grids may be used to increase slope stability. Engineering design guidance addressing geomembrane stability can be found in Reference 16.

When constructing a new landfill or when covering an existing landfill where the surface of the waste mass can be graded, EPA suggests that side slopes of a landfill cover not be less than 3 per cent or exceed 5 per cent [4, p. 24].

High air temperatures and dry conditions during construction may result in the loss of moisture from a clay barrier layer, causing desiccation cracking that can increase hydraulic conductivity. Desiccation cracking can be prevented by adding moisture to the clay surface and by installing the geomembrane in a composite barrier quickly after completion of the clay layer.

The hydraulic conductivity of compacted soil is also significantly influenced by the method of compaction, soil moisture content during compaction, compactive energy, clod size, and the degree of bonding between the individual lifts of soil in the barrier layer [11, p. 6].

Geomembranes are negatively influenced by different factors than soils during the construction process. Generally more care must be taken to prevent accidental punctures. Sunlight can heat the material, causing it to expand. If installed while hot, the geomembrane can then shrink to the point of seam rupture if compensating actions are not taken. Seams must be carefully constructed to ensure continuity and strength. They should run up and down slopes rather than horizontally in order to reduce seam stress. Details of geomembrane installation can be found in Reference 15.

Site Requirements

The construction of covers requires a variety of construction equipment for excavating, moving, mixing, and compacting soils. The equipment includes bulldozers, graders, various rollers, and vibratory compactors. Additional equipment is required in moving, placing, and seaming geosynthetic materials, e.g., forklifts and various types of seaming devices.

Storage areas are necessary for the materials to be used in the cover. If site soils are adequate for use in the cover, a borrow area needs to be identified and the soil tested and characterized. If site soils are not suitable, other low-permeability soils may have to be trucked in. An adequate supply of water may also be needed for application to the soil to achieve optimum soil density.

Performance Data

Once a cover is installed, it may be difficult to monitor or evaluate the performance of the system. Monitoring well systems or infiltration monitoring systems can provide some information, but it is often not possible to determine whether the water or leachate originated as surface water or groundwater. Few reliable data are available on cover performance other than records of cover condition and repairs.

The difficulty in monitoring the performance of covers accentuates the need for strict quality assurance and control for these projects during construction. It is important to note that no landfill cover is completely impervious. It is also important to note that small perforations or poorly seamed or jointed materials can increase leakage potential significantly.

Technology Status

The construction of landfill covers is a well-established technology. Several firms have experience in constructing covers. Similarly, there are several vendors of geosynthetic materials, bentonitic materials, and proprietary additives for use in constructing these barriers.

In EPA's FY 1989 ROD Annual Report [17], 154 RODs specified covers as part of the remedial action. Table 3 shows a selected number of Superfund sites employing landfill cover technology. While site-specific geophysical and engineering studies are needed to determine the appropriate materials and construction specifications, covers can effectively isolate wastes from rainfall and thus reduce leachate and control gas emissions. They can also be implemented rather quickly in conjunc-

Table 3
Selected Superfund Sites Employing Landfill Covers

SITE	*Location (Region)*	*Status*
Chemtronics	Swannada, NC (4)	In design phase
Mid-State Disposal Landfill	Cleveland Township, WI (5)	In pre-design phase
Bailey Waste Disposal	Bridge City, TX (6)	In design phase
Cleve Reber	Sorrento, LA (6)	In design phase
Northern Engraving	Sparta, WI (5)	In operation since 1988
Ninth Avenue Dump	Gary, IN (5)	In design phase
Charles George Reclamation	Tyngsborough, MA (1)	In operation
E.H. Shilling Landfill	Ironton, OH (5)	In design phase
Henderson Road	PA (3)	In design phase
Ordinance Works Disposal	WV (3)	In design phase
Industri-Plex	Woburn, MA (1)	In design phase
Combe Fill North	Mount Olive Township, NJ (2)	Completed in 1991
Combe Fill South	Chester and Washington Township, NJ (2)	In design phase

tion with other anticipated remedial actions. Long-term monitoring is needed to ensure that the technology continues to function within its design criteria.

EPA Contact

Technology-specific questions regarding landfill covers may be directed to:

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The following contractor personnel have contributed their time and comments by participating in the expert review meetings or in peer reviewing the document:

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Superfund | EPA/540/S-92/008 | October 1992

Engineering Bulletin
Slurry Walls

Purpose

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

Abstract

Slurry walls are used at Superfund sites to contain the waste or contamination and to reduce the potential of future migration of waste constituents. In many cases slurry walls are used in conjunction with other waste treatment technologies, such as covers and ground water pump-and-treat systems.

The use of this well-established technology is a site-specific determination. Geophysical investigations and other engineering studies need to be performed to identify the appropriate measure or combination of measures (e.g., landfill cover and slurry wall) to be implemented and the necessary materials of construction based on the site conditions and constituents of concern at the site. Site-specific compatibility studies may be necessary to document the applicability and performance of the slurry wall technology. The EPA contact whose name is listed at the end of this bulletin can assist in the location of other contacts and sources of information necessary for such studies.

This bulletin discusses various aspects of slurry walls including their applicability, limitations on their use, a description of the technology including innovative techniques, and materials of construction including new alternative barrier materials, site requirements, performance data, the status of these methods, and sources of further information.

Technology Applicability

Slurry walls are applicable at Superfund sites where residual contamination or wastes must be isolated at the source in order to reduce possible harm to the public and environment by minimizing the migration of waste constituents present. These subusurface barriers are designed to serve a number of functions, including isolating wastes from the environment thereby containing the leachate and contaminated ground water, and possibly returning the site to future land use.

Slurry walls are often used where a waste mass is too large for practical treatment, where residuals from the treatment are landfilled, and where soluble and mobile constituents pose an imminent threat to a source of drinking water. Slurry walls can generally be implemented quickly, and the construction requirements and practices associated with their installation are well understood.

The design of slurry walls is site specific and depends on the intended function(s) of the system. A variety of natural, synthetic, and composite materials and construction techniques are available for consideration when they are selected for use at a Superfund site.

Slurry walls can be used in a number of ways to contain wastes or contamination in the subsurface environment, thereby minimizing the potential for further contamination. Typical slurry wall construction involves soil-bentonite (SB) or cement-bentonite (CB) mixtures. These structures are often used in conjunction with covers and treatment technologies such as in situ treatment and ground water collection and treatment systems. Source containment can be achieved through a number of mechanisms including diverting ground water flow, capturing contaminated ground water, or creating an upward ground water gradient within the area of confinement (e.g., in conjunction with a ground water pump-and-treat system). Containment may also be achieved by lowering the groundwater level inside the containment area. This will help to reduce hydraulically driven transport (known as "advective transport") from the containment area. However, even if the hydraulic

gradient is directed towards the containment area, transport of the contaminants (although thought to be minimal) is still possible. In many cases slurry walls are expected to be in contact with contaminants, therefore, chemical compatibility of the barrier materials and the contaminants may be an issue [1, p. 373-374].

The effectiveness of slurry walls and high density polyethylene (HDPE) geomembranes on soils and ground water contaminated with general contaminant groups is shown in Table 1. Examples of constituents within contaminant groups are provided in the "Technology Screening Guide for Treatment of CERCLA Soils and Sludges" [2]. This table is based on current available information or on professional judgment where no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the containment efficiencies achieved will be acceptable at other sites. For ratings used in this table, demonstrated effectiveness means that, at some scale, compatibility tests showed that the technology was effective or compatible with that particular contaminant and matrix.

Table 1
Effectiveness of HDPE Geomembranes and Slurry Walls on General Contaminant Groups for Soil and Groundwater

		Effectiveness		
		HDPE	Slurry Walls	
	Contaminant Groups	Geomembranes	SB	CB
Organic	Halogenated volatiles	■	▼	▼
	Halogenated semivolatiles	■	▼	▼
	Nonhalogenated volatiles	■	▼	▼
	Nonhalogenated semivolatiles	■	▼	▼
	PCBs	■	▼	▼
	Pesticides (halogenated)	■	▼	▼
	Dioxins/Furans	▼	▼	▼
	Organic cyanides	■	▼	▼
	Organic corrosives	▼	❑	❑
Inorganic	Volatile metals	■	▼	▼
	Nonvolatile metals	■	▼	▼
	Asbestos	■	▼	▼
	Radioactive materials	▼	▼	▼
	Inorganic corrosives	❑	❑	❑
	Inorganic cyanides	■	▼	▼
Reactive	Oxidizers	❑	❑	❑
	Reducers	▼	▼	▼

■ Demonstrated Effectiveness: Short-term effectiveness demonstrated at some scale.

▼ Potential Effectiveness: Expert opinion that technology will work.

❑ No Expected Effectiveness: Expert opinion that technology will not work.

The ratings of potential effectiveness and no expected effectiveness are both based on expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully containing the contaminant groups in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given.

Limitations

In the construction of most slurry walls it is important that the barrier is extended and properly sealed into a confining layer (aquitard) so that seepage under the wall does not occur. For a light, non-aqueous phase liquid a hanging slurry may be used. Similarly, irregularities in the wall itself (e.g., soil slumps) may also cause increased hydraulic conductivity.

Slurry walls also are susceptible to chemical attack if the proper backfill mixture is not used. Compatibility of slurry wall materials and contaminants should be assessed in the project design phase.

Slurry walls also may be affected greatly by wet/dry cycles which may occur. The cycles could cause excessive desiccation which can significantly increase the porosity of the wall.

Once the slurry walls are completed, it is often difficult to assess their actual performance. Therefore, long-term ground water monitoring programs are needed at these sites to ensure that migration of waste constituents does not occur.

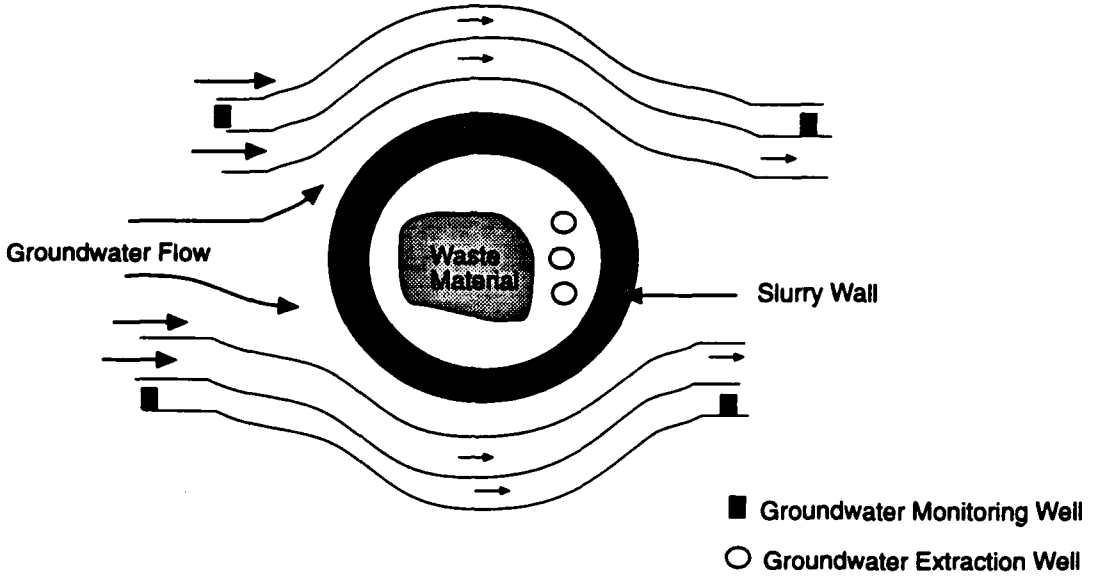
Technology Description

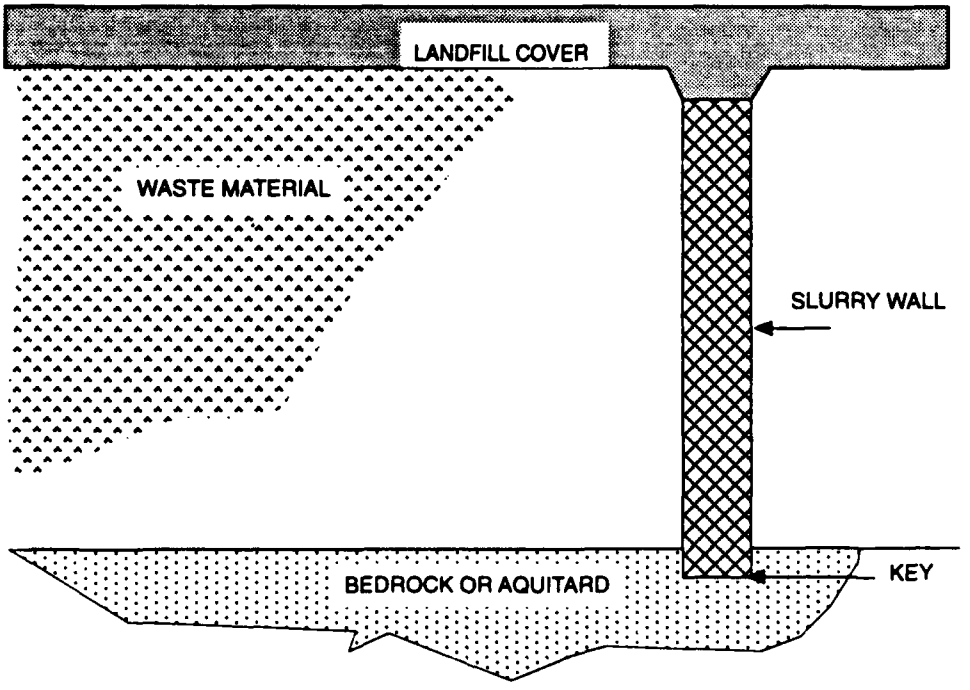
Low-permeability slurry walls serve several purposes including redirecting ground water flow, containing contaminated materials and contaminated ground water, and providing increased subsurface structural integrity. The use of vertical barriers in the construction business for dewatering excavations and building foundations is well established.

The construction of slurry walls involves the excavation of a vertical trench using a bentonite-water slurry to hydraulically shore up the trench during construction and seal the pores in the trench walls via formation of a "filter cake" [3, p. 2-17]. Slurry walls are generally 20 to 80 feet deep with widths 2 to 3 feet. These dimensions may vary from site to site. There are specially designed "long stick" backhoes that dig to 90 foot depths. Generally, there will be a substantial cost increase for walls deeper than 90 feet. Clam shell excavators can reach depths of more than 150 feet. Slurry walls constructed at water dam projects have extended to 400 feet using specialized milling cutters. Depending on the site conditions and contaminants, the trench can be either excavated to a level below the water table to capture chemical "floaters" (this is termed a "hanging wall") or extended ("keyed") into a lower confining layer (aquitard) [3, p. 3-1]. Similarly, on the horizontal plane the slurry wall can be constructed around the entire perimeter of the waste material/site or portions thereof (e.g., upgradient,

* [reference number, page number]

Figure 1
Aerial and Cross-section View Showing Implementation of Slurry Walls (4)

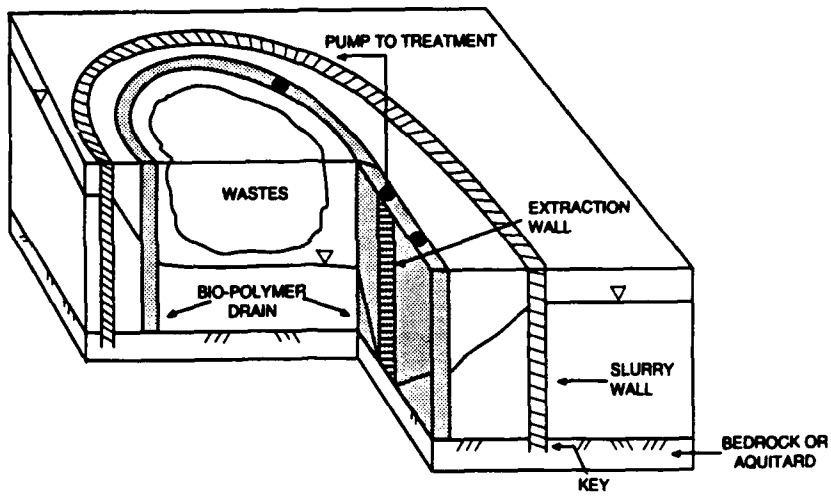




downgradient). Figure 1 diagrams a waste area encircled by a slurry wall with extraction and monitoring wells inside and outside of the waste area, respectively along with a cross-section view of a slurry wall being used with the landfill cover technology [4, p. 1].

The principal distinctions among slurry walls are differences in the low-permeability materials used to fill the trenches. The ultimate permeability of the wall is controlled by water content and ratios of bentonite/soil or bentonite/cement. In the case of a SB wall, the excavated soil is mixed with bentonite outside of the trench and used to backfill the trench. During the construction of a CB slurry wall, the CB mixture serves as both the initial slurry and the trench backfill. When this backfill gels (SB) or sets (CB), the result is a continuous barrier with lower permeability than the surrounding soils. A landfill cover, if

Figure 2
Schematic Diagram of Typical Slurry Wall and Bio-polymer Slurry Trench (9)*



* Drawing not to scale

employed, must extend over the finished slurry wall to complete the containment and to avoid desiccation.

Soil-bentonite slurry walls are the most popular since they have a lower permeability than CB walls, and are less costly [3, p. 1-6] [5, p. 2]. Attapulgite may also be used in situations where the bentonite is not compatible with the waste [5, p.16]. A newer development is the use of fly ash as a high carbon additive not only to lower the permeability of the SB but also to increase the adsorption capacity of the SB with respect to the transport of organic chemicals [6, p. 1][7, p. 444]. Permeabilities of SB walls as low as 5.0×10^{-9} cm/sec have been reported although permeabilities around 1×10^{-7} cm/sec are more typical [3, p. 2-28]. The primary advantage of the CB wall is its greater shear strength and lower compressibility. CB walls are often used on unstable slopes and steep terrain or where soils of low permeability are not accessible [3, p. 2-40]. The lowest permeabilities of CB walls are typically 1×10^{-6} cm/sec or greater [3, p. 2-42] [5, p. 14]. It should be noted that organic and inorganic contaminants in ground water/leachate can have a detrimental effect on bentonite and the trench backfill material in both SB and CB walls. Therefore, it is imperative that a compatibility testing program be conducted in order to determine the appropriate backfill mixture.

Composite slurry walls incorporate an additional barrier, such as a geomembrane, within the trench to improve impermeability and chemical resistance. The geomembranes often are plastic screens that are comprised of HDPE pile plank sections which lock together. The locking mechanism is designed to minimize the leakage of the contaminated ground water. Table 2 shows one vendor's experience in using HDPE as a geomembrane [8]. The membrane: is easy to install; has a long life; and is resistant to animal and vegetation intrusion, microorganisms, and decay. Combining the membrane with a bentonite slurry wall may be the most effective combination. It is usually effective to construct the bentonite-cement slurry wall and then install the membrane in the middle of the wall. The toe of the membrane sheet is stabilized in the backfill material, cement, or in a special grout [5, p.4]. The installation is reported to be effective in most every type of soil, is watertight and may be constructed to greater depths.

A relatively new development in the construction of slurry walls is the use of mixed-in-place walls (also referred to as soil-mixed walls). The process was originally developed in Japan. A drill rig with multi-shaft augers and mixing paddles is used to drill into the soil. During the drilling operation a fluid slurry or grout is injected and mixed with the soil to form a column. In constructing a mixed-in-place wall the columns are overlapped to form a continuous barrier. This method of vertical barrier construction is recommended for sites where contaminated soils will be encountered, soils are soft, traditional trenches might fail due to hydraulic forces, or space availability for construction equipment is limited. Both this method and a modified method termed "dry jet mixing" are usually more expensive than traditional slurry walls [5, p. 7] [9].

Another application of traditional slurry wall construction techniques is the construction of permeable trenches called bio-polymer slurry drainage trenches [10] [11]. Figure 2 diagrams a slurry wall and a bio-polymer slurry drainage trench constructed around a waste source; this will typically involve the use of a landfill cover in conjunction with the wall. Rather than restricting ground water flow, these trenches are constructed as interceptor drains or extraction trenches for collecting or removing leachate, ground water, and ground water-borne contaminants. These trenches also can be used as recharge systems. The construction sequence is the same as the traditional method described above. However, a biodegradable material (i.e., bio-polymer) with a high gel strength is used in the place of bentonite in the slurry, and the trench is backfilled with permeable materials such as sand or gravel. Once the trench is completed, the bio-polymer either degrades

or is broken with a breaker solution that is applied to the trench. Once the bio-polymer filter cake is broken the surrounding soil formation returns to its original hydraulic conductivity. Groundwater collected in the trench can be removed by use of an extraction well or other collection system installed in the trench [10]. A bio-polymer trench can be used in conjunction with an SB or CB slurry wall to collect leachate or a contaminated plume within the wall (similar to the function of a well-point collection system). A geomembrane also can be installed with the bio-polymer wall to restrict ground water flow beyond the bio-polymer wall.

Grouting, including jet grouting, employs high pressure injection of a low-permeability substance into fractured or unconsolidated geologic material. This technology can be used to seal fractures in otherwise impermeable layers or construct vertical barriers in soil through the injection of grout into holes drilled at closely spaced intervals (i.e., grout curtain) [5, p.8] [12, p. 5-97]. A number of substances can be used as grout including cement, alkali silicates, and organic polymers [12, p. 5-97 – 5-101]. However, concerns surround the use of grouting for the construction of vertical barriers in soils because it is difficult to achieve and verify complete permeation of the soil by the grout. Therefore, the desired low permeabilities may not be achieved as expected [5, p.8] [13, p. 7].

Site Requirements

Treatment of contaminated soils or other waste materials requires that a site safety plan be developed to provide for personnel protection and special handling measures.

The construction of slurry walls requires a variety of construction equipment for excavation, earth moving, mixing, and pumping. Knowledge of the site, local soil, and hydrogeologic conditions is necessary. The identification of underground utilities is especially important during the construction phase [8].

In slurry wall construction, large backhoes, clamshell excavators, or multi-shaft drill rigs are used to excavate the trenches. Dozers or graders are used for mixing and placement of backfill. Preparation of the slurry requires batch mixers, hydration ponds, pumps, and hoses. An adequate supply of water and storage tanks is needed as well as electricity for the operation of mixers, pumps, and lighting. Areas adjacent to the trench need to be available for the storage of trench spoils (which could potentially be contaminated) and the mixing of backfill. If excavated soils will not be acceptable for use in the slurry wall backfill suitable backfill material must be imported from off the site. In the case of CB walls, plans must be made for the disposal of the spoils since they are not backfilled. In marked contrast, deep soil mixing techniques require less surface storage area, use less heavy equipment, and may produce a smaller volume of trench spoils.

Performance Data

Performance data presented in this bulletin should not be considered directly applicable to all sites. A number of variables such as geographic region, topography, and material availability can affect the walls performance. A thorough characterization of the site and a compatability study is highly recommended.

At the Hill Air Force Base in northern Utah the installation of a slurry wall, landfill covers, groundwater extraction and treatment, and monitoring was implemented to respond to ground water and soil contamination at the site. The slurry wall was installed along the upgradient boundary on three sides of Operable Unit No. 1 to intercept and divert ground water away from the disposal site. Operable Unit No. 1 consists of Landfill No. 3, Landfill No. 4, Chem Pits No. 1 and 2, and Fire Training Area No. 1. Shallow perched groundwater and soils present were contaminated with halogenated organics and heavy metals. The performance of the slurry wall had been questioned because it was not successfully keyed into the underlying clay layer. This oversight was attributed to both the inadequate number and depth of soil borings. The combination of landfill caps, slurry wall, and ground water extraction and treatment has resulted in a significant reduction in the concentrations of organics and inorganics detected seeping at the toe of Landfill No. 4. Organics were reduced to levels below 5 percent of their pre-remedial action levels and iron was reduced to 20 percent of its original observed concentration. Three seperate QA/QC projects were implemented to assess the in situ effectiveness of the slurry wall. The determination of ground water levels in monitoring wells on the inside and outside of the wall provided the most the useful data [14].

Table 2
Relative Chemical Resistivity of an HDPE Geomembrane (8)[a]

Aromatic Compounds		*Inorganic Contamination*	
Benzene	+	NH_4	++
Ethylene Benzene	++	Fluorine	++
Toluene	+	CN	++
Xylene	++	Sulphides	++
Phenol	++	PO_4	++
Polycyclic Hydrocarbons		*Other Sources of Contamination*	
Naphthalene	++	Tetrahydrofurane	+
Anthracene	++	Pyrides	++
Phenanthrene	++	Tetrahydrothiophene	++
Pyrene	++	Cyclohexanone	++
Benzopyrene	++	Styrene	++
		Petrol	++
		Mineral Oil	++
Chlorinated Hydrocarbons		*Pesticides*	
Chlorobenzenes	+	Organic Chlorine	
Chlorophenols	++	Compounds	++
PCBs	++	Pesticides	++

Key: ++ Good Resistance
+ Average Resistance

[a] Adapted from vendor's marketing brochure

At the Lipari Landfill Superfund Site in New Jersey, a SB slurry wall was installed to encircle the landfill. A landfill cover, incorporating a 40 mil HDPE geomembrane, also was installed at the site. Heavy rains and snowmelt prior to the complete cap installation resulted in the need to perform an emergency removal (i.e., dewatering). Several years after completion of the slurry wall and landfill cover their effectiveness was evaluated during a subsequent feasibility study. The study concluded that the goal of an effective permeability of 1×10^{-7} cm/sec had been achieved in the slurry wall. Monitoring wells will be located at least 5 feet from the slurry wall on the upgradient side and 7 feet on the down gradient side [15]. The combination of technologies being used along with the slurry wall appears to be effectively containing the waste and its constituents.

A SB slurry wall, up to 70 feet deep, was installed at a municipal landfill Superfund site in Gratiot County, Michigan. The slurry wall was needed to prevent leachate from migrating into the local ground water. Approximately 250,000 $ft.^2$ of SB slurry wall was installed at the site. The confirmation of achieving a goal of a laboratory permeability of less than 1×10^{-7} cm/sec for the soil-bentonite backfill was reported by an independent laboratory [16].

A SB slurry wall, extending through three aquifers, was installed at the Raytheon NPL site in Mountain View, California. Soil and ground water at the site were contaminated with industrial solvents. Permeability tests performed on the backfilled material achieved the goal of 1×10^{-7} cm/sec or less. Associated activities at the site included the rerouting of underground utilities, construction of 3-foot-high earthen berms around all work areas, construction of two bentonite slurry storage ponds ,and construction of three lined ponds capable of storing 300,000 gallons of storm water. A ground water extraction and stripping/filtration system is also in place at the site. The slurry wall, purposely, was not keyed into an aquitard so that the ground water extraction program would create an upward gradient, thus serving to further contain the contaminants. The system appears to be functioning properly with the implementation of the combination of the technologies [17] [18]. However, this is the exception rather than the rule.

Technology Status

The construction and installation of slurry walls is considered a well-established technology. Several firms have experience in constructing this technology. Similarly, there are several vendors of geosynthetic materials, bentonitic materials, and proprietary additives for use in these barriers.

In EPA's FY 1989 ROD Annual Report [19] 26 RODs specified slurry walls as part of the remedial action. Of the RODs specifying slurry walls, 22 also indicated that covers would be used. Table 3 presents the status of selected superfund sites employing slurry walls.

While site-specific geophysical and engineering studies (e.g., compatibility testing of ground water and backfill materials) are needed to determine the appropriate materials and construction specifications, this technology can effectively isolate wastes and contain migration of hazardous constituents. Slurry walls also may be implemented rather quickly in conjunction with other remedial actions. Long-term monitoring is needed to evaluate the effectiveness of the slurry wall.

EPA Contact

Technology-specific questions regarding slurry walls may be directed to:

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Dr. David Daniel	University of Texas
Dr. Charles Shackelford	Colorado State University
Ms. Mary Boyer	SAIC

Table 3
Selected Superfund Sites Employing Slurry Walls (19)

SITE	*Location (Region)*	*Status*
Ninth Avenue Dump	Gary, IN (5)	In design phase
Outboard Marine	Waukegan, IL (5)	In operation
Liquid Disposal	Utica, MI (5)	In design phase
Industrial Waste Control	Fort Smith, AR (6)	In operation since 3/91
E.H. Shilling Landfill	Ironton, OH (5)	In design phase
Allied/Ironton Coke	Ironton, OH (5)	In pre-design phase
Florence Landfill	Florence Township, NJ (2)	Design completed; remedial action beginning soon
South Brunswick	New Brunswick, NJ (2)	In operation since 1985
Sylvester	Nashua, NH (1)	In operation since 1983
Waste Disposal Engineering	Andover, MN (5)	In design phase
Diamond Alkali	Neward, NJ (2)	In pre-design phase
Hooker - 102nd St.	Niagra Falls, NY (2)	In remedial design phase
Scientific Chemical Processing	Carlstadt, NJ (2)	Completed 1992

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Description of Technology

Slurry walls are subsurface, low-permeability barriers that have been widely used since the 1940s to control groundwater flow. Slurry walls have been used extensively in civil engineering applications such as construction area dewatering and dam construction. More recent applications of slurry walls have been in the areas of waste site remediation and pollution control. In these applications, slurry walls have been used to redirect groundwater away from or around a waste site, contain a contaminated groundwater plume, and generally control the potential for contaminant migration through soil and groundwater. An example application of the slurry wall to redirect groundwater around a waste site is shown in Figure 1. For the purposes of effective and complete site remediation, slurry walls are often used in conjunction with other control techniques (see "Interface With Other Technologies").

Most slurry walls are constructed of a soil, bentonite, and water mixture; walls of this composition provide a barrier with low permeability and chemical resistance at the lowest cost. Other wall compositions such as cement, bentonite, and water may be used if greater structural strength is required or if chemical incompatibilities between the bentonite and site contaminants exist. The desired permeability of the completed wall will typically be 1 x 10^{-3} cm/sec to 1 x 10^{-6} cm/sec.

Slurry walls are typically placed at depths less than 150 feet and are generally 2 to 4 feet in thickness. The most effective application of the slurry wall for site remediation or pollution control is to base (or key) the slurry wall 2 to 3 feet into a low permeability layer such as clay or bedrock, as shown in Figure 2. This "keying-in" provides for an effective foundation with minimum leakage potential. An alternate configuration for slurry wall installation is a "hanging" wall in which the wall projects into the groundwater table to block the movement of lower density or floating contaminants such as oils, fuels, or gases. Hanging walls are used less frequently than keyed-in walls.

In the construction of soil-bentonite slurry walls, a trench is excavated and a slurry (referred to as a "support slurry") of 4 to 7 percent bentonite in water is pumped into the open trench. This support slurry is used to fill the excavated trench to provide for sufficient hydrostatic pressure to hold the trench open and to

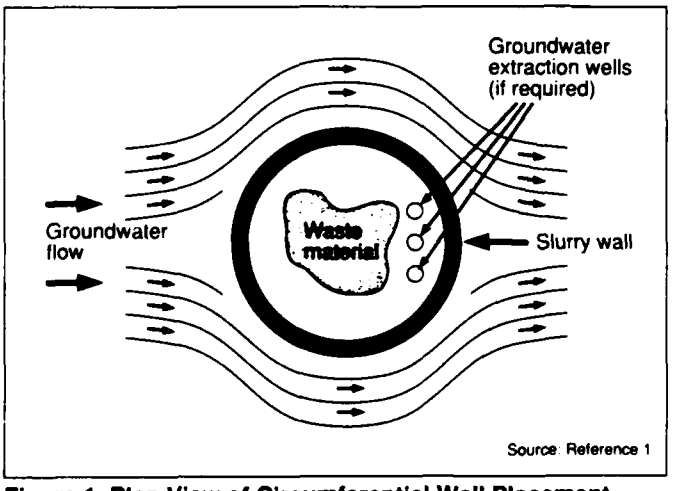


Figure 1. Plan View of Circumferential Wall Placement

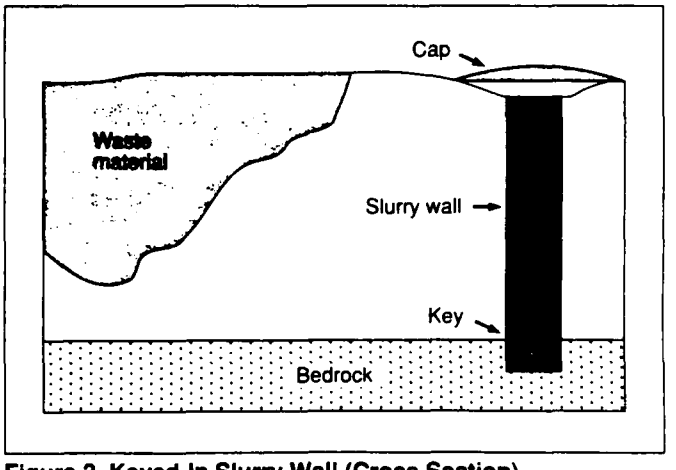
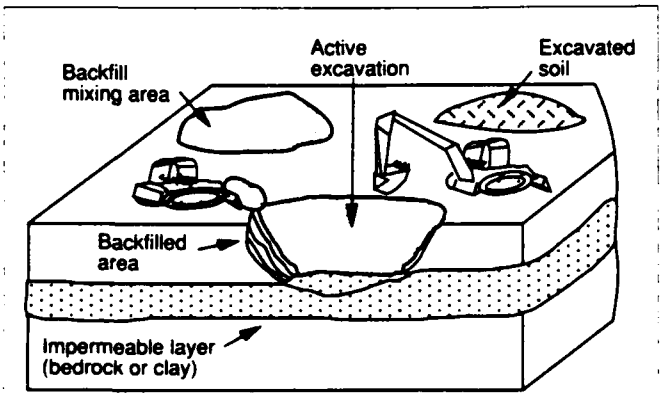


Figure 2. Keyed-In Slurry Wall (Cross Section)

allow for the formation of a thin seal ("filter cake") of low permeability on the surfaces of the trench. A "backfill" of soil mixed with bentonite-water slurry is then placed into the trench while displacing the support slurry. Normally, this backfill is formed with soil that has been excavated from the trench. However, quality control (QC) requirements for backfill specifications such as grain size, density, viscosity, and permeability may dictate the use of alternative or pretreated soil.

Wall construction is performed in a continuous manner, with trench excavation, support slurry fill, backfill mixing, and backfill emplacement occurring nearly simultaneously. A site layout illustrating this approach is provided in Figure 3.



Source: Reference 1

Figure 3. Slurry Wall Construction

Once the slurry wall is in place, a surface barrier or cap is typically employed to minimize water infiltration vertically along the slurry wall, to control erosion, and/or to contain contaminants. If the site is to be reused or will be subjected to heavy traffic, a strong and durable (normally asphalt or concrete) "traffic cap" is placed over the slurry wall.

Technology Status

Slurry walls have been widely used in civil construction activities such as site dewatering and dam construction. The installation of slurry walls is considered relatively conventional construction; however, there are a number of critical parameters that must be taken into consideration in the design and construction of slurry walls, particularly for site remediation and pollution control. For this reason, slurry wall construction is typically performed by a relatively small number of specialty contractors.

Contaminants Mitigated

Slurry walls are used to limit and control groundwater flow. In this respect, they can be used to mitigate the presence of a wide variety of organic and inorganic contaminants contained in the groundwater. Slurry walls may be applicable to a wide variety of wastes such as sanitary landfill leachates, oil and grease, low-level radioactive material, acid mine drainage, phenols, PCBs, mine tailings, fly ash impoundments, and organic solvents.

Despite their versatility, the integrity of slurry walls may be threatened by contact with incompatible contaminants, including strong acids and bases, other electrolytes (i.e., salt solutions including sea water), and alcohols. Contact with these and other incompatible materials can cause drying and cracking in the slurry wall, resulting in greatly increased permeability. For this reason, a thorough chemical characterization of the waste to be contained or controlled is required. Based on this characterization, compatibility testing of contaminants and slurry wall components may be required prior to a final decision of whether to use soil-bentonite walls in a specific application.

Applications and Limitations

Slurry walls have the potential to provide an effective, long-term, low-cost, and low-maintenance solution to the control of contaminant migration in soil and groundwater. Slurry walls are typically quick to implement and may provide for a fast-response solution to an acute groundwater contamination problem. However, it is important to consider that slurry walls alone do not eliminate the source of the contamination or reduce its toxicity, and that additional technologies may be required to permanently eliminate the threat of contamination.

Soil-bentonite slurry walls may not provide the ideal solution to specific waste site requirements, depending on factors such as waste characteristics, site surface characteristics, and site subsurface characteristics. Examples of potential limitations imposed by these factors are illustrated in Figure 4.

To address the limitations outlined in Figure 4, a thorough waste site assessment is necessary prior to design and construction of the soil-bentonite slurry wall. This assessment should include, at a minimum, consideration of the following:

- Physical and chemical characterization of soil;
- Hydrogeological conditions;
- Physical site layout; and
- Identification of a suitable substrate into which the wall can be keyed.

Once the wall is completed, special attention must be paid to the requirements for short-term and long-term monitoring requirements to provide assurance that contamination is adequately controlled.

Source	Potential Limitations
Waste characteristics	Chemical incompatibility between wall materials and electrolytic or strongly acidic or basic wastes
Site surface characteristics	Irregular contours and steep slopes may add complexity to design and construction of slurry walls Construction of slurry walls requires considerable site access and workspace
Site subsurface characteristics	If it is to be used for backfill, the excavated soil must have specific characteristics in terms of particle size distribution, water content, permeability, and chemical composition Depths of more than 150 feet or the presence of debris or boulders requires increasingly complex construction techniques in terms of equipment selection and use Effectiveness of the slurry wall may depend on the presence of a suitable impermeable layer into which the wall can key

Figure 4. Potential Limitations of Slurry Wall Use

Interface With Other Technologies

To provide for their maximum effectiveness in remedial and pollution control applications, slurry walls are often used in conjunction with other control methods and technologies. At a minimum, surface infiltration barriers or caps may be used to maintain wall integrity and further control contaminant migration. Additional technology interfaces may include:

- Use of grouts to seal the slurry wall to the surrounding surface or to seal the key into the impermeable barrier layer;
- Employment of a synthetic membrane placed within the wall to further decrease wall permeability;
- Groundwater extraction for surface treatment (see Figure 1);
- Containment of wastes that have been, or are to be, treated; and
- Capping of entire containment site to prevent infiltration of water into waste area.

A common application of slurry walls is their use in conjunction with a drain system, as shown in Figure 5.

Design Criteria

The following factors, at a minimum, must be assessed prior to designing effective soil-bentonite slurry walls:

- Maximum allowable permeability;
- Anticipated hydraulic gradients;
- Required wall strength;
- Accessibility and grade of bentonite to be used;
- Boundaries of contamination;
- Compatibility of wastes and contaminants in contact with slurry wall materials;
- Characteristics (i.e., depth, permeability, and continuity) of substrate into which the wall is to be keyed;
- Characteristics of backfill material (i.e., fines content);
- Site terrain and physical layout; and
- Cost.

Resulting design factors will include:

- Wall location, length, depth, and width;
- Requirements for sealing wall to existing structures;
- Type and quality of materials to be used and slurry composition;
- Requirements for pretreatment of excavated soil for use as backfill; and
- Methods and procedures to be used.

Construction Considerations

Major construction activities during installation of the soil-bentonite slurry wall include:

- Mobilization and site preparation;
- Slurry preparation;
- Excavation;
- Slurry placement;
- Backfill preparation;
- Backfill placement; and
- Capping.

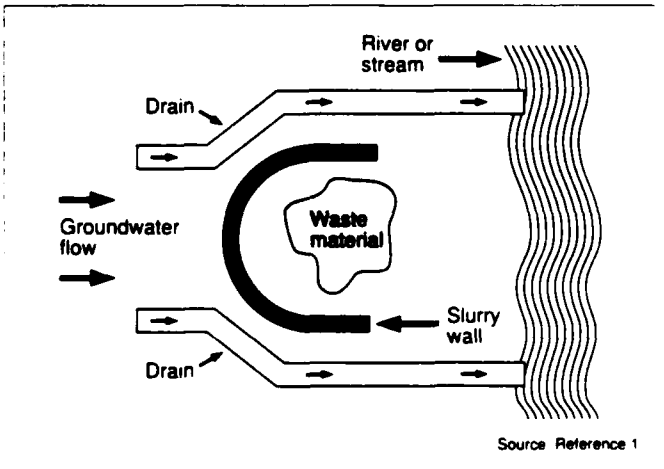


Figure 5. Slurry Wall/Drain System

Mobilization will include equipment selection based on site-specific conditions, such as depth of excavation and the type of barrier material in which the wall is to be keyed. For walls up to 80 feet deep, a hydraulic backhoe can be used; at greater depths, clamshells or draglines may be required. In order to key the slurry wall into hard bedrock, drilling or blasting may be required.

The size of the job will influence the selection of mixers to be used in slurry preparation. For small jobs, high-speed batch mixers are generally used. Larger jobs often require the use of flash (or venturi) mixers. Bulldozers are typically used to mix backfill and slurry in an established mixing area outside the excavated trench. Bulldozers and clamshells may be used to carefully place the soil-bentonite mixture in the trench.

Site preparation construction activities may include clearing, utility and water hookups, and equipment and construction material delivery.

Preparation of the bentonite and water support slurry consists of mixing bentonite—with specific purity, pH, particle size, and gel strength characteristics—with water that is low in hardness, relatively neutral in pH, and low in dissolved salts. It is critical that the slurry be completely hydrated and of proper viscosity prior to use. The viscosity of the support slurry is typically 40 seconds as measured in the Marsh Funnel Test (see Reference 2).

In soil-bentonite slurry wall construction, backfill used to fill the excavated trench is typically a mixture of the soil excavated from the trench and bentonite-water slurry. The soil is mixed with the slurry while adhering to specific criteria, such as fines content (10 to 45% passing a No. 200 sieve), wet density (typically 15 lb/ft^3 greater than that of the support slurry or 90 to 100 lb/ft^3), and slump. If on-site soils are too coarse, imported fines or extra bentonite must be added. Slump is indicative of the resulting slope of the backfill once placed into the trench; this slope is normally in the range of 5:1 to 10:1 (see Reference 1).

The construction of the slurry wall is performed in a continuous manner. The bentonite-water slurry is introduced into the trench just as the trench is opened and before the water table is reached. Backfilling is initiated once a sufficient length of trench has been excavated to the design depth. This length is dependent on backfill properties and the characteristics of excavation equipment used. Backfill is initially placed using a clamshell to carefully lower mixed backfill through the bentonite-water slurry to the trench bottom. When the backfill is visible from the surface, the remaining backfill can be pushed into the trench with a bulldozer or poured from trucks using a trough. The backfill should flow, not fall, down the sloped backfill already in place. This minimizes the potential for pockets of the support slurry to be trapped in the backfill that would reduce the slurry wall's effectiveness and performance. The viscosity of the backfill must be such that it can flow easily into the trench. The wet density of the backfill must be greater than that of the bentonite-water slurry so that the backfill can displace the slurry in the trench. The displaced slurry is pumped to a holding area where it is adjusted for density and viscosity. It may then be reintroduced into the excavated trench.

Once the backfill is completed and the slurry wall is formed, the top 1 to 3 feet of the wall is removed to eliminate any cracks that form as the soil-bentonite slurry dries. A fresh soil-bentonite slurry is then placed over the removed section of the wall, thereby providing a low permeability cap to protect the slurry wall. This cap is then covered with soil and seeding or gravel to prevent erosion. If the site is to be subjected to traffic, a reinforced traffic cap may be employed over the slurry wall. Reinforcing materials may include asphalt, aggregate, or geotextiles.

Quality Control

A critical part of the successful implementation of a soil-bentonite slurry wall for environmental protection applications is the adherence to strict QC measures throughout the construction of the wall. Specific QC requirements relate to all aspects of slurry wall construction, including support slurry preparation; trench excavation; and backfill selection, preparation, and placement. Examples of primary QC parameters relative to these construction components and their potential impact on the ultimate quality of the slurry wall are provided in Figure 6. Further details regarding QC measurements and instrumentation are provided in References 1 and 2.

Residuals Generated

The construction of soil-bentonite slurry walls can generate large quantities of excess slurry and excavated materials. Management of excess excavated materials can be a significant consideration if the excavated soil cannot be used as backfill. In most cases, it would be expected that these excess materials would not be hazardous; however, proper management of the residuals is still a requirement.

Criteria Ranking

The use of soil-bentonite slurry walls has been rated by a team of remedial action and engineering experts with respect to the ability of the walls to meet specific performance criteria. The results of this rating are provided in Figure 7.

Construction Component	QC Parameter	Quality Factor Impacted
Support slurry	Density Viscosity Filtrate loss	Trench support; backfill placement Filter cake formation; slurry workability Filter cake quality
Trench excavation	Trench continuity Depth and continuity of key penetration Trench stability	Long-term effectiveness Long-term effectiveness Support slurry placement
Backfill	Density Slump Hydraulic conductivity Bentonite content Fines content	Support slurry displacement Flowability of backfill; support slurry displacement Permeability Permeability Permeability

Figure 6. Quality Control During Slurry Wall Construction

Criteria	Ranking
Effect of reducing the overall threat to human health and the environment	
Vulnerability to ARARs (Applicable or Relevant and Appropriate Requirements)	
Long-term effectiveness	
Effectiveness at reducing toxicity, mobility, and volume	
Short-term effectiveness	
Implementability (including transportability)	
Cost	
Readiness of acceptance by the state and community	

Figure 7. Performance Criteria Rating

It should be noted that the use of slurry walls alone does not result in the removal of the contaminant from the environment or a reduction in toxicity, but rather limits the migration of the contaminant from the controlled area. For this reason, the technology may not be favorably comparable to those technologies that completely eliminate the threat of contamination.

Key Cost Factors

The primary cost components of soil-bentonite slurry wall design and construction include:

- Soil and hydrogeological characterization;
- Site preparation;
- Wall installation; and
- Site cleanup.

Factors that have the most significant impact on the final cost of soil-bentonite slurry wall installation include:

- Depth, length, and width of wall;
- Geological and hydrological characteristics;
- Nonstandard construction requirements that may be required;
- Distance from source of materials and equipment;
- Requirements for wall protection and maintenance;
- Type of slurry and backfill used; and
- Other site-specific requirements as identified in the initial site assessment (i.e., presence of contaminants or debris).

Costs likely to be incurred in the design and installation of a standard soil-bentonite wall in soft to medium soil range from $5 to $7 per square foot (1991 dollars). These costs do not include variable costs required for chemical analyses, feasibility, or compatibility testing. Testing costs depend heavily on site-specific factors.

Points to Remember

The following points are essential to consider in the selection, design, or construction of soil-bentonite slurry walls. These points are not intended to be all-inclusive, but represent critical elements as noted by those experienced in the implementation of slurry walls.

√ Adequate site investigation and characterization is required to identify hydrogeological, physical, and chemical conditions or constraints to slurry wall implementation;

√ Testing to identify potential chemical incompatibilities between contaminants and slurry wall components prior to design and construction may be required to ensure wall integrity;

√ Identification of a suitable impermeable layer into which the slurry wall can be keyed must be made;

√ Availability of suitable, quality backfill material must be determined;

√ A determination must be made of required wall strength and permeability limitations;

√ Factors such as future use of site or interfacing treatment technologies must be considered prior to design; and

√ Strict QC must be maintained throughout the slurry wall construction process.

Application Examples

Examples of applications of slurry walls constructed within the last five years are provided in Figure 8. These examples were selected to provide a representation of the variety of site or contaminant conditions that may be encountered.

In the first example, slurry walls were constructed for the purpose of hazardous waste landfill containment. These walls, more than 5,000 feet long, up to 40 feet deep, and 5 feet wide, were constructed of soil-bentonite and soil-attapulgite (a similar clay). The site was in a salt water environment, which presented a problem due to the known incompatibility of salt water and bentonite. In addition, laboratory testing indicated incompatibility between land-fill leachates and bentonite. This latter factor illustrates the importance of compatibility testing. The site contamination profile indicated the presence of a wide variety of organics including gasoline and xylene. Normally, the individual contaminants alone would not have indicated the potential for incompatibility, but testing indicated that the mixture of contaminants was incompatible with a soil-bentonite matrix. To address these incompatibilities, attapulgite was effectively used in sections of the wall to be exposed to salt water or to landfill leachates.

An example of a circumferential application of a slurry wall (see Figure 1) keyed into an underlying impervious layer (see Figure 2) is provided in the application of containing a coal tar disposal pond.

An example of the use of a slurry wall to contain a sanitary landfill is included because of the magnitude of the application. In this application, over 6 miles of slurry wall were constructed at depths of up to 53 feet. Due to the relative ease of excavation, the construction was completed in three months.

References

1. Spooner, P. A., et al. 1984. *Slurry Trench Construction for Pollution Migration Control.* EPA/540/2-84/001.

2. Goldberg-Zoino and Assoc. Inc., 1987. *Construction Quality Control and Post-Construction Performance for the Gilson Road Hazardous Waste Site Cutoff Wall.* EPA/600/2-87/065.

3. Geo-Con, Inc., Vendor Literature, 1991.

4. *Reclamation and Redevelopment of Contaminated Land: U.S. Case Studies,* 1986, U.S. Environmental Protection Agency, EPA/600/2-86/066.

Site	Wall Length	Wall Depth	Special Considerations	Reference
Hazardous waste landfill	5,000 ft.	40 ft.	Presence of loose sand and refuse. Salt water environment and presence of incompatible organic compound mixtures dictated use of bentonite alternative in some sections of the slurry wall.	3
Sanitary landfill	6 miles	< 52 ft.	Limited working area. 700,000 sq. ft. wall constructed in 3 months.	3
Coal tar disposal pond	735 ft.	13–20 ft.	Circumferential containment of leachate from pond containing metals and phenols. Wall-keyed into underlying impervious till.	4

Figure 8. Slurry Wall Application Examples

Additional Sources of Information

The following sources provide additional slurry wall application, design, and construction information.

- *Civil Works Construction Guide Specification for Soil-Bentonite Slurry Trench Cutoffs,* 1986, U.S. Army Corps of Engineers. National Institute of Building Sciences, Construction Criteria Base. CW-02214.

- *Guidelines for Preliminary Selection of Remedial Action for Hazardous Waste Sites,* 1986, U.S. Army Corps of Engineers. National Institute of Building Sciences, Construction Criteria Base. Engineer Manual No. 1110-2-505.

- McCandless, R. M. and Bodocsi, A. 1987. *Investigation of Slurry Cutoff Wall Design and Construction Methods for Containing Hazardous Wastes.* EPA/600/2-87/063.

Points of Contact

The following points of contact represent firms with demonstrated experience in slurry wall design and construction.

- Steve Day or Christopher Ryan, Geo-Con, Inc., Pittsburgh, PA, (412) 856-7700.

- Larry Duhaime, Griffin Remediation Services, Inc., Chesapeake, VA, (804) 543-6809.

- Tom O'Malley, Case International Company, Roselle, IL, (312) 625-1250.

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Composting of Contaminated Soil

Port Hueneme, CA 93043 | NEESA Document No. 20.2-051.9 | October 1993

Introduction

Composting is an innovative technology for the treatment of soil contaminated with nonvolatile organic compounds. As an engineered and enhanced form of biotreatment, composting has the potential to degrade hazardous compounds at faster rates than other types of biotreatment. In addition, composting can result in the decomposition of compounds that are less likely to be degraded by other biotreatment methods.

Although composting is one of the oldest techniques of organic material decomposition, investigations into its use in treating contaminated soils have been relatively recent. For the most part, experiences and data relating to the treatment of soil by composting are based on laboratory, pilot, and demonstration-scale studies. One of the most active areas of investigation for composting is in the treatment of soil contaminated with ordnance compounds including explosives and propellants. This Tech Data Sheet describes aspects of the technology as it applies to these ordnance compound-contaminated soils. In addition, application of the technology to other contaminants in soil is discussed.

Separate Tech Data Sheets have been prepared to address two other types of bioremediation: "Soil Bioremediation—Naturally Aerated Processes," and "Heap Pile Bioremediation."

Purpose and Audience

Tech Data Sheets are designed to:

- Disseminate practical, implementation-related information to minimize design and construction problems;
- Help Remedial Project Managers (RPMs) evaluate a technology (one recommended in a Feasibility Study [FS], for example) and decide if it is practical and cost-effective;
- Aid RPMs in writing a Remedial Action (RA) Delivery Order;
- Help Engineering Field Division (EFD) Remedial Design personnel write a Statement of Work (SOW) for, and RPMs to review, Remedial Design Plans; and
- Enable field personnel such as Project Superintendents, Engineers in Charge, On-Scene Coordinators (OSCs), and Resident Officers in Charge of Construction (ROICCs) to become familiar with a technology at a site they will oversee.

Description of Technology

Composting uses naturally occurring microorganisms (various bacteria and fungi) in a controlled environment to break down organic materials. When successfully applied to the treatment of soil contaminated with toxic organic compounds, composting results in the degradation of the contaminants to simpler, nontoxic compounds.

Composting differs from other types of ex situ aerobic processes (such as landfarming or heap pile bioremediation) by relying on a much higher concentration of organic matter in the material to be composted. These high concentrations of organic matter increase microbial activity to the point that heat is generated. In fact, if left unchecked, the compost can self-heat enough to significantly kill off microorganisms and decrease microbial activity (see **Design Criteria**). However, the compost is adequately self-regulating so that cessation of microbial activity is unlikely.

This high level of microbial activity and the resulting elevated temperatures will usually result in higher degradation rates and more extensive degradation levels than those typically achieved at ambient temperatures. In addition, the increased level of microbial activity provides an opportunity for cometabolism in which recalcitrant (i.e., resistant to biodegradation) compounds are degraded by microorganisms that obtain their carbon and energy from other, more usable sources (1). This latter feature of composting is what makes degradation of typically recalcitrant ordnance compounds feasible.

Despite the enhanced environment for biodegradation of recalcitrant compounds such as explosives, complete (100%) mineralization of the contaminants will not occur. As long as the toxicity of the contaminated material is reduced to levels that are protective of human health and the environment, complete mineralization is not necessary.

Incomplete mineralization may result in transformation products that are:

- Tightly bound or incorporated into the humic material of the compost;
- Degraded and incorporated into bacteria cell material;
- Left in a water-soluble form that may leach out (although research has shown that leachability is generally not a problem [2]);

- Less or more toxic than the original target contaminant; and/or
- Volatilized.

Because of concern about the potential toxicity of transformation products of compounds for which biodegradation pathways are not clearly understood (such as explosives), treatability studies should be performed (see **Limiting Factors** and **Design Criteria**).

In soil remediation applications, the material to be composted (compost) is made up of the contaminated soil and various amendments necessary for composting to be sustained. These amendments will:

- Structurally improve the compost matrix (e.g., reduce bulk weight and increase air voids);
- Increase the amount of biodegradable organics in the mixture; and
- Increase the amount of inorganic nutrients in the mixture.

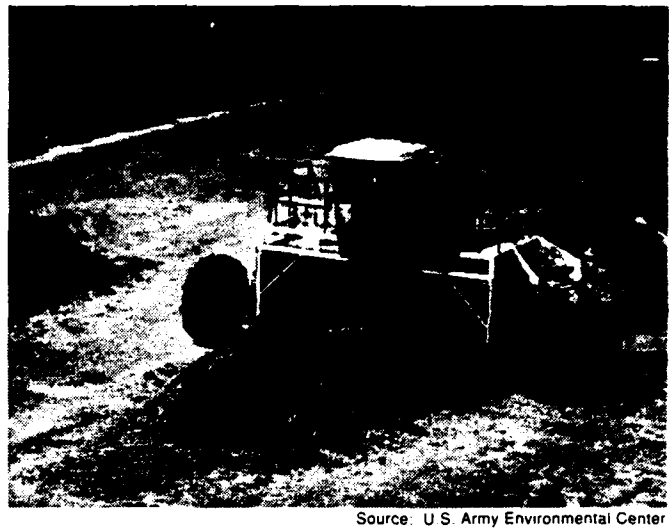
Common structural amendments include materials such as wood chips, straw, and sawdust. Many materials can be added to increase the concentration of biodegradable organics and inorganic nutrients. Often, agricultural materials such as manure, vegetable processing wastes, and/or field crops are used.

There are several process configurations for composting. The selection of the optimum configuration will usually depend on site-specific implications and requirements (see **Advantages and Disadvantages**). General types of composting configurations include: windrow, aerated static pile, and mechanical in-vessel composting. The primary features of each of these are described below. Additional design and operational details are provided in subsequent sections of this Tech Data Sheet.

Windrow composting, the most frequently used (and often least expensive) method, is a relatively simple form of composting in terms of process control and implementation. Material to be composted is shaped into long narrow piles. Aeration and temperature control are accomplished by periodically turning the compost. Turning can be done by hand (with shovels) or with a mechanical windrow machine specifically made for this purpose (see Figure 1).

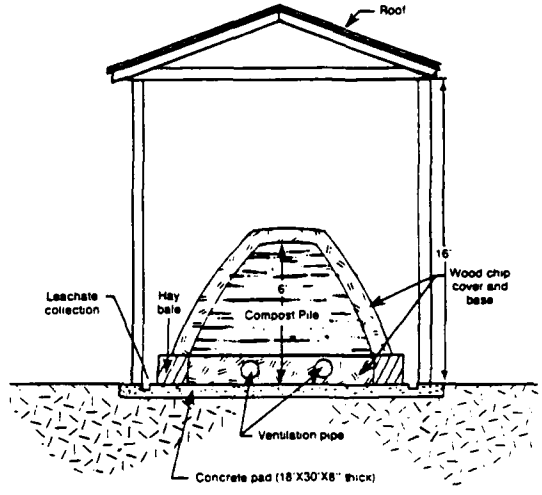
Aerated static pile composting is a more sophisticated method using an aeration system that is physically a part of the compost pile. This aeration system is used to aerate as well as to control temperatures within the compost. As shown in Figure 2, the compost is placed over a network of perforated pipes connected to a blower. Air is drawn or forced through the compost. The blower may be operated on an automatic on/off cycle as necessary to achieve the required aeration and/or temperature in the pile. Aerated static piles can take a number of forms. The compost can be constructed as an elongated, free-standing pile (as shown in Figure 2 [end view]); placed in long narrow piles (windrow-shaped); or placed in bins.

A third major configuration of composting includes mechanical composting systems. One of the many types of mechanical systems is a mechanical in-vessel composter. This configuration provides a high degree of process control and automation. Such a composter is illustrated in Figure 3. This composter was used by the Army in a field demonstration of composting explosive-contaminated soil (see **Application Examples**). As



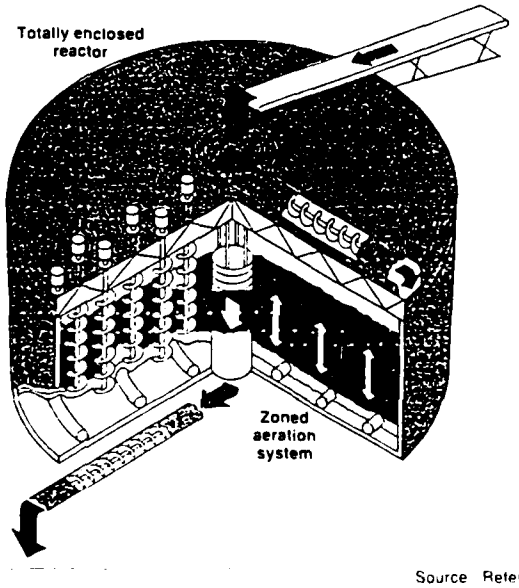
Source: U.S. Army Environmental Center

Figure 1. Windrow Machine Turning Compost



Source: Reference 3

Figure 2. Schematic of Aerated Static Pile



Source: Reference 4

Figure 3. In-Vessel Composter (manufactured by Fairfield Equipment Co.)

shown, this in-vessel composter consists of a totally enclosed reactor outfitted with augurs to provide for controlled mixing of the compost and a forced air ventilation system to aerate the compost and control temperature. Material handling (loading and discharge), mixing, aeration, and temperature control operations are usually performed automatically. These systems may be operated as continuous or batch processes.

Regardless of the composting configuration, a number of factors can be controlled in composting that affect its effectiveness (see **Design Criteria**). These include:

- Moisture content (by adding water);
- Temperature (reduced by turning the compost or increasing air flow through the pile);
- Concentration of organic matter (by adding selected amendments);
- Concentration of inorganic nutrients such as nitrogen (by adding selected amendments); and
- Oxygen content (increased by turning the compost or increasing air flow through the pile).

Although the composting process is usually a net consumer of water, a means for leachate collection and control will usually be required. To the maximum extent possible, collected leachate will be recycled to the compost to provide moisture. Excess leachate may require treatment if the compost is exposed to rainfall (see **Interface with Other Technologies** and **Residuals Generated**). However, leachate is seldom generated in a well-managed pile.

In addition, off-gas control may be required—particularly if the soil contains volatile organic compounds (see **Interface with Other Technologies** and **Residuals Generated**).

Technology Status

Since the 1960s, composting, as an engineered process, has been seriously investigated and implemented for the treatment of municipal wastewater treatment sludges (5). However, in remedial applications involving the treatment of contaminated soil typically containing low concentrations of organic compounds, composting is considered an innovative technology.

Interest in the use of composting for the treatment of hazardous wastes began in the late 1970s. In the 1980s, pilot tests and demonstrations of composting began to be conducted to determine its effectiveness for soil remediation. There are few reported full-scale applications of composting in remedial actions.

Composting has been actively investigated in the treatment of soils contaminated with energetic compounds such as explosives or propellants. The Army has conducted a number of pilot tests and field demonstrations of its use (see **Application Examples**). As a result of these successful tests and demonstrations, composting was selected as the recommended alternative for treatment of explosive-contaminated soils at an Army Superfund site (6).

Based on available information, there are at least five full-service bioremediation vendors that will use composting to treat contaminated soils. In addition, because of the extensive use of composting for treatment of wastewater sludges and other nonhazardous wastes, there are over 30 vendors of equipment to support composting (7). Although equipment is readily available, its use with explosives-contaminated soil is subject to explosive safety hazards analysis prior to use (see **Design Criteria**).

Types of Applications

At its current stage of development, potential applications of composting include the remediation of soils contaminated with:

- Low-volatility petroleum products as a result of leaks from underground storage tanks, spills, and past disposal practices (see **Application Examples**); and
- Ordnance compounds (e.g., explosives and propellant-related compounds) resulting from munition production, testing, and demilitarization operations (see **Application Examples**).

Types of Contaminants

Composting has been demonstrated to be effective in the treatment of soil contaminated with the following compounds:

- Diesel fuel;
- Polyaromatic hydrocarbons (PAH) (see **Application Example 6**);
- 2,4,6-trinitrotoluene (TNT);
- Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX);
- Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX);
- N-methyl-N-2,4,6-tetranitroaniline (tetryl);
- Nitrocellulose (NC); and
- Benzene, toluene, ethylbenzene, xylene (BTEX)—although these compounds may be volatilized at elevated temperatures.

Since the explosive and propellant ingredients listed above represent compounds that are generally considered to be recalcitrant, composting will most likely apply to a wider range of more biodegradable organic contaminants. However, applications have not been reported for other contaminants.

Advantages and Disadvantages

In general, composting offers advantages similar to those of other ex situ remedial technologies. These advantages include:

- Contaminants are not transferred to other environmental media (so there is typically nothing else to treat);
- The cost is low relative to other treatment alternatives (such as incineration); and
- It is permanent (in that contaminants may be completely degraded to nontoxic gases and water or detoxified).

Potential advantages of composting over other ex situ remedial technologies include:

- Reduction in treatment time due to controlled increase in microbial activity;
- Less dependence on soil characteristics because of the amendments and mixing processes used;
- In general, less land area may be required for composting than for landfarming;
- Enhancement in process optimization due to a greater degree of control of operating parameters (e.g., aeration, temperature, mixing);

- Ability to control off-gas releases if required (primarily applicable to static pile and in-vessel composting processes; more difficult in windrow processes); and
- Composting end product is material with high organic content that makes quality top soil, mulch, or fill material.

On the other hand, a potential disadvantage of composting over other bioremediation techniques is the large quantity of amendments that may be required. These amendments can significantly increase the volume of the compost (for example, a 200% to 300% increase may be expected for explosive-contaminated soil treatment [8]) and may be expensive based on their availability at the remediation site. The additional volume will be a concern if the treatment is not successful and a greater volume of contaminated material must be disposed.

Other disadvantages of composting include:

- The technology is innovative. There are few applications and little full-scale experience to demonstrate its effectiveness and likely cost with a wide variety of contaminants;
- The results of composting metal-containing soil are unknown;
- Toxic intermediate compounds may be end products (further complicated by potential difficulties in identifying these compounds); and
- There may be an odor problem (particularly if anaerobic conditions develop).

For soil contaminated with ordnance compounds, the only technology that has been successfully implemented in full-scale remediations is incineration. The primary advantages of composting over incineration in treating these soils are:

- Better public acceptance;
- Potentially lower cost;
- Easier to implement; and
- Reduced threats to the environment.

The disadvantages of composting when compared to incineration include:

- An increase in time required to complete the remediation;
- Applicability to a much narrower range of contaminants; and
- Incineration achieves a lower cleanup level.

Relative advantages and disadvantages of the various configurations of composting are provided in Figure 4.

Limiting Factors

The use of composting may be limited by a number of factors including:

- Degradability of the contaminant(s)—the contaminant must be biodegradable;
- Presence of other contaminants that may be toxic to the degradation organisms (e.g., metals);
- Availability and cost of amendments—the success of composting, especially in treating soil with low organic concentrations, relies on the use of large quantities of amendments that can significantly affect the practicality and cost of composting at a given site;
- Volatility of contaminant(s)—due to the elevated temperatures generated during composting, some contaminants may be more prone to volatilization than degradation; and
- Potential for generation of toxic byproducts—a reduction in toxicity to acceptable health-based risk levels will have to be demonstrated.

This latter factor is of particular concern when biodegradation pathways for the contaminants are not well understood. For such contaminants (including ordnance compounds), treatability studies will be required. To fully demonstrate a reduction in toxicity of transformation products bound to the soil, toxicological studies may be required (8) (see **Design Criteria** and **Application Example 2**).

In addition, the use of composting to treat explosive-contaminated soil may be limited by the presence of other compounds that increase potential explosive safety hazards (see **Design Criteria**).

Interface with Other Technologies

Depending on practical considerations and regulatory requirements, other technologies may interface with composting. These include:

- Carbon adsorption to control the emission of volatile organic-laden off-gas; and
- Technologies used for leachate collection and treatment (see **Residuals Generated**).

At many sites, the contamination goes below the water table. At these sites, some form of ground water treatment may be integrated with soil bioremediation. Such ground water treatment technologies may include pump-and-treat (where ground water is pumped to the surface and treated) or in situ techniques (e.g., biological treatment or air stripping).

Design Criteria

The first steps in preparing a sound design for composting contaminated soil include:

- Site characterization;
- Soil sampling and characterization;
- Contaminant characterization;
- Laboratory and/or field treatability studies; and
- Pilot testing and/or field demonstrations.

Site, soil, and contaminant characterizations are always a part of developing design criteria for the remediation of soil. However, their importance increases in applications where ordnance compounds may be present (see **Points to Remember**). These characterizations will be used to:

- Identify and quantify contaminants;
- Determine requirements for organic and inorganic amendments;
- Identify the presence of organic compounds that may be volatilized during composting;
- Identify potential safety issues;
- Determine requirements for excavation, staging, and movement of contaminated soil; and
- Determine availability and location of utilities (electricity and water).

Compost Type	Advantages	Disadvantages
Turned Windrow	• Simple process, easy to implement • Lower cost • Periodic turning of compost provides for better uniformity of temperature and moisture • Amendments and soil can be mixed during pile construction by windrow machine	• Difficult to control air emissions • Less control over oxygen content and temperature • Steam and dust generated during turning may impact worker safety • May require more land surface area
Aerated Static Pile	• Often better control of temperature and oxygen content than with windrows • In some cases, costs of operation may be less than windrows due to lack of frequent turning	• Increased utility costs due to blower use • Less homogeneous than windrows with respect to moisture and temperature • Potential for surfaces of pile to dry out • Soil and amendments must be well-mixed prior to pile construction
In-Vessel Composter	• May be totally enclosed—provides for better containment of wastes and odors • High degree of control of operating parameters • Usually faster degradation rates (allow for shorter treatment times) • System can be completely automated • Stirred reactor provides for better mixing and uniformity of moisture and aeration	• Higher capital, operating, and maintenance costs • Systems designed to handle explosive-contaminated soil are not commercially-available—they must be custom-made

Figure 4. Relative Advantages and Disadvantages of Composting Systems Source: References 2 and 8, and Arthur D. Little, Inc.

Laboratory or field treatability studies are needed to identify:

- Amendment mixtures that best promote microbial activity;
- The maximum quantity of soil in the composting matrix;
- Potential toxic degradation byproducts;
- The percent reduction and lower concentration limit of contaminant achievable; and
- The potential degradation rate.

Bench-scale treatability studies are needed to confirm that the contaminants of concern can be degraded as well as to optimize process parameters. Results of these tests will also be used to identify leachate treatment requirements as well as the disposition of the composted material.

As of August 1993, the Army's Waterways Experiment Station is nearing completion of a bench-scale adiabatic compost reactor that should predict full-scale treatability. As of this writing, there are at least two sources for the conduct of bench-scale treatability studies for explosives-contaminated soil (8). For additional information on treatability studies, contact Dr. Kurt Preston and/or Major Kevin Keehan (see **Points of Contact**).

Developing design criteria for composting involves ensuring that the proper environment is maintained to rapidly decompose the organic contaminant. The following factors must be considered.

Amendment selection—Amendments serve a number of purposes. They help provide for a suitable texture of the compost matrix to enhance air circulation. Amendments will be used to reduce the bulk density of the contaminated soil—typically, a bulk density of 1,000 lbs/yd^3 will be desirable for the compost.

In addition, amendments help develop a suitable chemical environment for biodegradation. They provide a carbon source for the development and maintenance of optimum levels of microbial activity.

Amendments will also be a source of inorganic nutrients required for degradation. One of the most important of the inorganic nutrients is nitrogen. A typical maximum carbon to nitrogen ratio used in composting is 30:1.

Two other important considerations in amendment selection include availability and cost. Amendments should be available year-round in the locality of the remedial site (ideally within a 100-mile radius [8]). The amendment cost may be particularly significant due to the large quantities required per unit of contaminated soil and/or the specific amendment (or mixture of amendments) selected (see **Key Cost Factors**).

Relative concentrations of soil and amendments—Because soils often contain only very low levels of biodegradable material, soil concentration is limited in the compost. This limitation will affect the throughput of the composting process. Based on optimization studies for composting explosive-contaminated soil, maximum soil loadings in the compost range from 25% to 40% by volume, depending on system configuration, amendment mixture, and contaminant type (4). However, for soil contaminated with petroleum hydrocarbons, soil loading can vary from 50% to 75% based on contaminant concentration (9).

Moisture content—A moisture content of 50% to 60% of total weight is typically desirable (10). Excess moisture should be avoided to reduce the potential for generation of leachate and impeding oxygen transfer (leading to anaerobic conditions). Design criteria will usually specify how much water should be added and at what frequency.

Aeration—Aeration of compost serves two purposes. First, it provides for an adequate level of oxygen to be maintained. Typical oxygen concentrations in the compost are 5% to 15% by volume (10). Excess air should be avoided, however, to prevent excessive cooling of the compost and limit moisture evaporation.

Aeration is also used to remove heat from the pile as necessary to prevent overheating. Ideal temperatures for composting are usually in the 55° to 70°C range—specific optimum temperatures will depend on the amendments, contaminants, and microorganisms involved.

Aeration can be accomplished by turning the compost material over by machine or by hand, as in the turned windrow method. In static pile composting, the piles are usually aerated by using aeration pipes located in the bottom of the piles to either pull or blow air through the compost (see **Field Implementation Considerations**).

pH—A neutral pH in the range of 6 to 8 is considered optimum. The pH may vary throughout the pile and throughout the composting operation. However, organic materials in the compost are usually buffered well enough to avoid sudden downshifts in pH and adjustments are seldom necessary.

In addition to the above factors, the design of a composting system to treat soil contaminated with explosive ordnance compounds will include consideration of explosive safety issues. The degree to which explosive safety will impact the design will be primarily determined by the concentration of the explosives in the soil, the type of explosives, and the likelihood of initiating compounds being present. Any equipment to be used will need to undergo a hazards analysis to identify potential explosive and fire hazards.

Field Implementation Considerations

Specific field activities for composting will vary depending on the selected configuration of composting. General field activities will include:

- Site selection and preparation;
- Earth work (excavation and handling of soil);
- Soil preparation (screening and mixing of soil and amendments);
- Operation and maintenance of composting system; and
- Facility monitoring.

Site selection will take the following issues into consideration:

- Needs for excavation, staging, and movement of contaminated soil;
- Area required for mixing of soil and amendments; and
- Availability and location of utilities (electricity and water).

In addition, a site for turned windrow operations must consider the requirements for a greater land surface area and the regular operation of heavy equipment.

Site preparation may include site surveying, staking, and grading (to ensure adequate drainage of leachate and runoff).

A foundation (pad) for the composting operation will be required. Pads are usually curbed and made of concrete or asphalt.

Enclosing (or, at a minimum, covering) aerated static pile and windrow composting operations is usually desirable. The benefits of enclosing the piles include:

- Prevention of runon and runoff that will add to the amount of leachate generated;
- Better control of temperature and moisture in the pile; and
- Better control of dust, volatilized organics, and nuisance odors.

If the composting operation is to be enclosed, a suitable enclosure will have to be identified or constructed. Temporary structures are available that can enclose static piles or windrows. These structures consist of an external frame covered with plastic or fabric under tension.

Soil excavation and movement will normally be done with conventional equipment (e.g., backhoes, front-end loaders, dump trucks). However, if explosives are present in concentrations that present an explosive safety hazard (see **Design Criteria**), the site safety plan should address special precautions to be taken for soil excavation and handling.

Once excavated, the soil may be screened to remove rocks and debris to avoid damage to the windrow machine or the in-vessel composter. The mixed compost is then loaded into a dump truck and transported to the composting site.

A front-end loader can be used to mix amendments with the soil and to construct static piles and windrows (final shaping of the windrow can be done by the windrow machine). Static piles are usually formed over a network of perforated pipe (typically 6-inch diameter) connected to a blower so that air may be forced or pulled through the compost.

Windrows are usually constructed in long parallel rows. The cross section of the windrows may be trapezoidal or triangular depending on the equipment used to turn the piles. Typical dimensions of a windrow are 15 feet wide and 3 to 7 feet tall (5).

In the case of the in-vessel composter, the compost will be placed into a feeding bin and charged to the composter.

Operation of the composting system will depend on the selected configuration. Once a windrow has been established, a windrow machine may be used to turn the compost to provide for aeration and temperature control. Alternatively, the compost can be turned manually if labor is available. Moisture will be added to the windrow as needed by handwatering with a hose and sprayer. A water spray may be required during turning to minimize fugitive dust generation.

Operation of the aerated static pile will generally be more automated than the turned windrow. The blower used to force or draw air through the compost may be cycled on and off automatically, based on pile temperatures and oxygen content. By blowing air through the compost, it is possible to humidify the air to add moisture. Additional moisture will be provided to the static pile as needed by handwatering or using a fixed spray or drip (soaker) system.

The in-vessel composter provides for a high degree of system automation. In the composter shown in Figure 3, aeration and mixing of the compost is accomplished by screw augers that rotate throughout the reactor. Air and water are added to the reactor as needed via a manifold. Other configurations of in-vessel composters are available. If used to compost explosive-contaminated soils, the in-vessel composter should be subjected to a safety review prior to use.

During operation, routine activities will include the regular monitoring of system performance parameters (see **Quality Control**).

It should be noted that the presence of spore and fungi during composting may affect hypersensitive workers (8).

Quality Control

A number of parameters may be monitored to ensure proper compost operation, including temperature, moisture, and pH. Microbial activity need only be monitored during treatability testing if problems occur.

Long-stemmed thermometers or thermocouples may be used to monitor temperature in the compost. Handheld instruments can be used to measure temperatures at various locations throughout the pile. Thermocouples can be used to continuously monitor temperatures and provide feedback to an automated control system to operate a blower (in an aerated static pile) or to operate the agitation/aeration system of an in-vessel composter. Temperature is the predominant controlling variable in composting. In most cases, providing air to control temperature may be adequate to ensure that the level of aeration necessary for microbial activity is maintained. It has been demonstrated that the drop of soil oxygen content to below detection limits does not necessarily affect compost efficiency (8).

Actual sampling of the compost for laboratory analysis should be performed in accordance with the Environmental Protection Agency Standard Method 8330. To reduce analytical variability, the samples should be homogenized according to the sample preparation protocol in Reference 11.

Periodic monitoring of moisture content is best done by laboratory gravimetric analyses on compost samples. Tensiometers can be used to roughly estimate relative compost moisture; however, they are not very reliable.

Measuring respiration rates provides a quick check on system performance. As organics degrade, oxygen is consumed and carbon dioxide is generated. Oxygen and carbon dioxide (respiration) measurements in gas from the compost can warn of potential problems in system performance. However, it should be noted that carbon dioxide may be converted to insoluble carbonates in an alkaline compost and may not be detected even though degradation is occurring (12). In addition, carbon dioxide may be lost to the atmosphere during the turning of windrows.

Chemical extraction—and thus analysis—of the compost may be impeded by the potential for contaminants and transformation products to absorb into or bind to the humic material of the compost.

Residuals Generated

Residuals generated during composting are limited to liquids (leachate and runoff) if generated during operations, off-gases from aeration processes, and the compost itself.

Leachate and runoff can be reduced by covering or enclosing the compost operation and further reduced by using collected liquids for moisture addition. However, excess liquids will require proper management. Options for managing these excess liquids include discharge to a publicly-owned treatment works (POTW) and treatment by carbon adsorption or air stripping.

The ability to discharge the liquids to a POTW is a function of the quantity of liquids, the quality of the liquids (in terms of contaminant or degradation product concentrations), and the capacity of the POTW. It should be noted that leachate generation in composting may be less than in other types of biotreatment because of increased evaporation at higher operating temperatures.

Off-gases may be controlled at the blower effluent if air is pulled through the compost (for static pile and in-vessel systems) or may be contained by enclosing the compost (applicable to all composting processes). Activated carbon adsorption is the most common means of treating off-gases.

After treatment, the compost product is usually returned to the site as backfill if it meets the treatment criteria.

Regulatory Issues

A review of local, state, and federal regulations should be the first step in planning the remedial action. The primary federal regulatory programs that will impact the feasibility, design, and operation of composting as a remedial action are the Comprehensive Environmental Response Compensation & Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA).

Specific regulatory requirements will be affected by site-specific factors and local (and state) regulatory issues. In general, the required regulatory permits are site- and system-specific. In remedial actions involving leachate collection and runoff control, permits regarding the management of the collected liquids may be required. Air permits may be required if volatile organics are involved in the remediation.

Regulatory issues associated with composting explosive-contaminated soil are complicated and evolving (13). The potential applicability of RCRA must be considered when dealing with soil contaminated with ordnance compounds such as explosives. Such soils could be considered a listed hazardous waste if they contain explosive wastes that are listed as RCRA wastes KO44 (wastewater treatment sludges generated during the original manufacture and loading, assembling, and packing of reactive explosives) or KO47 (wastewater generated during the production and formulation of TNT). Such wastes are listed solely because of reactivity. If it can be proven that these wastes are no longer reactive, they may be delisted. Explosive-contaminated soils may also be RCRA characteristic wastes due to reactivity or the results of the Toxicity Characteristic Leaching Procedure (TCLP). If the results of the TCLP exceed 0.013 mg/l of 2,4-DNT, then the compost is subject to regulation under Subtitle C of RCRA (8,14).

If RCRA does apply, potentially applicable requirements include Part 264 permitting standards for treatment facilities (including design and operating requirements), Part 270 permitting requirements, and RCRA Land Disposal Restrictions (LDR) (13). These requirements will increase the cost and time of the remedial action considerably.

Based on data developed for the Army (15), a concentration of less than 12% explosives (by weight) in soil should not, under normal circumstances, react explosively when subjected to flame initiation or shock. As a safety measure, the Army uses a

conservative reference explosives concentration of 10%. However, it is important to consider the possibility that initiating compounds (e.g., lead azide, lead styphnate, lead fulminate) may be present. If initiating compounds are present, the 10% explosive threshold does not apply and a thorough analysis of explosive reactivity should be conducted. The presence of initiating compounds can be predicted by a historical review of site activities and confirmed by analysis (8).

Feasibility Study (FS) Criteria Ranking

The use of composting to treat contaminated soil has been rated with respect to certain performance and regulatory criteria. The results of this rating are presented in Figure 5.

If composting results in adequate reduction in toxicity and the sufficient binding/stabilization of transformation products, criteria for long-term effectiveness and permanence and reduction in toxicity or mobility of contaminant(s) are met. However, because of the uncertainty of knowing how tightly transformation products (which may be toxic) are bound to humic material, composting may rank less favorably with respect to these criteria.

As a biotreatment technology that can be carried out under carefully controlled conditions, composting is likely to receive state and community acceptance.

Although easily implemented, composting may require months to achieve required treatment standards. Therefore, short-term effectiveness may be less desirable than if other (nonbiological) techniques are used.

In some cases, composting may be a lower-cost technology to employ. However, there are a number of factors that will affect the final cost of composting, including the types and quantities of amendments required and the selected process configuration (see **Key Cost Factors**).

Criteria	Ranking
Effect of reducing the overall threat to human health and the environment	⊜
Compliance with applicable or relevant and appropriate requirements (ARARs)	○
Long-term effectiveness and permanence	○
Reduction of toxicity, mobility, or volume	○
Short-term effectiveness	◐
Implementability	◐
Cost	○
State and community acceptance	⊜

⊜ ◐ ○ ◑ ● Favorable ◄——► Unfavorable

Source: Reference 2 and Arthur D. Little, Inc.

Figure 5. FS Criteria Ranking

Key Cost Factors

The primary factors affecting the overall cost of composting contaminated soil are:

- Time to treat;
- Volume of contaminated soil;
- Allowable percentage of soil in the compost (and therefore the land area and quantity of amendments required);
- The cost of amendments; and
- Regulatory requirements.

Regulatory requirements may affect facility and operational standards such as type of pad or foundation, frequency of monitoring, and enclosure of compost. These, together with requirements for permitting, may significantly impact cost.

Amendment use is a significant concern when evaluating the cost of composting. Economic composting is reliant on the local, year-round availability of suitable amendments. Based on previous investigations involving composting of explosive-contaminated soil, the Army has developed a baseline amendment cost of $50/ton for preparation of their cost estimates (8). For amendment costs greater than this, a cost analysis should be conducted to determine the competitiveness of composting with other treatment methods.

Figure 6 illustrates the affect of amendment mixture selection on cost. These figures are based on an economic analysis of composting of explosives-contaminated soil in a field demonstration at an Army site (see **Application Examples**).

An additional factor impacting the cost of composting is the process configuration used. Turned windrow composting is typically less expensive than aerated static piles. However, overall costs may be affected by the use of manual, rather than mechanical, labor to turn the compost. In addition, the costs of aerated static piles are affected by pile construction activities (e.g., laying aeration pipe).

Cost estimates have indicated that the use of the highly automated in-vessel composter configuration involves higher capital, operating, and maintenance costs.

Estimates performed by the Army have resulted in costs for composting of explosive-contaminated soil as shown in Figure 7. For the purpose of comparison, estimated costs to incinerate explosive-contaminated soil are also provided. These costs include site preparation, capital costs, excavation, backfill, and operation and maintenance.

Reported costs for composting of soil contaminated with petroleum hydrocarbons (diesel oil) are around $100 per cubic yard (9). Amendment costs in these applications are usually in the range of $5 to $10 per cubic yard of soil treated (assuming that cow manure is the primary amendment)(9).

In one successful, low-tech application of static pile composting to treat petroleum-contaminated soil, costs as low as $13 per

Amendment	Mixture A	Mixture B	Mixture C
Sawdust	30%		22%
Apple pomace	15%		6%
Chicken manure	20%		
Chopped potato	35%		17%
Horse manure/straw		50%	
Buffalo manure		10%	
Alfalfa		32%	22%
Horse feed		8%	
Cow manure			33%
Cost Per Ton	$15	$200	$11

Source: Reference 8

Figure 6. Costs of Selected Compost Amendment Mixtures

cubic yard were achieved (16). This application involved mixing 3.5 parts (by volume) contaminated soil with one part manure/wood chips, piling the compost on drain tiles to facilitate passive air exchange, and covering the pile with plastic sheeting.

Ranges of costs likely to be incurred as a result of treatability and feasibility assessments (assumed to be independent of volume to be treated) are: $25,000 to $75,000 for laboratory studies; and $100,000 to $1,000,000 for pilot tests or field demonstrations. For studies, tests, and demonstrations involving explosive-contaminated soil, costs are most likely to be at the high end of each of these ranges.

Application Examples

A summary of application examples is presented in Figure 8. Additional information is provided below. See **Points to Remember** for additional application information.

Example 1—Pilot Test of Composting Explosive-Contaminated Soil, Louisiana Army Ammunition Plant in Shreveport, Louisiana (3)

In 1988, a pilot program was conducted by the Army to determine the ability of composting to treat soils and sediments contaminated with TNT, RDX, and HMX. The pilot tests were conducted at an Army installation using soils and sediments that had been contaminated as a result of the lagooning of explosive-contaminated wastewaters over a period of about 30 years.

These pilot tests involved the operation of static piles. Each pile contained a system of perforated and nonperforated four-inch diameter polyethylene pipe placed on a concrete and wood chip base and connected to a blower. The blowers were used to pull air through the pile to promote aeration and remove heat. Operation of the blowers was controlled automatically based on temperatures in each pile.

Explosive-Contaminated Soil (Tons)	Estimated Cost ($/Ton Soil)		
	Windrow Composting	In-Vessel Composting	Incineration
3,700	390	650	740
6,800	290	480	660
30,000	210	330	280

Source: Reference 6

Figure 7. Composting Cost Comparison

To determine the affect of temperature on the composting process, piles were operated at two temperature ranges: one in an approximate range of 30° to 50°C; the other in an approximate range of 40° to 60°C.

The compost consisted of contaminated sediment and a mixture of amendments. The amendments included alfalfa, manure, straw, and horse feed. Contaminated sediment content in the compost was 24% (by weight). The sediment and amendments were well-mixed and the compost piles were constructed. The volume of compost in each pile was about 12 cubic yards. After pile construction, the piles were watered with garden hoses. Approximately 400 gallons of water were applied to each pile. Water was added periodically throughout the composting operation.

The piles were allowed to compost for 153 days. Results of composting at the lower temperature range indicated a reduction in TNT from approximately 11,000 to 50 mg/kg; a reduction in RDX from approximately 4,600 to 240 mg/kg; and a reduction in HMX from approximately 640 to 85 mg/kg. Results in the higher temperature pile reflected a reduction in TNT from approximately 12,000 to 3 mg/kg; a reduction in RDX from approximately 5,300 to 45 mg/kg; and a reduction in HMX from approximately 750 to 26 mg/kg. As can be seen, the higher temperature operation achieved the lower levels of explosives.

Additional information regarding this field study can be obtained from Wayne Sisk, U.S. Army Environmental Center (USAEC) (see **Points of Contact**).

Example 2—Field Optimization Study of Composting Explosive-Contaminated Soil, Umatilla Army Depot Activity in Hermiston, Oregon (4)

In 1991, a field study was conducted at an Army installation in an attempt to optimize various parameters associated with the composting of explosive-contaminated soil in order to demonstrate that composting can be conducted at a lower cost than incineration.

Six field tests were conducted using an aerated static pile system. Four field tests were conducted using a mechanically agitated in-vessel system (as shown in Figure 3).

The static pile systems consisted of 500-gallon fiberglass containers. A perforated wooden platform was placed six inches from the bottom of the container. Wood chips were placed between the platform and the bottom. Two air inlet ports were located at the bottom of the container. One inlet port was connected to a blower that was used to force air through the pile.

Application	Contaminants	Results	Comments	Ref.
1 Pilot Test at Army Facility	TNT, RDX, and HMX	Initial concentrations of TNT (11,000 to 12,000 mg/kg), RDX (4,600 to 5,300 mg/kg), and HMX (640 to 750 mg/kg) in compost reduced in 153 days to levels in the range of: TNT (3 to 50 mg/kg); RDX (45 to 240 mg/kg); and HMX (26 to 85 mg/kg). Better reductions achieved at higher compost pile temperatures.	Two aerated static piles operated at temperatures in the range of 30 to 50°C; two piles operated in the range of 40 to 60°C. Blowers were cycled automatically to draw air through piles. Contaminated soil comprised about 24% (by weight) of the compost mixture. Amendments included alfalfa, manure, straw, and horse feed.	3
2 Field Study at Army Facility	TNT, RDX, and HMX	90 days of composting resulted in reductions in TNT ranging from 79 to 99%; reductions in RDX ranging from 0 to 99%; and reductions in HMX ranging from 0 to 39%. Better results were achieved at lower soil concentrations and using an in-vessel composter.	Six tests were conducted using an aerated static pile. Four tests were conducted using a mechanically agitated in-vessel composter. Soil content in the compost ranged from 7 to 40% (by volume). Amendments included various mixtures of sawdust, apple waste, manures, potato wastes, straw, alfalfa, and horse feed.	4
3 Field Demonstration at Army Facility	TNT, RDX, and HMX	By day 20, reductions in TNT, RDX, and HMX were 99.3, 99.5, and 98.7%, respectively. See text for more information.	Demonstration of windrow composting. Two 20-feet long, 8-feet wide, and 4-feet high windrows each containing 28 cubic yards of compost were operated. Windrow machine used to turn compost once a day. In addition to turning, one pile was aerated by forced air. See text for more information.	8, 18
4 Pilot Study	RDX, HMX, and PETN	Initial concentrations of RDX (220 mg/kg), HMX (220 mg/kg), TATB (1500 ppm) and PETN (400 mg/kg) in soil. After composting for 18 days, levels of RDX, HMX, and PETN were below detection limits.	Aerated static pile used to compost soil spiked with explosives. Soil was mixed with horse manure, alfalfa, and horse feed (20:20:10) to achieve a compost with 30% by volume of dry soil. Estimated cost for full-scale was $225 per cubic yard of soil.	19
5 Bioremediation at Marine Corps site	Diesel Oil	Soil contaminated with an average of 5,000 ppm of TPH composted. In eight weeks, TPH reduced to target goal of 100 ppm.	525 cubic yards of soil were treated by composting in a turned windrow. One part cow manure was added to two parts contaminated soil. Pile was inoculated with an enzyme to activate bacteria.	9
6 Pilot Study of Creosote Composting	Creosote Compounds	Soil contaminated with 2216 to 8268 ppb total PAH composted. Non-volatile PAH were reduced from 818 ppb to 91 ppb in 35 days of composting.	Tumbler-type composter used to treat soil contaminated by creosote solution spill. Compost matrix consisted of a 1:1:1 ratio of soil to corn silage to fresh cow manure. Estimated cost was $300 per ton of soil.	20

Figure 8. Summary of Application Examples

The in-vessel system consisted of a nine-foot diameter tank with a capacity of approximately seven cubic yards. The reactor was totally enclosed.

A variety of amendments were used in these tests. The amendments included different combinations of sawdust, apple wastes, manures, potato wastes, straw, alfalfa, and horse feed. Soil content in the compost for the tests ranged from 7% to 40% (by volume).

In each test, the compost was operated for 90 days. Results of static pile composting indicated reductions of TNT ranging from 79% to 98%; reductions in RDX ranging from 0% to 93%; and reductions in HMX ranging from 2% to 39%. Results of in-vessel composting indicated reductions of TNT ranging from 97% to 99%; reductions in RDX ranging from 18% to 99%; and reductions in HMX ranging from 0% to 29%. Generally, RDX and HMX reductions were improved as the soil content in the compost was reduced.

Conclusions of the study were that both static pile and in-vessel systems were effective at degrading explosives. In addition, the maximum soil loading level for achieving effective degradation appears to be 30% by volume.

These results were supplemented by a series of chemical and toxicological characterizations performed with the composted material (17). These characterizations included a determination of explosives and TNT metabolites in the composts and their leachates, leachate aquatic toxicity, and mutagenicity of the leachates and organic solvent extracts of the composts on selected bacterial strains. The primary conclusion of these studies was that composting can reduce the concentrations and bacterial mutagenicity in explosive-contaminated soil, as well as the aquatic toxicity of leachable compounds. However, small levels of explosives and metabolites, bacterial mutagenicity, and leachable aquatic toxicity remain. The ultimate fate of the biotransformed explosives and the sources of residual toxicity and mutagencity remain unknown.

Additional information can be obtained from Wayne Sisk or Kevin Keehan, USAEC (see **Points of Contact**).

Example 3—Demonstration Windrow Composting of Explosive-Contaminated Soil, Umatilla Army Depot Activity in Hermiston, Oregon (8, 18)

A field demonstration of windrow composting has recently been completed at an Army site on the National Priority List. A Feasibility Study conducted for remediation of this site has selected composting as the preferred remedial alternative based on the results of the optimization study described in Application Example 2. This demonstration will provide further data to support this preference as well as complete a full-scale design.

In this field test, two 28-cubic yard windrows approximately 4 feet high, 8 feet wide, and 20 feet long were constructed. Both piles were placed on a bermed (8 inch) asphalt pad. In addition, one of the piles was placed on a bed of wood chips in which 6-inch diameter perforated pipe was embedded. This allowed this pile to receive additional aeration by forced air.

To reduce the potential dust hazard caused by turning the piles, the piles were enclosed in a temporary structure.

The piles were handwatered with hoses as necessary to adjust moisture content. The piles were designed to operate at about 55° to 60°C.

One of the piles was aerated only by daily turning with a windrow machine (see Figure 1). The other pile (placed over wood chips and perforated pipe) was subjected to forced-air aeration in addition to the daily turning. A thermocouple placed in this pile was used to control blowers that were activated when the temperature or the pile exceeded 60°C.

The compost in both piles consisted of a 30% soil/70% amendment (by volume) mixture. The amendments used were sawdust (17.8%), chicken manure (3.4%), chopped potato (10%), cow manure (21%), and alfalfa (17.8%).

Both windrows were effective in decontaminating the soil—even under the wintertime conditions experienced during operations. The turned-only pile proved to be more efficient than the forced-air aerated pile. Most of the detoxification and explosives transformation occurred by day 15. By day 20, TNT, RDX, and HMX levels in the turned-only pile were reduced by 99.3, 99.5, and 98.7%, respectively.

Additional information is available from Major Kevin Keehan or Wayne Sisk, USAEC (see **Points of Contact**).

Example 4—Pilot Tests: Composting Explosive-Contaminated Soil (19)

In 1991-1992, pilot tests were conducted at a vendor's facility using an aerated static pile. Enclosed composters were used to compost approximately 230 lb of soil spiked with RDX (220 mg/kg), HMX (220 mg/kg), TATB (1500 ppm), and PETN (400 ppm). This soil was mixed with amendments to achieve a compost soil content of 30% (dry weight). The amendment used was a 20:20:10 mixture of horse manure, alfalfa hay, and horse feed.

The composters used were 500-gallon, dish-bottomed, stainless steel tanks. A perforated wooden platform was placed in each tank allowing for drainage of leachate and for fresh air to be pulled down through the compost.

Temperatures were maintained in the 60° to 70°C range. Air flow through the piles was based on a timed cycle.

Results of the pilot tests indicated that RDX, HMX, and PETN were reduced below detection limits within 18 days. TATB degraded slower than the other contaminants. It was felt that this might have been due to the use of formulated TATB in the spike. Laboratory tests with unformulated TATB demonstrated complete breakdown under similar conditions within 3 weeks. Analyses of the final compost indicated that there were no persistent degradation byproducts.

Based on these tests, estimated full-scale costs to compost similarly-contaminated soils are approximately $225 per cubic yard.

Example 5—Bioremediation of Diesel Fuel-Contaminated Site, U.S. Marine Corps Camp Pendleton in California (9)

As a result of a leaking underground storage tank, 525 cubic yards of soil were contaminated with diesel oil at an average concentration of 5,000 ppm of oil (measured as total petroleum hydrocarbons [TPH]). This soil was excavated and remediated in 1992.

The remediation site selected was an asphalt parking lot. The asphalt was sprayed with an impermeable polyurethane barrier. This barrier is capable of withstanding the heavy traffic of trucks and front end loaders while still retaining its integrity. The sides and one end of the remediation area were blocked by using concrete highway barriers. A sump was installed at the lowest corner of the site to collect leachate and return it to the soil as irrigation.

The contaminated soil was piled on the prepared site and mixed with a bulking amendment (cow manure) in a 2:1 soil to manure ratio (by volume). The completed compost pile was eight to nine feet high. Once completed, the pile was inoculated with an enzyme to accelerate activation of bacteria. Five to ten gallons of water were added per cubic yard of compost. The compost was turned by front-loading tractors for aeration once a week and water was added at the rate of two to three gallons per cubic yard each week. Typical pile temperatures were about 55°C.

Composting was conducted over an eight-week period during adverse winter rain conditions. At the end of the eight-week period, a target goal of 100 ppm of TPH was reached. Monitoring of air emissions indicated little or no volatilization of diesel oil compounds during the remediation. There were also no obnoxious odors from the pile, even at the peak of degradation. The cost of this remediation was $100 per cubic yard of soil treated.

Example 6—Treatability Study of Creosote-Contaminated Soil in New York (20)

A pilot composting treatability study was performed on soil contaminated with creosote solution that spilled from high-pressure tanks at an abandoned railway tie-treating facility. A tumbler-type composter treated 15-30 lbs of soil per test. Non-volatile creosote compounds were reduced up to 88.9% (i.e., from about 818 ppb to 91 ppb) in 35 days. Starting concentrations of total PAH (including semivolatiles and nonvolatiles) ranged from 2216 to 8268 ppb. The optimum amendment mixture in this study was a 1:1:1 ratio of contaminated soil to corn silage to fresh cow manure. The optimum moisture content was 64%. The total estimated treatment cost was $300 per ton.

Points to Remember

The following points to remember were generated during discussions with remedial personnel with laboratory and field experience in the composting of contaminated soil.

√ It is important to have backup plans for aeration in the event that the primary aeration system fails. In the absence of aeration, self heating of the compost could reach temperatures sufficient to significantly decrease microbial activity.

√ Availability of amendments may be a driving force behind the competitiveness of composting as a remedial alternative. Finding a low-cost source of amendments close to the remedial site (within a 100-mile radius, for example) should be a first step in evaluating the applicability of composting. In addition, locally-available amendments may only be available seasonally, potentially limiting the period during which composting can be performed.

√ If explosives are the contaminants of concern, one of the most important elements in composting is safety. It is necessary to fully characterize the soil contamination and develop an appropriate safety plan for operation (to include a hazards analysis). Important considerations include:

- Presence of visible signs of explosive (explosives may be in the soil in "chunks");
- Concentrations of explosives in soil;
- Type of explosives in soil (e.g., RDX is more sensitive than TNT); and
- Presence of initiating compounds (e.g., lead azide, lead styphnate, and lead fulminate).

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Points of Contact

Additional information regarding the technical, regulatory, and practical aspects of composting may be obtained from:

- Major Kevin Keehan, USAEC, Aberdeen Proving Ground, MD, (410) 671-1278.
- Wayne Sisk, USAEC, Aberdeen Proving Ground, MD, (410) 671-1280.
- Dr. Kurt Preston, Environmental Laboratory, U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, MS, (601) 634-4106.
- John Fringer, NEESA, (805) 982-4856.
- Harry Craig, U.S. Environmental Protection Agency, Region 10, Portland OR, (503) 326-3689.

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Heap Pile Bioremediation

Port Hueneme, CA 93043 NEESA Document No. 20.2–051.8 August 1993

Introduction

Bioremediation is an innovative technology being considered more frequently, and more positively, for the remediation of soil contaminated with organic compounds. The main advantages of soil bioremediation are that it can be done on site at relatively low cost and results in the destruction of contaminants rather than transferring them to another medium.

While many points discussed will be applicable to soil bioremediation in general, this Tech Data Sheet focuses on heap pile bioremediation. Heap pile bioremediation, a solid-phase and aboveground process, uses forced aeration to increase oxygen availability and thus increase the rate of contaminant degradation. Naturally aerated processes are described in a separate Tech Data Sheet titled "Soil Bioremediation (Naturally Aerated Processes)."

Purpose and Audience

The Tech Data Sheets are designed to:

- Disseminate practical, implementation-related information to minimize design and construction problems;
- Help Remedial Project Managers (RPMs) to evaluate a technology (recommended in a Feasibility Study [FS], for example) and decide if it is practical and cost-effective;
- Aid RPMs in writing a Remedial Action (RA) Delivery Order;
- Help Engineering Field Division (EFD) Remedial Design personnel write a Statement of Work (SOW) for, and RPMs review, Remedial Design Plans; and
- Enable field personnel such as Project Superintendents, Engineers in Charge, On-Scene Coordinators (OSCs), and Resident Officers in Charge of Construction (ROICCs) to become familiar with a technology at a site they will oversee.

Description of Technology

Bioremediation uses microorganisms—typically, naturally occurring bacteria, fungi, and/or actinomycetes (metabolically advanced bacteria)—to degrade and/or detoxify contaminants. This degradation results in the breaking down of contaminants into simpler compounds that may or may not be less toxic. These simpler intermediate compounds may themselves be biodegraded. If the process leaves only carbon dioxide and water as end products, biodegradation is complete, and mineralization is said to have occurred.

Aboveground bioremediation is usually an aerobic process. That is, the microorganisms use oxygen to grow and metabolize contaminants. (In contrast, anaerobic microorganisms grow in the absence of oxygen.) Heap pile bioremediation is an ex situ version of soil bioventing in which air is pulled or blown through soil to aerate indigenous hydrocarbon-degrading microorganisms. This is in contrast to naturally aerated prepared bed processes that rely on the natural diffusion of oxygen through the soil.

Heap pile bioremediation is performed with excavated contaminated soil that has been placed in piles 8 to 12 feet high. Throughout the period of bioremediation, the soil is physically undisturbed while the proper environment is maintained to enhance and maintain acceptable rates of degradation. A schematic of a representative heap pile bioremediation system is provided in Figure 1. See **Field Implementation Considerations** for specific heap pile construction and operation details.

Once excavated, the contaminated soil may be pretreated before being placed in piles. For example, if large rocks or debris are present, they may be removed by screening. In addition, additives such as fertilizer (to provide nitrogen and phosphorus), mulch or sand (to increase porosity), and lime (to raise pH) may be added.

The excavated soil (with rocks and debris removed) is then placed on a prepared bed. The bed is typically prepared by spreading a 12-inch layer of contaminated soil over a watertight liner. Perforated pipes are then placed over the soil layer in regularly-spaced intervals. A layer of gravel is usually placed over the pipes, and the excavated and prepared soil is then dumped in 8- to 12-foot-high piles on the gravel.

The perforated pipe systems provide for aeration in the soil piles by either blowing (injecting) air through the pipes into the soil (forced air) or drawing (sucking) air from the ambient atmosphere around the pile through the soil. The preferred method is to draw air through the pile. In this way, off-gases can be

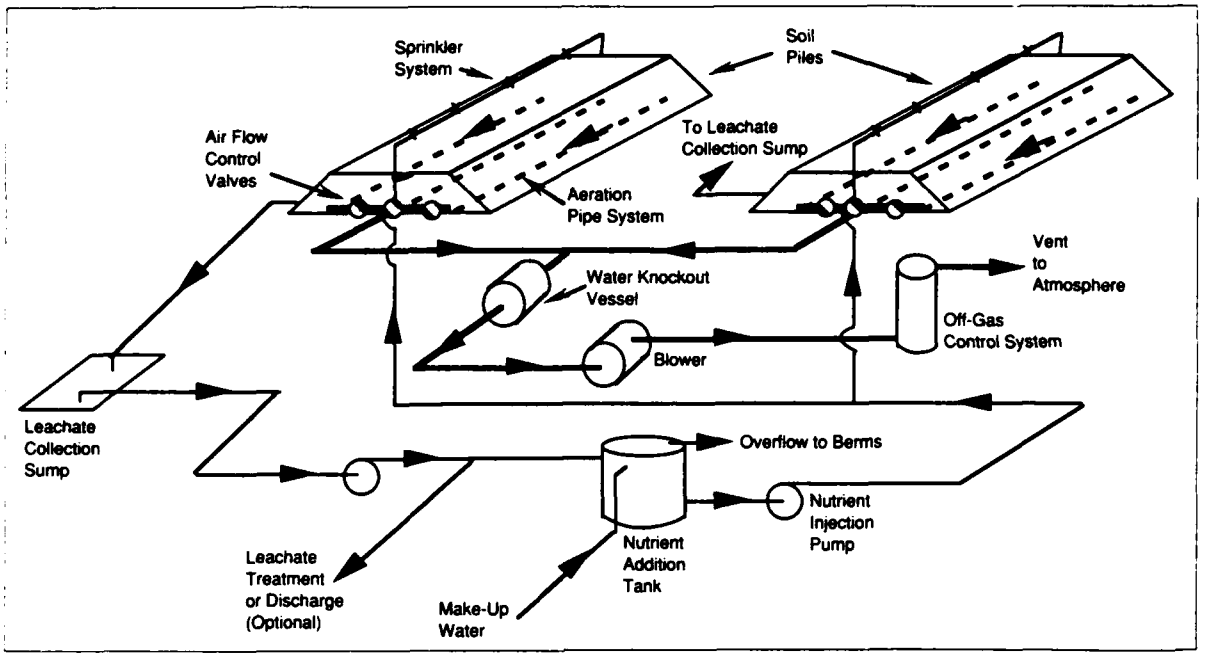

Figure 1. Representative Layout of Heap Pile Bioremediation System Source: Derived from Reference 1

controlled at the blower effluent and air flow can be more easily monitored.

Moisture content within the pile can be maintained with an irrigation system (e.g., overhead sprinkler or drip or soaker hoses). If air is injected into the soil, the air can be moisture-saturated with an air humidifier prior to injection. Liquid nutrients can be applied to the top of the pile and allowed to percolate through the pile. Alternatively, solid nutrients can be mixed with the excavated soil prior to construction of the pile, added to the pile during construction, or broadcast over the surface of the completed pile.

Air drawn from the pile may contain volatile components and will require treatment prior to discharge to the atmosphere if permitted levels are exceeded. Activated carbon adsorption is the most common means of treating the off-gases (see **Interface with Other Technologies**).

A leachate collection system will usually be required. To the maximum extent possible, leachate will be collected in drums or tanks and recycled to the pile via the irrigation system. Excess leachate may require treatment (see **Interface with Other Technologies**).

In summary, heap pile bioremediation technology consists of site (i.e., lined bed) preparation, soil pretreatment, design and placement of aeration pipes, an air handling system, water and nutrient delivery, and ancillary features such as leachate collection and off-gas treatment.

Technology Status

Heap pile bioremediation has been used since the early 1980s, primarily for the cleanup of soils contaminated with petroleum hydrocarbons. Although bioremediation is generally considered innovative (particularly for contaminants other than petroleum hydrocarbons), the technology involved in heap pile bioremediation is fairly well established. However, improvements are continually being introduced to increase effectiveness and reduce costs.

There are at least five firms that specialize in heap pile bioremediation, and many more have a broad range of bioremediation experience.

Types of Applications

Heap pile bioremediation has mostly been used to remediate soil contaminated with low-volatility petroleum hydrocarbons released by leaking underground storage tanks (USTs) (and related piping), spills, and past disposal practices (e.g., leaking drums).

If the contaminants consist solely of lighter, more volatile compounds (such as those in gasoline), they may be treated more effectively by in situ processes (e.g., soil vapor [vacuum] extraction and bioventing [2]) that take advantage of their volatility. However, if heavier hydrocarbons are present, aboveground bioremediation may be more appropriate (see **Types of Contaminants**).

Contaminated soil less than 10 feet deep and not adjacent to structures may be cost-effectively treated by heap pile bioremediation.

Heap pile bioremediation works best with sandy soils of near-neutral pH (6.5 to 8.5). However, a variety of soil amendments can be used to improve the quality of clayey, less permeable soils as well as to adjust the pH.

Types of Contaminants

Aboveground soil bioremediation has proven to be successful in treating soil contaminated with low-to-medium volatility petroleum hydrocarbons such as waste oil, grease, jet fuels,

diesel fuels, and crude oil. In addition, aboveground soil bioremediation has been shown to be effective with more volatile components of petroleum hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX)(1); although, as mentioned above, these contaminants may be more effectively treated in situ.

Aboveground soil bioremediation has also been used to treat soil contaminated with polynuclear aromatic hydrocarbons (PAHs) (3). Generally, the higher the molecular weight (and the more rings with a PAH), the slower the degradation rate. In addition, the more chlorinated the compound, the more difficult it is to degrade.

Despite demonstrated effectiveness with many compounds, there are too many site-specific considerations to extrapolate success in degrading a given compound from one site to another. Consequently, treatability studies (see **Design Criteria**) must be conducted using representative samples of soil from the site.

Advantages

Heap pile bioremediation in general has several advantages:

- It is a fairly straightforward process and is therefore typically easy to implement;
- The cost is low relative to other remedial alternatives (such as incineration);
- Non-volatile contaminants are destroyed—not transferred to another medium; and
- It is permanent (in that contaminants may be completely degraded to carbon dioxide and water).

Heap pile bioremediation has the following advantages over naturally aerated processes:

- Increased degradation rates (and thus reduced treatment times);
  Smaller land surface area requirements (particularly in contrast with landfarming);
- Better control of process parameters such as moisture, nutrients, and temperature;
- Easier control of off-gases, if required;
- Easier, and less costly, leachate collection and recycle; and
- Dirt clods that impede air diffusion are less likely to be formed in heap pile bioremediation than in processes that rely on tilling.

Disadvantages

Potential disadvantages of bioremediation in general include:

- Technology is in the innovative stage for contaminants other than petroleum hydrocarbons (the process is still evolving; cost data are inaccurate because of site variability and lack of good data; and results cannot be guaranteed within a specific time frame);
- Degradation of some compounds (e.g., PAHs of four or more rings and highly chlorinated compounds such as polychlorinated biphenyls [PCBs]) may be too slow to be practical;
- Treatment may be lengthy (some contaminants may take several months to degrade); and
- Toxic intermediate compounds may be end products (although this is more likely with anaerobic than aerobic biodegradation).

Disadvantages of heap pile bioremediation as compared to naturally aerated bioremediation processes include:

- Additional equipment requirements (e.g., pipes, blowers, pumps) add to cost;
- Site preparation is more complicated due to the placement of perforated pipes; and
- The pipes make decommissioning of the piles more complicated—it is difficult to remove soil without breaking the piping.

When compared to in situ treatment methods such as bioventing, heap pile bioremediation has several disadvantages primarily related to the excavation of contaminated soil:

- Increased costs due to excavation and handling of soil;
- Volatilization of lighter hydrocarbons during soil excavation and handling;
- Increased health and safety concerns associated with excavating and handling contaminated materials;
- Potential for damage to adjacent buildings and other structures during excavation; and
- Increased potential to trigger Land Disposal Restrictions (LDRs) (see **Regulatory Issues**).

Limiting Factors

The key to biodegradation at high rates is providing an environment that:

- Allows for rapid growth in the population of contaminant-degrading microorganisms;
- Maintains a high population of such microorganisms; and
- Provides maximum contact between the contaminant and the microorganisms.

The main criterion for achieving and maintaining high microbial populations is the availability of oxygen and nutrients (primarily nitrogen and phosphorus) to the microorganisms. This can be achieved in heap pile bioremediation. Factors affecting the availability of oxygen and nutrients, as well as other microbial growth conditions, are presented in Figure 2. Note that many of these factors are common to any type of aboveground bioremediation.

Interface with Other Technologies

Other technologies may interface with heap pile bioremediation as dictated by practical considerations and regulatory requirements. These include:

- Carbon adsorption or thermal destruction techniques (e.g., incineration or catalytic oxidation) to control the emission of off-gas containing volatile organic compounds (VOCs); and
- Technologies used for excess leachate disposal (such as discharge to a publicly owned treatment works [POTW]) and treatment with carbon adsorption or air stripping (see **Residuals Generated**).

Component	Factor	Potential Limitations
Contaminant	Biodegradability	Contaminant must be biodegradable at an acceptable rate
	Acclimation	If soil recently contaminated, degrading microorganisms have not been acclimated to contaminant or site conditions
	Volatility	Volatile components may be removed by volatilization rather than biodegradation; treatment of off-gases containing volatiles may be required
	Toxicity	Contaminant must be present in (or diluted to) a concentration not toxic to the degrading microorganisms
Soil	Physical characteristics	Clumping may limit exposed surface area and thus contaminant, water, and nutrient availability
	Moisture content	Excessive water limits diffusion of oxygen; very low moisture reduces contact between microorganisms and contaminants, as well as microbial activity
	Clay content	High clay content may affect physical characteristics and thus affect moisture control, oxygen diffusion, and contaminant binding to soil
	Organic content	Low organic material content may limit growth of degrading bacteria, but high content may cause bacteria to utilize that instead of contaminant as food source
	pH	Degrading microorganisms have an optimum range; pH may require adjustment
Site	Climate	Rainy climate may dictate special rainfall runoff and soil drainage controls; cold or excessively hot soil temperatures slow degradation

Figure 2. Limiting Factors of Heap Pile Bioremediation

Source. Arthur D. Little, Inc. and NEESA

At many sites, the contamination goes below the water table. At these sites, some form of ground water treatment may be integrated with soil bioremediation. Such ground water treatment technologies may include pump-and-treat (where ground water is pumped to the surface and treated) or in situ biological treatment.

Design Criteria

The success of a heap pile bioremediation operation is dependent on sound design based on site-specific information and data. The first steps in preparing such a design include:

- Site characterization;
- Soil sampling and characterization;
- Contaminant characterization;
- Laboratory and field treatability studies; and
- Pilot testing and/or field demonstrations.

Typical parameters to be considered in site, soil, and contaminant characterization are shown in Figure 3. Characterizations are conducted to:

- Identify and quantify contaminants;
- Determine the presence of microorganisms capable of degrading the contaminants involved; and
- Identify factors that affect biodegradability.

Laboratory (bench-scale) and/or field-scale treatability studies are needed to confirm that the contaminants of concern can be degraded as well as to optimize biodegradation parameters. Depending on site and contaminant complexity, field-scale pilot tests or demonstrations may also be needed to optimize full-scale design.

Currently, the U.S. Army Waterways Experiment Station (USAWES) is developing a 10-cubic-yard portable pilot-scale "biocell" that can be used to do on-site treatability studies. The biocell is housed in a commercially available, off-the-shelf "dumpster" at the bottom of which is slotted PVC aeration piping used to push or pull air through the soil. Off-gases will be monitored by oxygen, volatile organic, and carbon dioxide meters and purified with granular activated carbon before being released into the atmosphere. These meters, along with dissolved oxygen, temperature, and humidity soil probes, will be connected to an automatic data logging system. The unit will be equipped with soaker hoses connected to a leachate collection and recycling system. This portable unit will be used in conjunction with four 40-cubic-yard biocells (also in commercially available dumpsters) in a U.S. Army Corps of Engineers New Orleans District pilot-scale demonstration. In this demonstration, soil contaminated with 100 to 150 ppm of Total Petroleum Hydrocarbons (TPH) will be treated to less than 50 ppm. Total treatment costs are expected to be between $18 and $60 per cubic yard. Information gathered from these pilot systems will be used to validate treatability tests done with an eight-gallon bench-scale biocell (5).

To obtain more information on, or to arrange for, a treatability study, contact Mark Zappi (USAWES) or Bill Major (see **Points of Contact**).

Criteria for full-scale heap pile bioremediation include the following:

Design of air flow system and soil piles—The air flow system and the size and configuration of the soil piles should be designed as a package. There are computer models available that can aid in this integrated design. One model is CSUGAS, a computer-based model developed at Colorado State University (6). It can be used to determine maximum pile height, minimum blower size, and minimum air flow required to adequately stimulate microbial activity in active soil piles. This model was used in the design of a heap pile bioremediation system at the Marine Corps Air Ground Combat Center (MCAGCC) Twentynine Palms (see **Application Examples**).

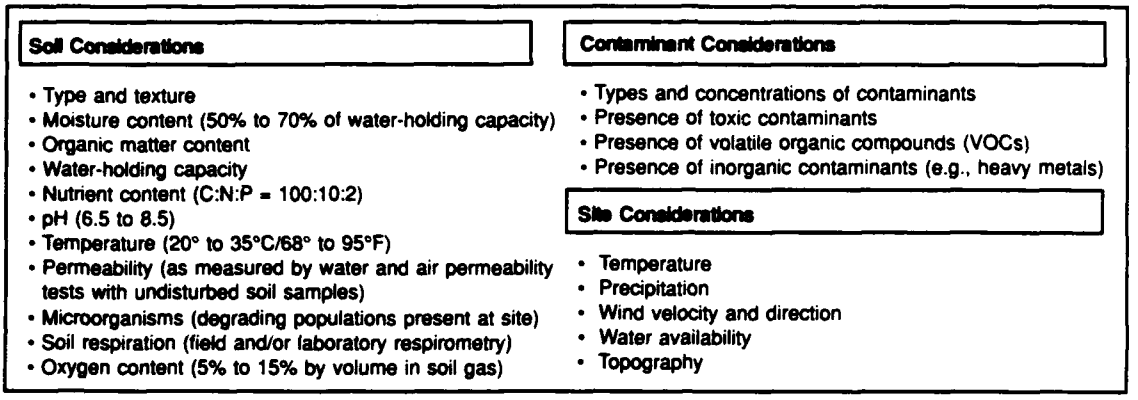

Figure 3. Site and Contaminant Characterization Parameters (With Usual Optimum Ranges When Applicable)

Source: Reference 4 and Arthur D. Little, Inc.

Soil physical property data are input to this model. Design aeration rate, air flow patterns, and air pressure distribution are generated. This output can be used to develop design criteria for blower size and pile configuration.

It should be noted that oversizing the blower wastes energy, increases the cost of the blower, and could cause shortcircuiting of air flow.

Perforated (or slotted) polyvinylchloride (PVC) pipes (typically with 0.02-inch slots)(6,7) are used for pile aeration. One end of each pipe is capped, and the other end is connected to a header pipe (manifold) that is connected to a blower. Valves are installed in the piping to allow for flow adjustments during start-up and operation. Sampling ports should be installed in the pipes to facilitate air flow monitoring throughout the remediation.

In addition to designing a pile configuration that can achieve design aeration rates, it is important that the design consider the potential for compaction of the soil during and after pile construction. Compaction of the soil or formation of a surface crust can limit the air flow through the pile or cause channelling of air. For this reason, heavy equipment should not run over the soil as the pile is constructed. This will usually limit the height of the piles to 8 to 12 feet.

Selection of liner—The most commonly used liner in heap pile bioremediation is a 60 to 80 mil high-density polyethylene (HDPE). Liner seams should be double-seam hot welded to maintain the integrity of the liner (6).

Design of irrigation system—An irrigation system is used to maintain the desired moisture content within the pile (typically 50% to 70% of the soil's water-holding capacity) as well as to add liquid nutrients. Spray or drip (soaker) systems can be used. Spray systems will usually provide better distribution of moisture. Drip (or soaker) systems may be preferred if the piles are covered to prevent moisture and temperature loss.

Design of leachate collection and distribution system—Collected leachate is usually recycled to the piles via the irrigation system. As leachate is generated in the pile, it may flow (by gravity) to a sump. A sump pump will transfer the leachate in the sump to irrigation water storage tanks.

Design of berms—Berms are constructed to contain the contaminated soil as well as runoff due to rainfall. Because of the cost and effort required in constructing berms, their height is kept to a minimum while maintaining required controls. Typical berm heights are two to three feet. One of the factors in design of the berms is that the berms and collection systems should be able to contain a volume that meets the requirements of a 50- or 100-year rainfall event.

Other design features may be required, including off-gas control and treatment systems; and leachate or run-off collection, recycle, and treatment systems.

In addition, design criteria may address details of the specific operations to be used in the establishment and operation of heap piles (*see* **Field Implementation Considerations**), including:

- Pretreatment requirements (e.g., dewatering, pH adjustment, soil screening);
- Process control requirements (e.g., pH, moisture, oxygen, nutrient addition, etc.);
- Process monitoring needs; and
- Construction and installation procedures.

Field Implementation Considerations

The field work for heap pile bioremediation includes:

- Site (lined bed) preparation;
- Earth work (excavation and handling of soil);
- Soil pretreatment;
- Soil pile construction;
- Installation of irrigation, leachate control, and nutrient addition systems;
- Installation of off-gas control system (if necessary);
- Operation and maintenance; and
- Facility monitoring.

Site preparation may include site surveying, staking, grading (to ensure adequate drainage of leachate and run-off), and bed construction.

Bed construction typically begins with the construction of berms (usually made of native soil). The liner is then cut and/or welded

to the required size and placed over the treatment site with edges extending over the berms. The liner should be covered by a 12-inch layer of contaminated soil (with minimal rock content) to protect it from puncture.

The slotted pipe used for aeration should be placed on top of the soil layer. Gravel should then be placed over the pipe to separate the pipe from the soil to be treated. Once in place, the slotted pipe is connected to a manifold or header line. This manifold or header should be equipped with a drain valve to allow for the periodic removal of standing water.

Methods used to excavate contaminated soil should be selected to minimize soil handling and time while maintaining worker safety. Soil excavation may cause concern if VOCs are present. It has often been observed that soil excavation is responsible for a significant portion of VOC emissions during soil bioremediation (8). For this reason, air monitoring for worker protection should be performed during excavation if VOCs are present.

Once excavated, soil may be pretreated prior to being placed in the piles. Usually, the soil is screened to remove rocks (greater than two to four inches) and debris (such as lumber). Larger rocks and debris increase the potential for liner damage. If soil is clayey and clumps are present, the soil should be broken up (pulverized) and mixed with a small amount of sand.

Soil additives are usually mixed with the excavated soil prior to, or during, pile construction. These additives may include:

- Soil amendments such as manures or plant materials (mulch);
- Lime or acidifying materials to adjust the pH (typically maintained within a range of 6.5 to 8.5); and/or
- Nutrient elements such as nitrogen and phosphorus (a typical carbon-nitrogen-phosphorus ratio is 100:10:2 by weight) (8).

Once the soil has been pretreated, it is placed in 8- to 12-foot piles on the prepared bed as specified in the design. The soil piles may be covered with mulch for insulation.

The irrigation system will consist of water (and leachate) storage tanks, pumps, and related piping. A sump is usually constructed downgradient from the soil piles to collect leachate and runoff from the piles. A sump pump is used to transfer collected liquid in the sump to the water storage tanks.

When a blower is used to draw air through the piles, water knockout vessels should be installed between the piles and the blowers. Water knockout vessels remove condensed water from the air to protect the blower motors. The vessels should contain a level switch to shut off the blower when they become full. The vessels are then drained and the blower reactivated.

The blowers also need to be protected from particulates by filtering the air from the piles.

Once system installation is complete (including pile construction), the blower should be turned on and air flow should be monitored throughout the piles to ensure that adequate aeration is being achieved. Air flow valves can be adjusted at this time.

During operation of the heap pile, routine activities will include regular monitoring of system performance parameters, including oxygen and carbon dioxide gas concentrations in off-gas, soil temperature, flow rates, and pressure (see **Quality Control**).

Soil samples are taken periodically to monitor the progress of the remediation as well as to ensure that the proper soil environment is being maintained. Analyses usually performed include oxygen and carbon dioxide levels in soil gas (measured from soil gas probes placed in the piles), pH, moisture, nutrient content, and microbial activity (see **Quality Control**). Most of these tests can be performed in the field with portable instruments.

A rigid schedule should be established to check system components including (at a minimum):

- Blower operation (belt tension, motor and blower fluid levels, electrical connections, and air flow connections)(6);
- Irrigation and leachate collection system (to guard against leaks); and
- Air flow lines running to and from the soil piles (checking for leaks by monitoring pressure drops across the bed).

Liner leaks are usually detected during decommissioning of the heap pile by inspecting the soil under the liner and analyzing soil if necessary or by smoke tests.

Quality Control

The field operator will need to monitor a number of parameters to ensure that the heap piles are operating satisfactorily. These parameters include aeration characteristics (air flow and composition) and soil pile characteristics (e.g., temperature, moisture and nutrient content, microbial activity).

Air flow characteristics typically monitored include air flow rates within the pipes (to ensure that there are no blockages in the air flow system) and pressure (to ensure that air flow is uniform throughout the soil pile). Air flow can be measured by placing a hot wire anemometer probe into the center of the air pipe cross-section. Pressure is measured with pressure probes (placed at various locations and depths in the soil piles) and a manometer.

Oxygen can be measured with soil gas probes placed in the piles. Oxygen and carbon dioxide levels can be determined with special portable meters. Oxygen within the piles should be maintained above the level where oxygen becomes a growth-limiting factor (generally 2% to 3% oxygen by volume in soil gas). Oxygen measurements provide an opportunity to optimize bioremediation operations while reducing blower utilization. Blower operation can thus be cycled to maintain the desired oxygen concentration.

Soil temperatures can be monitored easily with thermocouples placed in the piles. Temperatures should be adequate to maintain biodegradation (ideally, greater than 20° C) but should not be so high as to inhibit growth of some microorganisms (in excess of 35°C).

Soil samples are typically taken from the middle of the piles. Analyses will typically include:

- Moisture content (moisture levels should be maintained at between 50% and 70% of the soil's water-holding capacity);
- pH (usually maintained within a range of 6.5 to 8.5); and
- Nutrient content (a typical carbon-nitrogen-phosphorus ratio is 100:10:2) (8).

A determination of moisture in soil is most reliably performed by sampling the soil and performing a standard laboratory gravimetric analysis. Tensiometers can be used in the pile to roughly estimate pile moisture, but they are not very accurate.

Nutrient content is usually determined by analyzing for phosphorus as soluble (ortho-) phosphate and nitrogen as ammonia.

Measuring respiration rates provides a quick check on system performance. As organics degrade aerobically, oxygen is consumed and carbon dioxide is generated. Oxygen and carbon dioxide (respiration) measurements in soil gas indicate degradation rate and can warn of potential problems in system performance. However, it should be noted that carbon dioxide may be converted to insoluble carbonates in alkaline soils and thus may not be detected even though degradation is occurring (9).

Residuals Generated

Residuals generated during heap pile bioremediation are limited to liquids (leachate and runoff) from the operations, the off-gases from the aeration process, and the treated soil itself. The design of the overall project should include the means for managing these residuals.

Although accumulated leachate and runoff can be minimized if recycled during irrigation, excess liquids will require proper management. Options for managing excess liquids include discharge to a POTW and treatment by carbon adsorption or air stripping. The ability to discharge the leachate to a POTW is a function of the quantity of leachate, the quality of the leachate, and the capacity of the POTW.

Treated soil is usually returned to the site as backfill. The treated soil may also be disposed of in a suitable manner (e.g., as a landfill cover) depending on site-specific regulatory requirements.

Regulatory Issues

Regulations both drive and constrain the use of bioremediation in general. A regulatory review should be the first step in planning the remedial action.

Regulatory coordination and documentation requirements will be affected by site-specific factors, local regulatory issues, and the applicability of CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act as amended by the Superfund Amendments and Reauthorization Act) and/or RCRA (Resource Conservation and Recovery Act). As soon as heap pile bioremediation is considered for implementation, a project manager should coordinate with regulators to determine the treatment levels to be achieved. These levels will be incorporated into a Record of Decision and remedial design (CERCLA) or a corrective action plan (RCRA). These documents will describe what will be accomplished and may take into account the following:

- Treatment criteria;
- Analytical methodology to be used;
- Monitoring requirements (during and after field operations);
- System design requirements;
- Management of treatment residuals;
- Worker protection; and
- Site closure.

The types of regulatory permits that may be required are site- and system-specific. For soil bioremediations involving leachate collection and runoff control, permits regarding the management of the collected liquids may be required. Air permits may be required if volatile organics are involved.

Because heap pile bioremediation is usually conducted on site, permitting under RCRA is typically not required for CERCLA actions. However, parts of RCRA such as LDRs may apply as Applicable or Relevant and Appropriate Requirements (ARARs). Note that the applicability of LDRs is subject to interpretation—although the remediation is performed on site, it does involve excavation and placement of contaminated soil.

Feasibility Study (FS) Criteria Ranking

The use of heap pile bioremediation has been rated with respect to certain performance and regulatory criteria. The results of this rating are presented in Figure 4. It should be noted that these ratings are subjective and may be dependent on specific site and contaminant factors.

Criteria	Ranking
Effect of reducing the overall threat to human health and the environment	
Compliance with applicable or relevant and appropriate requirements (ARARs)	
Long-term effectiveness and permanence	
Reduction of toxicity, mobility, or volume	
Short-term effectiveness	
Implementability	
Cost	
State and community acceptance	

Favorable ◄——► Unfavorable

Figure 4. FS Criteria Ranking

Heap pile bioremediation is easy to implement compared to technologies that require large pieces of equipment or are energy- or labor-intensive (e.g., incineration). As a contained system, the technology minimizes the overall threat to human health and the environment. Heap pile bioremediation has been proven a lower-cost remedial technology (particularly for petroleum hydrocarbons) and provides for a permanent long-term solution, so related criteria are favorable.

Since heap pile bioremediation is carried out under carefully controlled conditions, state and community acceptance will most likely be favorable.

Although relatively easy to implement, successful bioremediation may require months to achieve (depending on volumes, contaminant type and concentration, and other site-specific factors). Therefore, short-term effectiveness may be less favorable than if other (nonbiological) techniques are used. However, biodegradation is usually faster in heap pile than in naturally-aerated bioremediation.

Key Cost Factors

The cost of heap pile bioremediation is primarily a function of the various construction activities associated with its implementation. Often, a significant portion of the cost is due to earth moving and construction management.

Operation and maintenance costs typically represent 25% to 30% of the total remediation costs, with an inverse relation to the volume of soil treated (1).

Costs associated with treatability and feasibility studies can be significant depending on the level and type of contaminants, the degree of clean-up required, and regulatory constraints (e.g., off-gas treatment).

Ranges of costs likely to be encountered are:

- Treatability and feasibility assessment costs (assumed to be independent of volume to be treated): $15,000 to $50,000;
- Pilot test or field demonstration costs: $20,000 to $500,000 (depending on scale and analytical requirements); and
- Costs of treatment (including site preparation, soil excavation and movement, and actual treatment operations): $35 to $120 per cubic yard of contaminated soil.

The wide range of treatment costs reflects the variability due to site-specific conditions and requirements. Reported costs for the treatment of soils contaminated with petroleum hydrocarbons under relatively non-restrictive conditions are in the low range ($35 to $50 per cubic yard)(1,3).

Application Examples

The application examples described below are summarized in Figure 5.

The following two examples describe heap pile bioremediation at U.S. Naval facilities. If you have questions regarding these activities, or would like further details, contact Bill Major (see **Points of Contact**). In addition, see **Points to Remember/ Lessons Learned** for additional information relating to the implementation and operation of these systems.

Example 1—Fuel-Contaminated Soil at Marine Corps Site in Bridgeport, California (7,11,13)

A site at the Marine Corps Mountain Warfare Training Center (MCMWTC) Bridgeport was contaminated with diesel fuel, jet fuel (JP-5 was approximately 70% of the total contamination), and other petroleum fuels that had leaked from USTs over a two- to four-year period. In this 1989 pilot study, about 7,000 cubic yards of this contaminated soil containing TPH at concentrations of about 1,200 mg/kg were excavated and processed through a screen to remove rocks greater than four inches in diameter. The screened soil was then transferred to a site protected by a 40 mil HDPE liner on an eight-inch sand base. Contaminated soil was spread on the liner to a depth of three feet. A series of perforated pipes were then placed over the soil and manifolded to a vacuum blower to provide aeration. The final dimension of the soil pile was approximately 15 feet high, 55 feet wide, and 300 feet long.

Initially, 80,000 gallons of water were added with soaker hoses over a two-week period to establish a moisture content within the pile of 50% to 70% of the soil's water-holding capacity. 1.5 tons of granular urea (a nitrogen source) were spread into one-foot lifts of soil with a shovel.

Air was pulled through the pile at about 300 standard cubic feet per minute (scfm) with a 15-hp blower. This air flow proved much more than adequate. Off-gases from the process were treated by carbon adsorption at the blower effluent.

Because the contamination was two to four years old, indigenous bacteria were well acclimated to the contaminants. After approximately two months of operation (at ambient temperatures of 20° to 85°F), the average TPH concentration was 120 mg/kg (with a maximum of 260 mg/kg).

The cost to remediate this site was reported to be approximately $80 per ton of soil, including the costs of additional sampling for research purposes.

Example 2—Petroleum-Contaminated Soil at Marine Corps Site in Twentynine Palms, California (6,11,12,13)

A heap pile bioremediation project at Marine Corps Air Ground Combat Center (MCAGCC) Twentynine Palms was conducted from April through July, 1992. The plan for this research project called for the bioremediation of 1,500 cubic yards of soil contaminated with an average of 702 mg/kg TPH (80% upper confidence level of 1,455 mg/kg). Sources of contamination included: UST removal (diesel and unleaded gasoline); JP-5; diesel and unleaded fuel surface spills; and surface spills of oil during vehicle maintenance. The contamination was two to four years old.

Construction of the soil piles is illustrated in Figure 6. Figure 7 shows the overall system configuration during operation.

Treatment specifics for this project include the following:

- A 190-ft by 70-ft treatment area (total) was lined with 60 mil HDPE sheeting. An 8- to 12-inch layer of contaminated native soil (sandy, with minimal rock content) was

Site	Amount Treated	Contaminants	Results	Comments	Ref.
1 MCMWTC Bridgeport, CA	7,000 cu yds	Diesel fuel, jet fuel, and other petroleum fuels	Initial TPH concentrations were at a maximum of 1200 mg/kg. After two months of operation, the maximum concentration was 260 mg/kg (average of 120 mg/kg)	Pilot study. See detailed discussion in text.	7,11,13
2 MCAGCC Twentynine Palms, CA	1,500 cu yds	Petroleum hydrocarbons	Initial average TPH concentration of 702 mg/kg. Average final concentration of 234 mg/kg	Research project. See discussion in text.	6,11,12,13
3 Oil Refinery, CA	5,000 cu yds	Crude oil	Initial TPH concentrations were in a range of 800 to 4,500 mg/kg. After 3 weeks, concentrations ranged from 700 to 4,300 mg/kg. By the sixth week, reported TPH concentrations were below 5 mg/kg.	Windrow configuration. Windrows covered with perforated HDPE sheets to control odors. Off-gas treatment by carbon adsorption. TPH degradation tied to peak of microbial population.	1
4 Oil Refinery, CA	15,000 cu yds	Crude oil and other petroleum hydrocarbons	Initial TPH concentrations were 42 to 770 mg/kg. After 45 days of treatment, the average TPH concentration was 22 mg/kg.	Ten covered treatment cells (6 ft by 110 ft by 9 ft high) used. Carbon dioxide monitored in effluent air to track contaminant degradation. Off-gas treated by carbon adsorption.	1
5 Fuel Storage Facility, TX	1,500 cu yds	Crude oil and grease	Average initial TPH concentrations of 920 mg/kg. TPH concentration dropped to 300 mg/kg after 3 weeks of treatment. Within 8 weeks, TPH dropped below the analytical method detection limit of 50 mg/kg.	Contaminated soil was clay of very low permeability. Treatment cell dimensions were 100 ft by 120 ft. Cells covered with vented polyethylene sheet to divert rainwater to an area outside cell berms.	1

Figure 5. Application Examples

placed over the liner to allow the movement of heavy equipment over it during formation of the piles;

- The treatment area was divided into three individual treatment cells. Slotted 4-inch Schedule 40 PVC aeration pipes were placed on the initial 8- to 12-inch layer of soil and a 12-inch mound of pea gravel was formed over each pipe;
- Three soil piles were constructed (see Figure 6)—each containing 500 cubic yards of soil resulting in piles 8 feet high, 52 feet wide, and 52 feet long. One pile was maintained as a control; the other two piles were used to treat contaminated soil;
- A 3-hp blower was used to draw air through the two treatment piles at a rate of 70 scfm. A computer model was used to design heap pile components for uniform airflow throughout the piles;
- Air drawn from the pile was directed to a water knockout vessel to remove water. Air exiting the vessel was passed through an in-line filter to remove particulates (no other control was required);
- Initially, solid fertilizer (at a C:N:P ratio established during the treatability study) was mixed with the soil;
- An irrigation system provided for both nutrient addition (ammonium sulfate and ammonium phosphate) and moisture control;
- A leachate collection system was employed. Collected leachate was stored and recycled to the pile for moisture addition as needed; and
- The average final TPH concentration was 234 mg/kg (with an 80% upper confidence level of 454 mg/kg).

This project demonstrated that a batch process in which treated soil is removed from the pile and replaced with contaminated soil can be sucessfully implemented. In addition, it demonstrated that different types of contaminated soil can be effectively treated in separate cells.

Treatment costs for the research and development project were about $150 per cubic yard. These costs included an extensive treatability study, increased sampling and analysis, and detailed oxygen and carbon dioxide monitoring. The full-scale remediation of 5600 cubic yards performed under NEESA's Remedial Action Contract was conducted at a cost of $27.30 per cubic yard. This cost included ongoing operation and maintenance, consolidation of three piles into one, the moving of dirt onto and off of the piles, and the implementation of improvements based on lessons learned from the pilot study.

The following examples provide descriptions of recent private sector applications of heap pile bioremediation. These examples are not intended to provide guidance for the implementation of heap pile bioremediation systems, but instead to provide representative examples of heap pile use and results.

Example 3—Crude Oil-Contaminated Soil in California (1)

About 5,000 cubic yards of soil were found to be contaminated with crude oil with a maximum concentration of 4,500 mg/kg. Results of a feasibility study indicated good biodegradation potential.

A series of negative pressure windrows was constructed. To minimize nuisance odors, the windrows were covered with perforated HDPE sheets. During the construction phase, a nutrient solution of ammonium chloride (a nitrogen source) and disodium phosphate (a phosphorus source) was added by spraying. Air was drawn through slotted pipes within the windrows manifolded to a 3/4-hp blower. Off-gas from the blower was treated by carbon adsorption.

Baseline TPH concentrations ranged between 800 and 4,500 mg/kg. After three weeks of operation, the concentrations ranged from 700 to 4,300 mg/kg. Subsequently, a rapid decrease in TPH concentrations was detected. By the sixth week

Figure 6. Construction of Piles Source: NCEL

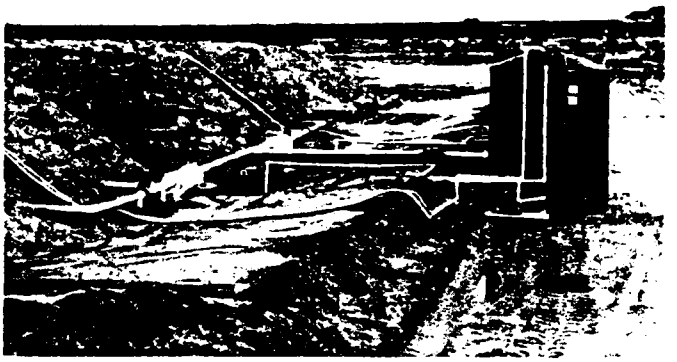

Figure 7. Heap Pile Bioremediation System Source: NCEL

of operation, TPH concentrations were observed to have dropped to levels below 5 mg/kg. A review of microbial enumeration data indicated that this coincided with a peak in microbial population five weeks after system start-up.

Example 4—Crude Oil-Contaminated Soil in California (1)
At another site in California, about 15,000 cubic yards of soil were contaminated with crude oil and other petroleum hydrocarbons. Initial TPH concentrations were 42 to 770 mg/kg. Soil was treated using ten treatment cells, each 6 ft by 110 ft by 9 ft high. The cells were covered with perforated polyethylene sheeting to control nuisance odors. A vacuum blower was used to pull air through the piles. The blower effluent was treated by carbon adsorption.

After 45 days of treatment, TPH levels had dropped off to an average of 22 mg/kg with nearly 60% of the results below the 10 mg/kg detection limit for the analytical method used.

Throughout the course of this remediation, microbial activity was monitored by measuring carbon dioxide concentrations in the vacuum system effluent. Initial carbon dioxide levels from the treatment cells exceeded 12,000 ppm (compared to atmospheric carbon dioxide levels of approximately 350 ppm). After two weeks, carbon dioxide in the air pulled from the piles approached 4,000 ppm and continued to decline slowly.

Example 5—Crude Oil-Contaminated Soil in Texas (1)
At a fuel storage facility in Texas, approximately 1,500 cubic yards of soil had been contaminated by crude oil and grease during years of operation. Initial TPH levels were on the order of 1,000 mg/kg. The contaminated soil was a gumbo-type clay with very low permeability. A 100-ft by 120-ft treatment cell lined with HDPE sheeting was constructed. The berms along the treatment cell perimeters were three to five feet in height. Two-inch diameter slotted PVC piping was placed in trenches in the soil pile and packed with gravel to prevent plugging. Nutrients (ammonium chloride for nitrogen and dipotassium phosphate for phosphorus) and moisture were added through a one-inch soaker pipe system. A French drain was constructed along the length of the pile to collect leachate that was then recycled to the pile.

Vented polyethylene sheeting was placed over the cells to prevent contamination of rainwater runoff by diverting rainwater from the cells to a point outside the bermed area.

The average initial TPH concentration was 920 mg/kg. After three weeks of treatment, the concentration dropped to 300 mg/kg. By the eighth week of treatment, sampling indicated that contaminant levels had dropped below the detection limit of 50 mg/kg for the analytical method used.

Closure of the site was requested after final samples were collected and analyzed. The results of these final analyses indicated an average concentration of 59 mg/kg TPH, which was less than the 75 mg/kg background concentration established for the site. Based on these results closure was granted.

Points to Remember/Lessons Learned

General points to remember for implementing a remedial technology such as heap pile bioremediation include:

- √ Regulatory review and coordination should be initiated as soon as possible in the technology selection and planning process.
- √ Remedial personnel should enter into regulatory negotiations with specific goals and objectives (e.g., whether the pile should be covered, target treatment levels, leachate collection requirements, etc.) in mind. They should be prepared to negotiate to develop realistic and practical criteria and operational requirements.
- √ Process design must take into consideration the local regulatory requirements for management or treatment of residuals (including off-gases, accumulated leachate and runoff, and treated soil).
- √ The success of heap pile bioremediation depends on the quality of system design, construction, and operation—the use of experienced contractors will provide the best assurance that success will be achieved with a minimum of problems.

The following points to remember/lessons learned were generated during discussions with Navy and contractor personnel with first-hand knowledge and experience with implementing heap pile bioremediation in the field (such as the Application Examples just presented). These issues reflect potential pitfalls and problems encountered in field implementation and provide some pointers on how to avoid these problems.

For clarity, these issues have been divided into the different phases of heap pile bioremediation.

Soil Preparation:

√ In applications involving soil contaminated with a variety of contaminants, it is beneficial to segregate (if possible) the soil by contaminant type. This will enhance the uniformity of contaminants within the soil pile. In addition, because different contaminants will have different degradation characteristics, the process can be optimized to better meet the requirements for specific contaminants.

√ If possible, soil that is classified as hazardous waste should be separated from soil that is not. In addition, care should be taken to avoid the contamination of fuel-contaminated soil with other hazardous wastes.

√ Rocks and debris greater than two to four inches in diameter should be screened from the soil prior to pile construction to avoid potential damage to the liner.

√ The soil on which the liner is placed (soil base) must be free of rocks to avoid liner damage. This can be accomplished by screening rocks from the soil or by placing an 8- to 12-inch layer of sand over the soil. Liner manufacturers will usually guarantee a liner only if the soil base is adequate. A company representative should inspect the soil base prior to arrival of the installation crews if there is any doubt about its quality.

√ Heap pile bioremediation works best with sandy soils. However, if soil is clayey and clumps are present, the clumps should be broken up using a soil mixer or by screening in order to maximize surface area exposed to the degradative microorganisms, air, and nutrients. Sand can be added to the soil to increase porosity.

√ In rare instances when pH adjustment is necessary, care should be taken to avoid potential shock to microorganisms already acclimated to the low or high pH of the contaminated soil. Amendments (such as phosphate fertilizers) can be used to adjust pH.

Pile Construction:

√ A 12-inch layer of contaminated soil should be placed over the liner. This layer protects the liner during pile construction. In addition, this layer helps to keep the aeration pipes off the surface of the liner, preventing shortcircuiting of airflow along the pipe/liner interface.

√ To prevent soil from clogging the aeration pipe and to extend the aeration zone, a 10- to 12-inch layer of rounded pea gravel should be placed over the aeration pipe in the pile before adding the soil to be treated. The use of geotextiles to separate the contaminated soil from the pipes is not recommended due to clogging of the textile by soil fines or clay.

√ Running heavy equipment over soil during construction of the piles should be avoided to prevent compaction of the soil. A front-end loader should be used to loosely form piles approximately 8 feet high without running over previously placed soil (see Figure 6).

√ Wet soil should not be added to the pile. Wet soil will easily compact and result in poor permeability and channelling (shortcircuiting) of air through the pile.

√ Nutrients are most effectively applied during the construction of the soil pile. Nutrients in solid or liquid form (time-released fertilizers work best) can be distributed over layers of soil as they are placed on the pile.

√ A layer of mulch on the soil pile can provide insulation. With mulch, the pile can be kept cooler in the summer and warmer in the winter.

√ Plastic sheeting may be placed over the pile for temperature and moisture control. A white, opaque plastic should be used to avoid overheating the pile. Plastic sheeting may also be used to divert rainwater to a location outside the berms.

√ Once piles have been constructed, the uniformity of air flow should be verified (see ***Monitoring and Measurements***). If necessary, valves in the aeration pipe system should be adjusted.

Pile Operation:

√ Temperatures within the soil piles should be prevented from going below approximately 20°C (68°F) or above 35°C (95°F) to avoid inhibiting the growth of some microorganisms. Within this range, the degradation rate will roughly double for every 10°C (18°F) increase in temperature.

√ Spray irrigation systems will provide for better distribution of moisture and minimal maintenance. (At the Marine Corps remediation described in Application Example 2, the primary maintenance problem was the need to constantly clean the drip irrigation system clogged by silt). Drip (or soaker) systems may be necessary, however, if the piles are covered.

√ After pile construction, nutrient levels should be adjusted through the irrigation system for a more controlled and even distribution.

√ By monitoring oxygen content and temperature in the piles, blowers can be cycled on and off depending on oxygen and temperature set points. This will reduce energy requirements and blower wear.

√ Power outages will cut off the source of oxygen to the piles. Depending on the specific microorganisms involved, a power outage of greater than one day may be detrimental. Once power is returned, a period of 1 to 2 days may be required for reacclimatization of the microorganisms (although a steady state oxygen concentration in the pile will take only a few hours). Recommendations to minimize the impact of a power outage include: (1) installation of an automatic restart mechanism to restart the blower once power is restored and (2) installation of an hour event meter to indicate periods of power outages.

√ Water knockout vessels should be used to remove moisture pulled from the pile to prevent damage to the blower motor. In addition, a particulate filter should be used to prevent entrained solids from entering the blower. An automatic blower shutoff switch should be installed in the event the water knockout vessels fill up.

√ The potential for overflow of berms, sumps, knockout vessels, or liquid storage tanks is a source of regulatory concern. This potential can be minimized by ensuring that the total capacity of the berms, sumps, vessels, and tanks meets 50-year (or 100-year, if required) rainfall event guidelines. Additional measures that can provide overflow protection include: (1) automatic drainage of knockout vessels (based on liquid level in the vessels) into the berms and (2) an automated sump pump system to pump excess liquid inside the berm system into liquid storage tanks.

Monitoring and Measurements:

√ Several methods can be used to determine if air flow is uniform throughout the soil pile. Air flow measurements can be made using manometers to measure pressure differential between different areas within the pile or by using soil gas pressure probes to determine discreet pressures.

√ It may be difficult to maintain optimum moisture content without inducing channeling of air through the piles. Too much soil moisture will result in reduced air flow. Channelling will usually be identified by a pressure drop at the blower inlet or as a large difference between measurements of pressure probes.

√ To ensure that there are no blockages in the aeration pipe system, hot wire anemometers are used to monitor air flow within the pipes. For accurate readings, care should be taken to ensure that these anemometers are placed in the center of the pipe cross-section.

√ The most reliable method to determine moisture content in the soil is by standard gravimetric analysis. Tensiometers, although less accurate, can provide relative measurements of moisture content in soil piles.

√ Soil gas probes should be installed and monitored periodically to ensure that required oxygen levels (between 5% and 15% by volume in soil gas) in the soil are maintained.

√ Carbon dioxide concentrations in soil gas (measured by soil gas probes) can provide a quick check on microbial respiration. However, it should be noted that if soils are alkaline (pH greater than 7), carbon dioxide may be converted to insoluble carbonates that will not be measured in the soil gas.

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Points of Contact

Additional information regarding the technical, regulatory, and practical aspects of heap pile bioremediation may be obtained from:

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EPA

Engineering Bulletin
Rotating Biological Contactors

Purpose

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

Abstract

Rotating biological contactors (RBCs) employ aerobic fixed-film treatment to degrade either organic and/or nitrogenous (ammonia-nitrogen) constituents present in aqueous waste streams. Treatment is achieved as the waste passes by the media, enabling fixed-film systems to acclimate biomass capable of degrading organic waste [1, p. 91]*. Fixed-film RBC reactors provide a surface to which soil organisms can adhere; many indigenous soil organisms are effective degraders of hazardous wastes.

An RBC consists of a series of corrugated plastic discs mounted on a horizontal shaft. As the discs rotate through the aqueous waste stream, a microbial slime layer forms on the surface of the discs. The microorganisms in this slime layer degrade the waste's organic and nitrogenous constituents. Approximately 40 percent of the RBC's surface area is immersed in the waste stream as the RBC rotates through the liquid. The remainder of the surface area is exposed to the atmosphere, which provides oxygen to the attached microorganisms and facilitates oxidation of the organic and nitrogenous contaminants [2, p. 6]. In general, the large microbial population growing on the discs provides a high degree of waste treatment in a relatively short time. Although RBC systems are capable of performing organic removal and nitrification concurrently, they may be designed to primarly provide either organic removal or nitrification singly [3, p. 1-2].

RBCs were first developed in Europe in the 1950s [1, p. 6]. Commercial applications in the United States did not occur until the late 1960s. Since then, RBCs have been used in the United States to treat municipal and industrial wastewaters. Because biological treatment converts organics to innocuous products such as CO_2, investigators have begun to evaluate whether biological treatment systems like RBCs can effectively treat liquid waste streams from Superfund sites. Treatability studies have been performed at at least three Superfund sites to evaluate the effectiveness of this technology at removing organic and nitrogenous constituents from hazardous waste leachate. A full-scale RBC treatment system is presently operating in at least one Superfund site in the United States.

Technology Applicability

Research demonstrates that RBCs can potentially treat aqueous organic waste streams from some Superfund sites. During the treatability studies for the Stringfellow, New Lyme, and Moyer Superfund sites, RBC systems efficiently removed the major organic and nitrogenous constituents in the leachates. Because waste stream composition varies from site to site, treatability testing to determine the degree of contaminant removal is an essential element of the remedial action plan. Although recent Superfund applications have been limited to the treatment of landfill leachates, this technology may be applied to groundwater treatment [4].

In general, biological systems can degrade only the soluble fraction of the organic contamination. Thus the applicability of RBC treatment is ultimately dependent upon the solubility of the contaminant. RBCs are generally applicable to influents containing organic concentrations of up to 1 percent organics, or between 40 and 10,000 mg/l of SBOD. (Note: Soluble biochemical oxygen demand, or SBOD, measures the soluble fraction of the biodegradable organic content in terms of oxygen demand.) RBCs can be designed to reduce influent biochemical oxygen demand (BOD) concentrations below 5 mg/l SBOD and ammo-

*[reference number, page number]

Table 1
Effectiveness of RBCs on General Contaminant Groups for Liquid Waste Streams

	Contaminant Groups	Effectiveness
Organic	Halogenated volatiles	■
	Halogenated semivolatiles	■
	Nonhalogenated volatiles	■
	Nonhalogenated semivolatiles	■
	PCBs	▼
	Pesticides	▼
	Dioxins/Furans	❑
	Organic cyanides	▼
	Organic corrosives	▼
Inorganic	Volatile metals	❑
	Nonvolatile metals	❑
	Asbestos	❑
	Radioactive materials	❑
	Inorganic corrosives	❑
	Inorganic cyanides	▼
Reactive	Oxidizers	❑
	Reducers	❑

■ Demonstrated Effectiveness: Successful treatability test at some scale completed.
▼ Potential Effectiveness: Expert opinion that technology will work.
❑ No Expected Effectiveness: Expert opinion that technology will not work.

nia-nitrogen (NH_3-N) levels below 1.0 mg/l [5, p. 2] [6, p. 60]. RBCs are effective for treating solvents, halogenated organics, acetone, alcohols, phenols, phthalates, cyanides, ammonia, and petroleum products [7, p. 6] [8, p. 69]. RBCs have fully nitrified leachates containing ammonia-nitrogen concentrations up to 700 mg/l [6, p. 61].

The effectiveness of RBC treatment systems on general contaminant groups is shown in Table 1. Examples of constituents within contaminant groups are provided in "Technology Screening Guide for Treatment of CERCLA Soils and Sludges" [9]. Table 1 is based on the current available information or professional judgment where no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability was tested to show the technology was effective for that particular contaminant group. The ratings of potential effectiveness or no expected effectiveness are based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular medium. When the technology is not applicable or will probably not work for a particular combination of contaminant group and medium, a no expected effectiveness rating is given.

Limitations

Although RBCs have proven effective in treating waste streams containing ammonia-nitrogen and organics, they are not effective at removing most inorganics or non-biodegradable organics. Wastes containing high concentrations of heavy metals and certain pesticides, herbicides, or highly chlorinated organics can resist RBC treatment by inhibiting microbial activity. Waste streams containing toxic concentrations of these compounds may require pretreatment to remove these materials prior to RBC treatment [10, p. 3].

RBCs are susceptible to excessive biomass growth, particularly when organic loadings are elevated. If the biomass fails to slough off and a blanket of biomass forms which is thicker than 90 to 125 mils, the resulting weight may damage the shaft and discs. When necessary, excess biofilm may be reduced by either adjusting the operational characteristics of the RBC unit (e.g., the rotational speed or direction) or by employing air or water to shear off the excess biomass [11, p. 2].

In general, care must be taken to ensure that organic pollutants do not volatilize into the atmosphere. To control their release, gaseous emissions may require offgas treatment [12, p. 31].

All biological systems, including RBCs, are sensitive to temperature changes and experience drops in biological activity at temperatures lower than 55°F. Covers should be employed to protect the units from colder climates and extraordinary weather conditions. Covers should also be used to protect the plastic discs from degradation by ultraviolet light, to inhibit algal growth, and to control the release of volatiles [13]. In general, organic degradation is optimum at a pH between 6 and 8.5. Nitrification requires the pH be greater than 6 [6, p. 61].

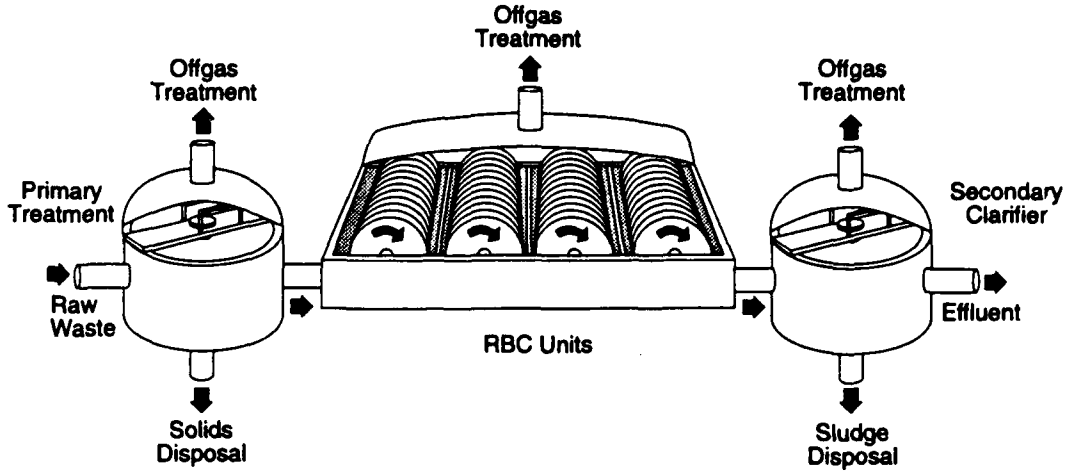
Additionally, nutrient and oxygen deficiencies can reduce microbial activity, causing significant decreases in biodegradation rates [14, p. 39]. Extremes in pH can limit the diversity of the microbial population and may suppress specific microbes capable of degrading the contaminants of interest. Fortunately, these variables can be controlled by modifying the system design.

Technology Description

A typical RBC unit consists of 12-foot-diameter plastic discs mounted along a 25-foot horizontal shaft. The total disc surface area is normally 100,000 square feet for a standard unit and 150,000 square feet for a high density unit. Figure 1 is a diagram of a typical RBC system.

As the RBC slowly rotates through the groundwater or leachate at 1.5 rpm, a microbial slime forms on the discs. These microorganisms degrade the organic and nitrogenous contaminants present in the waste stream. During rotation, approximately 40 percent of the discs' surface area is in contact with the aqueous waste while the remaining surface area is exposed to the atmosphere. The rotation of the media through the atmosphere causes the oxygenation of the attached organisms. When

Figure 1
Typical RBC Plant Schematic (12)



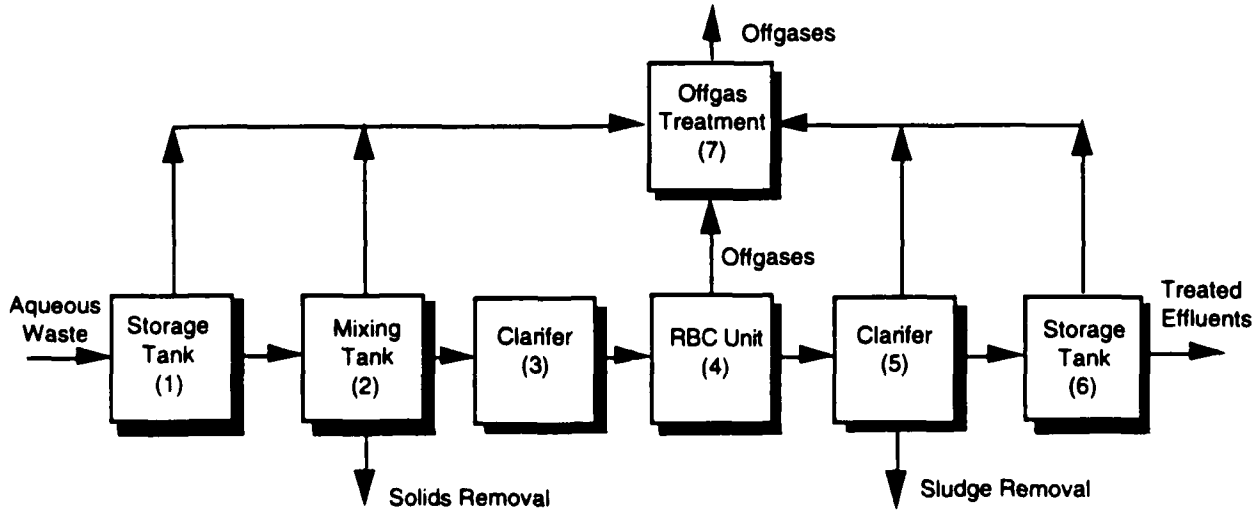
operated properly, the shearing motion of the discs through the aqueous waste causes excess biomass to shear off at a steady rate. Suspended biological solids are carried through the successive stages before entering the secondary clarifier [2, p. 13.101].

Primary treatment (e.g., clarifiers or screens), to remove materials that could settle in the RBC tank or plug the discs, is often essential for good operation. Influents containing high concentrations of floatables (e.g., grease, etc.) will require treatment using either a primary clarifier or an alternate removal system [11, p. 2].

The RBC treatment process may involve a variety of steps, as indicated by the block diagram in Figure 2. Typically, aqueous waste is transferred from a storage or equalization tank (1) to a mixing tank (2) where chemicals may be added for metals precipitation, nutrient adjustment, and pH control. The waste stream then enters a clarifier (3) where the solids are separated from the liquid. The effluent from the clarifier enters the RBC (4) where the organics and/or ammonia are converted to innocuous products. The treated waste is then pumped into a second clarifier (5) for removal of the biological solids. After secondary clarification the effluent enters a storage tank (6) where, depending upon the contamination remaining in the effluent, the waste may be stored pending additional treatment or discharged to a sewer system or surface stream. Throughout this treatment process the offgases from the various stages should be collected for treatment (7). The actual treatment train will, of course, depend upon the nature of the waste and will be selected after the treatability study is conducted.

Staging, which employs a number of RBCs in series, enhances the biochemical kinetics and establishes selective biological cultures acclimated to successively decreasing organic load-

Figure 2
Block Diagram of the RBC Treatment Process



ings. As the waste stream passes from stage to stage, progressively increasing levels of treatment occur [2, p. 13.105].

In addition to maximizing the system's efficiency, staging can improve the system's ability to handle shock loads by absorbing the impact of a shock load in the initial stages, thereby enabling subsequent stages to operate until the affected stages recover [15, p. 10.200].

Factors effecting the removal efficiency of RBC systems include the type and concentration of organics present, hydraulic residence time, rotational speed, media surface area exposed and submerged, and pre- and post-treatment activities. Design parameters for RBC treatment systems include the organic and hydraulic load rates, design of the disc train(s), rotational velocity, tank volume, media area submerged and exposed, retention time, primary treatment and secondary clarifier capacity, and sludge production [8, p. 69].

Process Residuals

During primary clarification, debris, grit, grease, metals, and suspended solids (SS) are separated from the raw influent. The solids and sludges resulting from primary clarification may contain metallic and organic contaminants and may require additional treatment. Primary clarification residuals must be disposed of in an appropriate manner (e.g., land disposal, incineration, solidification, etc.).

Following RBC treatment, the effluent undergoes secondary clarification to separate the suspended biomass solids from the treated effluent. Refractory organics may contaminate both the clarified effluent and residuals. Additional treatment of the solids, sludges, and clarified effluent may be required. Clarified secondary effluents which meet the treatment standards are generally discharged to a surface stream, while residual solids and sludges must be disposed of in an appropriate manner, as outlined above for primary clarification residuals [2, p. 13.120].

Volatile organic compound (VOC)-bearing gases are often liberated as a byproduct of RBC treatment. Care must be taken to ensure that offgases do not contaminate the work space or the atmosphere. Various techniques may be employed to control these emissions, including collecting the gases for treatment [13].

Site Requirements

RBCs vary in size depending upon the surface area needed to treat the hazardous waste stream. A single full size unit with a walkway for access on either side of the unit takes up approximately 550 square feet [16]. The total area required for an RBC system is site-specific and depends on the number, size, and configuration of RBC units installed.

Contaminated groundwater, leachates, or waste materials are often hazardous. Handling and treatment of these materials requires that a site safety plan be developed to provide for personnel protection and special handling measures. Storage should be provided to hold the process product streams until they have been tested to determine their acceptability for disposal, reuse, or release. Depending on the site, a method to store waste that has been prepared for treatment may be necessary. Storage capacity will depend on waste volume.

Onsite analytical equipment capable of determining site-specific organic compounds for performance assessment make the operation more efficient and provide better information for process control.

Performance Data

Limited information is available on the effectiveness of RBCs in treating waste from Superfund sites. Most of the data came from studies done on leachate from the New Lyme, Ohio; Stringfellow, California; and Moyer, Pennsylvania Superfund sites. The results of these studies are summarized below.

In order to compensate for the lack of Superfund performance data, non-Superfund applications are also discussed. The majority of the performance data for non-Superfund applications were obtained from industrial RBC operations. Theoretically this information has a high degree of application to Superfund leachate and groundwater treatment.

The quality of the information present in this section has not been determined. The data are included as a general guidance, and may not be directly transferrable to a specific Superfund site. Good characterization and treatability studies are essential in further refining and screening of RBC technology.

New Lyme Treatability Study

The EPA performed a remedy selection study on the leachate from the New Lyme Superfund site located in New Lyme Township, Ashtabula County, Ohio, to help determine the applicability of an RBC to treat hazardous waste from a Superfund site. Samples of leachate collected from various seeps surrounding the landfill showed that the leachate was highly concentrated. Results indicated that the leachate contained up to 2,000 mg/l dissolved organic carbon (DOC), 2,700 mg/l SBOD, and 5,200 mg/l soluble chemical oxygen demand (SCOD) [17, p. 12]. (Note: SCOD measures the soluble fraction of the organics amenable to chemical oxidation, as well as certain inorganics such as sulfides, sulfites, ferrous iron, chlorides, and nitrites.)

Leachate from the New Lyme site was transported from New Lyme to a demonstration-scale RBC located at the EPA's Testing and Evaluation Facility in Cincinnati, Ohio. After an adequate biomass was developed on the RBC discs using a primary effluent supplied by Mill Creek Treatment Facility (a local industrial wastewater treatment facility), the units were gradually acclimated to an influent consisting of 100 percent leachate. Results indicated that within 20 hours the RBC removed 97 percent of the gross organics, as represented by DOC, from the leachate (see Figure 3 and Table 2) [18, p. 7]. Priority pollutants were either converted and/or stripped from the leachate during treatment. After normal clarification, the effluent from the RBC was

eligible for disposal into the sewer system leading to the Mill Creek facility.

Stringfellow Treatability Study

A remedy selection study using an RBC was conducted on leachate from the Stringfellow Superfund site located in Glen Avon, California. After the leachate from this site received lime treatment to remove metal contamination, the leachate was transported to the EPA's Testing and Evaluation Facility in Cincinnati for testing similar to the New Lyme study. The objective of this study was to determine whether the leachate from Stringfellow could be treated economically with an RBC system.

The leachate from this site was generated at a daily rate of 2,500 gallons. Compared to the New Lyme leachate, it contained moderate concentrations of gross organics with DOC values of 300 mg/l, SBOD values of 420 mg/l, and SCOD values of 800 mg/l [4, p. 44].

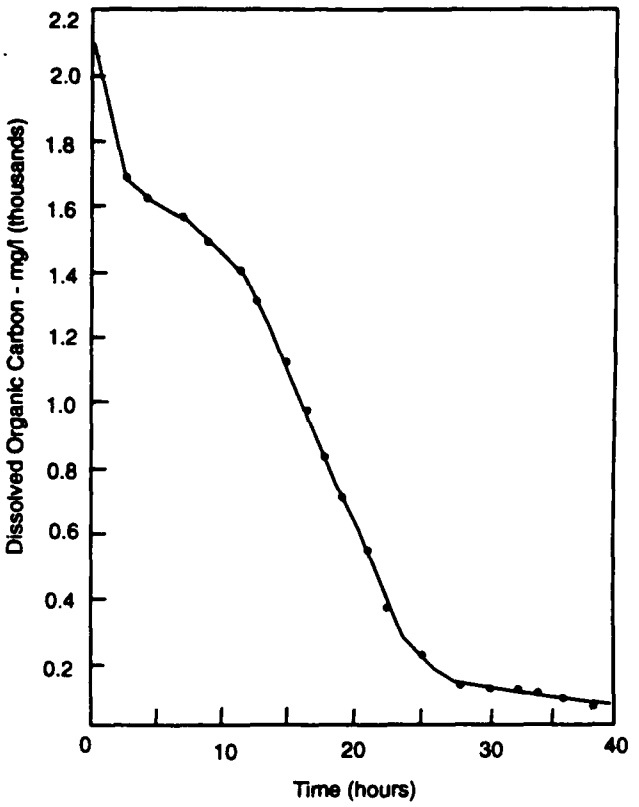
Results indicated that greater than 99 percent of SBOD was removed, 65 percent of DOC was removed, and 54 percent SCOD was removed within four days using the RBC laboratory-scale treatment system [4, p. 44]. Table 3 presents pertinent information on the treatment of 100 percent leachate. Since the DOC and SCOD conversion rates were low, a significant fraction of the refractory organics remained following treatment. Activated carbon was used to reduce the DOC to limits acceptable to the Mill Creek Treatment Facility.

Table 2
Removal of Pollutants from New Lyme Leachate (17, p. 17)
Experiment 5

	Influent (mg/l)	*Effluent (mg/l)*
SBOD	2700	4
BOD_T	3000	6.6
DOC	2000	17
TOC	2100	19
SCOD	5200	33
NO_3-N	<1	60
SS	1400	6600
VSS	240	2600
Volatile PP		
Benzene	0.28	<0.002
Toluene	4.9	<0.002
Additional Volatiles		
Cis 1,2-Dichloroethene	0.94	ND
Xylenes	2.8	ND
Acetone	140	ND
Methyl Ethyl Ketone	470	ND
Total Organic Halides	-	1.2
Total Toxic Organics	<0.250	<0.010

BOD_T = Total Biochemical Oxygen Demand
NO_3-N = Nitrogen as Nitrate
VSS = Volatile Suspended Soilds

Figure 3
Disappearance of DOC with Time (17, p. 14)
Experiment 5*



* The influent for Experiment 5 consisted of 100 percent leachate and the biomass on the RBCs was acclimated. Nutrient addition was also employed (at a ratio of 160/5/2 for C/N/P).

Moyer Treatability Study

During a recent remedy selection study, three treatability-scale RBCs were used to degrade a low-BOD (26 mg/l), high ammonia (154 mg/l) leachate from the Moyer Landfill Superfund site in Lower Providence Township near Philadelphia, Pennsylvania [19, p. 971]. The leachate has low organic strength (e.g., 26 mg/l BOD, 358 mg/l COD, and 68 mg/l TOC) which is typical of an older landfill and it also contains mainly non-biodegradable organic compounds [19, p. 972]. (Note: Total organic carbon, or TOC, is a measure of all organic carbon expressed as carbon.) The abundance of ammonia found in the leachate prompted investigators to attempt ammonia oxidation with an RBC system. Relatively low substrate loading rates were employed during the study (0.2, 0.4, and 0.6 gpd/square foot of disc surface area per stage). Ammonia oxidation was essentially complete (98 percent) and a maximum of 80 percent of the BOD and 38 percent of the COD in the leachate was oxidized [19, p. 980]. Runs performed using lower loading rates experienced the largest removals. A limited denitrification study was also performed using an anoxic RBC to treat an RBC effluent generated during the aerobic segment of the treatability investigation. This study demonstrated the feasibility of using denitrification to treat

the nitrate produced by aerobic ammonia oxidation [19, p. 980].

Non-Superfund Applications

The Homestake Mine in Lead, South Dakota has operated an RBC wastewater treatment plant since 1984. Forty-eight RBCs treat up to 5.5 million gallons per day (MGD) (21,000 m^3) of discharge water per day. The system was designed to degrade thiocyanate, free cyanide, and metal-complexed cyanides, to reduce heavy metal concentrations, and to remove ammonia, which is a byproduct of cyanide degradation [20, p. 2]. Eight parallel treatment trains, utilizing five RBCs in series, were employed to degrade and nitrify the metallurgical process waters (see Table 4 for a characterization of the influent). The first two RBCs in each train were used to degrade the cyanides and remove heavy toxic metals and particulate solids through biological adsorption. The last three RBCs employed nitrification to convert the ammonia to nitrate. Table 5 provides an average performance breakdown for the system. During its operation, overall performance improved significantly, as demonstrated by an 86 percent increase in the systems ability to reduce total effluent cyanide concentrations (e.g., from 0.45 to 0.06 mg/l). Concurrently, the cost per kg to treat cyanide dropped from $11.79 to $3.10, while the cost per m^3 to treat effluent decreased by 50 percent [21, p. 9]. In general, the system has responded well to any upsets or disturbances. Diesel fuels, lubricants, degreasers, biocides, dispersants, and flocculants have been periodically found in the influent wastewater but normally only create minor upsets in the performance of the plant. During the life of the system, the number of upsets and the biomass's ability to recuperate have both improved [21, p. 6].

A significant difference between the Homestake system and the other RBC systems described within this report is that instead of removing the metals contaminating the wastewater in the pretreatment stage, metal reduction is accomplished through bioadsorption during the treatment phase. Bioadsorption of metals by biological cells is not unlike the use of activated carbon, however the number and complexity of binding sites on the cell wall are enormous in comparison [20, p. 2].

In a study by Israel's Institute of Technology, a laboratory-scale RBC was used to treat an oil refinery wastewater. The wastewater had been pretreated using oil-water separation and dissolved air flotation. As summarized in Table 6, 91 percent of the hydrocarbon and 97 percent of the phenol were removed, as well as 96 percent of the ammonia-nitrogen [22, p. 4]. By gradually increasing the concentration of phenols present in the influent (e.g., over a 5 day period) from 5 mg/l to 30 mg/l, the system demonstrated that it was capable of quickly adapting to influent changes and higher phenolic loads [22, p. 6]. During this period, the RBC was able to maintain effluent COD concentrations at levels comparable to previous loadings. The system's resiliency was further demonstrated by its ability to recover from a major disturbance (e.g., such that effluent COD removal was interrupted) within 4 days [22, p. 7].

Technology Status

RBCs have been used commercially in the United States since

Table 3
Treatment of 100% Stringfellow Leachate (4, p. 44)

	Leachate (mg/l)	*RBC Effluent (mg/l)*	*Use APC plus Effluent (mg/l)*
SBOD	420	<3.0	0.9
BOD	440		22
DOC	300	110	20
TOC	310		22
SCOD	800	360	79
COD	840		95
SS	43		23
VSS	31		14
NH_3-N	3.4		6.3
NO_3-N	44		34

APC = Activated Powered Carbon
COD = Chemical Oxygen Demand

Table 4
Homestake Mine Wastewater Matrix *

	Decant Water (mg/l)	*Mine Water (mg/l)*	*Influent Blend (mg/l)*
Thiocyanate	110-350	1-33	35-110
Total Cyanide	5.5-65.0	0.30-2.50	0.50-11.50
WAD Cyanide	3.10-38.75	0.50-1.10	0.50-7.15
Copper	0.5-3.1	0.10-2.65	0.15-2.95
Ammonia-N	5-10	5.00-19.00	6-12
Phosphorus-P	0.10-0.20	0.10-0.15	0.10-0.15
Alkalinity	50-200	150-250	125-225
pH	7-9	7-9	7.5-8.5
Hardness	400-500	650-1400	500-850
Temperature°C	1.0-27.2	24-33	5-25

WAD = Weak Acid Dissociable
*Adapted from reference [20, p. 8]

Table 5
Influent, Effluent and Permit Concentrations at the Homestake Mines (20, p. 8)

	Influent (mg/l)	*Effluent (mg/l)*	*Permit (mg/l)*
Thiocyanate	62.0	<0.5	-
Total Cyanides	4.1	0.06	1.00
WAD Cyanide	2.3	<0.02	0.10
Total Copper	0.56	0.07	0.13
Total Suspended Soilds	-	6.0	10.0
Ammonia-Nitrogen	5.60*	<0.50	1.0-3.9

*Ammonia peaks at 25 mg/l within the plant as a cyanide degradation byproduct

Table 6
Refinery Wastewater Quality Before and After RBC Treatment (22, p. 4)

Constituent		*Influent (mg/l)*	*Effluent (mg/l)*
COD	Total	715	197
	Soluble	685	186
BOD	Total	140	8
	Soluble	128	6
Phenols		7.5	0.22
Suspended Solids			
	Total	32	7
	Volatile	29	6
NH_3-N		12.8	0.48

the late 1960s to treat municipal and industrial wastes. In the past decade, studies have been performed to evaluate the effectiveness of RBCs in treating leachate from hazardous waste sites.

Treatability studies have been performed on leachate from the Stringfellow, New Lyme, and Moyer Superfund sites. Results of these studies indicate that RBCs are effective in removing organic and nitrogenous constituents from hazardous waste leachate. Additional research is needed to define the effectiveness of an RBC in treating leachates and contaminated groundwater and to determine the degree of organic stripping that occurs during the treatment process. RBCs are being used to treat leachate from the New Lyme Superfund site.

RBCs require a minimal amount of equipment, manpower, and space to operate. Staging of RBCs will vary from site to site depending on the waste stream. The cost to install a single RBC unit with a protective cover and a surface area of 100,000 to 150,000 square feet ranges from $80,000 to $85,000 [16] [23].

During the Stringfellow treatability study researchers determined that by augmenting the existing carbon treatment system with RBCs, reductions in carbon costs would pay for the RBC plant within 3.3 years [4, p. 44]. The RBC plant model used to formulate this estimate was a scaled-up version of the pilot unit used during the treatability study.

EPA Contact

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Superfund | EPA/540/2-90/016 | September 1990

Engineering Bulletin

EPA Slurry Biodegradation

Purpose

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

Abstract

In a slurry biodegradation system, an aqueous slurry is created by combining soil or sludge with water. This slurry is then biodegraded aerobically using a self-contained reactor or in a lined lagoon. Thus, slurry biodegradation can be compared to an activated sludge process or an aerated lagoon, depending on the case.

Slurry biodegradation is one of the biodegradation methods for treating high concentrations (up to 250,00 mg/kg) of soluble organic contaminants in soils and sludges. There are two main objectives for using this technology: to destroy the organic contaminant and, equally important, to reduce the volume of contaminated material. Slurry biodegradation is not effective in treating inorganics, including heavy metals. This technology is in developmental stages but appears to be a promising technology for cost-effective treatment of hazardous waste.

Slurry biodegradation can be the sole treatment technology in a complete cleanup system, or it can be used in conjunction with other biological, chemical, and physical treatment. This technology was selected as a component of the remedy for polychlorinated biphenyl (PCB)-contaminated oils at the General Motors Superfund site at Massena, New York, [11, p. 2]* but has not been a preferred alternative in any record of decision [6, p. 6]. It may be demonstrated in the Superfund Innovative Technology Evaluation (SITE) program. Commercial-scale units are in operation. Vendors should be contacted to determine the availability of a unit for a particular site. This bulletin provides information on the technology applicability, the types of residuals produced, the latest performance data, site requirements, the status of the technology, and sources for further information.

Technology Applicability

Biodegradation is a process that is considered to have enormous potential to reduce hazardous contaminants in a cost-effective manner. Biodegradation is not a feasible treatment method for all sites. Each vendor's process may be capable of treating only some contaminants. Treatability tests to determine the biodegradability of the contaminants and the solids/liquid separation that occurs at the end of the process are very important.

Slurry biodegradation has been shown to be effective in treating highly contaminated soils and sludges that have contaminant concentrations ranging from 2,500 mg/kg to 250,000 mg/kg. It has the potential to treat a wide range of organic contaminants such as pesticides, fuels, creosote, pentachlorophenol (PCP), PCBs, and some halogenated volatile organics. It is expected to treat coal tars, refinery wastes, hydrocarbons, wood-preserving wastes, and organic and chlorinated organic sludges. The presence of heavy metals and chlorides may inhibit the microbial metabolism and require pretreatment. Listed Resource Conservation and Recovery Act (RCRA) wastes it has treated are shown in Table 1[10, p. 106].

*[Reference number, page number]

Table 1
RCRA-Listed Hazardous Wastes

Wood Treating Wastes	K001
Dissolved Air Floatation (DAF) Float	K048
Slop Oil Emulsion Solids	K049
American Petroleum Institute (API) Separator Sludge	K051

The effectiveness of this slurry biodegradation on general contaminant groups for various matrices is shown in Table 2 [12, p. 13]. Examples of constituents within contaminant groups are provided in Reference 12, "Technology Screening Guide for Treatment of CERCLA Soils and Sludges." This table is based on current available information or professional judgment when no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. For the ratings used for this table, demonstrated biodegradability means that, at some scale, treatability was tested to show that, for that particular contaminant and matrix, the technology was effective. The ratings of potential biodegradability and no expected biodegradability are based upon expert judgment. Where potential biodegradability is indicated, the technology is believed capable of successfully treating the contaminant group. When the technology is not applicable or will probably not work for a particular contaminant group, a no-expected-biodegradability rating is given. Another source of general observations and average removal efficiencies for different treatability groups is contained in the Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS [10], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," (OSWER Directive 9347.3-07FS [9].

Limitations

The various characteristics limiting the process feasibility, the possible reasons for these, and actions to minimize impacts of these limitations are listed in Table 3 [11, p. 2]. Some of these actions could be a part of the pretreatment process. The variation of these characteristics in a particular hardware design, operation, and/or configuration for a specific site will largely determine the viability of the technology and cost-effectiveness of the process as a whole.

Table 2
Degradability Using Slurry Biodegradation Treatment on General Contaminant Groups for Soils, Sediments, and Sludges

	Contaminant Groups	Biodegradability All Matrices
Organic	Halogenated volatiles	▼
	Halogenated semivolatiles	■
	Nonhalogenated volatiles	▼
	Nonhalogenated semivolatiles	■
	PCBs	▼
	Pesticides	■
	Dioxins/Furans	❑
	Organic cyanides	▼
	Organic corrosives	❑
Inorganic	Volatile metals	❑
	Nonvolatile metals	❑
	Asbestos	❑
	Radioactive materials	❑
	Inorganic corrosives	❑
	Inorganic cyanides	▼
Reactive	Oxidizers	❑
	Reducers	❑

■ Demonstrated Effectiveness: Successful treatability test at some scale completed
▼ Potential Effectiveness: Expert opinion that technology will work
❑ No Expected Effectiveness: Expert opinion that technology will not work

Technology Description

Figure 1 is a schematic of a slurry biodegradation process.

Waste preparation (1) includes excavation and/or moving the waste material to the process where it is normally screened to remove debris and large objects. Particle size reduction, water addition, and pH and temperature adjustment are other important waste preparation steps that may be required to achieve the optimum inlet feed characteristics for maximum contaminant reduction. The desired inlet feed characteristics [6, p. 14] are:

Organics:	.025-25%	by weight	Temperature:15-35°C
Solids:	10-40%	by weight	pH: 4.5-8.8
Water:	60-90%	by weight	
Solids particle size:		Less than 1/4"	

After appropriate pretreatment, the wastes are suspended in a slurry form and mixed in a tank (2) to maximize the mass transfer rates and contact between contaminants and microorganisms capable of degrading those contaminants. Aerobic treatment in batch mode has been the most common mode of operation. This process can be performed in contained reactors (3) or in lined lagoons [7, p. 9]. In the latter case, synthetic liners have to be placed in existing unlined lagoons, complicating the operation and maintenance of the system. In this case, excavation of a new lagoon or above-ground tank reactors should be considered. Aeration is provided by floating or submerged aerators or by compressors and spargers. Mixing is provided by aeration alone or by aeration and mechanical mixing. Nutrients and neutralizing agents are supplied to relieve any chemical limitations to microbial activity. Other materials, such as surfactants, dispersants, and compounds supporting growth and inducing degradation of contaminant compounds, can be used to improve the materials' handling characteristics or increase substrate availability for degradation [8, p. 5]. Microorganisms may be added initially to seed the bioreactor or added continuously to maintain the correct concentration of biomass. The residence time in the bioreactor varies with the soil or sludge matrix; physical/chemical nature of the contaminant, including concentration; and the biodegradability of the contaminants. Once biodegradation of the contaminants is completed, the treated slurry is sent to a separation/dewatering system (4). A clarifier for gravity separation, or any standard dewatering equipment, can be used to separate the solid phase and the aqueous phase of the slurry.

Process Residuals

There are three main waste streams generated in the slurry biodegradation system: the treated solids (sludge or soil), the process water, and possible air emissions. The solids are dewatered and may be further treated if they still contain organic contaminants. If the solids are contaminated with inorganics and/or heavy metals, they can be stabilized before disposal. The process water can be treated in an onsite treatment system prior to discharge, or some of it (as high as 90 percent by weight of solids) is usually recycled to the front end of the system for slurrying. Air emissions are possible during operation of the system (e.g., benzene, toluene, xylene [BTX] compounds); hence, depending on the waste characteristics, air pollution control, such as activated carbon, may be necessary [4, p. 29].

Site Requirements

Slurry biodegradation tank reactors are generally transported by trailer. Therefore, adequate access roads are required to get the unit to the site. Commercial units require a setup area of 0.5-1 acre per million gallons of reactor volume.

Standard 440V three-phase electrical service is required. Compressed air must be available. Water needs at the site can be high if the waste matrix must be made into slurry form. Contaminated soils or other waste materials are hazardous and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures.

Climate can influence site requirements by necessitating covers over tanks to protect against heavy rainfall or cold for long residence times.

Large quantities of wastewater that results from dewatering the slurried soil or that is released from a sludge may need to be stored prior to discharge to allow time for analytical tests to verify that the standard for the site has been met. A place to discharge this wastewater must be available.

Onsite analytical equipment for conducting dissolved oxygen, ammonia, phosphorus, pH, and microbial activity are needed for process control. High-performance liquid chromatographic and/or gas chromatographic equipment is desirable for monitoring organic biodegradation.

Performance Data

Performance results on slurry biodegradation systems are provided based on the information supplied by various vendors. The quality assurance for these results has not been evaluated. In most of the performances, the cleanup criteria were based on the requirements of the client; therefore, the data do not necessarily reflect the maximum degree of treatment possible.

Remediation Technologies, Inc.'s (ReTeC) full-scale slurry biodegradation system (using a lined lagoon) was used to treat wood preserving sludges (K0001) at a site in Sweetwater, Tennessee, and met the closure criteria for treatment of these sludges. The system achieved greater than 99 percent removal efficiency and over 99 percent reduction in volume attained for PCP and polynuclear aromatic hydrocarbons (PAHs) (Table 4 and Table 5).

Figure 1
Slurry Biodegradation Process

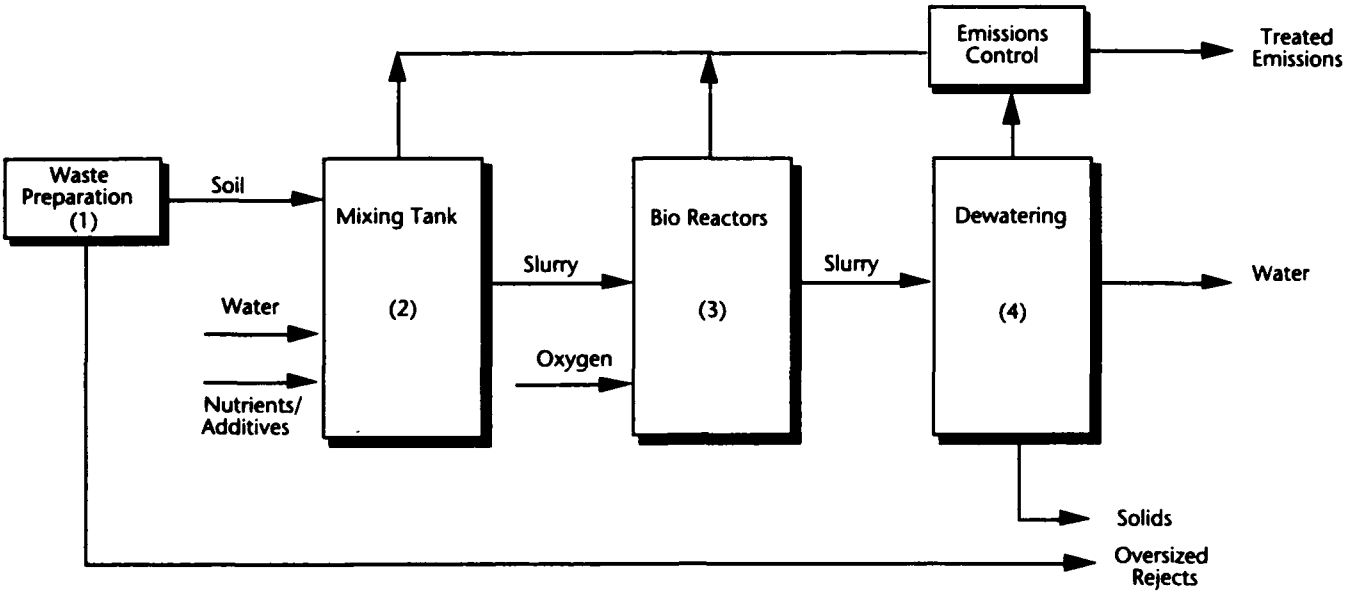


Table 3
Characteristics Limiting the Slurry Biodegradation Process

CHARACTERISTICS LIMITING THE PROCESS FEASIBILITY	REASONS FOR POTENTIAL IMPACT	ACTIONS TO MINIMIZE IMPACTS
Variable waste composition	Inconsistent biodegradation caused by variation in biological activity	Dilution of waste stream. Increase mixing
Nonuniform particle size	Minimize the contact with microorganisms	Physical separation
Water solubility	Contaminants with low solubility are harder to biodegrade	Addition of surfactants or other emulsifiers
Biodegradability	Low rate of destruction inhibits process	Addition of microbial culture capable of degrading particularly difficult compounds or longer residence time
Temperature outside 15-35°C range	Less microbial activity outside this range	Temperature monitoring and adjustments
Nutrient deficiency	Lack of adequate nutrients for biological activity	Nutrient monitoring; adjustment of the carbon/nitrogen/phosphorus ratio
Oxygen deficiency	Lack of oxygen is rate limiting	Oxygen monitoring and adjustments
Insufficient Mixing	Inadequate microbes/solids/organics contact	Optimize mixing characteristics
pH outside 4.5 - 8.8 range	Inhibition of biological activity	Sludge pH monitoring. Addition of acidic or alkaline compounds
Microbial population	Insufficient population results in low biodegradation rates	Culture test, addition of culture strains
Water and air emissions discharges	Potential environmental and/or health impacts	Post-treatment processes (e.g., air scrubbing, carbon filtration)
Presence of elevated, dissolved levels of: • Heavy metals • Highly chlorinated organics • Some pesticides, herbicides • Inorganic salts	Can be highly toxic to microorganisms	Pretreatment processes to reduce the concentration of toxic compounds in the constituents in the reactor to nontoxic range

Table 4
Results Showing Reduction in Concentration for Wood Preserving Wastes

Compounds	Initital Concentration		Final Concentration		Percent Removal	
	Solids (mg/kg)	Slurry (mg/kg)	Solids (mg/kg)	Slurry (mg/kg)	Solids (mg/kg)	Slurry (mg/kg)
Phenol	14.6	1.4	0.7	<0.1	95.2*	92.8
Pentachlorophenol	687	64	12.3	0.8	98.2	92.8
Naphthalene	3,670	343	23	1.6	99.3*	99.5*
Phenanthrene & Anthracene	30,700	2,870	200	13.7	99.3	99.5
Fluoranthene	5,470	511	67	4.6	98.8	99.1
Carbazole	1,490	139	4.9	0.3	99.7	99.8

*May be due to combined effect of Volatilization and Biodegradation. [Source: ReTec, 50,000 gal. reactor]

Table 5
Results Showing Reduction in Volume For Wood Preserving Wastes

Compounds	Before Treatment (Total pounds)	After Treatment (Total pounds)	Percent Volume Reduction
Phenol	368	41.4	88.8*
Pentachlorophenol	141,650	193.0	99.9
Naphthalene	179,830	36.6	99.9*
Phenanthrene & Anthracene	2,018,060	303.1	99.9
Fluoranthene	190,440	341.7	99.8
Carbazole	114,260	93.7	99.9

*May be due to combined effect of Volatilization and Biodegradation. [Source: ReTec, 50,000 gal. reactor]

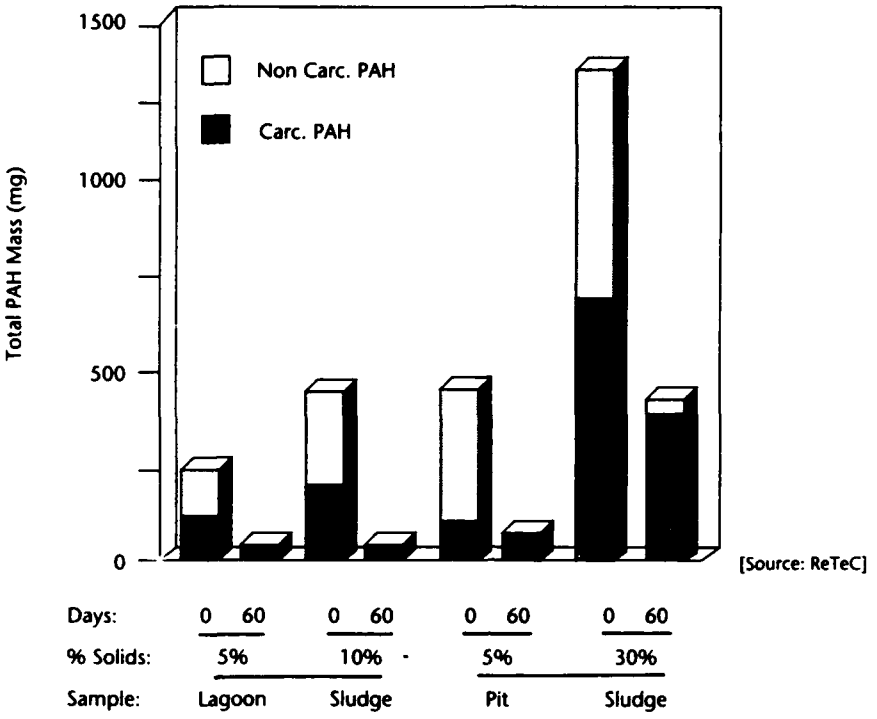
Data for one of these pilot-scale field demonstrations, which treated 72,000 gallons of oil refinery sludges, are shown in Figure 2 [8, p. 24]. In this study, the degradation of PAHs was relatively rapid and varied depending on the nature of the waste and loading rate. The losses of carcinogenic PAHs (principally the 5- and 6-ring PAHs) ranged from 30 to 80 percent over 2 months while virtually all of the noncarcinogenic PAHs were degraded. The total PAH reduction ranged from 70 to 95 percent with a reactor residence time of 60 days.

ECOVA's full-scale, mobile slurry biodegradation unit was used to treat more than 750 cubic yards of soil contaminated with 2,4-Dichlorophenoxy acetic acid (2,4-D) and 4-chloro-2-methyl-phenoxyacetic acid (MCPA) and other pesticides such as alachlor, trifluralin, and carbofuran. To reduce 2,4-D and MCPA levels from 800 ppm in soil and 400 ppm in slurry to less than 20 ppm for both in 13 days, 26,000-gallon bioreactors capable of handling approximately 60 cubic yards of soil were used. The residuals of the process were further treated through land application [3, p. 4]. Field application of the slurry bio-degradation system designed by ECOVA to treat PCP-contaminated wastes has resulted in a 99-percent decrease in PCP concentrations (both in solid and aqueous phase) over a period of 24 days [3, p. 5].

Performance data for Environmental Remediation, Inc. (ERI) is available for the treatment of American Petroleum Institute (API) separator sludge and wood-processing wastes. Two lagoons containing an olefin sludge from an API separator were treated. In one lagoon, containing, 4,000 cubic yards of sludge, a degradation time of 21 days was required to achieve 68 percent volume reduction and 62 percent mass oil and grease reduction at an operating temperature of 18°C. In the second lagoon, containing 2,590 cubic yards of sludge, a treatment time of 61 days was required to achieve 61 percent sludge reduction and 87.3 percent mass oil and grease reduction at an operating temperature of 14°C [1, p. 367].

At another site, the total wood-preserving constituents were reduced to less than 50 ppm. Each batch process was

Figure 2
Pilot Scale Results on Oil Refinery Sludges



carried out with a residence time of 28 days in 24-foot-diameter, 20-foot-height tank reactors handling 40 cubic yards per batch [6]. The mean concentrations of K001 constituents before treatment and the corresponding concentrations after treatment, for both settled solids and supernatant, are provided in Table 6 [2, p. 11]. The supernatant was discharged to a local, publicly owned wastewater treatment works.

RCRA Land Disposal Restrictions (LDRs) that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements (ARARs) for CERCLA response actions. Slurry biodegradation can produce a treated waste that meets treatment levels set by BDAT, but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where slurry biodegradaton does not meet these levels, it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. EPA has made the treatability variance process available in order to ensure that LDRs do not unnecessarily restrict the use of alternative and innovative treatment technologies. Treatability variances may be justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS) [10] and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-07FS) [9]. Another approach could be to use other treatment techniques in series with slurry biodegradation to obtain desired treatment levels.

Technology Status

Biotrol, Inc. has a pilot-scale slurry bioreactor that consists of a feed storage tank, a reactor tank, and a dewatering system for the treated slurry. It was designed to treat the fine-particle slurry from its soil-washing system. Biotrol's process was included in the SITE program demonstration of its soil-washing system at the MacGillis and Gibbs wood-preserving site in New Brighton, Minnesota, during September and October of 1989. Performance data from the SITE demonstration are not currently available; the Demonstration and Applications Analysis Report is scheduled to be published in late1990.

Table 6
Results of Wood Preserving Waste Treatment

Wood Preserving Waste Constituents	Before treatment	After Treatment	
	In Soil (mg/kg)	In Settled Soil (mg/kg)	In Supernatant (mg/L)
2-Chlorophenol	1.89	<0.01	<0.01
Phenol	3.91	<0.01	<0.01
2,4-Dimethylphenol	7.73	<0.01	<0.01
2,4,6-Trichlorophenol	6.99	<0.01	<0.01
p-Chloro-m-cresol	118.62	<0.01	<0.01
Tetrachlorophenol	11.07	<0.02	<0.02
2,4-Dinitrophenol	4.77	<0.03	<0.03
Pentachlorophenol	420.59	3.1	<0.01
Naphthalene	1078.55	<0.01	0.04
Acenaphthylene	998.80	1.4	1.60
Phenanthrene + Anthracene	6832.07	3.8	3.00
Fluoranthene	1543.06	4.9	16.00
Chrysene + Benz(a)anthracene	519.32	1.4	8.20
Benzo(b)fluoranthene	519.32	<0.03	4.50
Benzo(a)pyrene	82.96	0.1	2.50
Indeno(1,2,3-cd)pyrene + Dibenz(a,h)anthracene	84.88	0.5	1.70
Carbazole	135.40	<0.05	1.70

[Source: Environmental Solutions, Inc.]

ECOVA Corporation has a full-scale mobile slurry biodegradation system. This system was demonstrated in the field on soils contaminated with pesticides and PCP. ECOVA has developed an innovative treatment approach that utilizes contaminated ground water on site as the make up water to prepare the slurry for the bioreactor.

ERI has developed a full-scale slurry biodegradation system. ERI's slurry biodegradation system was used to reduce sludge volumes and oil and grease content in two wastewater treatment lagoons at a major refinery outside of Houston, Texas, and to treat 3,000 cubic yards of wood-preserving waste (creosote-K001) over a total cleanup time of 18 months.

Environmental Solutions, Inc. reportedly has a full-scale slurry biodegradation system, with a treatment capacity of up to 100,000 cubic yards, that has been used to treat petroleum and hydrocarbon sludges.

Groundwater Technology, Inc. reportedly has a full-scale slurry biodegradation system, which employs flotation, reactor, and clarifier/sedimentation tanks in series, that has been used to treat soils contaminated with heavy oils, PAHs, and light organics.

ReTeC's full-scale slurry biodegradation system was used in two major projects: Valdosta, Georgia, and Sweetwater, Tennessee. Both projects involved closure of RCRA-regulated surface impoundments containing soils and sludges contaminated with creosote constituents and PCP. Each project used in-ground, lined slurry-phase bioreactor cells operating at 100 cubic yards per week. Residues were chemically stabilized and further treated by tillage. For final closure, the impoundment areas and slurry-phase cells were capped with clay and a heavy-duty asphalt paving [5]. ReTeC has also performed several pilot-scale field demonstrations with their system on oil refinery sludges (RCRA K048-51).

One vendor estimates the cost of full-scale operation to be $80 to $150 per cubic yard of soil or sludge, depending on the initial concentration and treatment volume. The cost to use slurry biodegradation will vary depending upon the need for additional pre- and post-treatment and the addition of air emission control equipment.

EPA Contact

Technology-specific questions regarding slurry biodegradation may be directed to:

Dr. Ronald Lewis
U.S. EPA Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
Telephone: FTS 684-7856 or (513) 569-7856.

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Soil Bioremediation

(Naturally Aerated Processes)

Port Hueneme, CA 93043 **NEESA Document No. 20.2–051.3** **June 1992**

Introduction

Bioremediation is an innovative technology being considered more frequently, and more positively, for the remediation of soil contaminated with organic compounds. The main advantages of soil bioremediation are that it can be done on site (possibly avoiding land disposal restrictions) at relatively low cost and involves destruction of contaminants without transferring them to another media.

While many points discussed will be applicable to soil bioremediation in general, this Tech Data Sheet focuses on treatment of soil in the vadose zone (the unsaturated soil above the water table) by solid phase processes (in contrast to the use of liquid phase slurries) using natural aeration. Processes using forced aeration (mechanically pumping air through the soil as in heap piles and bioventing) will be covered in a separate Tech Data Sheet titled "Heap Pile Bioremediation."

Purpose and Audience

Tech Data Sheets are designed to:

- Disseminate practical, implementation-related information to minimize design and construction problems;
- Help Remedial Project Managers (RPMs) to evaluate a technology (one recommended in a Feasibility Study [FS], for example) and decide if it is practical and cost-effective;
- Aid RPMs in writing a Remedial Action (RA) Delivery Order;
- Help Engineering Field Division (EFD) Remedial Design personnel to write a Statement of Work (SOW) for, and RPMs to review, Remedial Design Plans; and
- Enable field personnel such as Project Superintendents, Engineers in Charge, On-Scene Coordinators (OSCs), and Resident Officers in Charge of Construction (ROICCs) to become familiar with a technology at a site they will be overseeing.

Description of Technology

Bioremediation uses microorganisms—typically, naturally occurring bacteria, fungi, and/or actinomycetes (metabolically advanced microorganisms)—to degrade and, desirably, detoxify contaminants. This degradation is the breaking down of contaminants into simpler compounds that may or may not be less toxic. These simpler intermediate compounds may themselves be degraded. If the process leaves only carbon dioxide and water as end products, degradation is complete, and mineralization is said to have occurred.

Aboveground bioremediation is an aerobic process. That is, the microorganisms need oxygen to live and metabolize contaminants. In contrast, anaerobic microorganisms propagate in the absence of oxygen.

There are two basic approaches to naturally aerated soil bioremediation: landfarming and prepared beds. With natural aeration, oxygen consumed by bacterial respiration can be replaced only by diffusion of air through the soil. This means both approaches operate on thin layers of soil (about one-foot thick).

Landfarming is defined in this Tech Data Sheet as the tilling and cultivating of soil in place (i.e., without excavation) to enhance the biodegradation of hydrocarbon compounds. Since most degradation takes place in the aerobic zone of soil, landfarming can be used only in cases of shallow, widespread contamination, where no downward migration into ground water can be expected. Landfarming historically has involved the application of liquid hydrocarbon sludges from refineries to initially uncontaminated land and plowing to mix the sludge into the soil. After a certain degree of degradation has occurred, more sludge is applied.

Using lined landfarming treatment beds known as "prepared beds" or "treatment cells" is the most common form of soil bioremediation because: 1) most contamination is too deep for a plowing device to reach; and 2) placing the soil on a liner guards against the spread of contamination. Soil is excavated and spread above ground on specially prepared beds, usually at the site in order to minimize the cost of transporting hazardous waste and to avoid triggering Land

Disposal Restrictions (LDRs) (see **Regulatory Issues**). The sites are designed to prevent the migration of contaminants to ground or surface water. They are surrounded by berms to control runoff and may be lined with clay or polymeric liners. Ancillary features may include systems for leachate collection/treatment and systems for water, nutrient, enzyme, and cultured bacteria delivery.

Soil conditions are often controlled to optimize the rate of contaminant degradation. Conditions normally controlled include:

- Moisture content (usually by irrigation or spraying);
- Oxygen level (by mixing the soil via tilling, etc.);
- Nutrients, primarily nitrogen and phosphorus (by fertilizing);
- pH (increased slightly by adding lime); and
- Soil clumping (by adding soil amendments and by mixing via tilling, etc.).

In landfarming and prepared beds, mixing of the soil and contaminant is important. Mixing aerates the soil while evenly distributing concentrations of soil, contaminant, moisture, nutrients, oxygen, and bacteria. It also maximizes the surface area of soil and contaminant available to the bacteria.

Standard agricultural practices and equipment are often used in both landfarming and prepared beds. Disk harrows, tillers, and other plowing devices are used for mixing, and normal fertilizing implements are often used to add nutrients and for liming.

Technology Status

Naturally aerated soil bioremediation is one of the best-established and most cost-effective methods for treating soil contaminated with petroleum hydrocarbons. As of November 1990, the Environmental Protection Agency (EPA) had identified approximately 32 sites where soil bioremediation projects are either under consideration or are operational (1). Most of the sites involve bioremediation of nonvolatile, heavier petroleum hydrocarbons and polynuclear aromatic hydrocarbons (PAHs).

Landfarming involving sludge spreading has been practiced near refineries for more than 30 years, and prepared beds have been used for about 10 years (2). While the agricultural practices involved are conventional, bioremediation technology continues to evolve with respect to:

- Optimization of degradation rate and degree;
- Identification of intermediate products; and
- Combination with other processes such as soil venting.

Types of Applications

The most common applications of landfarming and prepared beds have been remediating soils contaminated by low-volatility petroleum products released from leaking underground storage tanks, spills, or past disposal practices (e.g., leaking drums).

Types of Contaminants

Soil bioremediation has been proven most successful in treating petroleum hydrocarbons. Since lighter, more volatile hydrocarbons such as gasoline are treated very successfully by processes that utilize their volatility (i.e., soil vapor [vacuum] extraction and bioventing), use of aboveground bioremediation is usually limited to heavier hydrocarbons—and products and wastes that include them. As a rule of thumb, the higher the molecular weight (and the more rings with a PAH), the slower the degradation rate. Also, the more chlorinated or nitrated the compound, the more difficult it is to degrade. (Note: Many mixed products and wastes include some volatile components that transfer to the atmosphere before they can be degraded.)

Contaminants that have been successfully treated include diesel fuel, #2 and #6 fuel oils, JP-5, oily sludge, wood-preserving wastes (creosote), coke wastes, and certain pesticides (3,4,5).

Despite demonstrated effectiveness with many compounds, there are too many site-specific considerations to extrapolate success in degrading a given compound from one site to another. Consequently, treatability studies must be conducted using a site's particular contaminant and soil characteristics.

Advantages

Natural aeration bioremediation in general has several advantages:

- It is easy to implement (since it uses conventional agricultural practices and equipment);
- The cost is low relative to other alternatives (such as incineration);
- Contaminants are not transferred to another media (so there is nothing else to treat);
- It is permanent (in that contaminants may be completely degraded to nontoxic gases and water); and
- It may not trigger LDRs—being *in situ*, landfarming definitely does not—but whether the use of on-site prepared beds does may be subject to interpretation.

Landfarming has the additional advantages of not requiring the expense of liners and leachate collection/treatment. Only rainfall run-off control is used.

The leachate collection/treatment systems, run-off collection/treatment systems, and liners (optional) used with prepared beds allow complete control of contaminant migration in a liquid phase. If necessary, volatile components can be controlled by enclosing the beds.

Disadvantages

Natural aeration bioremediation in general has several disadvantages:

- Technology is in the innovative stage for contaminants other than petroleum hydrocarbons (the process is still evolving; the exact cost to remediate a given compound is not known because of site variability, and results cannot be guaranteed);
- Treatment of some compounds, such as PAHs of four or more rings and chlorinated compounds like polychlorinated biphenyls (PCBs), is too slow to be practical (high molecular weight compounds, such as creosote, degrade slowly);
- Treatment may be long-term (some compounds may take months to degrade);
- Site conditions can make treatment impractical (e.g., biodegradation can be very slow in cold climates or during winter in northern latitudes); and
- Toxic intermediate compounds may be end products, although this is more likely with anaerobic than aerobic biodegradation.

Limiting Factors

The key to biodegradation at high rates is providing an environment that initially supports exponential growth of contaminant-degrading bacteria and then maintains that population. The main factors that affect achieving such an environment are presented in Figure 1. This figure also illustrates some of the considerations involved in rating the applicability of landfarming or prepared beds to a given site.

Interface with Other Technologies

At many sites, contamination goes below the water table. At these sites, some form of ground-water remediation technology may be integrated with soil bioremediation. Such ground-water treatment technologies may include pump and treat (where ground water is pumped to the surface and treated) or *in situ* biological treatment. When ground water is treated, remediation of the soil may be required, because contaminants held by the soil may recontaminate the ground water.

Design Criteria

The following activities are often done before preparing full-scale design plans and specifications:

- Site and contaminant characterization;
- Laboratory and field treatability studies; and
- Pilot testing and/or field demonstration.

Component	Factor	Potential Limitations
Contaminant	Biodegradability	Contaminant must be biodegradable at an acceptable rate
	Volatility	Volatile components are removed by volatilization rather than biodegradation; air quality regulations may restrict use of naturally aerated bioremediation
	Toxicity	Contaminant must be present in (or diluted to) a concentration not toxic to the degradation organisms
Soil	Physical characteristics	Presence of rock or debris may impact the use of agricultural equipment; clumping may limit exposed surface area and thus degradation
	Moisture content	Excessive water limits diffusion of oxygen
	Clay content	High clay content may affect physical characteristics and thus affect moisture control and exposed surface area
	Organic content	Low organic-material content may limit growth of degrading bacteria, but high content may cause bacteria to utilize that instead of the contaminant
Site	pH	Bacteria have an optimum range; pH may require adjustment
	Hydrological features	A high water table may dictate ground-water protection controls
	Geological features	Landfarming may be physically impeded
	Climate	Rainy climate may dictate special rainfall runoff and soil drainage controls; colder climates slow degradation and may prevent agricultural operations

Figure 1. Limiting Factors

Source: Arthur D. Little, Inc., and NEESA

Contaminant Considerations

- Types and concentrations of contaminants
- Depth, profile, and distribution of contaminants
- Presence of toxic contaminants
- Presence of volatile organic compounds (VOCs)
- Presence of inorganic contaminants (e.g., metals)

Site Considerations

- Surface geological features (e.g., topography, vegetative cover)
- Subsurface geological and hydrogeological features
- Temperature
- Precipitation
- Wind velocity and direction
- Water availability
- Surface water features

Soil Considerations

- Type and texture
- Moisture content
- Organic matter content
- Cation exchange capacity
- Water-holding capacity
- Nutrient content
- pH
- Temperature
- Electrical conductivity
- Permeability
- Microorganisms (degradative populations present at site)
- Soil respirometry (field and/or laboratory)

Source: Reference 7 and Arthur D. Little, Inc.

Figure 2. Site and Contaminant Characterization Parameters

Typical parameters to be considered in site and contaminant characterizations are shown in Figure 2. These characterizations are conducted to:

- Identify and quantify contaminants;
- Determine the level of productive microbial activity in the soil; and
- Identify factors that will affect biodegradability.

Laboratory studies are conducted to determine the biodegradability of the contaminant(s) in the type of soil at the site. In addition, results of these studies will be used to optimize process design and operating parameters.

Pilot tests and field demonstrations can be expensive and may not be necessary. For sites contaminated with materials that have been repeatedly proven treatable, experienced contractors are able to scale up for full-scale design based on laboratory study results (5). However, pilot and demonstration tests may be necessary if a site is complicated or there are many unknowns.

Design criteria for full-scale soil bioremediation will address elements including:

- Rate of degradation (or time required for treatment);
- Pretreatment requirements (dewatering, pH adjustment, soil screening);
- Soil moisture control;
- Aeration of soil (method and frequency of tilling or plowing);
- Requirements for monitoring and adjustment of pH during treatment operations;
- Addition of nutrients (type, quantity, frequency);
- Requirements for bioaugmentation (addition of microorganisms); and
- Requirements for support systems such as run-off control, liners, and leachate collection and treatment.

In addition, design criteria will address all the specifications, construction, and necessary installation procedures. Design criteria for prepared beds will address treatment bed size, bed slope, orientation, berm height, and installation procedures for liners.

Field Implementation Considerations

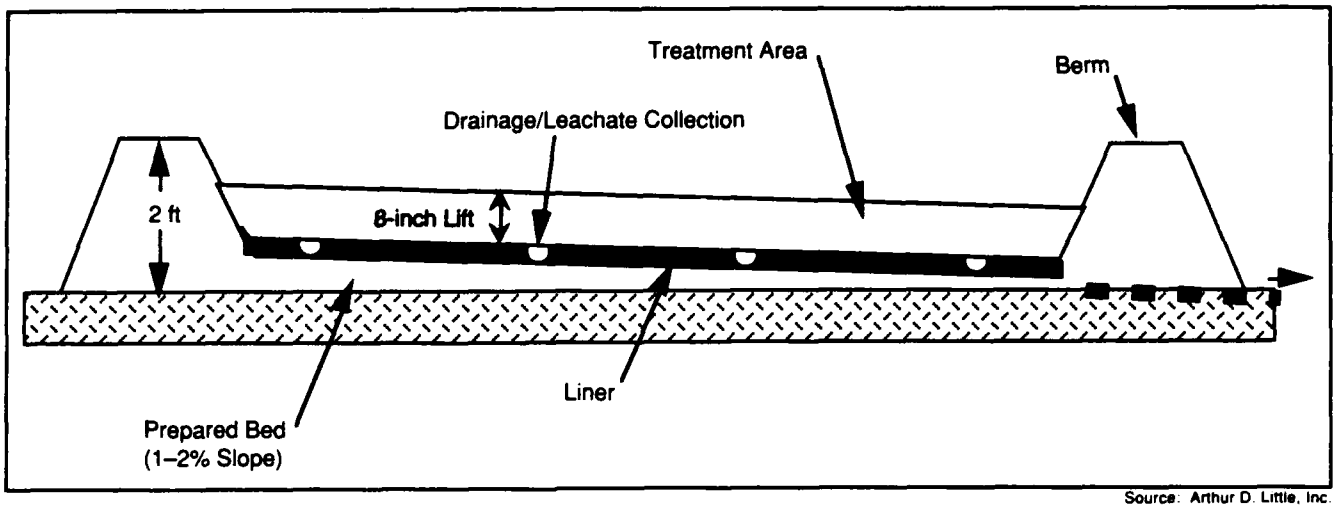
Field activities are much simpler in landfarming processes than in prepared bed processes. The following discussion primarily addresses the use of prepared beds while recognizing that some of the activities are common to landfarming.

Figure 3 shows a typical prepared bed. Actual dimensions can vary according to site conditions.

Typical prepared bed operations are conducted in cycles with successive lifts (or layers) of soil. As a general rule of thumb, a single treatment cycle of 1,000 cubic yards of soil can be conducted per acre, assuming a lift of approximately 8 inches (5).

Primary field activities of naturally aerated soil bioremediation include:

- Site preparation;
- Liner installation (prepared bed only);
- Excavation and screening of contaminated soil (prepared bed only);
- Material addition (e.g., nutrients, lime, amendments, additional microorganisms);
- Soil aeration; and
- Moisture control.



Source: Arthur D. Little, Inc.

Figure 3. Prepared Bed

For prepared beds, site preparation may include grading the site to provide adequate drainage for runoff and leachate collection. Typical bed slopes range from one to two percent. Berms are constructed to contain the contaminated soil. The height of the berm depends on the depth of the prepared bed, including foundation and liner, the depth of soil (or lift) to be treated, and potential rainfall amounts. Because of the costs and efforts associated with the construction of berms, their height is kept to a minimum while maintaining required controls. Typical berm heights may be 2 to 3 feet.

Liners are installed before placing the contaminated soil in prepared beds. Low-cost liners may be constructed of clay if locally available. Synthetic materials may also be used. Synthetic liners are placed over a prepared surface free of rocks and debris. Often, a layer of sand is placed over both clay and synthetic liners to protect the liners as well as accommodate leachate collection systems.

Methods used to excavate contaminated soil should be selected to minimize soil handling and time while maintaining worker safety. If large rocks or debris are present, the contaminated soil should be screened prior to placement. If multiple zones of contamination exist, the soil may be segregated according to contaminant type or concentration to optimize treatment. Usually, however, a uniform contaminant concentration is preferred.

Soil excavation may cause concern if VOCs are present. It has been observed that often soil excavation is responsible for the majority of VOC emissions during soil bioremediation (5). For this reason, if VOCs are present, air monitoring for worker protection should be performed during excavation.

Materials may be added to the soil to optimize the biodegradation processes. These materials may be added with power implements, tillers, and applicators (6). Types of added materials may include:

- Lime or acidifying materials for pH control;
- Nutrients;
- Soil amendments to improve soil quality; and
- Adapted, naturally occurring microorganisms (bioaugmentation).

A pH near neutral (pH 7) is usually desirable. As biodegradation occurs, acids may be generated that decrease pH. For this reason, pH should be monitored and controlled as necessary, usually by adding lime throughout the bioremediation.

Nutrients are added based on soil nutrient analyses. The most common nutrients required are nitrogen and phosphorus. Additional carbon sources may be required if the concentration of organic contaminants is insufficient to support an active microbial population or if treatability studies show improved degradation rates. A typical carbon-nitrogen-phosphorus ratio to be maintained is 100:10:2 (5). Nutrients are often supplied in the form of readily available agricultural fertilizers.

Amendments such as manures or plant materials (e.g., mulch) may be added to the soil to:

- Improve the soil structure;
- Enhance diffusion of oxygen;
- Provide for moisture control; and/or
- Stimulate microbial activity and populations (6).

Bioaugmentation with naturally occurring microorganisms is typically not required in most naturally aerated soil bioremediations (5,7,8). If bioaugmentation is required to achieve a desired rate or degree of biodegradation, the isolation and growth of acclimated microorganisms from the site (as opposed to the introduction of foreign microorganisms) is the most effective approach.

In naturally aerated bioremediations, tilling enhances oxygen diffusion into the soil. Available equipment and site and soil conditions will determine how and how often the soil should be tilled. Tilling frequency is generally dictated by soil type. The heavier or more claylike the soil, the more frequent the tilling. Sandier types of soil may require less frequent tilling. A weekly tilling frequency in soil of average texture is typical.

The depth of tilling is determined by the equipment used. Typical tractor/tiller combinations are operated to depths of approximately 8 inches.

Tilling operations may require special consideration due to:

- Increased susceptibility of the site to erosion;
- Increased potential for air emissions such as particulate (dust) and VOCs; and
- Compaction of wet, clayey soils.

Moisture is required to keep the microorganisms alive; however, too much moisture can saturate the soil and limit the diffusion of oxygen. Optimal moisture contents are typically 70 to 80 percent of the soil's water-holding capacity (5).

If local precipitation is insufficient to maintain proper soil moisture, irrigation may be necessary. Standard methods such as overhead or sprinkler irrigation are employed. Irrigation should be applied frequently in relatively small amounts to minimize the potential for leaching or to prevent saturation of the soil (6). In prepared beds, collected leachate may often be used to supplement irrigation.

If an overly high moisture content seems likely because of heavy rainfall, drainage systems should be built to remove excess water.

Naturally aerated soil bioremediation will generally be conducted during warmer weather periods. This limitation is due in part to a decrease in the rate of biodegradation as temperatures decrease, but also due to the physical operations involved. Usually, bioremediation operations will be initiated in the spring once the soil is dry enough and tilling or plowing is feasible. Field operations will usually be stopped at, or soon after, the first freeze when tilling becomes difficult or impossible.

If necessary, prepared beds can be covered with black plastic or mulches to insulate the bed, transmit heat in winter, and/or control moisture.

Quality Control

Regular monitoring of critical parameters during field operations will be required to provide for the most efficient operation. Among these parameters are:

- Nutrients (maintaining optimum levels of nutrients such as nitrogen and phosphorus);
- Soil pH (maintain within a 6.5 to 8.5 range);
- Soil moisture (maintain between 60 and 80 percent of moisture-holding capacity); and
- Oxygen (maintain at levels above which oxygen becomes a growth-limiting factor).

System performance can be rapidly assessed by measuring respiration rates. As organics degrade, oxygen is consumed and carbon dioxide is generated. Oxygen and carbon dioxide (respiration) measurements in soil gas from the site (compared to an adjacent, uncontaminated site) or through laboratory respirometric determinations can warn of potential problems beforehand or serve to determine aeration frequency. However, carbon dioxide may be converted to insoluble carbonates in alkaline soils (8).

Residuals Generated

Residuals generated during naturally aerated soil bioremediation should be minimal. Successful treatment should result in a product that can be maintained or replaced on site, with few contaminated residuals left to be transported off site.

Potential residuals that may result during soil bioremediation include:

- Liquid and solid residues resulting from personnel and equipment decontamination and cleaning; and
- Liquids accumulated as a result of leachate collection and/or run-off control.

Although the latter can be minimized if recycled during irrigation, there may be potential for this water to be contaminated. In most cases, management of these liquids (including treatment and disposal) will be a part of the action plan.

Regulatory Issues

A regulatory review should be the first step in planning the remedial action. Subsequent coordination with regulators is often accomplished through negotiations affecting various aspects of the remediation, including:

- Treatment criteria;
- Analytical methodology to be used;
- Monitoring requirements (during and after field operations);
- System design requirements;
- Management of water or treatment residues;
- Worker protection; and
- Site closure.

It is best that the most experienced personnel participate in regulatory negotiations to provide for the most practical and cost-effective remedial design.

The types of regulatory permits that may be required are site- and system-specific. In soil bioremediations involving leachate collection and run-off control, permits regarding the management of the collected liquids may be required. Air permits are often required for operations of any kind in environmentally sensitive areas (e.g., California).

At many U.S. Navy sites, selecting a site for soil bioremediation may be affected by on-site wetlands issues (9).

Because naturally aerated soil bioremediation is conducted on site, permitting under the Resource Conservation and Recovery Act (RCRA) is typically not required. However, parts of RCRA (such as LDRs) may apply as Applicable or Relevant and Appropriate Requirements (ARARs). Landfarming, since performed *in situ*, may not trigger LDRs. The applicability of LDRs to the use of on-site prepared beds may be subject to interpretation.

Specific regulatory coordination and documentation requirements will be affected by site-specific factors and local regulatory issues. Typically, an RPM should tell regulators what the proposed plan is. The RPM can then prepare a Corrective Action (or Remedial Action) Plan according to regulatory input. This plan, prepared after the final remedial design, will document what will be accomplished (7). Features of the plan may include:

- Description of process and procedures;
- Parameters to be measured and controlled;
- Sampling and analysis procedures and methodology;
- Quality assurance and quality control procedures to be employed;
- Treatment endpoint verification; and
- Post-treatment closure and monitoring requirements.

Feasibility Study (FS) Criteria Ranking

The use of naturally aerated soil bioremediation has been rated by remedial engineers with respect to certain performance and regulatory criteria. The results of this rating are presented in Figure 4. It should be noted that performance ratings may change with the contaminant being degraded.

Successful soil bioremediation will result in destruction or detoxification of contaminant(s) of concern. For this reason, long-term effectiveness and reduction of toxicity criteria are rated favorable.

Although relatively quick to implement, successful bioremediation may require months to achieve. As such, short-term effectiveness may be less favorable than other techniques such as incineration.

Experience has shown that naturally aerated soil bioremediation has the potential to be a lower-cost remedy for soil treatment.

Key Cost Factors

Costs associated with naturally aerated soil bioremediation include the costs of:

- Pretreatment tasks, including site characterization, treatability study, and pilot-scale testing or field demonstration (often optional for petroleum products); and

- Actual field implementation, including site and soil preparation, prepared bed construction, establishment and operation of rainfall runoff and leachate controls, irrigation, nutrient addition, pH control, sampling and analyses, and site cleanup and closure.

As with any RA, total costs are site- and application-specific. Costs often heavily depend on the time required to achieve specified treatment levels. Thus, the more concentrated the contaminant or the slower the rate of degradation, the longer and therefore more costly is the required treatment time. Other issues that may affect total cost include:

Criteria	Ranking
Effect of reducing the overall threat to human health and the environment	
Compliance with ARARs	
Long-term effectiveness and permanence	
Reduction of toxicity, mobility, or volume	
Short-term effectiveness	
Implementability	
Cost	
State and community acceptance	

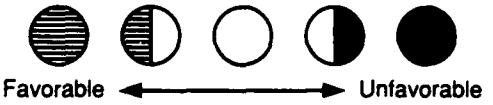


Figure 4. FS Criteria Ranking

- Excavation of contaminated soil;
- Liner use;
- Rainfall runoff and leachate treatment; and
- Additives needed for nutrient enhancement and pH control.

Ranges of costs likely to be encountered are:

- ***Costs prior to treatment (assumed to be independent of volume to be treated)***: $25,000 to $50,000 for laboratory studies; $100,000 to $500,000 for pilot tests or field demonstrations;

- ***Cost of landfarming (in situ treatment requiring no excavation of soil)***: $25 to $50 per cubic yard; and

- ***Cost of prepared bed (with liner)***: $100 to $200 per cubic yard.

Treatment costs are exclusive of sampling/analysis and monitoring costs.

Points to Remember

The following points to remember reflect issues identified by those experienced in bioremediation.

- √ Regulatory review and coordination should be initiated as soon as possible in the technology selection and planning process;
- √ Remedial personnel should enter into regulatory negotiations with specific goals and objectives in mind. They should be prepared to negotiate to develop realistic and practical criteria and operational requirements;
- √ Making use of contractors with experience and proven capabilities provides for the best assurance that success will be achieved with a minimum of unforeseen problems;
- √ If prepared bed treatment is to be used, site selection should be carefully considered with respect to space requirements, moisture control, and the potential impact of natural or cultural resources;
- √ Laboratory treatability studies are required in order to define the factors affecting biodegradation and to allow for necessary process optimization; and
- √ Site climate (particularly with respect to temperature) may dictate the timing of naturally aerated soil bioremediation.

Application Examples

Examples of recent applications of naturally aerated soil bioremediation actions are summarized in Figure 5. The first six examples were selected as representative of a variety of treatment conditions that may be encountered. Examples 7, 8, and 9 represent U.S. Navy applications. The U.S. Navy examples are described below in greater detail.

Example 1—Petroleum Products Terminal

Naturally aerated bioremediation was used in the cleanup of a decommissioned petroleum products terminal proposed for residential development. The first stage of the bioremediation was a thorough subsurface site characterization to define areas of mixed contamination and areas contaminated by a single product. Soils were then segregated by contaminant, and laboratory treatability studies were performed with each soil type to demonstrate applicability and optimize treatment parameters. In the full-scale remediation, soils were treated separately.

Example 2—Fuel Oil Spill

Soil contaminated as a result of a 20,000-gallon fuel oil spill was excavated and treated. The soil was a heavy clay, and amendments were required to improve the soil consistency for bioremediation.

Example 3—California Industrial Site

Naturally aerated bioremediation was conducted at a California industrial site contaminated with a variety of petroleum products, including waste oil, crude oil, and diesel fuel. Prior to treatment, the contaminated soil was excavated and screened to remove trash and debris. Because of different action levels established for refined and crude oil contaminants (100 and 1,000 ppm, respectively), the contaminated soil was segregated by contaminant for separate treatment.

Example 4—Creosote Waste Impoundments

Two creosote waste impoundments at a Superfund site in Minnesota were treated by naturally aerated bioremediation. These impoundments contained approximately 10,000 cubic yards of sludge and contaminated soils at an average concentration of 4,000 ppm of total PAHs. A three-acre lined facility was constructed and operated to treat these wastes. Cleanup levels were based on visual criteria; treatment was considered complete when the contaminated sludges and soils were no longer black and agglomerated. Corresponding analyses indicated that this occurred at levels of approximately 1,000 ppm of total PAHs.

Example 5—Pesticide Storage Facility

This example represents an application of naturally aerated bioremediation in which prepared beds were used to successfully reduce concentrations of pesticides to limits at or below regulatory cleanup guidelines.

Example 6—Contaminated Soil from Leaking Underground Storage Tanks (USTs)

Soil at a site in Marina del Rey, California, was contaminated with gasoline, diesel fuel, transmission fluid, lube oil, kerosene, and trichloroethylene. The "Safesoil Biotreatment System" was used by ENSITE, Inc., to remediate the site (10,11).

Since soil particles greater than 3 inches in diameter cannot be treated in this system, the contaminated soil is first screened to remove rocks and debris. The soil is then conveyed to a horizontal shaft ribbon blender, where it is mixed with various organic and inorganic nutrients, naturally occurring surfactants, soil conditioners, and water. Ten gallons of this additive/nutrient mix and five gallons of water are typically added per each cubic yard of soil. During the final mixing phase, air is injected and entrained in the soil matrix.

The mixed soil is placed into piles (roughly 3.5-ft square and 2.5-ft high) and left undisturbed while curing. Curing results in a honeycomblike structure through which air can passively diffuse. According to the vendor, a crust forms on the surface of the soil that prevents volatile contaminants from escaping but allows for natural infusion of air.

The "Safesoil Biotreatment System" is best suited for soil contaminated with an average of less than 2,000 ppm of Total Petroleum Hydrocarbons (TPH). At higher concentrations, especially where longer-chain, weathered petroleum residuals are present, the soil may have to be processed a second time. Indigenous, acclimated microorganisms capable of degrading the contaminants must be present.

Treatability studies are required to optimize process conditions for this system. Typically, ambient temperatures of greater than 75°F are optimal. No biodegradation will occur if ambient temperatures drop below 40°F or rise above 100°F (10).

Site	Amount Treated	Contaminants	Results	Comments	Ref.
1 Petroleum Products Terminal	100,000 yd^3	Petroleum hydrocarbons	TPH reduced from 1,000 ppm to 100 ppm. Treatment complete in 3 years of seasonal operation.	Soils segregated for treatment by contaminant type. 30-acre treatment area.	5
2 Fuel Oil Spill Site	4,000 yd^3	Fuel oil	TPH reduced from 4,000–6,000 ppm to less than 100 ppm in 120 on-site treatment days.	Clay soil required amendments to improve soil texture.	7
3 Industrial Dump Site	6,000 yd^3	Waste oil, diesel fuel, and crude oil	TPH reduced from 4,000 ppm to less than 100 ppm in 140 treatment days for one action level. TPH reduced from 2,000 ppm to less than 1,000 ppm in 100 treatment days for the other action level.	Soil screened prior to treatment to remove trash and debris. Two action levels established for different contaminants.	7
4 Creosote Waste Impoundments	10,000 yd^3	Creosote (PAHs)	TPAH reduced from 4,000 ppm to 1,000 ppm. Ongoing seasonal treatment operation.	Superfund site. Visual criteria established.	5
5 Pesticide Storage Facility	10,000 yd^3	Pesticides (2,4-D and MCPA)	Pesticide concentrations reduced from 86 ppm to 5 ppm in 5 months.	12-inch clay liner with drainage employed.	3
6 Leaking USTs	35,000 yd^3	Petroleum hydrocarbons	70% of soil reduced to <50 ppm TPH from 100–10,000 ppm in 14 days. Nine of 14 samples were nondetect for TPH and BTXE in less than 30 days.	California emission standards met. No further treatment required; soil backfilled on site. See text for further details.	10,11
7 Craney Island Fuel Terminal	20,000 yd^3	Petroleum hydrocarbons	Target is to reduce TRPH from 2,000–5,000 ppm to 1,000 ppm.	Planned remediation. See text for details.	9
8 Marine Corps Base Camp Pendleton	50 tons (pilot study) and 1,000 tons (spill cleanup)	Petroleum hydrocarbons	Pilot study reduced TPH from 34,000–51,000 ppm to 88 ppm. Spill cleanup action reduced TPH from about 34,000 ppm to nondetect.	Two applications at Camp Pendleton. See text for details.	12,13, 14
9 NCBC Port Hueneme	1,250 yd^3 - additional volumes from UST removal	Gasoline, diesel fuel, fuel oil, and waste oil	Target treatment levels not yet established; background TPH (100 ppm) levels assumed.	Planned remediation under U.S. Navy Remedial Action Contract. See text for details.	15,16, 17

TPH - Total Petroleum Hydrocarbons
TRPH - Total Recoverable Petroleum Hydrocarbons
TPAH - Total PAH
UST - Underground Storage Tanks

Figure 5. Application Examples (Summary)

Reported costs for mobilization, setup, excavation, treatment, backfill, compaction, and demobilization range from approximately $40/cubic yard for the treatment of 5,000 cubic yards to $60/cubic yard for the treatment of 1,000 cubic yards. Treatability study costs necessary for process optimization range from approximately $2,000 to $15,000 (10). All reported costs are exclusive of sampling and analytical costs.

Example 7—Craney Island Fuel Terminal

At Craney Island Fuel Terminal, soil has been contaminated with fuel oil and other petroleum hydrocarbons from tank bottom sludges and tank cleaning wastes over roughly the last 40 years. Thus, bacteria in the soil are well-acclimated and primed to degrade the petroleum compounds when supplied with air, water, and fertilizer. A risk assessment conducted using volatiles, semivolatiles, and metals data from a soil sample location with a TRPH (Total Recoverable Petroleum Hydrocarbon) level of 3,690 ppm yielded a conclusion of no significant risk to site workers. As a result, a safe cleanup level of 1,000 ppm TRPH was chosen. (Starting TRPH concentrations range from 2,000 to 5,000 ppm.) A Corrective Action Plan will be reviewed by the Virginia State Water Control Board once the remedial design is finalized.

Since 10 percent of the 23 acres of the tank construction site at Craney Island is classified as wetlands, and 0.4 acres of the wetlands area is located on the biocell treatment site, the U.S. Navy has applied for Wetlands Permits. The Army Corps of Engineers routes the permit applications through other environmental agencies for approval. These permits, which may be granted by June 1992, are needed before the contract can be advertised. Another hurdle has been a soil stabilization study that caused the design firm to question whether the soil on the treatment cell site is too soft to support construction equipment or the treatment cells. A preliminary examination of the soil

boring data showed that the soil can be stabilized. Using a geotextile will probably ensure stability. The question remaining is whether it will be too expensive to stabilize the soil versus downsizing the present biocell construction site.

The treatment cell will be about 16 acres. The base sand layer will be up to one-foot thick. Excess water will be collected by PVC pipe in a ditch and recycled. Optimistically, construction could begin in mid-October 1992, and the cells could be constructed by December 1992. Approximately 120 days of biodegradation would be needed to reduce the TPH level to below 1,000 ppm. Since the ambient temperature must be 50°F for efficient bioremediation to occur, the earliest the treatment could begin is mid-March 1993. After verification sampling and analysis of the soil in June, it could be backfilled (on site) in July 1993.

Example 8—Marine Corps Base Camp Pendleton

A pilot study was done under RCRA to demonstrate InPlant BioRemedial Services' prepared bed (or biocell) treatment process in March and April 1991 at Marine Corps Base Camp Pendleton, with 50 tons of petroleum-contaminated soil that had been stockpiled for about 90 days before remediation began (Example 7). Half the soil was contaminated with #2 heating fuel that had leaked into the ground; the other half was contaminated with diesel fuel, hydraulic oils, and glycols from sandy oil/water separator grit chamber waste, which was dewatered before it was stockpiled. Four samples were taken one foot below the surface of the stockpiled soil, which was divided into four quarters and analyzed for benzene, toluene, xylene (BTXE) and TPH. After treatment, the soil was again divided into four quarters and analyzed using EPA test 8015. Starting TPH concentrations ranged from 34,000 to 51,000 ppm.

A 60-foot by 120-foot prepared bed was constructed by placing hay bales as berms on the concrete slab of an old washrack facility. The slab's 1 percent downslope funneled any runoff into a drainage ditch connected to an oil/water separator. Visqueen® was used as a liner for the beds. A six-inch base layer of decomposed granite (a porous, sandy material) was placed on the Visqueen®. Next, 50 tons of the contaminated soil was placed in a 1.5-foot (approximately) layer on the decomposed granite. A surfactant was then sprayed on the soil to reduce air emissions. Bacteria had meanwhile been extracted from the contaminated soil and cultured in InPlant's lab. Using a 30-day treatment process, this cultured bacteria was sprayed onto the soil every other week. On successive days, a mixture of enzymes and nutrients was also applied biweekly. A "polyphasic suspension agent" was sprayed onto the soil five times, three to four days apart. The soil was rototilled using a 28-hp garden tractor after each product application and also once a week. On one day out of the 30-day period, it rained lightly and the treatment site was covered with Visqueen®. The average temperature during the period was about 63°F. Total TPH concentration was reduced to an average of 88 ppm TPH (which is below San Diego County's treatment level of 100 ppm) in 30 days, while all except toluene out of BTXE were reduced to "nondetect" (using EPA test 8020). After the 30 days, the soil was left in place (without treatment) an additional 60 days. Four additional samples were taken and analyzed using EPA test 8020. Toluene levels were reduced to nondetect in all samples. The treated soil was used as a final cover in the Box Canyon Landfill in San Diego. The total cost of treatment was $13,930: $250 per ton of contaminated soil and $1,430 for soil sampling.

In June 1991, about 10,000 gallons of #2 heating fuel leaked from an underground pipe near the Navy Regional Medical Center at Camp Pendleton. About 1,000 tons of soil was contaminated at an average of about 34,000 ppm. Because the contaminated soil was adjacent to a watershed, the San Diego County Department of Health Services and Regional Water Quality Control Board authorized the use of InPlant's prepared bed treatment to clean up the soil under emergency response guidelines. Camp Pendleton contracted InPlant under an emergency sole-source justification. The procedure used was the same as that described above, except the bed was lined with 20-mil polyethylene; rocks were screened from the soil and washed; the base layer consisted of only four inches of decomposed granite; the contaminated soil layer was 20- to 24-inches deep; bacteria and additives were applied with a 1,200-gallon water truck and pump; and the prepared bed, whose dimensions were 110 feet by 220 feet, was constructed on an asphalt parking lot. Thirty-two soil samples were taken immediately before remediation began and on the 30th day of treatment. All samples were analyzed for TPH, and two or three were analyzed for BTXE. Mainly because treatment conditions were optimized in the pilot study, all samples were reduced to nondetect for all analytes. The total cost of treatment, including analytical and design costs, was about $125 per cubic yard of contaminated soil.

Example 9—Naval Construction Battalion Center (NCBC) Port Hueneme

The U.S. Navy CLEAN (Comprehensive Long-Term Environmental Action, Navy) contractor will conduct a treatability study to determine how effective prepared bed biodegradation will be on contaminated soil from leaking USTs at the NCBC in Port Hueneme, California. The treatability study results will also support the establishment of target treatment levels. Primary soil contaminants are gasoline and diesel fuels.

Sixty to 70 USTs will be removed from July 1992 to August 1993. Construction of a 3.9-acre biocell (or prepared bed) with an asphalt slab base should be completed in August 1992. Although the Corrective Action Plan has not been finalized, it has been proposed that soil be sampled, excavated, and segregated into stockpiles in a staging area according to primary contaminant type (gasoline or diesel fuels). The stockpiles will be covered and monitored throughout the project.

Soil in which the primary contaminant is gasoline will first be aerated to remove volatile hydrocarbons. This volatilization step will be conducted by spreading the contaminated soil over the asphalt in layers one- to two-feet thick and disking the soil periodically. If resulting TPH levels indicate additional treatment is necessary, water and nutrients can then be added to stimulate biodegradation. A soil aeration permit from the local air pollution control district will be necessary for these activities if soils are contaminated with gasoline from 50 to 5,000 ppm. At concentrations above 5,000 ppm, volatilization is not allowed.

Diesel-contaminated soil will be placed on the asphalt and bioremediated by adding water and nutrients and disking.

Treatment of gasoline- and diesel-contaminated soils is expected to take place from January 1993 to September 1994. Treated soils will be backfilled in designated areas at NCBC Port Hueneme. If soils are found to be contaminated with inorganics such as lead, chromium IV, and other metals, they will be disposed of off site.

This remediation, classified as an UST removal action, will be funded under the Defense Environmental Restoration Account (DERA) and implemented by one of NEESA's Remedial Action Contractors (RACs).

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There are additional bibliographical references that pertain to naturally aerated bioremediation. For additional references, contact Mr. Hoeppel (see **Points of Contact**).

Points of Contact

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Superfund | EPA/540/2-91/022 | October 1991

EPA

Engineering Bulletin
Air Stripping of Aqueous Solutions

Purpose

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

Abstract

Air stripping is a means to transfer contaminants from aqueous solutions to air. Contaminants are not destroyed by air stripping but are physically separated from the aqueous solutions. Contaminant vapors are transferred into the air stream and, if necessary, can be treated by incineration, adsorption, or oxidation. Most frequently, contaminants are collected in carbon adsorption systems and then treated or destroyed in this concentrated form. The concentrated contaminants may be recovered, incinerated for waste heat recovery, or destroyed by other treatment technologies. Generally, air stripping is used as one in a series of unit operations and can reduce the overall cost for managing a particular site. Air stripping is applicable to volatile and semivolatile organic compounds. It is not applicable for treating metals and inorganic compounds.

During 1988, air stripping was one of the selected remedies at 30 Superfund sites [1]*. In 1989, it was a component of the selected remedy at 38 Superfund sites [2]. An estimated 1,000 air-stripping units are presently in operation at sites throughout the United States [3]. Packed-tower systems typically provide the best removal efficiencies, but other equipment configurations exist, including diffused-air basins, surface aerators, and cross-flow towers [4, p. 2] [5, p. 10-48]. In packed-tower systems, there is no clear technology leader by virtue of the type of equipment used or mode of operation. The final determination of the lowest cost alternative will be more site specific than process equipment dominated.

This bulletin provides information on the technology applicability, the technology limitations, a description of the technology, the types of residuals produced, site requirements, the latest performance data, the status of the technology, and sources of further information.

Technology Applicability

Air stripping has been demonstrated in treating water contaminated with volatile organic compounds (VOCs) and semivolatile compounds. Removal efficiencies of greater than 98 percent for VOCs and greater than or equal to 80 percent for semivolatile compounds have been achieved. The technology is not effective in treating low-volatility compounds, metals, or inorganics [6, p. 5-3]. Air stripping has commonly been used with pump-and-treat methods for treating contaminated groundwater.

This technology has been used primarily for the treatment of VOCs in dilute aqueous waste streams. Effluent liquid quality is highly dependent on the influent contaminant concentration. Air stripping at specific design and operating conditions will yield a fixed, compound-specific percentage removal. Therefore, high influent contaminant concentrations may result in effluent concentrations above discharge standards. Enhancements, such as high temperature or rotary air stripping, will allow less-volatile organics, such as ketones, to be treated [6, p. 5-3].

Table 1 shows the effectiveness of air stripping on general contaminant groups present in aqueous solution. Examples of constituents within contaminant groups are provided in Reference 7, "Technology Screening Guide for Treatment of CERCLA Soils and Sludges." This table is based on the current available information or professional judgment

* [reference number, page number]

Table 1
Effectiveness of Air Stripping on General Contaminant Groups from Water

	Contaminant Groups	Effectiveness
Organic	Halogenated volatiles	■
	Halogenated semivolatiles *	▼
	Nonhalogenated volatiles	■
	Nonhalogenated semivolatiles	❑
	PCBs	❑
	Pesticides	❑
	Dioxins/Furans	❑
	Organic cyanides	❑
	Organic corrosives	❑
Inorganic	Volatile metals	❑
	Nonvolatile metals	❑
	Asbestos	❑
	Radioactive materials	❑
	Inorganic corrosives	❑
	Inorganic cyanides	❑
Reactive	Oxidizers	❑
	Reducers	❑

■ Demonstrated Effectiveness: Successful treatability test at some scale completed
▼ Potential Effectiveness: Expert opinion that technology will work
❑ No Expected Effectiveness: Expert opinion that technology will not work
* Only some compounds in this category are candidates for air stripping.

where no information was available. The proven effectiveness of the technology for a particular site or contaminant does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability testing demonstrated the technology was effective for that particular contaminant group. The ratings of potential effectiveness and no expected effectiveness are both based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular contaminant group, a no-expected-effectiveness rating is given.

Limitations

Because air stripping of aqueous solutions is a means of mass transfer of contaminants from the liquid to the air stream, air pollution control devices are typically required to capture or destroy contaminants in the offgas [8]. Even when offgas treatment is required, air stripping usually provides significant advantages over alternatives such as direct carbon adsorption from water because the contaminants are more favorably sorbed onto activated carbon from air than from water. Moreover, contaminant destruction via catalytic oxidation or incineration may be feasible when applied to the offgas air stream.

Aqueous solutions with high turbidity or elevated levels of iron, manganese, or carbonate may reduce removal efficiencies due to scaling and the resultant channeling effects. Influent aqueous media with pHs greater than 11 or less than 5 may corrode system components and auxiliary equipment. The air stripper may also be subject to biological fouling. The aqueous solution being air stripped may need pretreatment to neutralize the liquid, control biological fouling, or prevent scaling [6][9].

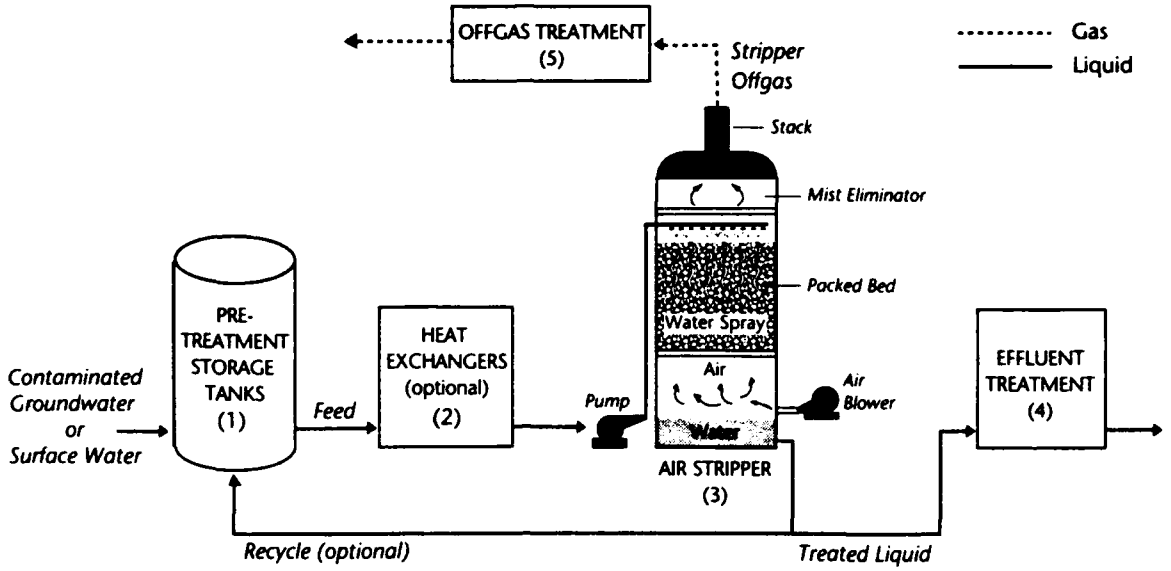
Contaminated water with VOC or semivolatile concentrations greater than 0.01 percent generally cannot be treated by air stripping. Even at lower influent concentrations, air stripping may not be able to achieve cleanup levels required at certain sites. For example, a 99 percent removal of trichloroethene (TCE) from groundwater containing 100 parts per million (ppm) would result in an effluent concentration of 1 ppm, well above drinking water standards. Without heating, only volatile organic contaminants with a dimensionless Henry's Law constant greater than 10^{-2} are amenable to continuous-flow air stripping in aqueous solutions [6][5]. In certain cases, where a high removal efficiency is not required, compounds with lower Henry's Law constants may be air stripped. Ashworth et al. published the Henry's Law constants for 45 chemicals [10, p. 25]. Nirmalakhandan and Speece published a method for predicting Henry's Law constants when published constants are unavailable [11]. Air strippers operated in a batch mode may be effective for treating water containing either high contaminant concentrations or contaminants with lower Henry's Law constants. However, batch systems are normally limited to relatively low average flow rates.

Several environmental impacts are associated with air stripping. Air emissions of volatile organics are produced and must be treated. The treated wastewater may need additional treatment to remove metals and nonvolatiles. Deposits, such as metal (e.g., iron) precipitates may occur, necessitating periodic cleaning of air-stripping towers [6, p. 5-5]. In cases where heavy metals are present and additional treatment will be required, it may be beneficial to precipitate those metals prior to air stripping.

Technology Description

Air stripping is a mass transfer process used to treat groundwater or surface water contaminated with volatile or semivolatile organic contaminants. At a given site, the system is designed based on the type of contaminant present, the contaminant concentration, the required effluent concentration, water temperature, and water flow rate. The major design variables are gas pressure drop, air-to-water ratio, and type of packing. Given those design variables, the gas and liquid loading (i.e., flows per cross-sectional area), tower diameter and packing height can be determined. Flexibility in the system design should allow for changes in contaminant concentration, air and water flow rates, and water temperature. Figure 1 is a schematic of a typical process for the air stripping of contaminated water.

Figure 1
Schematic Diagram of Air-Stripping System [8, p. 20][13, p. 43]



In an air-stripping process, the contaminated liquid is pumped from a groundwater or surface water source. Water to be processed is directed to a storage tank (1) along with any recycle from the air-stripping unit.

Air stripping is typically performed at ambient temperature. In some cases, the feed stream temperature is increased in a heat exchanger (2). Heating the influent liquid increases air-stripping efficiency and has been used to obtain a greater removal of semi-volatile organics such as ketones. At temperatures close to 100°C, steam stripping may be a more practical treatment technique [8, p. 3].

The feed stream (combination of the influent and recycle) is pumped to the air stripper (3). Three basic designs are used for air strippers: surface aeration, diffused-air systems, and specially designed liquid-gas contactors [4, p. 3]. The first two of these have limited application to the treatment of contaminated water due to their lower contaminant removal efficiency. In addition, air emissions from surface-aeration and diffused-air systems are frequently more difficult to capture and control. These two types of air strippers will not be discussed further. The air stripper in Figure 1 is an example of a liquid-gas contactor.

The most efficient type of liquid-gas contactor is the packed tower [4, p. 3]. Within the packed tower, structures called packing provide surface area on which the contaminated water can form a thin film and come in contact with a countercurrent flow of air. Air-to-water ratios may range from 10:1 to 300:1 on a volumetric basis [14, p. 8]. Selecting packing material that will maximize the wetted surface area will enhance air stripping. Packed towers are usually cylindrical and are filled with either random or structured packing. Random packing consists of pieces of packing dumped onto a support structure within the tower. Metal, plastic, or ceramic pieces come in standard sizes and a variety of shapes. Smaller packing sizes generally increase the interfacial area for stripping and improve the mass-transfer kinetics. However, smaller packing sizes result in an increased pressure drop of the air stream and an increased potential for precipitate fouling. Tripacks®, saddles, and slotted rings are the shapes most commonly used for commercial applications. Structured packing consists of trays fitted to the inner diameter of the tower and placed at designated points along the height of the tower. These trays are made of metal gauze, sheet metal, or plastic. The choice of which type of packing to use depends on budget and design constraints. Random packing is generally less expensive. However, structured packing reportedly provides advantages such as lower pressure-drop and better liquid distribution characteristics [4, p. 5].

The processed liquid from the air-stripper tower may contain trace amounts of contaminants. If required, this effluent is treated (4) with carbon adsorption or other appropriate treatments.

The offgas can be treated (5) using carbon adsorption, thermal incineration, or catalytic oxidation. Carbon adsorption is used more frequently than the other control technologies because of its ability to remove hydrocarbons cost-effectively from dilute (< 1 percent) air streams [8, p. 5].

Process Residuals

The primary process residual streams created with air-stripping systems are the offgas and liquid effluent. The offgas is released to the atmosphere after treatment; activated carbon is the treatment most frequently applied to the offgas stream. Where activated carbon is used, it is recommended that the relative humidity of the air stream be reduced. Once spent, the carbon can be regenerated onsite or shipped to the original supplier for reactivation. If spent carbon is replaced, it may have to be handled as a hazardous waste. Catalytic oxidation and thermal incineration also may be used for offgas treatment [15, p. 10] [8, p. 5]. Sludges, such as iron precipitates, build up

within the tower and must be removed periodically [6, p. 5-5]. Spent carbon can also result if carbon filters are used to treat effluent water from the air-stripper system. Effluent water containing nonvolatile contaminants may need additional treatment. Such liquids are treated onsite or stored and removed to an appropriate facility. Biological, chemical, activated carbon, or other appropriate treatment technologies may be used to treat the effluent liquid. Once satisfactorily treated, the water is sent to a sewage treatment facility, discharged to surface water, or returned to the source, such as an underground aquifer.

Site Requirements

Air strippers are most frequently permanent installations, although mobile systems may be available for limited use. Permanent installations may be fabricated onsite or may be shipped in modular form and constructed onsite. Packing is installed after fabrication or construction of the tower. A concrete pad will be required to support the air-stripper tower in either case. Access roads or compacted soil will be needed to transport the necessary materials.

Standard 440V, three-phase electrical service is needed. Water should be available at the site to periodically clean scale or deposits from packing materials. The quantity of water needed is site specific. Typically, treated effluent can be used to wash scale from packing.

Contaminated liquids are hazardous, and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures. Spent activated carbon may be hazardous and require similar handling. Storage may be needed to hold the treated liquid until it has been tested to determine its acceptability for disposal or release. Depending upon the site, a method to store liquid that has been pretreated may be necessary. Storage capacity will depend on liquid volume.

Onsite analytical equipment for conducting various analyses, including gas chromatography capable of determining site-specific organic compounds for performance assessment, make the operation more efficient and provide better information for process control.

Performance Data

System performance is measured by comparing contaminant concentrations in the untreated liquid with those in the treated liquid. Performance data on air-stripping systems, ranging from pilot-scale to full-scale operation, have been reported by several sources, including equipment vendors. Data obtained on air strippers at Superfund sites also are discussed below. The data are presented as originally reported in the referenced documents. The quality of this information has not been determined. The key operating and design variables are provided when they were available in the reference.

An air-stripping system, which employed liquid-phase GAC to polish the effluent, was installed at the Sydney Mine site in Valrico, Florida. The air-stripping tower was 4 feet in diameter, 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 (gpm) with a hydraulic loading rate of 12 gpm/ft² and a volumetric air-to-water ratio of approximately 200:1. The air-stripping tower was oversized for use at future treatment sites. Effluent water from the air stripper was polished in a carbon adsorption unit. Table 2 summarizes the performance data for the complete system; it is unclear how much removal was accomplished by the air stripper and how much by the activated carbon. Influent concentrations of total organics varied from approximately 25 parts per billion (ppb) to 700 ppb [13, p. 41].

Table 2
Performance Data for the Groundwater Treatment System at the Sydney Mine Site, FL [13, p. 42]

Contaminant	Concentration	
	Influent (µg/L)	Effluent (µg/L)
Volatile organics		
Benzene	11	ND*
Chlorobenzene	1	ND
1,1-dichloroethane	39	ND
Trans-1,2-dichloropropane	1	ND
Ethylbenzene	5	ND
Methylene chloride	503	ND
Toluene	10	ND
Trichlorofluoromethane	71	ND
Meta-xylene	3	ND
Ortho-xylene	2	ND
Extractable organics		
3-(1,1-dimethylethyl) phenol	32	ND
Pesticides		
2,4-D	4	ND
2,4,5-TP	1	ND
Inorganics		
Iron (mg/L)	11	< 0.03

*ND = Not detected at method detection limit of 1 µg/L for volatile organics and 10 µg/L for extractable organics and pesticides

Air stripping was used at well 12A in the city of Tacoma, Washington. Well 12A had a capacity of 3,500 gpm and was contaminated with chlorinated hydrocarbons, including 1,1,2,2-tetrachloroethane; trans-1,2-dichloroethene (DCE); TCE; and perchloroethylene. The total VOC concentration was approximately 100 ppb. Five towers were installed and began operation on July 15, 1983. Each tower was 12 feet in diameter and was packed with 1-inch polypropylene saddles to a depth of 20 feet. The water flow rate was 700 gpm for each tower, and the volumetric air-to-water ratio was 310:1. The towers consistently removed 94 to 98 percent of the influent 1,1,2,2-tetrachloroethane with an overall average of 95.5 percent removal. For the other contaminants, removal efficiencies in excess of 98 percent were achieved [16, p. 112].

Another remedial action site was Wurtsmith Air Force Base in Oscoda, Michigan. The contamination at this site was the result of a leaking underground storage tank near a mainte-

Table 3
Air-Stripper Performance Summary
At Wurtsmith AFB
[17, p. 121]

G/L (vol)	Water Flow (L/min)	Single Tower (% Removed)	Series Operation (% Removed)
10	1,135	95	99.8
10	1,700	94	99.8
10	2,270	86	96.0
18	1,135	98	99.9
18	1,700	97	99.9
18	2,270	90	99.7
25	1,135	98	99.9
25 *	1,700	98	99.9
25	2,270	98	99.9

Influent TCE concentration: 50-8,000 µg/L Water temperature: 283°K

nance facility. Two packed-tower air strippers were installed to remove TCE. Each tower was 5 feet in diameter and 30 feet tall, with 18 feet of 16mm pall ring packing. The performance summary for the towers, presented in Table 3, is based on evaluations conducted in May and August 1982 and January 1983. Excessive biological growth decreased performance and required repeated removal and cleaning of the packing. Operation of the towers in series, with a volumetric air-to-water ratio of 25:1 and a water flow of 600 gpm (2,270 L/min), removed 99.9 percent of the contaminant [17, p. 119].

A 2,500 gpm air stripper was used to treat contaminated groundwater during the initial remedial action at the Verona Well field site in Battle Creek, Michigan. This well field is the major source of public potable water for the city of Battle Creek. The air stripper was a 10-foot diameter tower packed to a height of 40 feet with 3.5 inch pall rings. The air stripper was operated at 2,000 gpm with a 20:1 volumetric air-to-water ratio. Initial problems with iron oxide precipitating on the packed rings were solved by recirculating sodium hypochlorite through the stripper about four times per year [8, p. 8-9]. The total VOC concentration of 131 ppb was reduced by approximately 82.9 percent [15, p. 56]. The air stripper offgas was treated via vapor phase granular activated carbon beds. The offgas was heated prior to entering the carbon beds to reduce its humidity to 40 percent.

An air stripper is currently operating at the Hyde Park Superfund site in New York. Treatek, Inc., which operates the unit, reports the system is treating about 80,000 gallons per day (gpd) of landfill leachate. The contaminants are in the range of 4,000 ppm total organic carbon (TOC). The air stripper is reportedly able to remove about 90 percent of the TOCs [18]. A report describing the performance of the air stripper is expected to be published during 1991.

The primary VOCs at the Des Moines Superfund site were TCE; 1,2-DCE; and vinyl chloride. The TCE initial concentration was approximately 2,800 ppb and gradually declined to the 800 to 1,000 ppb range after 5 months. Initial groundwater concentrations of 1,2-DCE were unreported while the concentration of vinyl chloride ranged from 38 ppb down to 1 ppb. The water flow rate to the air stripper ranged from 500 to 1,850 gpm and averaged approximately 1,300 gpm. No other design data were provided. TCE removal efficiencies were generally above 96 percent, while the removal efficiencies for 1,2-DCE were in the 85 to 96 percent range. No detectable levels of vinyl chloride were observed in the effluent water [12, p. B-1].

VOCs were detected in the Eau Claire municipal well field in Eau Claire, Wisconsin, as part of an EPA groundwater supply survey in 1981. An air stripper was placed on-line in 1987 to protect public health and welfare until completion of the remedial investigation/feasibility study (RI/FS) and final remedy selection. Data reported on the Eau Claire site were for the period beginning August 31, 1987 and ending February 15,1989. During this period, the average removal efficiency was greater than

Table 4
Air-Stripper Performance at
Eau Claire Municipal Well Field [12, p. C-1]

Contaminant	Influent Concentration (ppb)	Removal Efficiency (%)
1,1-Dichloroethene	0.17-2.78	88
1,1-Dichloroethane	0.38-1.81	93
1,1,1-Trichloroethane	4.32-14.99	99
Trichloroethene	2.53-11.18	98

88 percent for the four chlorinated organic compounds studied. The average removal efficiencies are shown in Table 4. The air stripper had a 12-foot diameter and was 60 feet tall, with a packed bed of 26 feet. Water feed rates were approximately 5 to 6 million gallons per day (mgd). No other design parameters were reported [12, p. C-1].

In March 1990, an EPA study reviewed the performance data from a number of Superfund sites, including the Brewster Well Field, Hicksville MEK Spill, Rockaway Township, Western Processing, and Gilson Road Sites [15].

Reported removal efficiencies at the Brewster Well Field site in New York were 98.50 percent, 93.33 percent, and 95.59 percent for tetrachloroethene (PCE); TCE; and 1,2-DCE; respectively. Initial concentrations of the three contaminants were 200 ppb (PCE), 30 ppb (TCE) and 38 ppb (1,2-DCE) [15, p. 55]. The 300 gpm air stripper had a tower diameter of 4.75 feet, packing height of 17.75 feet, air-to-water ratio of 50:1, and used 1-inch saddles for packing material [15, p. 24].

A removal efficiency of 98.41 percent was reported for methyl ethyl ketone (MEK) at the Hicksville MEK spill site in New York. The reported influent MEK concentration was 15 ppm. The air stripper had a 100 gpm flowrate, an air-to-water ratio of 120:1, a tower diameter of 3.6 feet, a packing height of 15 feet, and used 2-inch Jaeger Tripack packing material. Water entering the air stripper was heated to approximately 180° to195°F by heat exchangers [15, p. 38].

Table 5
Air Stripper Performance at Rockaway Township, NJ [15, p. 53]

Contaminant	Influent Concentration (ppb)	Removal Efficiency (%)
Trichloroethylene	28.3	99.99
Methyl-tert-butyl ether	3.2	99.99
1,1-Dichloroethylene	4.0	99.99
cis-1,2-Dichloroethylene	6.4	99.99
Chloroform	1.3	99.99
1,1,1-Trichloroethane	20.0	99.99
1,1-Dichloroethane	2.0	99.99
Total VOC	65.2	99.99

The Rockaway Township air stripper had a flowrate of 1,400 gpm, tower diameter of 9 feet, packing height of 25 feet, air-to-water ratio of 200:1, and used 3-inch Tellerettes packing material. The performance data are shown in Table 5 [15, p. 18].

The Western Processing site had two air-stripping towers treating different wells in parallel. The first tower had a 100 gpm (initial) and 200 gpm (maximum) flowrate, a tower diameter of 40 feet, a packing height of 40.5 feet, an air-to-water ratio of 160:1 (initial) and 100:1 (maximum), and used 2-inch Jaeger Tripack packing material. The second tower had a 45 gpm (initial) and 60 gpm (maximum) flowrate, a tower diameter of 2 feet, packing height of 22.5 feet, air-to-water ratio of 83.1:1 (initial) and 62.3:1 (maximum), and used 2-inch Jaeger Tripack packing material [15, p. 31]. The performance data are presented in Table 6.

Table 6
Air-Stripper Performance at Western Processing, WA [15, p. 61]

Contaminant	Influent Concentration (ppb)	Removal Efficiency (%)
Benzene	73	93.15
Carbon tetrachloride	5	—
Chloroform	781	99.36
1,2-Dichloroethane	22	77.27
1,1-Dichloroethylene	89	94.38
1,1,1-Trichloroethane	1,440	99.65
Trichloroethylene	8,220	99.94
Vinyl chloride	159	99.37
Dichloromethane	8,170	99.63
Tetrachloroethylene	378	98.68
Toluene	551	99.09
1,2-Dichlorobenzene	11	54.55
Hexachlorobutadiene	250	96.00
Hexachloroethane	250	96.00
Isobutanol	10	0.00
Methyl ethyl ketone	1,480	70.27

Table 7
Air-Stripper Performance at the Gilson Road Site, NH [15, p. 65]

Contaminant	Influent Concentration (ppb)	Average Removal Efficiency (%)
Isopropyl alcohol	532	95.30
Acetone	473	91.93
Toluene	14,884	99.87
Dichloromethane	236	93.79
1,1,1-Trichloroethane	1,340	99.45
Trichloroethylene	1,017	99.71
Chloroform	469	99.06
Total VOC	18,951	99.41

The Gilson Road Site used a single column high-temperature air stripper (HTAS) which had a 300 gpm flowrate (heated influent), tower diameter of 4 feet, packing height of 16 feet, air-to-water ratio of 51.4:1, and used 16 Koch-type trays at 1-foot intervals [15, p. 42-45]. The performance data are provided in Table 7. Due to the relatively high influent concentration and the high (average) removal efficiency, this system required supplemental control of the volatiles in the offgas.

Another EPA study, completed in August 1987, analyzed performance data from 177 air-stripping systems in the United States. The study presented data on systems design, contaminant types, and loading rates, and reported removal efficiencies for 52 sites. Table 8 summarizes data from 46 of those sites, illustrating experiences with a wide range of contaminants [19]. Reported efficiencies should be interpreted with caution. Low efficiencies reported in some instances may not reflect the true potential of air stripping, but may instead reflect designs intended to achieve only modest removals from low-level contaminant sources. It is also important to recognize that, because different system designs were used for these sites, the results are not directly comparable from site to site.

Technology Status

Air stripping is a well-developed technology with wide application. During 1988, air stripping of aqueous solutions was a part of the selected remedy at 30 Superfund sites [1]. In 1989, air stripping was a part of the selected remedy at 38 Superfund Sites [2].

The factors determining the cost of an air stripper can be categorized as those affecting design, emission controls, and operation and maintenance (O&M). Design considerations such as the size and number of towers, the materials of construction, and the desired capacity influence the capital costs. Equipment cost components associated with a typical packed-tower air strip-

Table 8
Summary of Reported Air-Stripper Removal Efficiencies from 46 Sites [19]

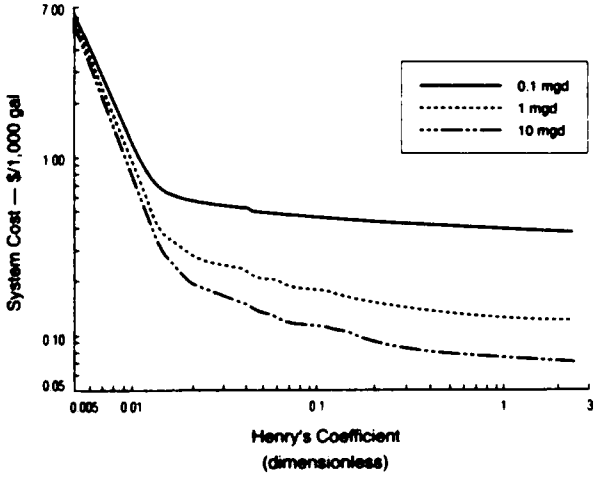
Contaminant	No. of Data Points	Influent Concentration (µg/L)		Reported Removal Efficiency[a] (%)	
		Average	Range	Average	Range
Aniline	1	226	NA[b]	58	NA
Benzene	3	3,730	200-10,000	99.6	99-100
Bromodichloromethane	1	36	NA	81	NA
Bromoform	1	8	NA	44	NA
Chloroform	1	530	1500	48	NA
Chlorobenzene	0	95	NA	ND[c]	ND
Dibromochloromethane	1	34	NA	60	NA
Dichloroethylene	7	409	2-3,000	98.6	96-100
Diisopropyl ether	2	35	20-50	97.0	95-99
Ethylbenzene	1	6,370	100-1,400	99.8	NA
Ethylene dichloride	7	173	5-1,000	99.3	79-100
Methylene chloride	1	15	9-20	100	NA
Methyl ethyl ketone	1	100	NA	99	NA
2-Methylphenol	1	160	NA	70	NA
Methyl tertiary butylether	2	90	50-130	97.0	95-99
Perchloroethylene	17	355	3-4,700	96.5	86-100
Phenol	1	198	NA	74	NA
1,1,2,2-Tetrachloroethane	1	300	NA	95	NA
Trichloroethane	8	81	5-300	95.4	70-100
Trichloroethylene	34	7,660	1-200,000	98.3	76-100
1,2,3-Trichloropropane	1	29,000	NA	99	NA
Toluene	2	6,710	30-23,000	98	96-100
Xylene	4	14,823	17-53,000	98.4	96-100
Volatile organic compounds	3	44,000	57-130,000	98.8	98-99.5
Total Volatile Organics	46	11,120	12-205,000	97.5	58.1-100

[a]Note that the averages and ranges presented in this column represent more data points than are presented in the second column of this table because the removal efficiencies were not available for all air strippers.

[b]NA = Not Applicable. Data available for only one stripper.

[c]ND = No Data. Insufficient data available.

Figure 2
Cost Estimates for Air Stripping without Air Emission Controls as a Function of the Henry's Law Coefficient



per include tower shell, packing support, water distributor, mist eliminator, packing, blower and motor, engineering, and contractor overhead and profit. The addition of an air treatment system roughly doubles the cost of an air-stripping system [3][6, p. 5-5]. Onsite regeneration or incineration of carbon may increase the cost associated with emission controls. The primary O&M cost components are operating labor, repair and upkeep, and energy requirements of blower motor and pumps [12].

Adams et al. made cost estimates based on flows from 0.1 to 10 mgd assuming a removal efficiency of 99 percent. The process was optimized for packed tower volume and energy consumption. Figure 2 presents general cost curves for three flow rates based on their work. Air emissions controls were not included in the costs. Within the range of Henry's Law Coefficients of 0.01 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 [20, p. 52].

According to Hydro Group, Inc., the cost of air stripping may range from $0.04 to $0.17 per 1,000 gallons [21, p. 7]. The Des Moines Superfund site unit cost for groundwater treatment is estimated to be about $0.45/1,000 gallons based on a 1,250 gpm treatment rate and an average O&M cost of $200,000/year for 10 years at 10 percent interest. The Eau Claire site had a unit cost of roughly $0.14/1,000 gallons assuming a 5-year operation period and an average treatment rate of 7 million gpd [12, p. C-6].

Recent developments in this technology include high-temperature air stripping (HTAS) and rotary air stripping. A full-scale HTAS system was demonstrated at McClellan AFB to treat groundwater contaminated with fuel and solvents from spills and storage tank leaks. The combined recycle and makeup was heated to 65°C, and a removal efficiency of greater than 99 percent was achieved [8, p. 9]. The rotary design, marketed under the name HIGEE, was demonstrated at a U.S. Coast Guard air station in East Bay Township, Michigan. At a gas-to-liquid ratio of 30:1 and a rotor speed of 435 rpm, removal efficiencies for all contaminants, except 1, 2-DCE, exceeded 99 percent. The removal efficiency for 1,2-DCE was not reported [4, p. 19].

Raising influent liquid temperature increases mass-transfer rates and the Henry's Law Constants. This results in improved removal efficiencies for VOCs and the capability to remove contaminants that are less volatile. Table 9 illustrates the influence that changes in liquid temperature have on contaminant removal efficiencies. Note that steam stripping may be the preferred treatment technology at a feed temperature approaching 100°C, because the higher temperatures associated with steam stripping allow organics to be removed more efficiently than in HTAS systems. However, steam stripping uses more fuel and therefore will have higher operating costs. Additionally, the capital costs for steam stripping may be higher than for HTAS if higher-grade construction materials are needed at the elevated temperatures used in steam stripping [8, p. 3].

Table 9
Influence of Feed Temperature on Removal of Water Soluble Compounds from Groundwater [8, p. 15]

Compound	*Percent Removed at Selected Temperature*		
	12°C	*35°C*	*73°C*
2 - Propanol	10	23	70
Acetone	35	80	95
Tetrahydrofuran	50	92	>99

Rotary air strippers use centrifugal force rather than gravity to drive aqueous solutions through the specially designed packing. This packing, consisting of thin sheets of metal wound together tightly, was developed for rotary air strippers because of the strain of high centrifugal forces. The use of centrifugal force reportedly results in high removal efficiencies due to formation of a very thin liquid film on wetted surfaces. The rotary motion also causes a high degree of turbulence in the gas phase. The turbulence results in improved liquid distribution over conventional gravity-driven air strippers. The biggest advantage of rotary strippers is the high capacity for a relatively small device. Disadvantages include the potential for mechanical failures and additional energy requirements for the drive motor. Water carryover into the air effluent stream may cause problems with certain emission control devices used to treat the contaminated air. Cost and performance data on rotary air strippers are very limited [4, p. 16].

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EPA

Engineering Bulletin
Granular Activated Carbon Treatment

Purpose

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

Abstract

Granular activated carbon (GAC) treatment is a physicochemical process that removes a wide variety of contaminants by adsorbing them from liquid and gas streams [1, p. 6-3]. This treatment is most commonly used to separate organic contaminants from water or air; however, it can be used to remove a limited number of inorganic contaminants [2, p. 5-17]. In most cases, the contaminants are collected in concentrated form on the GAC, and further treatment is required.

The contaminant (adsorbate) adsorbs to the surfaces of the microporous carbon granules until the GAC becomes exhausted. The GAC may then be either reactivated, regenerated, or discarded. The reactivation process destroys most contaminants. In some cases, spent GAC can be regenerated, typically using steam to desorb and collect concentrated contaminants for further treatment. If GAC is to be discarded, it may have to be handled as a hazardous waste.

Site-specific treatability studies are generally necessary to document the applicability and potential performance of a GAC system. This bulletin provides information on the technology applicability, technology limitations, a technology description, the types of residuals produced, site requirements, latest performance data, status of the technology, and sources for further information.

Technology Applicability

Adsorption by activated carbon has a long history of use as a treatment for municipal, industrial, and hazardous waste streams. The concepts, theory, and engineering aspects of the technology are well developed [3]. It is a proven technology with documented performance data. GAC is a relatively nonspecific adsorbent and is effective for removing many organic and some inorganic contaminants from liquid and gaseous streams [4].

The effectiveness of GAC as an adsorbent for general contaminant groups is shown in Table 1. Examples of constituents within contaminant groups are provided in "Technology Screening Guide for Treatment of CERCLA Soils and Sludges" [5]. This table is based on current available information or professional judgment when no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability was tested to show that, for that particular contaminant and matrix, the technology was effective. The ratings of potential effectiveness and no expected effectiveness are based upon expert judgement. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given.

The effectiveness of GAC is related to the chemical composition and molecular structure of the contaminant. Or-

* [reference number, page number]

Table 1
Effectiveness of Granular Activated Carbon on General Contaminant Groups

	Contaminant Groups	Liquid /Gas
Organic	Halogenated volatiles	■
	Halogenated semivolatiles	■
	Nonhalogenated volatiles[a]	■
	Nonhalogenated semivolatiles	■
	PCBs	■
	Pesticides	■
	Dioxins/Furans	■
	Organic cyanides [a]	▼
	Organic corrosives [a]	■
Inorganic	Volatile metals[a]	■
	Nonvolatile metals [a]	■
	Asbestos	❑
	Radioactive materials [a]	■
	Inorganic corrosives	❑
	Inorganic cyanides [b]	■
Reactive	Oxidizers[b]	■
	Reducers	❑

■ Demonstrated Effectiveness: Successful treatability test at some scale completed

▼ Potential Effectiveness: Expert opinion that technology will work.

❑ No Expected Effectiveness: Expert opinion that technology will not work

[a] Technology is effective for some contaminants in the group; it may not be effective for others.

[b] Applications to these contaminants involve both adsorption and chemical reaction.

ganic wastes that can be treated by GAC include compounds with high molecular weights and boiling points and low solubility and polarity [6]. Organic compounds treatable by GAC are listed in Table 2. GAC has also been used to remove low concentrations of certain types of inorganics and metals; however, it is not widely used for this application [1, p. 6-13].

Almost all organic compounds can be adsorbed onto GAC to some degree [2, p. 5-17]. The process is frequently used when the chemical composition of the stream is not fully analyzed [1, p. 6-3]. Because of its wide-scale use, GAC has probably been inappropriately selected when an alternative technology may have been more effective [7]. GAC can be used in conjunction with other treatment technologies. For example, GAC can be used to remove contaminants from the offgas from air stripper and soil vapor extraction operations [7] [8, p. 73] [9].

Table 2
Organic Compounds Amenable to Adsorption by GAC [1]

Class	Example
Aromatic solvents	Benzene, toluene, xylene
Polynuclear aromatics	Naphthalene, biphenyl
Chlorinated aromatics	Chlorobenzene, PCBs, endrin, toxaphene, DDT
Phenolics	Phenol, cresol, resorcinol, nitrophenols, chlorophenols, alkyl phenols
Aromatic amines and high molecular weight aliphatic amines	Aniline, toluene diamine
Surfactants	Alkyl benzene sulfonates
Soluble organic dyes	Methylene blue, textile dyes
Fuels	Gasoline, kerosene, oil
Chlorinated solvents	Carbon tetrachloride, perchloroethylene
Aliphatic and aromatic acids	Tar acids, benzoic acids
Pesticides/herbicides	2,4-D, atrazine, simazine, aldicarb, alachlor, carbofuran

Limitations

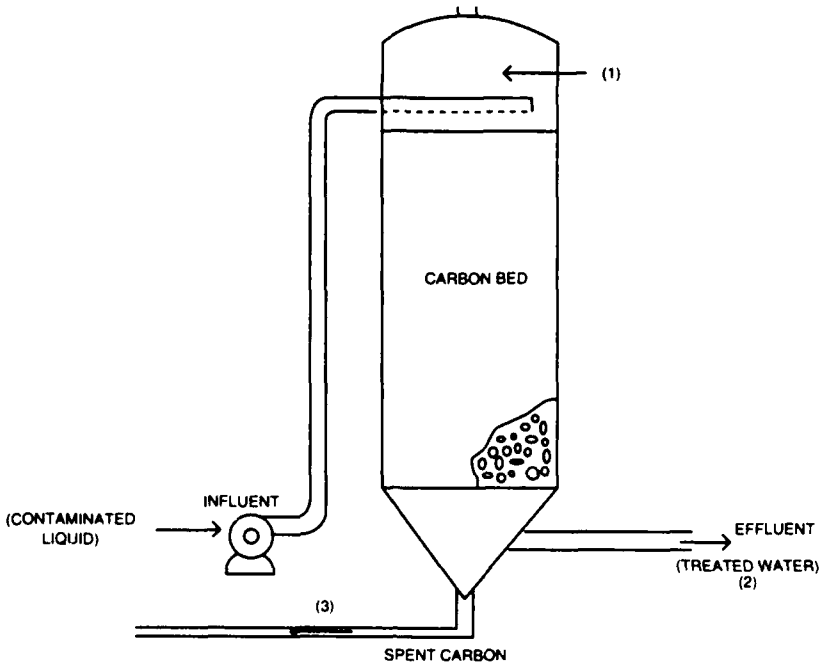
Compounds that have low molecular weight and high polarity are not recommended for GAC treatment. Streams with high suspended solids (≥ 50 mg/L) and oil and grease (≥ 10 mg/L) may cause fouling of the carbon and require frequent backwashing. In such cases, pretreatment prior to GAC, is generally required. High levels of organic matter (e.g., 1,000 mg/L) may result in rapid exhaustion of the carbon. Even lower levels of background organic matter (e.g., 10-100 mg/L) such as fulvic and humic acids may cause interferences in the adsorption of specifically targeted organic contaminants which are present in lower concentrations. In such cases, GAC may be most effectively employed as a polishing step in conjunction with other treatments.

The amount of carbon required, regeneration/reactivation frequency, and the potential need to handle the discarded GAC as a hazardous waste are among the important economic considerations. Compounds not well adsorbed often require large quantities of GAC, and this will increase the costs. In some cases the spent GAC may be a hazardous waste, which can significantly add to the cost of treatment.

Technology Description

Carbon is an excellent adsorbent because of its large surface area, which can range from 500-2000 m^2/g, and because its diverse surfaces are highly attractive to many different types of contaminants [3]. To maximize the amount of surface available

Figure 1. Schematic Diagram of Fixed-Bed GAC System



for adsorption, an activation process which increases the surface-to-volume ratio of the carbon is used to produce an extensive network of internal pores. In this process, carbonaceous materials are converted to mixtures of gas, tars, and ash. The tar is then burned off and the gases are allowed to escape to produce a series of internal micropores [1, p. 6-6]. Additional processing of the GAC may be used to render it more suitable for certain applications (e.g. impregnation for mercury or sulfur removal).

The process of adsorption takes place in three steps [3]. First the contaminant migrates to the external surface of the GAC granules. It then diffuses into the GAC pore structure. Finally, a physical or chemical bond forms between the contaminant and the internal carbon surface.

The two most common reactor configurations for GAC adsorption systems are the fixed bed and the pulsed or moving bed [3]. The fixed-bed configuration is the most widely used for adsorption from liquids, particularly for low to moderate concentrations of contaminants. GAC treatment of contaminated gas streams is done almost exclusively in fixed-bed reactors. The following technical discussion applies to both gas and liquid streams.

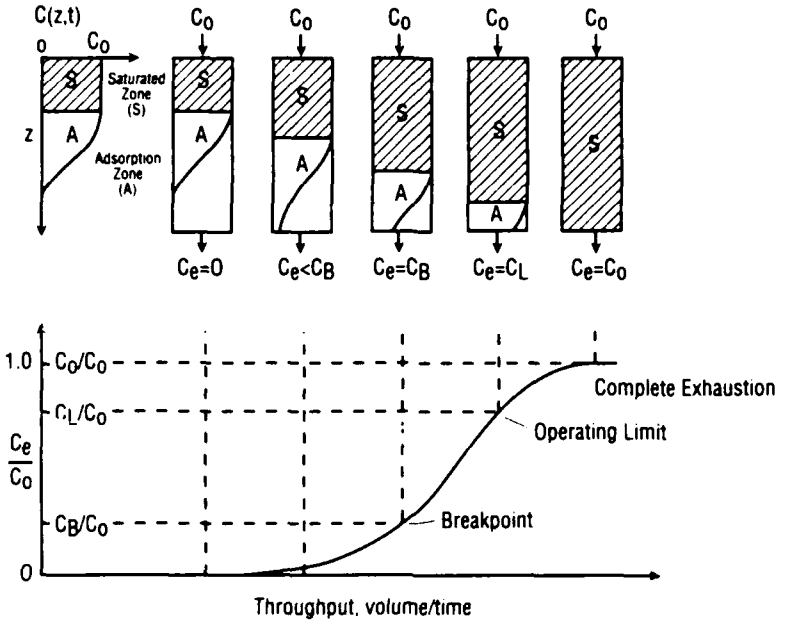
Figure 1 is a schematic diagram of a typical single-stage, fixed-bed GAC system for use on a liquid stream. The contaminant stream enters the top of the column (1). As the waste stream flows through the column, the contaminants are adsorbed. The treated stream (effluent) exits out the bottom (2). Spent carbon is reactivated, regenerated, or replaced once the effluent no longer meets the treatment objective (3). Although Figure 1 depicts a downward flow, the flow direction can be upward, depending on design considerations.

Suspended solids in a liquid stream or particulate matter in a gaseous stream accumulate in the column, causing an increase in pressure drop. When the pressure drop becomes too high, the accumulated solids must be removed, for example by backwashing. The solids removal process necessitates adsorber downtime, and may result in carbon loss and disruption of the mass transfer zone. Pretreatment for removal of solids from streams to be treated by GAC is, therefore, an important design consideration.

As a GAC system continues to operate, the mass-transfer zone moves down the column. Figure 2 shows the adsorption pattern and the corresponding effluent breakthrough curve [3]. The breakthrough curve is a plot of the ratio of effluent concentration (C_e) to influent concentration (C_o) as a function of water volume or air volume treated per unit time. When a predetermined concentration appears in the effluent (C_B), breakthrough has occurred. At this point, the effluent quality no longer meets treatment objectives. When the carbon becomes so saturated with the contaminants that they can no longer be adsorbed, the carbon is said to be spent ($C_e=C_o$). Alternative design arrangements may allow individual adsorbers in multi-adsorber systems to be operated beyond the breakpoint as far as complete exhaustion. This condition of operation is defined as the operating limit ($C_e=C_L$) of the adsorber.

The major design variables for liquid phase applications of GAC are empty bed contact time (EBCT), GAC usage rate, and system configuration. Particle size and hydraulic loading are often chosen to minimize pressure drop and reduce or eliminate backwashing. System configuration and EBCT have an impact on GAC usage rate. When the bed life is longer than 6 months and the treatment objective is stringent ($C_e/C_o < 0.05$),

Figure 2
Breakthrough Characteristics of Fixed-Bed GAC Adsorber [3]



a single adsorber or a combination of single beds operating in parallel is preferred. For a single adsorber, the EBCT is normally chosen to be large enough to minimize GAC usage rate. When less stringent objectives are required ($C_e/C_o > 0.3$), blending of effluents from partially saturated adsorbers can be used to reduce GAC usage rate. When stringent treatment objectives are required ($C_e/C_o < 0.05$) and GAC bed life is short (less than 6 months) multiple beds in series may be used to decrease GAC usage rate.

For gas-phase applications, the mass transfer zone is usually very short if the relative humidity is low enough to prevent water from filling the GAC pores. The adsorption zone (Figure 2) for gas-phase applications is small relative to bed depth, and the GAC is nearly saturated at the breakpoint. Accordingly, EBCT and system configuration have little impact on GAC usage rate and a single bed or single beds operated in parallel are commonly used.

GAC can be reactivated either onsite or offsite. The choice is usually dictated by costs which are dependent on the site and on the proximity of offsite facilities that reactivate carbon. Generally onsite reactivation is not economical unless more than 2,000 pounds per day of GAC are required to be reactivated. Even so, an offsite reactivation service may be more cost effective [10].

The basic evaluation technique for initial assessment of the feasibility of GAC treatment is the adsorption isotherm test. This test determines if a compound is amenable to GAC adsorption and can be used to estimate minimum GAC usage rates. More detailed testing such as small-scale column tests and pilot tests should be conducted if the isotherms indicate GAC can produce an effluent of acceptable quality at a reasonable carbon usage rate [10].

Process Residuals

The main process residual produced from a GAC system is the spent carbon containing the hazardous contaminants. When the carbon is regenerated, the desorbed contaminants must be treated or reclaimed. Reactivation of carbon is typically accomplished by thermal processes. Elevated temperatures are employed in the furnace and afterburners to destroy the accumulated contaminants. If the carbon cannot be economically reactivated, the carbon must be discarded and may have to be treated and disposed of as a hazardous waste. In some cases, the influent to GAC treatment must be pretreated to prevent excessive head loss. Residues from pretreatment (e.g. filtered suspended solids) must be treated or disposed. Solids collected from backwashing may need to be treated and disposed of as a hazardous waste.

Site Requirements

GAC equipment generally has small space requirements and sometimes can be incorporated in mobile units. The rapidity of startup and shutdown also makes GAC amenable to mobile treatment. Carbon beds or columns can be skid-mounted and transported by truck or rail [2, p. 5-19].

As previously stated, spent carbon from the treatment of streams containing hazardous substances is generally considered hazardous, and its transportation and handling requires that a site safety plan be developed to provide for personnel protection and special handling measures. Storage may have to be provided to hold the GAC-treated liquid until its acceptability for release has been determined. If additional treatment is required, adequate space must be provided for these systems.

Performance Data

Performance data on full-scale GAC systems have been reported by several sources including equipment vendors. Data on GAC systems at several Superfund sites and other cleanup sites are discussed in this section. The data presented for specific contaminant removal effectiveness were obtained from publications developed by the respective GAC system vendors. The quality of this information has not been determined; however, it does give an indication of the efficiency of GAC.

A GAC system was employed for leachate treatment at the Love Canal Superfund site in Niagara Falls, New York. The results of this operation are listed in Tables 3 and 4 [11].

Table 5 summarizes a number of experiences by Calgon Corporation in treating contaminated groundwater at many other non-Superfund sites. Table 5 identifies the sources of contamination along with operating parameters and results [12]. While these sites were not regulated under CERCLA, the type and concentration of contaminants are typical of those encountered at a Superfund site.

The Verona Well Field Superfund site in Battle Creek, Michigan used GAC as a pretreatment for the air stripper. This arrangement reduced the influent concentrations which allowed the air stripper to comply with the National Pollution Discharge Elimination System (NPDES) permit. The system had two parallel trains: a single unit and two units in series. Approximately one-third of the total flow was directed to the first train while the remaining flow went to the other train. Performance data for removal of total volatile organic compounds (TVOC) on selected operating days are given in Table 6 [13].

A remediation action at the U.S. Coast Guard Air Station in Traverse City, Michigan, resulted in GAC being used to treat contaminated groundwater. The groundwater was pumped from the extraction well system to the GAC system. The treated water was then discharged to the municipal sewer system. Concentrations of toluene in the monitoring wells were reduced from 10,329 parts per billion (ppb) to less than 10 ppb in approximately 100 days [14].

Technology Status

GAC is a well-proven technology. It has been used in the treatment of contaminated groundwater at a number of Superfund sites. Carbon adsorption has also been used as a polishing step following other treatment units at many sites. In 1988, the number of sites where activated carbon was listed in the Record of Decision was 28; in 1989, that number was 38.

Costs associated with GAC are dependent on waste stream flow rates, type of contaminant, concentrations, and site and timing requirements. Costs are lower with lower concentration levels of a contaminant of a given type. Costs are also lower at higher flow rates. At liquid flow rates of 100-million gallons per day (mgd), costs range from $0.10 - 1.50/1,000 gallons treated. At flow rates of 0.1 mgd, costs increase to $1.20 - 6.30/1,000 gallons treated [12].

Table 3
Love Canal Leachate Treatment System[a] (March 1979) [11]

Priority Pollutant Compounds Identified	*Carbon System Influent µg/l*	*Carbon System Effluent µg/l*
Hexachlorobutadiene	109	<20
1,2,4-trichlorobenzene	23	<20
Hexachlorobenzene	32	<20
α-BHC	184	<0.01
γ-BHC	392	0.12
β-BHC	548	<0.01
Heptachlor	573	<0.01
Phenol	4,700[b]	<5[b]
2,4-dichlorophenol	10	<5
Methylene chloride	180	<10
1,1-dichloroethylene	28	<10
Chloroform	540	<10
Carbon tetrachloride	92	<10
Trichloroethylene	240	<10
Dibromochloromethane	21	<10
1,1,2,2-tetrachloroethylene	270	<10
Chlorobenzene	1,200	<10

[a] Samples were analyzed by Recra Research, Inc., according to EPA protocol dated April 1977 (sampling and analysis procedures of screening for industrial effluents for priority pollutants).
[b] The data represent phenol analysis conducted by Calgon in June 1979, as earlier results were suspect

Table 4
Love Canal Leachate Treatment System[a] (June 1979) [11]

Priority Pollutant Compounds Identified	*Raw Leachate µg/l*	*Carbon System Effluent µg/l*
2,4,6-trichlorophenol	85	<10
2,4-dichlorophenol	5,100	N.D.
Phenol	2,400	<10
1,2,3-trichlorobenzene	870	N.D.
Hexachlorobenzene	110	N.D.
2-chloronaphthalene	510	N.D.
1,2-dichlorobenzene	1,300	N.D.
1,3 & 1,4-dichlorobenzene	960	N.D.
Hexachlorobutadiene	1,500	N.D.
Anthracene and phenanthrene	29	N.D.
Benzene	28,000	<10
Carbon tetrachloride	61,000	<10
Chlorobenzene	50,000	12
1,2-dichloroethane	52	N.D.
1,1,1-trichloroethane	23	N.D.
1,1-dichloroethane	66	N.D.
1,1,2-trichloroethane	780	<10
1,1,2,2-tetrachloroethane	80,000	<10
Chloroform	44,000	<10
1,1-dichloroethylene	16	N.D.
1,2-trans-dichloroethylene	3,200	<10
1,2-dichloropropane	130	N.D.
Ethylbenzene	590	<10
Methylene chloride	140	46
Methyl chloride	370	N.D.
Chlorodibromomethane	29	N.D.
Tetrachloroethylene	44,000	12
Toluene	25,000	<10
Trichloroethylene	5,000	N.D.

[a] Samples were analyzed by Carborundum Corporation according to EPA protocol dated April 1977 (sampling and analysis procedures for screening of industrial effluents for priority pollutants).
N.D. = nondetectable

Table 5
Performance Data at Selected Sites [12]

Source of Contaminants	*Typical Influent Conc. (mg/l)*	*Typical Effluent Conc. (µg/l)*	*Carbon Usage Rate (lb./1000 gal.)*	*Total Contact Time (min.)*
Truck spill				
Methylene chloride	21	<1.0	3.9	534
1,1,1-trichloroethane	25	<1.0	3.9	534
Rail car spills				
Phenol	63	<1.0	5.8	201
Orthochlorophenol	100	<1.0	5.8	201
Vinylidine chloride	2-4	<10.0	2.1	60
Ethyl acrylate	200	<1.0	13.3	52
Chloroform	0.020	<1.0	7.7	160
Chemical spills				
Chloroform	3.4	<1.0	11.6	262
Carbon tetrachloride	130-135	<1.0	11.6	262
Trichloroethylene	2-3	<1.0	11.6	262
Tetrachloroethylene	70	<1.0	11.6	262
Dichloroethyl ether	1.1	<1.0	0.45	16
Dichloroisopropyl ether	0.8	<1.0	0.45	16
Benzene	0.4	<1.0	1.9	112
DBCP	2.5	<1.0	0.7–3.0	21
1,1,1-trichloroethane	0.42	<10	1.5	53
Trichlorotrifloroethane	5.977	<10	1.5	53
Cis-1,2-dichloroethylene	.005	<1.0	0.25	121
Onsite storage tanks				
Cis-1,2-dichloroethylene	0.5	<1.0	0.8	64
Tetrachloroethylene	7.0	<1.0	0.8	64
Methylene chloride	1.5	<100	4.0	526
Chloroform	0.30-0.50	<100	1.19	26
Trichloroethylene	3-8	<1.0	1.54	36
Isopropyl alcohol	0.2	<10.0	1.54	36
Acetone	0.1	<10.0	1.54	36
1,1,1-trichloroethane	12	<5.0	1.0	52
1,2-dichloroethylene	0.5	<1.0	1.0	52
Xylene	8.0	<1.0	1.0	-52
Landfill site				
TOC	20	<5000	1.15	41
Chloroform	1.4	<1.0	1.15	41
Carbon tetrachloride	1.0	<1.	1.15	41
Gasoline spills, tank leakage				
Benzene	9-11	<100 Total	<1.01	214
Toluene	5-7		<1.01	214
Xylene	6-10		<1.01	214
Methyl t-butyl ether	0.030-0.035	<5.0	0.62	12
Di-isopropyl ether	0.020-0.040	<1.0	0.10-0.62	12
Trichloloethylene	0.050-0.060	<1.0	0.62	12
Chemical by-products				
Di-isopropyl methyl phosphonate	1.25	<50	0.7	30
Dichloropentadiene	0.45	<10	0.7	30
Manufacturing residues				
DDT	0.004	<0.5	1.1	31
TOC	9.0		1.1	31
1,3-dichloropropene	0.01	<1.0	1.1	31
Chemical landfill				
1,1,1-trichloroethane	0.060-0.080	<1.0	<0.45	30
1,1-dichloroethylene	0.005-0.015	0.005	<0.45	30

Table 6
TVOC Removal with GAC at Verona Well Superfund Site [13]

Operating Day	Influent Feed Concentration (ppb)	Effluent	
		Train (1) Concentration (ppb)	Train (2) Concentration (ppb)
1	18,812	NA	25
9	12,850	11	7
16	9,290	41	17
27	6,361	260	426
35	7,850	484	575
42	7,643	412	551
49	7,577	405	524
57	5,591	452	558
69	10,065	377	475
92	6,000	444	509
106	3,689	13	702
238	4,671	246	263

NA = not available

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Engineering Bulletin
In Situ Soil Flushing

Purpose

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

Abstract

In situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. Soil flushing is accomplished by passing the extraction fluid through in-place soils using an injection or infiltration process. Extraction fluids must be recovered and, when possible, are recycled. The method is potentially applicable to all types of soil contaminants. Soil flushing enables removal of contaminants from the soil and is most effective in permeable soils. An effective collection system is required to prevent migration of contaminants and potentially toxic extraction fluids to uncontaminated areas of the aquifer. Soil flushing, in conjunction with in situ bioremediation, may be a cost-effective means of soil remediation at certain sites [1, p. vi] [2, p. 11].* Typically, soil flushing is used in conjunction with other treatments that destroy contaminants or remove them from the extraction fluid and groundwater.

Soil flushing is a developing technology that has had limited use in the United States. Typically, laboratory and field treatability studies must be performed under site-specific conditions before soil flushing is selected as the remedy of choice. To date, the technology has been selected as part of the source control remedy at 12 Superfund sites. This technology is currently operational at only one Superfund site; a second is scheduled to begin operation in 1991 [3][4]. EPA completed construction of a mobile soil-flushing system, the In Situ Contaminant/Treatment Unit, in 1988. This mobile soil-flushing system is designed for use at spills and uncontrolled hazardous waste sites [5].

This bulletin provides information on the technology applicability, the technology limitations, a description of the technology, the types of residuals resulting from the use of the technology, site requirements, the latest performance data, the status of the technology, and sources of further information.

Technology Applicability

In situ soil flushing is generally used in conjunction with other treatment technologies such as activated carbon, biodegradation, or chemical precipitation to treat contaminated groundwater resulting from soil flushing. In some cases, the process can reduce contaminant concentrations in the soil to acceptable levels, and thus serve as the only soil treatment technology. In other cases, in situ biodegradation or other in situ technologies can be used in conjunction with soil flushing to achieve acceptable contaminant removal efficiencies. In general, soil flushing is effective on coarse sand and gravel contaminated with a wide range of organic, inorganic, and reactive contaminants. Soils containing a large amount of clay and silt may not respond well to soil flushing, especially if it is applied as a stand-alone technology.

A number of chemical contaminants can be removed from soils using soil flushing. Removal efficiencies depend on the type of contaminant as well as the type of soil. Soluble (hydrophilic) organic contaminants often are easily removed from soil by flushing with water alone. Typically, organics with octanol/water partition coefficients (K_{ow}) of less than 10 ($\log K_{ow}<1$) are highly soluble. Examples of such compounds include lower molecular weight alcohols, phenols, and carboxylic acids [6].

Low solubility (hydrophobic) organics may be removed by selection of a compatible surfactant [7]. Examples of such compounds include chlorinated pesticides, polychlorinated biphenyls (PCBs), semivolatiles (chlorinated benzenes and polynuclear aromatic hydrocarbons), petroleum products (gasoline,

* [reference number, page number]

jet fuel, kerosene, oils and greases), chlorinated solvents (trichloroethene), and aromatic solvents (benzene, toluene, xylenes and ethylbenzene) [8]. However, removal of some of these chemical classes has not yet been demonstrated.

Metals may require acids, chelating agents, or reducing agents for successful soil flushing. In some cases, all three types of chemicals may be used in sequence to improve the removal efficiency of metals [9]. Many inorganic metal salts, such as carbonates of nickel, zinc, and copper, can be flushed from the soil with dilute acid solutions [6]. Some inorganic salts such as sulfates and chlorides can be flushed with water alone.

In situ soil flushing has been considered for treating soils contaminated with hazardous wastes, including pentachlorophenol and creosote from wood-preserving operations, organic solvents, cyanides and heavy metals from electroplating residues, heavy metals from some paint sludges, organic chemical production residues, pesticides and pesticide production residues, and petroleum/oil residues [10, p. 13][11, p. 8][7][12].

The effectiveness of soil flushing for general contaminant groups [10, p. 13] is shown in Table 1. Examples of constituents within contaminant groups are provided in Reference 10, "Technology Screening Guide For Treatment of CERCLA Soils and Sludges." Table 1 is based on currently available information or professional judgment where definitive information is currently inadequate or unavailable. The demonstrated effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. For the ratings used in this table, demonstrated effectiveness means that, at some scale, treatability was tested to show that, for that particular contaminant and matrix, the technology was effective. The ratings of potential effectiveness and no expected effectiveness are based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given. Other sources of general observations and average removal efficiencies for different treatability groups are the Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.3-06FS) [13], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-07FS) [14].

Table 1
Effectiveness of Soil Flushing on General Contaminant Groups

	Contaminant Groups	*Effectiveness*
Organic	Halogenated volatiles	■
	Halogenated semivolatiles	▼
	Nonhalogenated volatiles	▼
	Nonhalogenated semivolatiles	■
	PCBs	▼
	Pesticides (halogenated)	▼
	Dioxins/Furans	▼
	Organic cyanides	▼
	Organic corrosives	▼
Inorganic	Volatile metals	▼
	Nonvolatile metals	■
	Asbestos	❑
	Radioactive materials	▼
	Inorganic corrosives	▼
	Inorganic cyanides	▼
Reactive	Oxidizers	▼
	Reducers	▼

■ Demonstrated Effectiveness: Successful treatability test at some scale completed.

▼ Potential Effectiveness: Expert opinion that technology will work.

❑ No Expected Effectiveness: Expert opinion that technology will not work.

Information on cleanup objectives, as well as the physical and chemical characteristics of the site soil and its contaminants, is necessary to determine the potential performance of this technology. Treatability tests are also required to determine the feasibility of the specific soil-flushing process being considered. If bench-test results are promising, pilot-scale demonstrations should be conducted before making a final commitment to full-scale implementation. Table 2 contains physical and chemical soil characterization parameters that should be established before a treatability test is conducted at a specific site. The table contains comments relating to the purpose of the specific parameter to be characterized and its impact on the process [15, p. 715] [16, p. 90] [17].

Soil permeability is a key physical parameter for determining the feasibility of using a soil-flushing process. Hydraulic conductivity (K) is measured to assess the permeability of soils. Soils with low permeability ($K < 1.0 \times 10^{-5}$ cm/sec) will limit the ability of flushing fluids to percolate through the soil in a reasonable time frame. Soil flushing is most likely to be effective in permeable soils ($K > 1.0 \times 10^{-3}$ cm/sec), but may have limited application to less permeable soils (1.0×10^{-5} cm/sec $< K < 1.0 \times 10^{-3}$ cm/sec). Since there can be significant lateral and vertical variability in soil permeability, it is important that field measurements be made using the appropriate methods.

Prior to field implementation of soil flushing, a thorough groundwater hydrologic study should be carried out. This should include information on seasonal fluctuations in water level, direction of groundwater flow, porosity, vertical and horizontal hydraulic conductivities, transmissivity and infiltration (data on rainfall, evaporation, and percolation).

Moisture content can affect the amount of flushing fluids required. Dry soils will require more flushing fluid initially to mobilize contaminants. Moisture content is also used to calculate pore volume to determine the rate of treatment [15].

The concentration and distribution of organic contami-

Table 2
Characterization Parameters

Parameter	*Purpose and Comment*
Soil permeability	Affects treatment time and efficiency of contaminant removal
$\geq 1.0 \times 10^{-3}$ cm/sec	Effective soil flushing
$< 1.0 \times 10^{-5}$ cm/sec	Limited soil flushing
Soil structure	Influences flow patterns (channeling, blockage)
Soil porosity	Determines moisture capacity of soil at saturation (pore volume)
Moisture content	Affects flushing fluid transfer requirements
Groundwater hydrology	Critical in controlling the recovery of injected fluids and contaminants
Organics Concentration Solubility Partition coefficient	Determine contaminants and assess flushing fluids required, flushing fluid compatibility, changes in flushing fluid with changes in contaminants.
Metals Concentration Solubility products Reduction potential Complex stability constants	Concentration and species of constituents will determine flushing fluid compatibility, mobility of metals, post treatment.
Total Organic Carbon (TOC)	Adsorption of contaminants on soil increases with increasing TOC. Important in marine wetland sites, which typically have high TOC.
Clay content	Adsorption of contaminants on soil increases with increasing clay content.
Cation Exchange Capacity (CEC)	May affect treatment of metallic compounds.
pH, buffering capacity	May affect treatment additives required, compatibility with equipment materials of construction, wash fluid compatibility.

nants and metals are key chemical parameters. These parameters determine the type and quantity of flushing fluid required as well as any post-treatment requirements. The solubility and partition coefficients of organics in water or other solutions are also important in the selection of the proper flushing fluids. The species of metal compounds present will affect the solubility and leachability of heavy metals.

High humic content and high cation exchange capacity tend to reduce the removal efficiency of soil flushing. Some organic contaminants may adsorb to humic materials or clays in soils and, therefore, are difficult to remove during soil flushing. Similarly, the binding of certain metals with clays due to cationic exchange makes them difficult to remove with soil flushing. The buffering capacity of the soil will affect the amount required of some additives, especially acids. Precipitation reactions (resulting in clogging of soil pores) can occur due to pH changes in the flushing fluid caused by the neutralizing effect of soils with high buffering capacity. Soil pH can affect the speciation of metal compounds resulting in changes in the solubility of metal compounds in the flushing fluid.

Limitations

Generally, remediation times with this technology will be lengthy (one to many years) due to the slowness of diffusion processes in the liquid phase. This technology requires hydraulic control to avoid movement of contaminants offsite. The hydrogeology of some sites may make this difficult or impossible to achieve.

Contaminants in soils containing a high percentage of silt- and clay-sized particles typically are strongly adsorbed and difficult to remove. Also, soils with silt and clay tend to be less permeable. In such cases, soil flushing generally should not be considered as a stand-alone technology.

Hydrophobic contaminants generally require surfactants or organic solvents for their removal from soil. Complex mixtures of contaminants in the soil (such as a mixture of metals, nonvolatile organics, and semivolatile organics) make it difficult to formulate a single suitable flushing fluid that will consistently and reliably remove all the different types of contaminants from the soil. Frequent changes in contaminant concentration and composition in the vertical and horizontal soil profiles will complicate the formulation of the flushing fluid. Sequential steps with frequent changes in the flushing formula may be required at such complex sites [10, p. 77].

Bacterial fouling of infiltration and recovery systems and treatment units may be a problem particularly if high iron concentrations are present in the groundwater or if biodegradable reagents are being used.

While flushing additives such as surfactants and chelants may enhance some contaminant removal efficiencies in the soil flushing process, they also tend to interfere with the downstream wastewater treatment processes. The presence of these additives in the washed soil and in the wastewater treatment sludge may cause some difficulty in their disposal. Costs associated with additives, and the management of these additives as part of the residuals/wastewater streams, must be carefully weighed against the incremental improvements in soil-flushing performance that they may provide.

Technology Description

Figure 1 is a general schematic of the soil flushing process [18, p. 7]. The flushing fluid is applied (1) to the contaminated soil by subsurface injection wells, shallow infiltration galleries, surface flooding, or above-ground sprayers. The flushing fluid is typically water and may contain additives to improve contaminant removal.

The flushing fluid percolates through the contaminated soil, removing contaminants as it proceeds. Contaminants are mobilized by solubilization into the flushing fluid, formation of emulsions, or through chemical reactions with the flushing fluid [19].

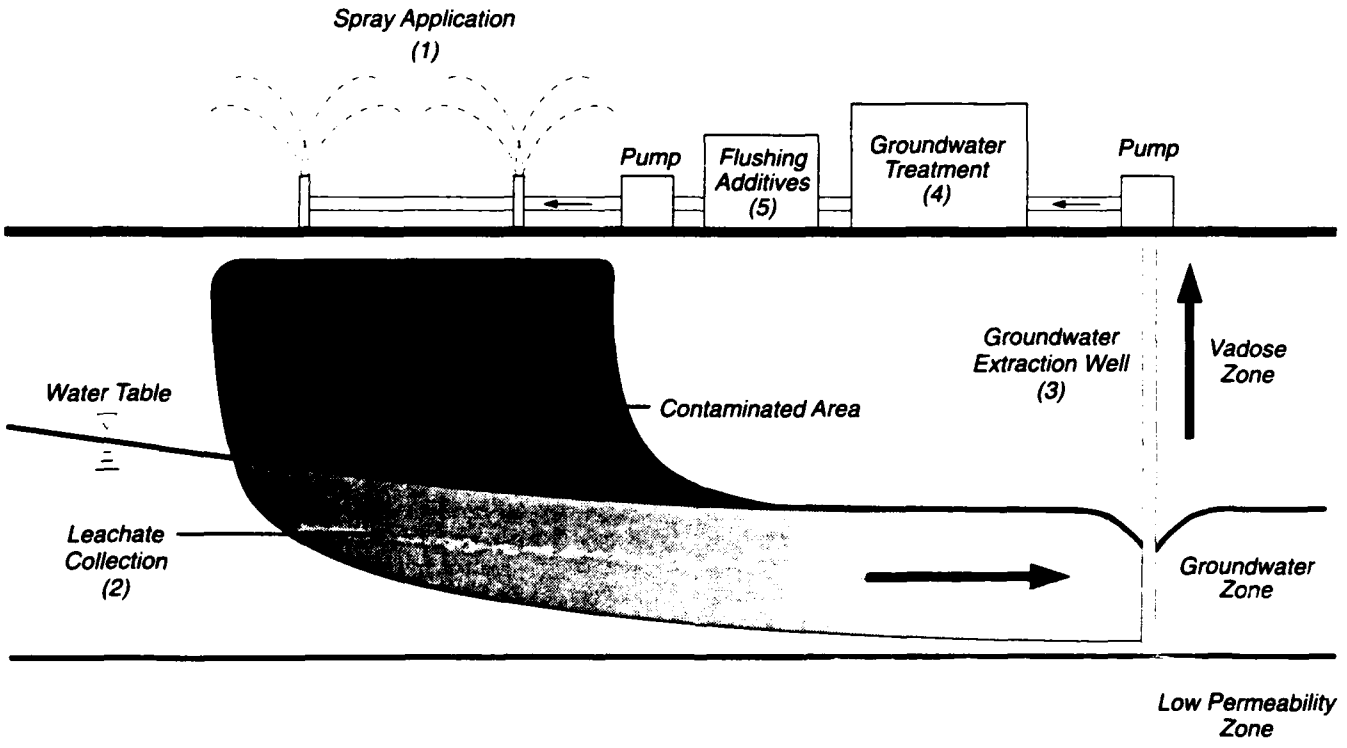
Contaminated flushing fluid or leachate mixes with groundwater and is collected (2) for treatment. The flushing fluid delivery and the groundwater extraction systems are designed to ensure complete contaminant recovery [7]. Ditches open to the surface, subsurface collection drains, or groundwater recovery wells may be used to collect flushing fluids and mobilized contaminants. Proper design of a fluid recovery system is very important to the effective application of soil flushing.

Contaminated groundwater and flushing fluids are captured and pumped to the surface in a standard groundwater extraction well (3). The rate of groundwater withdrawal is determined by the flushing fluid delivery rate, the natural infiltration rate, and the groundwater hydrology. These will determine the extent to which the groundwater removal rate must exceed the flushing fluid delivery rate to ensure recovery of all reagents and mobilized contaminants. The system must be designed so that hydraulic control is maintained.

The groundwater and flushing fluid are treated (4) using the appropriate wastewater treatment methods. Extracted groundwater is treated to reduce the heavy metal content, organics, total suspended solids, and other parameters until they meet regulatory requirements. Metals may be removed by lime precipitation or by other technologies compatible with the flushing reagents used. Organics are removed with activated carbon, air stripping, or other appropriate technologies. Whenever possible, treated water should be recycled as makeup water at the front end of the soil-flushing process.

Flushing additives (5) are added, as required, to the treated groundwater, which is recycled for use as flushing fluid. Water alone is used to remove hydrophilic organics and soluble heavy-metal salts [9]. Surfactants may be added to remove hydrophobic and slightly hydrophilic organic contaminants [12]. Chelating agents, such as ethylenediaminetetra-acetic acid (EDTA), can effectively remove certain metal compounds. Alkaline buffers such as tetrasodium pyrophosphate can remove metals bound to the soil organic fraction. Reducing agents such as hydroxylamine hydrochloride can reduce iron and manganese oxides that can bind

Figure 1
Schematic of Soil Flushing System



metals in soil. Insoluble heavy-metal compounds also can be reduced or oxidized to more soluble compounds. Weak acid solutions can improve the solubility of certain heavy metals [9]. Treatability studies should be conducted to determine compatability of the flushing reagents with the contaminants and with the site soils.

Process Residuals

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

Site Requirements

Access roads are required for transport of vehicles to and from the site. Stationary or mobile soil-flushing process systems are located on site. The exact area required will depend on the vendor system selected and the number of tanks or ponds needed for washwater preparation and wastewater treatment.

Because contaminated flushing fluids are usually considered hazardous, their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures during wastewater treatment operations. Fire hazard and explosion considerations should be minimal, since the soil-flushing fluid is predominantly water.

An Underground Injection Control (UIC) Permit may be necessary if subsurface infiltration galleries or injection wells are used. When groundwater is not recycled, a National Pollution Discharge Elimination System (NPDES) or State Pollution Discharge Elimination System (SPDES) permit may be required. Federal, State, and local regulatory agencies should be contacted to determine permitting requirements before implementing this technology.

Slurry walls or other containment structures may be needed along with hydraulic controls to ensure capture of contaminants and flushing additives. Climatic conditions such as precipitation cause surface runoff and water infiltration. Berms, dikes, or other runoff control methods may be required. Impermeable membranes may be necessary to limit infiltration of precipitation, which could cause dilution of flushing solution and loss of hydraulic control. Cold weather freezing must also be considered for shallow infiltration galleries and above-ground sprayers.

Performance Data

Some of the data presented for specific contaminant removal effectiveness were obtained from publications developed by the respective soil-flushing-system vendors. The quality of this information has not been determined; however it does give an indication of the effectiveness of in situ soil flushing.

Tetrachloroethylene was discharged into the aquifer at the site of a spill in Sindelfingen, Germany. The contaminated aquifer is a high-permeability ($k=5.10 \times 10^{-4}$ m/sec) layer overlaying a clay barrier. Soil flushing was accomplished by infiltrating water into the ground through ditches. The leaching liquid and polluted groundwater were pumped out of eight wells and treated with activated carbon. The treated water was recycled through the infiltration ditches. Within 18 months, 17 metric tons of chlorinated hydrocarbons were recovered [19, p. 565].

Two percolation basins were installed to flush contaminated soil at the United Chrome Products site near Corvallis, Oregon. Approximately 1,100 tons of soil containing the highest chromium concentrations were excavated and disposed of offsite. The resulting pits from the excavations were used as infiltration basins to flush the remaining contaminated soil. The soil-flushing operation for the removal of hexavalent chromium from an estimated 2.4 million gallons of contaminated groundwater began in August 1988. No information on the site soils was provided, but preliminary estimates were that a groundwater equilibrium concentration of 100 mg/L chromium would be reached in 1 to 2 years, but that final cleanup to 10 mg/L would take up to 25 years [20, p. H-1]. Since that time over 8-million gallons of groundwater, containing over 25,000 pounds of chromium, have been removed from the 23 extraction wells in the shallow aquifer. Average monthly chromium concentrations in the groundwater decreased from 1,923 mg/L in August 1988 to 96 mg/L in March 1991 [4].

Waste-Tech Services, Inc. performed two tests of soil-flushing techniques to remove creosote contamination at the Laramie Tie Plant site in Wyoming. The first test involved slowly flooding the soil surface with water to perform primary oil recovery (POR). Soil flushing reduced the average concentration of total extractable organics (TEO) from an estimated initial concentration of 93,000 mg/kg to 24,500 mg/kg, a 74 percent reduction. The second test involved sequential treatment with alkaline agents, polymers, and surfactants. During the 8-month treatment period, average TEO concentrations were reduced to 4,000 mg/kg. This represents an 84 percent reduction from the post-POR concentration (24,500 mg/kg) and a 96 percent reduction from the estimated initial concentration (93,000 mg/kg). The tests were performed in alluvial sands and gravels. The low permeability of adjacent silts and clays precluded soil flushing [22].

Laboratory tests were conducted on contaminated soils from a fire-training area at Volk Air Force Base. Initial concentrations of oil and grease in the soils were reported to be 10,000 and 6,000 mg/kg. A 1.5-percent surfactant solution in water was used to flush soil columns. The tests indicated that 75 to 94 percent of the initial hydrocarbon contamination could be removed by flushing with 12-pore volumes of liquid.

However, field tests were unsuccessful in removing the same contaminants. Seven soil-flushing solutions, including the solution tested in the laboratory studies, were tested in field studies. The flushing solutions were delivered to field test cells measuring 1 foot deep and 1 to 2 feet square. Only three of the seven tests achieved the target delivery of 14-pore volumes. Two of the test cells plugged completely, permitting no further infiltration of flushing solutions. There was no statistically significant removal of soil contaminants due to soil flushing. The plugging of test cells may be related to the use of a surfactant solution. By hydrolyzing in water, surfactants may block soil pores by forming either flocs or surfactant aggregates called micelles. In addition, if the surfactant causes fine soil particles to become suspended in the flushing fluid, narrow passages between soil particles could be blocked. If enough of these narrow passages are blocked along a continuous front, a "mat" is said to have formed, and fluid flow is halted in that area [23] [7].

Resource Conservation Recovery Act (RCRA) Land Disposal Restrictions (LDRs) that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements (ARARs) for CERCLA response actions. The soil-flushing technology can produce a treated waste that meets treatment levels set by BDAT, but may not reach these treatment levels in all cases. The ability of the technology to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where soil flushing does not meet these levels, it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. EPA has made the treatability variance process available in order to ensure that LDRs do not unnecessarily restrict the use of alternative and innovative treatment technologies. Treatability variances may be justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.3-06FS) [13], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-07FS) [14]. Another approach could be to use other treatment techniques in conjunction with soil flushing to obtain desired treatment levels.

Technology Status

In situ soil flushing is a developing technology that has had limited application in the United States. In situ soil flushing technology has been selected as one of the source control remedies at the 12 Superfund sites listed in Table 3 [3].

EPA Contact

Technology-specific questions regarding soil flushing may be directed to:

Michael Gruenfeld
U.S. EPA, Releases Control Branch
Risk Reduction Engineering Laboratory
2890 Woodbridge Avenue, Building 10
Edison, New Jersey 08837
Telephone FTS 340-6625 or (908) 321-6625.

Table 3
Superfund Sites Using In Situ Soil Flushing

Site	*Location (Region)*	*Primary Contaminants*	*Status*
Byron Barrel & Drum	Genesee County, NY (2)	VOCs (BTX, PCE, and TCE)	Pre-design: finalizing workplan
Goose Farm	Plumsted Township, NJ (2)	VOCs (Toluene, Ethylbenzene, Dichloromethane, and TCE), SVOCs, and PAHs	In design: 30% design phase
Lipari Landfill	Gloucester, NJ (2)	VOCs (Benzene, Ethylbenzene, Dichlormethane, and TCE), SVOCs, PAHs and Chlorinated ethers (bis-2-chloroethylether)	Operational, summer '91
Vineland Chemical	Vineland, NJ (2)	Arsenic and VOCs (Dichloromethane)	Pre-design
Harvey-Knott Drum	_____, DE (3)	Lead	In design: re-evaluating alternative
L.A. Clarke & Son	Spotsylvania, VA (3)	Creosote, PAHs, and Benzene	In design
Ninth Avenue Dump	Garry, IN (5)	VOCs (BTEX, TCE), PAHs, Phenols, Lead, PCBs, and Total Metals	In design: pilot failed
U.S. Aviex	Niles, MI (5)	VOCs (Carbon Tetrachloride, DCA, Ethylbenzene, PCE, TCE, Toluene, TCA, Freon, Xylene, and Chloroform)	Pre-design: re-evaluating alternatives
South Calvacale Street	Houston, TX (6)	PAHs	In design
United Chrome Products	Corvallis, OR (10)	Chromium	Operational since 8/88
Cross Brothers Pail	Pembroke, IL (5)	VOCs (Benzene, PCE, TCE, Toluene, and Xylenes) and PCBs	In desgn: developing workplan
Bog Creek Farm	Howell Township, NJ (2)	VOCs, Organics	In design: treatment plant completed, dump and treat not installed

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EPA

Engineering Bulletin
In Situ Soil Vapor Extraction Treatment

Purpose

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

Abstract

Soil vapor extraction (SVE) is designed to physically remove volatile compounds, generally from the vadose or unsaturated zone. It is an in situ process employing vapor extraction wells alone or in combination with air injection wells. Vacuum blowers supply the motive force, inducing air flow through the soil matrix. The air strips the volatile compounds from the soil and carries them to the screened extraction well.

Air emissions from the systems are typically controlled by adsorption of the volatiles onto activated carbon, thermal destruction (incineration or catalytic oxidation), or condensation by refrigeration [1, p. 26].*

SVE is a developed technology that has been used in commercial operations for several years. It was the selected remedy for the first Record of Decision (ROD) to be signed under the Superfund Amendments and Reauthorization Act of 1986 (the Verona Well Field Superfund Site in Battle Creek, Michigan). SVE has been chosen as a component of the ROD at over 30 Superfund sites [2] [3] [4] [5] [6].

Site-specific treatability studies are the only means of documenting the applicability and performance of an SVE system. The EPA Contact indicated at the end of this bulletin can assist in the location of other contacts and sources of information necessary for such treatability studies.

The final determination of the lowest cost alternative will be more site-specific than process equipment dominated. This bulletin provides information on the technology applicability, the limitations of the technology, the technology description, the types of residuals produced, site requirements, the latest performance data, the status of the technology, and sources for further information.

Technology Applicability

In situ SVE has been demonstrated effective for removing volatile organic compounds (VOCs) from the vadose zone. The effective removal of a chemical at a particular site does not, however, guarantee an acceptable removal level at all sites. The technology is very site-specific. It must be applied only after the site has been characterized. In general, the process works best in well drained soils with low organic carbon content. However, the technology has been shown to work in finer, wetter soils (e.g., clays), but at much slower removal rates [7, p. 5].

The extent to which VOCs are dispersed in the soil—vertically and horizontally—is an important consideration in deciding whether SVE is preferable to other methods. Soil excavation and treatment may be more cost effective when only a few hundred cubic yards of near-surface soils have been contaminated. If volume is in excess of 500 cubic yards, if the spill has penetrated more than 20 or 30 feet, or the contamination has spread through an area of several hundred square feet at a particular depth, then excavation costs begin to exceed those associated with an SVE system [8] [9] [10, p. 6].

The depth to groundwater is also important. Groundwater level in some cases may be lowered to increase the volume of the unsaturated zone. The water infiltration rate can be

* [reference number, page number]

Table 1
Effectiveness of SVE on General Contaminant Groups For Soil

	Contaminant Groups	Effectiveness Soil
Organic	Halogenated volatiles	■
	Halogenated semivolatiles	▼
	Nonhalogenated volatiles	■
	Nonhalogenated semivolatiles	■
	PCBs	❑
	Pesticides	❑
	Dioxins/Furans	❑
	Organic cyanides	❑
	Organic corrosives	❑
Inorganic	Volatile metals	❑
	Nonvolatile metals	❑
	Asbestos	❑
	Radioactive materials	❑
	Inorganic corrosives	❑
	Inorganic cyanides	❑
Reactive	Oxidizers	❑
	Reducers	▼

■ Demonstrated Effectiveness: Successful treatability test at some scale completed
▼ Potential Effectiveness: Expert opinion that technology will work
❑ No Expected Effectiveness: Expert opinion that technology will not work

controlled by placing an impermeable cap over the site. Soil heterogeneities influence air movement as well as the location of chemicals. The presence of heterogeneities may make it more difficult to position extraction and inlet wells. There generally will be significant differences in the air permeability of the various soil strata which will affect the optimum design of the SVE facility. The location of the contaminant on a property and the type and extent of development in the vicinity of the contamination may favor the installation of an SVE system. For example, if the contamination exists beneath a building or beneath an extensive utility trench network, SVE should be considered.

SVE can be used alone or in combination with other technologies to treat a site. SVE, in combination with groundwater pumping and air stripping, is necessary when contamination has reached an aquifer. When the contamination has not penetrated into the zone of saturation (i.e., below the water table), it is not necessary to install a groundwater pumping system. A vacuum extraction well will cause the water table to rise and will saturate the soil in the area of the contamination. Pumping is then required to draw the water table down and allow efficient vapor venting [11, p.169].

SVE may be used at sites not requiring complete remediation. For example, a site may contain VOCs and nonvolatile contaminants. A treatment requiring excavation might be selected for the nonvolatile contaminants. If the site required excavation in an enclosure to protect a nearby populace from VOC emissions, it would be cost effective to extract the volatiles from the soil before excavation. This would obviate the need for the enclosure. In this case it would be necessary to vent the soil for only a fraction of the time required for complete remediation.

Performance data presented in this bulletin should not be considered directly applicable to other Superfund sites. A number of variables such as the specific mix and distribution of contaminants affect system performance. A thorough characterization of the site and a well-designed and conducted treatability study are highly recommended.

The effectiveness of SVE on general contaminant groups for soils is shown in Table 1. Examples of constituents within contaminant groups are provided in the "Technology Screening Guide For Treatment of CERCLA Soils and Sludges" [12]. This table is based on the current available information or professional judgment where no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. For the ratings used in this table, demonstrated effectiveness means that, at some scale, treatability tests showed that the technology was effective for that particular contaminant and matrix. The ratings of potential effectiveness, or no expected effectiveness are both based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given. Another source of general observations and average removal efficiencies for different treatability groups is contained in the Superfund Land Disposal Restrictions (LDR) Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS, July 1989) [13] and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," (OSWER Directive 9347.3-07FS, December 1989) [14].

Limitations

Soils exhibiting low air permeability are more difficult to treat with in situ SVE. Soils with a high organic carbon content have a high sorption capacity for VOCs and are more difficult to remediate successfully with SVE. Low soil temperature lowers a contaminant's vapor pressure, making volatilization more difficult [11].

Sites that contain a high degree of soil heterogeneity will likely offer variable flow and desorption performance, which will make remediation difficult. However, proper design of the vacuum extraction system may overcome the problems of heterogeneity [7, p. 19] [15].

It would be difficult to remove soil contaminants with low vapor pressures and/or high water solubilities from a site. The lower limit of vapor pressure for effective removal of a compound is 1 mm Hg abs. Compounds with high water solubilities, such as acetone, may be removed with relative ease from arid soils. However, with normal soils (i.e., moisture content ranging from 10 percent to 20 percent), the likelihood of successful remediation drops significantly because the moisture in the soil acts as a sink for the soluble acetone.

Technology Description

Figure 1 is a general schematic of the in situ SVE process. After the contaminated area is defined, extraction wells (1) are installed. Extraction well placement is critical. Locations must be chosen to ensure adequate vapor flow through the contaminated zone while minimizing vapor flow through other zones [11, p. 170]. Wells are typically constructed of PVC pipe that is screened through the zone of contamination [11]. The screened pipe is placed in a permeable packing; the unscreened portion is sealed in a cement/bentonite grout to prevent a short-circuited air flow direct to the surface. Some SVE systems are installed with air injection wells. These wells may either passively take in atmospheric air or actively use forced air injection [9]. The system must be designed so that any air injected into the system does not result in the escape of VOCs to the atmosphere. Proper design of the system can also prevent offsite contamination from entering the area being extracted.

The physical dimensions of a particular site may modify SVE design. If the vadose zone depth is less than 10 feet and the area of the site is quite large, a horizontal piping system or trenches may be more economical than conventional wells.

An induced air flow draws contaminated vapors and entrained water from the extraction wells through headers—usually plastic piping—to a vapor-liquid separator (2). There, entrained water is separated and contained for subsequent treatment (4). The contaminant vapors are moved by a vacuum blower (3) to vapor treatment (5).

Vapors produced by the process are typically treated by carbon adsorption or thermal destruction. Other methods—such as condensation, biological degradation, and ultraviolet oxidation—have been applied, but only to a limited extent.

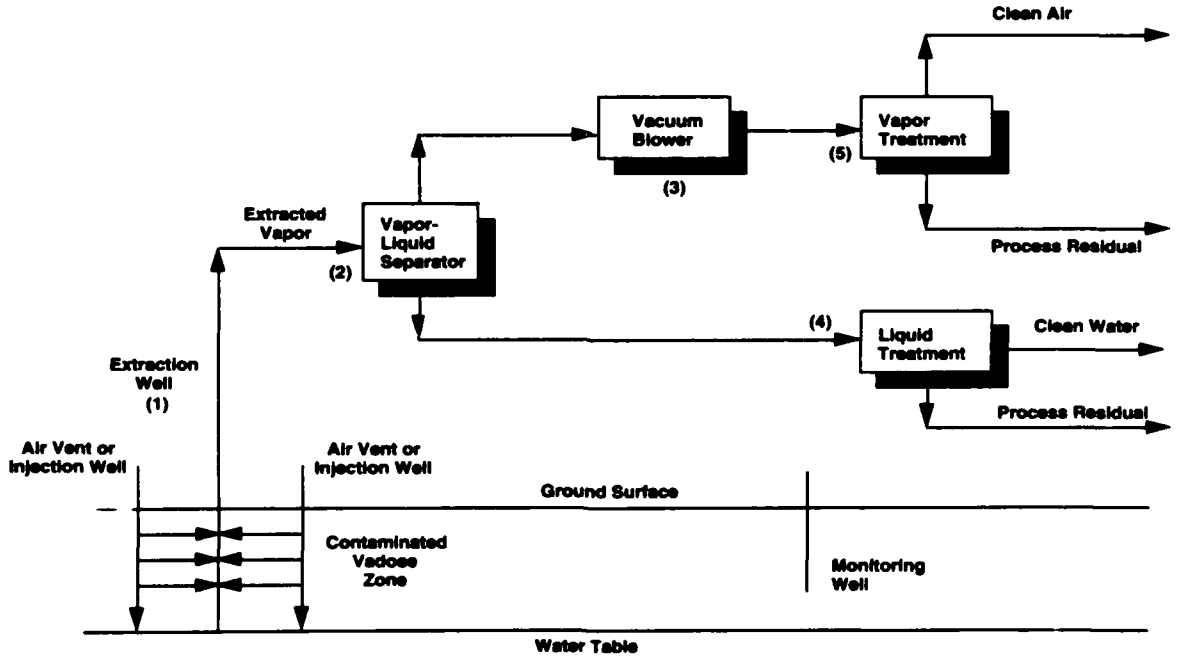
Process Residuals

The waste streams generated by in situ SVE are vapor and liquid treatment residuals (e.g., spent granular activated carbon [GAC]), contaminated groundwater, and soil tailings from drilling the wells. Contaminated groundwater may be treated and discharged onsite [12, p. 86] or collected and treated offsite. Highly contaminated soil tailings from drilling must be collected and may be either cleaned onsite or sent to an offsite, permitted facility for treatment by another technology such as incineration.

Site Requirements

SVE systems vary in size and complexity depending on the capacity of the system and the requirements for vapor and liquid treatment. They are typically transported by vehicles ranging from trucks to specifically adapted flatbed semitrailers; therefore, a proper staging area for these vehicles must be incorporated in the plans.

Figure 1
Process Schematic of the In Situ Soil Vapor Extraction System



Adequate access roads must be provided to bring mobile drilling rigs onsite for construction of wells and to deliver equipment required for the process (e.g., vacuum blowers, vapor-liquid separator, emission control devices, GAC canisters).

A small commercial-size SVE system would require about 1,000 square feet of ground area for the equipment. This area does not include space for the monitoring wells which might cover 500 square feet. Space may be needed for a forklift truck to exchange skid-mounted GAC canisters when regeneration is required. Large systems with integrated vapor and liquid treatment systems will need additional area based on vendor-specific requirements.

Standard 440V, three-phase electrical service is needed. For many SVE applications, water may be required at the site. The quantity of water needed is vendor- and site-specific.

Contaminated soils or other waste materials are hazardous, and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures. Storage should be provided to hold the process product streams until they have been tested to determine their acceptability for disposal or release. Depending upon the site, a method to store soil tailings from drilling operations may be necessary. Storage capacity will depend on waste volume.

Onsite analytical equipment, including gas chromatographs and organic vapor analyzers capable of determining site-specific organic compounds for performance assessment, make the operation more efficient and provide better information for process control.

Performance Data

SVE, as an in situ process (no excavation is involved), may require treatment of the soil to various cleanup levels mandated by federal and state site-specific criteria. The time required to meet a target cleanup level (or performance objective) may be estimated by using data obtained from bench-scale and pilot-scale tests in a time-predicting mathematical model. Mathematical models can estimate cleanup time to reach a target level, residual contaminant levels after a given period of operation and can predict location of hot spots through diagrams of contaminant distribution [16].

Table 2 shows the performance of typical SVE applications. It lists the site location and size, the contaminants and quantity of contaminants removed, the duration of operation, and the maximum soil contaminant concentrations before treatment and after treatment. The data presented for specific contaminant removal effectiveness were obtained, for the most part, from publications developed by the respective SVE system vendors. The quality of this information has not been determined.

Midwest Water Resources, Inc. (MWRI) installed its VAPORTECH™ pumping unit at the Dayton, Ohio site of a spill of uncombusted paint solvents caused by a fire in a paint warehouse [19]. The major VOC compounds identified were acetone, methyl isobutyl ketone (MIBK), methyl ethyl ketone (MEK), benzene, ethylbenzene, toluene, naphtha, xylene, and other volatile aliphatic and alkyl benzene compounds. The site is underlain predominantly by valley-fill glacial outwash within the Great Miami River Valley, reaching a thickness of over 200 feet. The outwash is composed chiefly of coarse, clean sand and gravel, with numerous cobbles and small boulders. There are two outwash units at the site separated by a discontinuous till at depths of 65 to 75 feet. The upper outwash forms an unconfined aquifer with saturation at a depth of 45 to 50 feet below grade. The till below serves as an aquitard between the upper unconfined aquifer and the lower confined to semiconfined aquifer. Vacuum withdrawal extended to the depth of groundwater at about 40 to 45 feet. During the first 73 days of operation, the system yielded 3,720 pounds of volatiles and after 56 weeks of operation, had recovered over 8,000 pounds of VOCs from the site. Closure levels for the site were developed for groundwater VOC levels of ketones only. These soil action levels (acetone, 810 µg/l; MIBK, 260 µg/l, and MEK, 450 µg/l) were set so that waters recharging through contaminated soils would result in

Table 2.
Summary of Performance Data for In Situ Soil Vapor Extraction

Site	*Size*	*Contaminants*	*Quantity removed*	*Duration of operation*	*Soil concentrations (mg/kg) max. before treatment*	*Soil concentrations (mg/kg) after treatment*
Industrial - CA [17]	–	TCE	30 kg	440 days	0.53	0.06
Sheet Metal Plant - MI [18]	5,000 cu yds	PCE*	59 kg	35 days	5600	0.70
Prison Const. Site - MI [19]	165,000 cu yds	TCA	–	90 days	3.7	0.01
Sherwin-Williams Site - OH [19]	425,000 cu yds	Paint solvents	4,100 kg	6 mo	38	0.04
Upjohn - PR [20][21]	7,000,000 cu yds	CCl_4	107,000 kg	3 yr	2200	<0.005
UST Bellview - FL [7]	–	BTEX	9,700 kg	7 mo	97	<0.006
Verona Wellfield - MI [7][22]	35,000 cu yds	TCE, PCE, TCA	12,700 kg	Over 1 yr	1380	Ongoing
Petroleum Terminal - Owensboro, KY [19]	12,000 cu yds	Gasoline, diesel	–	6 mo	>5000	1.0 (target)
SITE Program - Groveland MA [7]	6,000 cu yds	TCE	590 kg	56 days	96.1	4.19

*PCE = Perchloroethylene

groundwater VOC concentrations at or below regulatory standards. The site met all the closure criteria by June 1988.

A limited amount of performance data is available from Superfund sites. The EPA Superfund Innovative Technology Evaluation (SITE) Program's Groveland, Massachusetts, demonstration of the Terra Vac Corporation SVE process produced data that were subjected to quality assurance/quality control tests. These data appear in Table 2 [7, p. 29] and Table 3 [7, p. 31]. The site is contaminated by trichloroethylene (TCE), a degreasing compound which was used by a machine shop that is still in operation. The subsurface profile in the test area consists of medium sand and gravel just below the surface, underlain by finer and silty sands, a clay layer 3 to 7 feet in depth, and—below the clay layer—coarser sands with gravel. The clay layer or lens acts as a barrier against gross infiltration of VOCs into subsequent subsoil strata. Most of the subsurface contamination lay above the clay lens, with the highest concentrations adjacent to it. The SITE data represent the highest percentage of contaminant reduction from one of the four extraction wells installed for this demonstration test. The TCE concentration levels are weighted average soil concentrations obtained by averaging split spoon sample concentrations every 2 feet over the entire 24-foot extraction well depth. Table 3 shows the reduction of TCE in the soil strata near the same extraction well. The Groveland Superfund Site is in the process of being remediated using this technology [2].

The Upjohn facility in Barceloneta, Puerto Rico, is the first and, thus far, the only Superfund site to be remediated with SVE. The contaminant removed from this site was a mixture containing 65 percent carbon tetrachloride (CCl_4) and 35 percent acetonitrile [20]. Nearly 18,000 gallons of CCl_4 were extracted during the remediation, including 8,000 gallons that were extracted during a pilot operation conducted from January 1983 to April 1984. The volume of soil treated at the Upjohn site amounted to 7,000,000 cubic yards. The responsible party originally argued that the site should be considered clean when soil samples taken from four boreholes drilled in the area of high pretest contamination show nondetectable levels of CCl_4. EPA did not accept this criterion but instead required a cleanup criteria of nondetectable levels of CCl_4 in all the exhaust stacks for 3 consecutive months [21]. This requirement was met by the technology and the site was considered remediated by EPA.

Approximately 92,000 pounds of contaminants have been recovered from the Tyson's Dump site (Region 3) between November 1988 and July 1990. The site consists of two unlined lagoons and surrounding areas formerly used to store chemical wastes. The initial Remedial Investigation identified no soil heterogeneities and indicated that the water table was 20 feet below the surface. The maximum concentration in the soil (total VOCs) was approximately 4 percent. The occurence of dense nonaqueous-phase liquids (DNAPLs) was limited in areal extent. After over 18 months of operation, a number of difficulties have been encountered. Heterogeneities in soil grain size, water content, permeability, physical structure and compaction, and in contaminant concentrations have been identified. Soil contaminant concentrations of up to 20 percent and widespread distribution of DNAPLs have been found. A tar-like substance, which has caused plugging, has been found in most of the extraction wells. After 18 months of operation, wellhead concentrations of total VOCs have decreased by greater than 90 percent [23, p. 28].

As of December 31, 1990, approximately 45,000 pounds of VOCs had been removed from the Thomas Solvent Raymond Road Operable Unit at the Verona Well Field site (Region 5). A pilot-scale system was tested in the fall of 1987 and a full-scale operation began in March, 1988. The soil at the site consists of poorly-graded, fine-to-medium-grained loamy soils underlain by approximately 100 feet of sandstone. Groundwater is located 16 to 25 feet below the surface. Total VOC concentrations in the combined extraction well header have decreased from a high of 19,000 ug/1 in 1987 to approximately 1,500 ug/1 in 1990 [22].

Table 3
Extraction Well 4: TCE Reduction in Soil Strata—EPA Site Demonstration (Groveland, MA) [7, p. 31]

Depth (ft)	*Description of strata*	*Hydraulic Conductivity (cm/s)*	*Soil TCE concentration (mg/kg)* *Pre-treatment*	*Post-treatment*
0-2	Med. sand w/gravel	10^{-4}	2.94	ND
2-4	Lt. brown fine sand	10^{-4}	29.90	ND
4-6	Med. stiff lt. brown fine sand	10^{-5}	260.0	39.0
6-8	Soft dk. brown fine sand	10^{-5}	303.0	9.0
8-10	Med. stiff brown sand	10^{-4}	351.0	ND
10-12	V. stff lt. brown med. sand	10^{-4}	195.0	ND
12-14	V. Stiff brown fine sand w/silt	10^{-4}	3.14	2.3
14-16	M. stff grn-brn clay w/silt	10^{-8}	ND	ND
16-18	Soft wet clay	10^{-8}	ND	ND
18-20	Soft wet clay	10^{-8}	ND	ND
20-22	V. stiff brn med-coarse sand	10^{-4}	ND	ND
22-24	V. stiff brn med-coarse w/gravel	10^{-3}	6.17	ND

ND - Nondetectable level

An SVE pilot study has been completed at the Colorado Avenue Subsite of the Hastings (Nebraska) Groundwater Contamination site (Region 7). Trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), and tetrachloroethylene (PCE) occur in two distinct unsaturated soil zones. The shallow zone, from the surface to a depth of 50 to 60 feet, consists of sandy and clayey silt. TCE concentrations as high as 3,600 ug/1 were reported by EPA in this soil zone. The deeper zone consists of interbedded sands, silty sands, and gravelly sands extending from about 50 feet to 120 feet. During the first 630 hours of the pilot study (completed October 11, 1989), removal of approximately 1,488 pounds of VOCs from a deep zone extraction well and approximately 127 pounds of VOCs from a shallow zone extraction well were reported. The data suggest that SVE is a viable remedial technology for both soil zones [24].

As of November, 1989, the SVE system at the Fairchild Semi-conductor Corporation's former San Jose site (Region 9) has reportedly removed over 14,000 pounds of volatile contaminants. Total contaminant mass removal rates for the SVE system fell below 10 pounds per day on October 5, 1989 and fell below 6 pounds per day in December, 1989. At that time, a proposal to terminate operation of the SVE system was submitted to the Regional Water Quality Control Board for the San Francisco Bay Region [25, p.3].

Resource Conservation and Recovery Act (RCRA) LDRs that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements for CERCLA response actions. SVE can produce a treated waste that meets treatment levels set by BDAT but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where SVE does not meet these levels, it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. EPA has made the treatability variance process available in order to ensure that LDRs do not unnecessarily restrict use of alternative and innovative treatment technologies. Treatability variances are justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.3-06FS, July 1989) [13], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-07FS, December 1989) [14]. Another approach could be to use other treatment techniques in series with SVE to obtain desired treatment levels.

Technology Status

During 1989, at least 17 RODs specified SVE as part of the remedial action [5]. Since 1982, SVE has been selected as the remedial action, either alone or in conjunction with other treatment technologies, in more than 30 RODs for Superfund sites [2] [3] [4] [5] [6]. Table 4 presents the location, primary contaminants, and status for these sites [3] [4] [5]. The technology also has been used to clean up numerous underground gasoline storage tank spills.

A number of variations of the SVE system have been investigated at Superfund sites. At the Tinkhams Garage Site in New Hampshire (Region 1), a pilot study indicated that SVE, when used in conjunction with ground water pumping (dual extraction), was capable of treating soils to the 1 ppm clean-up goal [26, 3-7] [27]. Soil dewatering studies have been conducted to determine the feasability of lowering the water table to permit the use of SVE at the Bendix, PA Site (Region 3) [28]. Plans are underway to remediate a stockpile of 700 cubic yards of excavated soil at the Sodeyco Site in Mt. Holly, NC using SVE [29].

With the exception of the Barceloneta site, no Superfund site has yet been cleaned up to the performance objective of the technology. The performance objective is a site-specific contaminant concentration, usually in soil. This objective may be calculated with mathematical models with which EPA evaluates delisting petitions for wastes contaminated with VOCs [30]. It also may be possible to use a TCLP test on the treated soil with a corresponding drinking water standard contaminant level on the leachate.

Most of the hardware components of SVE are available off the shelf and represent no significant problems of availability. The configuration, layout, operation, and design of the extraction and monitoring wells and process components are site specific. Modifications may also be required as dictated by actual operating conditions.

On-line availability of the full-scale systems described in this bulletin is not documented. System components are highly reliable and are capable of continuous operation for the duration of the cleanup. The system can be shut down, if necessary, so that component failure can be identified and replacemnts made quickly for minimal downtime.

Based on available data, SVE treatment estimates are typically $50/ton for treatment of soil. Costs range from as low as $10/ton to as much as $150/ton [7]. Capital costs for SVE consist of extraction and monitoring well construction; vacuum blowers (positive displacement or centrifugal); vapor and liquid treatment systems piping, valves, and fittings (usually plastic); and instrumentation [31]. Operations and maintenance costs include labor, power, maintenance, and monitoring activities. Offgas and collected groundwater treatment are the largest cost items in this list; the cost of a cleanup can double if both are treated with activated carbon. Electric power costs vary by location (i.e., local utility rates and site conditions). They may be as low as 1 percent or as high as 2 percent of the total project cost.

Caution is recommended in using these costs out of context, because the base year of the estimates vary. Costs also are highly variable due to site variations as well as soil and contaminant characteristics that impact the SVE process. As contaminant concentrations are reduced, the cost effectiveness of an SVE system may decrease with time.

Table 4
Superfund Sites Specifying SVE as a Remedial Action

Site	*Location (Region)*	*Primary Contaminants*	*Status*
Groveland Wells 1 & 2	Groveland, MA (1)	TCE	SITE demonstration complete [2][7] Full-scale Remediation in design
Kellogg-Deering Well Field	Norwalk, CT (1)	PCE, TCE, and BTX	Pre-design [3] [5] [6]
South Municipal Water Supply Well	Peterborough, NH (1)	PCE, TCE, Toluene	Pre-design completion expected in the fall of 1991 [3] [5][6]
Tinkham Garage	Londonderry, NH (1)	PCE, TCE	Pre-design pilot study completed [26] [27]
Wells G & H	Woburn, MA (1)	PCE, TCE	In design [3] [5]
FAA Technical Center	Atlantic County, NJ (2)	BTX, PAHs, Phenols	In design [3] [5]
Upjohn Manufacturing Co.	Barceloneta, PR (2)	CCl_4	Project completed in 1988 [20] [21]
Allied Signal Aerospace-Bendix Flight System Div.	South Montrose, PA (3)	TCE	Pre-design tests and dewatering study completed [28]
Henderson Road	Upper Merion Township, PA (3)	PCE, TCE, Toluene, Benzene	Pre-design [3] [4]
Tyson's Dump	Upper Merion Township, PA (3)	PCE, TCE, Toluene, Benzene, Trichloropropane	In operation (since 11/88) [23]
Stauffer Chemical	Cold Creek, AL (4)	CCL_4, pesticides	Pre-design [5] [6]
Stauffer Chemical	Lemoyne, AL (4)	CCL_4, pesticides	Pre-design [5] [6]
Sodyeco	Mt. Holly, NC (4)	TCE, PAHs	Design approved [29]
Kysor Industrial	Cadillac, MI (5)	PCE, TCE,Toluene, Xylene	In design; pilot studies in progress [3] [5] [6]
Long Prairie	Long Prairie, MN (5)	PCE, TCE, DCE, Vinyl chloride	SVE construction expected in the Fall of 1991 [3] [6]
MIDCO 1	Gary, IN (5)	BTX, TCE, Phenol, Dichloro-methane, 2-Butanone, Chlorobenzene	In Design [3] [5] [6]
Miami County Incinerator	Troy, OH (5)	PCE; TCE; Toluene	Pre-design [3] [5] [6]
Pristine	Cincinnati, OH (5)	Benzene; Chloroform; TCE; 1,2-DCA; 1,2-DCE	Pre-design [3] [6]
Seymour Recycling	Seymour, IN (5)	TCE; Toluene; Chloromethane; cis-1, 2-DCE; 1,1,1-DCA; Chloroform	Pre-design investigation completed [32]
Verona Well Field	Battle Creek, MI (5)	PCE, TCA	Operational since 3/81 [22]
Wausau Groundwater Contamination	Wausau, WI (5)	PCE, TCE	Pre-design [3] [5] [6]
South Valley/ General Electric	Albuquerque, NM (6)	Chlorinated solvents	Pilot studies scheduled for Summer of 1991 [4] [6]
Hastings Groundwater Contamination	Hastings, NE (7)	CCL_4 ,Chloroform	Pilot studies completed for Colorado Ave. & Far-Marco subsites [24]
Sand Creek Industrial	Commerce City, CO (8)	PCE, TCE, pesticides	Pilot study completed [33]
Fairchild Semiconductor	San Jose, CA (9)	PCE, TCA, DCE, DCA, Vinyl chlorides, Phenols, and Freon	Operational since 1988, Currently conducting resaturation studies [25]
Fairchild Semiconductor/ MTV-1	Mountain View, CA (9)	PCE, TCA, DCE, DCA, Vinyl chlorides, Phenols, and Freon	Pre-design [3] [5]
Fairchild Semiconductor/ MTV-2	Mountain View, CA (9)	PCE, TCA, DCE, DCA, Vinyl chlorides, Phenols, and Freon	Pre-design [3] [5]
Intel Corporation	Mountain View, CA (9)	PCE, TCA, DCE, DCA, Vinyl chlorides, Phenols, and Freon	Pre-design [3] [5]
Raytheon Corporation	Mountain View, CA (9)	PCE, TCA, DCE, DCA, Vinyl chlorides, Phenols, and Freon	Pre-design [3] [5]
Motorola 52nd Street	Phoenix, AZ (9)	TCA, TCE, CCL_4, Ethylbenzene	Pre-design [3] [4] [6]
Phoenix-Goodyear Airport Area (also Litchfield Airport Area)	Goodyear, AZ (9)	TCE, DCE, MEK	North Unit - In design [34] South Unit - pilot study completed

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Engineering Bulletin
In Situ Steam Extraction Treatment

Purpose

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

Abstract

In situ steam extraction removes volatile and semivolatile hazardous contaminants from soil and groundwater without excavation of the hazardous waste. Waste constituents are removed in situ by the technology and are not actually treated. The use of steam enhances the stripping of volatile contaminants from soil and can be used to displace contaminated groundwater under some conditions. The resultant condensed liquid contaminants can be recycled or treated prior to disposal. The steam extraction process is applicable to organic wastes but has not been used for removing insoluble inorganics and metals. Steam is injected into the ground to raise the soil temperature and drive off volatile contaminants. Alternatively, steam can be injected to form a displacement front by steam condensation to displace groundwater. The contaminated liquid and steam condensate are then collected for further treatment.

In situ steam extraction is a developing technology that has had limited use in the United States. In situ steam extraction is currently being considered as a component of the remedy for only one Superfund site, the San Fernando Valley (Area 1), California site [1]* [2]. However, a limited number of commercial-scale in situ steam extraction systems are in operation. Two types of systems are discussed in this document: the mobile system and the stationary system. The mobile system consists of a unit that volatilizes contaminants in small areas in a sequential manner by injecting steam and hot air through rotating cutter blades that pass through the contaminated medium. The stationary system uses steam injection as a means to volatilize and displace contaminants from the undisturbed subsurface. Each system has specific applications; however, the lowest cost alternative will be determined by site-specific considerations. This bulletin provides information on the technology applicability, limitations, a description of the technology, types of residuals produced, site requirements, the latest performance data, the status of the technology, and sources for further information.

Technology Applicability

In situ steam extraction has been shown to be effective in treating soil and groundwater containing such contaminants as volatile organic compounds (VOCs) including halogenated solvents and petroleum wastes. The technology has been shown to be effective for extracting soluble inorganics (i.e., acids, bases, salts, heavy metals) on a laboratory scale [3]. The presence of semivolatile organic compounds (SVOCs) does not interfere with extraction of the VOCs [4, p. 12]. This process has been shown to be applicable for the removal of VOCs including chlorinated organic solvents [4, p. 9] [5, p. i], gasoline [6, p. 1265], and diesel [7, p. 506]. It has been shown to be particularly effective on alkanes and alkane-based alcohols such as octanol and butanol [8].

Steam extraction applies to less volatile compounds than ambient vacuum extraction systems. By increasing the temperature from initial conditions to the steam temperature, the vapor pressures of most contaminants will increase, causing them to become more volatile. Semivolatile components can volatilize at significant rates only if the temperature is increased [3, p. 3]. Steam extraction also may be used to remove low boiling point VOCs more efficiently.

* [reference number, page number]

Table 1
RCRA Codes for Wastes Applicable to Treatment by In Situ Steam Extraction

Spent Halogenated Solvents used in Degreasing	F001
Spent Halogenated Solvents	F002
Spent Non-Halogenated Solvents	F003
Spent Non-Halogenated Solvents	F004
Spent Non-Halogenated Solvents	F005

Table 2
Effectiveness of In Situ Steam Extraction on General Contaminant Groups for Soil and Groundwater

		Effectiveness		
		Mobile System		Stationary System
	Contaminant Groups	Soil	Groundwater	Soil/ Groundwater
Organic	Halogenated volatiles	■	▼	■
	Halogenated semivolatiles	▼	▼	▼
	Nonhalogenated volatiles	■	▼	■
	Nonhalogenated semivolatiles	▼	▼	▼
	PCBs	❑	❑	▼
	Pesticides	❑	❑	▼
	Dioxins/Furans	❑	❑	▼
	Organic cyanides	❑	❑	▼
	Organic corrosives	❑	❑	▼
Inorganic	Volatile metals	❑	❑	▼
	Nonvolatile metals	❑	❑	▼
	Asbestos	❑	❑	❑
	Radioactive materials	❑	❑	▼
	Inorganic corrosives	❑	❑	▼
	Inorganic cyanides	❑	❑	▼
Reactive	Oxidizers	❑	❑	▼
	Reducers	❑	❑	▼

■ Demonstrated Effectiveness: Successful treatability test at some scale completed
▼ Potential Effectiveness: Expert opinion that technology will work
❑ No Expected Effectiveness: Expert opinion that technology will not work

Table 1 lists specific Resource Conservation and Recovery Act (RCRA) wastes that are applicable to treatment by this technology. The effectiveness of the two steam extraction systems (mobile and stationary) on general contaminant groups for soil and groundwater is shown in Table 2. Examples of constituents within contaminant groups are provided in Reference 9, " Technology Screening Guide for Treatment of CERCLA Soils and Sludges." Table 2 is based on the current available information or professional judgment where no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at all sites. For the ratings used for this table, demonstrated effectiveness means that, based on treatability studies at some scale, the technology was effective for that particular contaminant and matrix. The ratings of potential effectiveness or no expected effectiveness are based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given. The table shows that the stationary system shows potential effectiveness for inorganic and reactive contaminants. This is only true if the compounds are soluble.

Limitations

Soil with high silt and clay content may become malleable and unstable when wet, potentially causing problems with support and mobility of the mobile steam extraction system. Remediation of low permeability soil (high clay content) requires longer treatment times [4, p. 8]. The soil must be penetrable by the augers and free of underground piping, wiring, tanks, and drums. Materials of this type must be relocated before treatment can commence. Surface and subsurface obstacles greater than 12 inches in diameter (e.g., rocks, concrete, wooden piles, trash, and metal) must be removed to avoid damage to the equipment. Substantial amounts of subsurface obstacles may preclude the use of a mobile system. A climate temperature range of 20–100°F is desirable for best operation of the mobile system [4, p. 18].

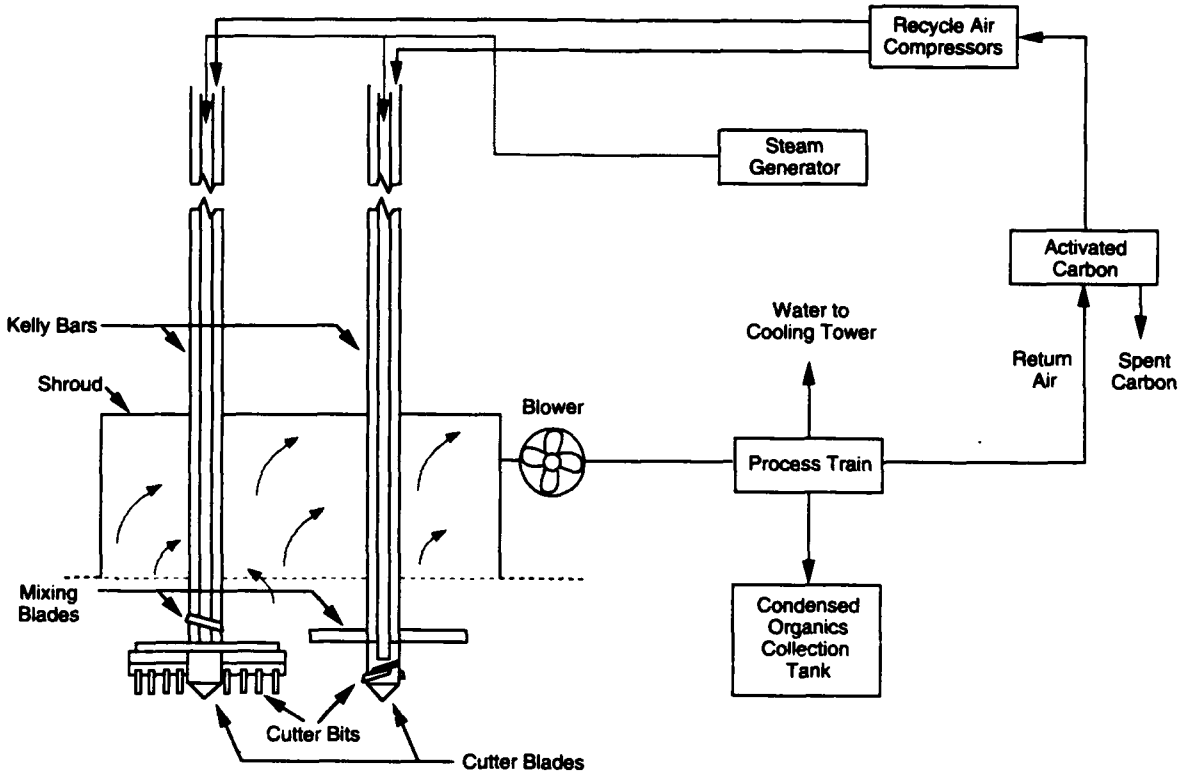
Mobile steam extraction systems can treat large contaminated areas but are limited by the depth of treatment. One system that has been evaluated can treat to a depth of 30 feet.

To be effective, the stationary steam extraction system requires a site with predominately medium- to high-permeability soil. Sites with homogeneous physical soil conditions are more amenable to the system. If impermeable lenses of contaminated soil exist, the stationary system may not remediate these areas to desired cleanup levels [5, p. 19]. However, a combination of steam injection followed by vacuum extraction (drying) may be effective on sites with heterogeneous soil conditions [10]. Steam extraction may be effective for remediation of contaminated groundwater near the source of contamination [5, p. 14] [10].

There may be residual soil contamination after application of in situ steam extraction. Study of a mobile system showed the average removal efficiency for volatile contaminants was 85%; 15% of the volatile compound contamination remained in the soil [4, p. 4]. If other organic or inorganic contamination exists, the cleaned soil may need subsequent treatment by some other technique (i.e., stabilization).

In situ steam extraction may not remove SVOCs and inorganics effectively. The operational costs of steam extraction are greater than ambient vacuum extraction, but may be offset by higher recovery and/or reduction in time required to remediate the site due to more efficient removal of contaminants.

Figure 1
Schematic of the Mobile Steam Extraction System



In situ steam extraction requires boilers to generate steam and a sophisticated process to capture and treat extracted steam and contaminants. Because the mobile system is mechanically complex its equipment may fail and shut down frequently; however, mechanical problems may be corrected fairly quickly. Equipment failure and shutdown are less frequent for the stationary system.

The increase in soil temperature may adversely affect other soil properties such as microbial populations, although some microbial populations can withstand soil temperatures up to 140°F.

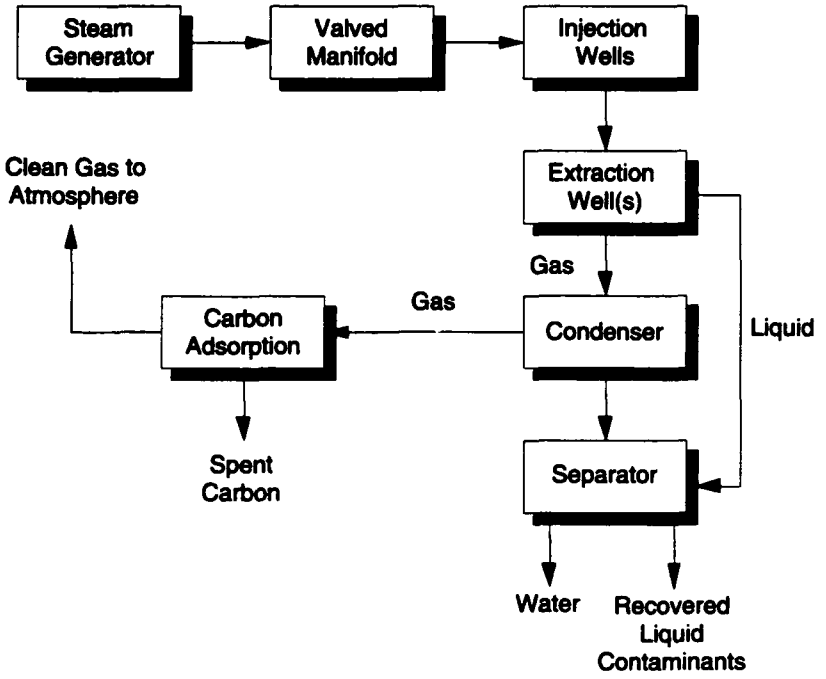
Technology Description

Figure 1 is a general schematic of a mobile steam extraction system [4, p. 48]. A process tower 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 through-flow of gases. Steam (at 400°F) and compressed air (at 275°F) are piped to nozzles located on the cutter blades. Heat from the injected steam and hot air volatilizes the organics. A steel shroud covers the area of soil undergoing treatment. Suction produced by the blower keeps the area underneath the shroud at a vacuum to pull gases from the soil and to protect against leakage to the outside environment. The offgases are pulled by the blower from the shroud to the treatment train, where water and organics are removed by condensation in coolers. The airstream is then treated by carbon adsorption, compressed, and returned to the soil being treated. Water is removed from the liquid stream with a gravity separator followed by batch distillation and carbon adsorption and is then recycled to a cooling tower. The condensed organics are collected and held for removal and transportation.

Mobile systems treat small areas of contamination until an entire site is remediated. The action of the cutter blades enables the process to treat low-permeability zones (high clay content) by breaking up the soil. Current systems treat blocks of soil measuring 7'4" x 4' by up to 30' deep.

Figure 2 is a schematic of a stationary steam extraction system [5, p. 9]. High-quality steam is delivered through individual valves and flow meters to the injection wells from the manifold. Gases and liquids are removed from the soil through the recovery wells. Gases flow through a condenser and into a separation tank where water and condensed gases are separated from the contaminant phase. Liquid organics are pumped from the separation tank through a meter and into a holding tank. The water may require treatment by carbon adsorption or another process to remove remaining contaminants. Noncondensible gases are passed through activated carbon tanks where contaminants are adsorbed before the cleaned air is vented to the atmosphere. A vacuum pump maintains the subatmospheric pressure on the recovery well and drives the flow of recovered gases. Contaminated liquids are pumped out of the recovery well to a wastewater tank.

Figure 2
Process Schematic of the Stationary Steam Extraction System



Process Residuals

At the conclusion of both processes, the contaminants are recovered as condensed organics in the produced water and on the spent carbon. Residual contamination will also remain in the soil. The recovered contaminants are temporarily stored on site and may require analysis to determine the need for further treatment before recycling, reuse, or disposal.

Separated, cleaned water is used as cooling tower makeup water in the mobile system. Also in this system, cleaned gas is heated and returned as hot air to the soil. Separated water from the stationary system must be treated to remove residual contaminants before disposal or reuse. The cleaned gas from this system is vented to the atmosphere. Both systems produce contaminated granular activated carbon from the gas cleaning. The carbon must be regenerated or disposed. There may be minor fugitive emissions of VOCs from the soil during treatment by the steam stripping systems and from the gas-phase carbon beds [4, p. 2].

Site Requirements

Power and telephone lines or other overhead obstacles must be removed or rerouted to avoid conflict with the 30-foot treatment tower on the mobile steam extraction system. Access roads must be available for transporting the mobile system. Sufficient land area must be available around the identified treatment zone to maneuver the unit and to place support equipment and trailers. The area to be treated by the mobile steam extraction system must be capable of supporting the treatment rig so that it does not sink or tip. The ground must be flat and gradable to less than 1% slope. A minimum treatment area of approximately 0.5 acre (20,000 ft^2) is necessary for economical use of the mobile system. Rectangular shaped treatment areas are most efficient. The mobile system requires a water supply of at least 8 to 10 gpm at 30 psig. Power for the process can be provided by on-board diesel generators [4, p. 18].

Boilers that generate steam for the stationary steam extraction system use no. 2 fuel oil or other hydrocarbon fuels. Water and electricity must be available at the site. The site must have sufficient room for a drilling rig to install the injection and extraction wells and for steam generation and waste treatment equipment to be set up, as well as room for support equipment and trailers.

Contaminated soils or waste materials are hazardous and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures. Storage should be provided to hold the process product streams until they have been tested to determine their acceptability for disposal, reuse, or release. Depending on the site, a method to store waste that has been prepared for treatment may be necessary. Storage capacity will depend on waste volume.

Onsite analytical equipment capable of determining site-specific organic compounds for performance assessment make the operation more efficient and provide better information for process control.

Performance Data

Toxic Treatments (USA) Inc. used a prototype of its mobile system to remediate a site in Los Angeles, California. The site soil had been contaminated by diesel and gasoline fuel

Table 3
Total Petroleum Hydrocarbons Removed by Toxic Treatments (USA) Inc. at Los Angeles, CA*

Calculated Value	Initial (mg/kg)	Final (mg/kg)	Percent Removal
Mean	2222	191	91

* This information is from vendor-published literature [7]; therefore, quality assurance has not been evaluated.

from underground storage tanks. For this application, the steam stripping was augmented with potassium permanganate to promote oxidation of hydrocarbons in the highly contaminated zones [7, p. 506]. Table 3 summarizes the results of the treatment by steam stripping. The level of petroleum hydrocarbons was reduced overall by an average of 91%. The mobile system was reported to have effectively reduced the level of petroleum hydrocarbon compounds found in the soil at a wide range of concentrations. However, the system's ability to remove the higher molecular weight, less volatile components of the diesel fuel was limited.

Under the Superfund Innovative Technology Evaluation (SITE) program, Toxic Treatments demonstrated an average VOC removal rate of 85 percent for a test area of 12 soil blocks [4, p. 10] as shown in Table 4. The average VOC post-treatment concentration was 71 ppm; the cleanup level for the site was 100 ppm. The primary VOCs were trichloroethene, tetrachloroethene, and chlorobenzene. The test achieved a treatment rate of 3 cu. yds./hr. in soils having high clay content and containing some high-boiling-point VOCs. Toxic Treatments obtained similar results in tests conducted throughout the site; baseline testing demonstrated an average post-treatment concentration of 61 ppm. The mobile technology also demonstrated the ability to diminish the level of SVOCs by approximately 50%, as shown in Table 5, although the fate of these SVOCs could not be determined [4, p. 45]. These tests were conducted on contamination in the unsaturated zone. A follow-up test was conducted on six soil blocks where treatment extended into the saturated zone. Pre-treatment data from the vendor indicated significant VOC contamination in this area. Post-treatment results showed that the average level of VOC contamination in the unsaturated zone was reduced to 53 ppm. Ketones (specifically acetone, 2-methyl-4-pentanone, and 2-butanone) were found to be the primary contaminants in the post-treatment soil. Data from the vendor indicated that similar reduction of VOCs occurred in the saturated zone.

The stationary steam extraction system using steam injection alone decreased soil contaminant concentrations by 90 percent in a recent pilot study [5]. High concentrations of individual contaminants were found in a low permeability zone by use of temperature logs. The residual high contaminant concentrations are thought to have been caused by: 1) retention of highly contaminated steam condensate found ahead of the condensation front in the dry, low-permeability zones and 2) the decreased evaporation rate of the high-boiling-point compounds due to the high water content in the low permeability zones [5, p. 19]. This issue is currently under study at the University of California, Berkeley [10]. Experimental testing has shown that a combination of steam

Table 4
Demonstration Test Results for Volatiles Removed by Toxic Treatments (USA) Inc. [4]

	12-Block Test Area		
Block Number	Pre-Treatment (µg/g)	Post-Treatment (µg/g)	Percent Removal
A-25-e	54	14	73
A-26-e	28	12	56
A-27-e	642	29	96
A-28-e	444	34	92
A-29-e	850	82	90
A-30-e	421	145	65
A-31-e	788*	61	92
A-32-e	479	64	87
A-33-e	1133	104	91
A-34-e	431	196	54
A-35-e	283	60	79
A-36-e	153	56	64

* Only analyses from two of the three sample cores taken were available.

Table 5
Demonstration Test Results for Semivolatiles Removed by Toxic Treatments (USA) Inc. [4]

	12-Block Test Area		
Block Number	Pre-Treatment (µg/g)	Post-Treatment (µg/g)	Percent Removal
A-25-e	595	82	86
A-26-e	1117	172	85
A-27-e	1403	439	69
A-28-e	1040	576	45
A-29-e	1310	726	45
A-30-e	1073	818	24
A-31-e	781	610	22
A-32-e	994	49	95
A-33-e	896	763	15
A-34-e	698	163	77
A-35-e	577	192	67
A-36-e	336	314	7

injection and vacuum extraction can effectively remove volatile contaminants from a heterogeneous soil type [10]. Steam injection followed by vacuum extraction produces an effective drying mechanism. The process achieves greater contaminant removals by enhancing the vapor flow from low- to high-permeability regions.

Performance data may be forthcoming from full-scale stationary system steam extraction projects being conducted by Solvent Service, Inc. and Hydro-Fluent, Inc. Data from laboratory-scale studies are also available [6] [3].

RCRA Land Disposal Restrictions (LDRs) that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements for CERCLA response actions. The in situ steam extraction technology produces liquid contaminants which may be recyclable or may require treatment to meet treatment levels set by BDAT. A common approach to treating liquid waste may be to use other treatment techniques in series with in situ steam extraction.

Technology Status

In situ extraction is being considered as a component of the selected remedy for the San Fernando Valley (Area 1) site in Burbank, California. The Area 1 site consists of an aquifer contaminated with VOCs, including TCE and PCE [1, p.145]. Toxic Treatments' mobile steam extraction technology (Detoxifier™) was used in 1986 to remediate 4,700 cu. yds. of soil contaminated with diesel fuel at the Pacific Commerce Center site in Los Angeles, California [7, p. 506].

In 1987, Toxic Treatments' mobile steam extraction system was selected as the remedial action to clean up approximately 8,700 cu. yds. of soil contaminated with VOCs and SVOCs at the GATX Annex Terminal site in San Pedro, California [11, p. I-1]. Treatability testing of the technology at the site has been underway to validate its performance prior to full site remediation. This system also has been evaluated under the SITE program at the site in San Pedro, California. Toxic Treatments expects to have a second generation Detoxifier™ available soon, which will be capable of operating on grades up to 5 percent.

For the mobile technology, the most significant factor influencing cost is the time of treatment or treatment rate. Treatment rate is influenced primarily by the soil type (soils with higher clay content require longer treatment times), the waste type, and the on-line efficiency. Cost estimates for this technology are strongly dependent on the treatment rate and range. A SITE demo indicated costs of $111-317/cu. yd. (for 10 and 3 cu. yd. treatment rates, respectively). These costs are based on a 70% on-line efficiency [4, p. 28].

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 20 feet of up to 41,000 cu. yds. of soil contaminated with numerous organic solvents [5, p. 3] [10]. Solvent Service hopes to make the SIVE system available for other applications in the future. The system consists of injection and extraction wells and a gas and liquid treatment process. Equipment for steam generation and extraction and contaminated gas/liquid treatment are trailer mounted.

Hydro-Fluent, Inc. is designing and constructing its first full-scale stationary steam extraction system to be used in Huntington Beach, California for recovery of 135,000 gallons of diesel fuel in soil to a depth of 40 feet at the Rainbow Disposal, Nichols Avenue site [12]. Bench and pilot-scale studies have been conducted.

For the stationary steam extraction system, the most significant factor influencing cost is the number of wells required per unit area, which is related to the depth of contamination and soil permeability. Shallow contamination requires lower operating pressures to prevent soil fracturing, and wells are placed closer together. Deeper contamination allows higher operating pressures and greater well spacing; therefore, fewer wells and lower capital cost. Cost estimates for this technology range from about $50–300/cu. yd., depending on site characteristics [10].

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Engineering Bulletin

EPA Soil Washing Treatment

Purpose

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

Abstract

Soil washing is a water-based process for mechanically scrubbing soils ex-situ to remove undesirable contaminants. The process removes contaminants from soils in one of two ways: by dissolving or suspending them in the wash solution (which is later treated by conventional wastewater treatment methods) or by concentrating them into a smaller volume of soil through simple particle size separation techn ies (similar to those used in sand and gravel operations). Soil washing systems incorporating both removal techniques offer the greatest promise for application to soils contaminated with a wide variety of heavy metal and organic contaminants.

The concept of reducing soil contamination through the use of particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically, to clay and silt soil particles. The silt and clay, in turn, are attached to sand and gravel particles by physical processes, primarily compaction and adhesion. Washing processes that separate the fine (small) clay and silt particles from the coarser sand and gravel soil particles effectively separate and concentrate the contaminants into a smaller volume of soil that can be further treated or disposed. The clean, larger fraction can be returned to the site for continued use. This set of assumptions forms the basis for the volume-reduction concept upon which most soil washing technology applications are being developed.

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

The final determination of the lowest cost alternative will be more site-specific than process equipment dominated. Vendors should be contacted to determine the availability of a unit for a particular site. This bulletin provides information on the technology applicability, the types of residuals resulting from the use of the technology, the latest performance data, site requirements, the status of the technology, and where to go for further information.

Technology Applicability

Soil washing can be used either as a stand-alone technology or in combination with other treatment technologies. In some cases, the process can deliver the performance needed to reduce contaminant concentrations to acceptable levels and, thus, serve as a stand-alone technology. In other cases, soil washing is most successful when combined with other technologies. It can be cost-effective as a pre-processing step in reducing the quantity of material to be processed by another technology such as incineration; it also can be used effectively to transform the soil feedstock into a more homogeneous condition to augment operations in the subsequent treatment system. In general, soil washing is effective on coarse sand and gravel contaminated with a wide range of organic, inorganic, and reactive contaminants. Soils containing a large amount of clay and silt typically do not respond well to soil washing, especially if it is applied as a stand-alone technology.

A wide variety of chemical contaminants can be removed from soils through soil washing applications. Removal efficiencies depend on the type of contaminant as well as the type of soil. Volatile organic contaminants often are easily removed from soil by washing; experience shows that volatiles can be removed with 90-99 percent efficiency or more. Semivolatile organics

may be removed to a lesser extent (40-90 percent) by selection of the proper surfactant. Metals and pesticides, which are more insoluble in water, often require acids or chelating agents for successful soil washing. The process can be applicable for the treatment of soils contaminated with specific listed Resource Conservation and Recovey Act (RCRA) wastes and other hazardous wastes including wood-preserving chemicals (pentachlorophenol, creosote), organic solvents, electroplating residues (cyanides, heavy metals), paint sludges (heavy metals), organic chemicals production residues, pesticides and pesticides production residues, and petroleum/oil residues [1, p. 659][2, p. 15][4][7 through 13]*.

The effectiveness of soil washing for general contaminant groups and soil types is shown in Table 1 [1, p. 659][3, p. 13][15, p.1]. Examples of constituents within contaminant groups are provided in Reference 3, "Technology Screening Guide For Treatment of CERCLA Soils and Sludges." This table is based on currently available information or professional judgment where definitive information is currently inadequate or unavailable. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. For the ratings used in this table, good to excellent applicability means the probability is high that soil washing will be effective for that particular contaminant and matrix. Moderate to marginal applicability indicates situations where care needs to be exercised in choosing the soil washing technology. When not applicable is shown, the technology will probably not work for that particular combination of contaminant group and matrix. Other sources of general observations and average removal efficiencies for different treatability groups are the Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.3-06FS), [16] and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-07FS) [17].

Information on cleanup objectives as well as the physical and chemical characteristics of the site soil and its contaminants is necessary to determine the potential performance of this technology and the requirements for waste preparation and pretreatment. Treatability tests are also required at the laboratory screening, bench-scale and/or pilot-scale level(s) to determine

Table 1
Applicability of Soil Washing on General Contaminant Groups for Various Soils

Contaminant Groups		*Matrix* *Sandy/ Gravelly Soils*	*Silty/Clay Soils*
Organic	Halogenated volatiles	■	▼
	Halogenated semivolatiles	▼	▼
	Nonhalogenated volatiles	■	▼
	Nonhalogenated semivolatiles	▼	▼
	PCBs	▼	▼
	Pesticides (halogenated)	▼	▼
	Dioxins/Furans	▼	▼
	Organic cyanides	▼	▼
	Organic corrosives	▼	▼
Inorganic	Volatile metals	■	▼
	Nonvolatile metals	■	▼
	Asbestos	❑	❑
	Radioactive materials	▼	▼
	Inorganic corrosives	▼	▼
	Inorganic cyanides	▼	▼
Reactive	Oxidizers	▼	▼
	Reducers	▼	▼

■ Good to Excellent Applicability: High probability that technology will be successful

▼ Moderate to Marginal Applicability: Exercise care in choosing technology

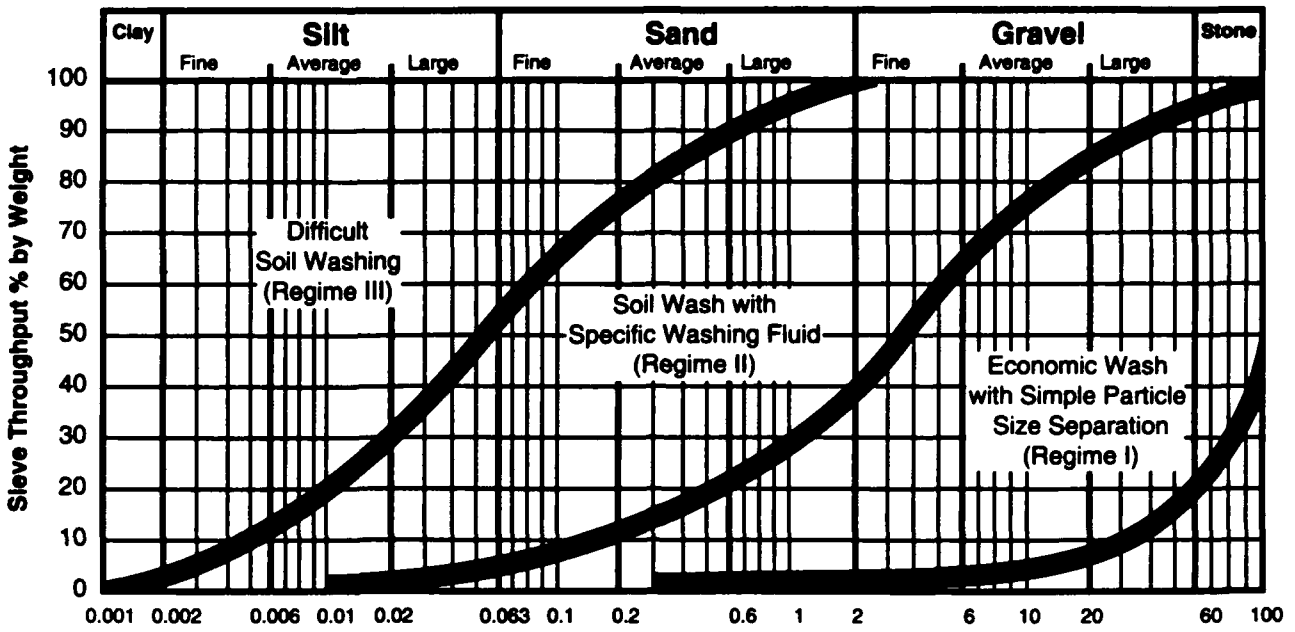
❑ Not Applicable: Expert opinion that technology will not work

* [reference number, page number]

Table 2
Waste Soil Characterization Parameters

Parameter	*Purpose and Comment*
Key Physical	
Particle size distribution:	
>2 mm	Oversize pretreatment requirements
0.25-2 mm	Effective soil washing
0.063-0.25 mm	Limited soil washing
<0.063 mm	Clay and silt fraction—difficult soil washing
Other Physical	
Type, physical form, handling properties	Affects pretreatment and transfer requirements
Moisture content	Affects pretreatment and transfer requirements
Key Chemical	
Organics Concentration Volatility Partition coefficient	Determine contaminants and assess separation and washing efficiency, hydrophobic interaction, washing fluid compatibility, changes in washing fluid with changes in contaminants. May require preblending for consistent feed. Use the jar test protocol to determine contaminant partitioning.
Metals	Concentration and species of constituents (specific jar test) will determine washing fluid compatibility, mobility of metals, posttreatment.
Humic acid	Organic content will affect adsorption characteristics of contaminants on soil. Important in marine/wetland sites.
Other Chemical	
pH, buffering capacity	May affect pretreatment requirements, compatibility with equipment materials of construction, wash fluid compatibility.

Figure 1
Soil Washing Applicable Particle Size Range



the feasibility of the specific soil washing process being considered and to understand waste preparation and pretreatment steps needed at a particular site. If bench-test results are promising, pilot-scale demonstrations should normally be conducted before final commitment to full-scale implementation. Treatability study procedures are explained in the EPA's forthcoming document entitled "Superfund Treatability Study Protocol: Bench-Scale Level of Soils Washing for Contaminated Soils" [14].

Table 2 contains physical and chemical soil characterization parameters that must be established before a treatability test is conducted on a specific soil washing process. The parameters are defined as either "key" or "other" and should be evaluated on a site-specific basis. Key parameters represent soil characteristics that have a direct impact on the soil washing process. Other parameters should also be determined, but they can be adjusted prior to the soil washing step based on specific process requirements. The table contains comments relating to the purpose of the specific parameter to be characterized and its impact on the process [6, p. 90][14, p. 35].

Particle size distribution is the key physical parameter for determining the feasibility of using a soil washing process. Although particle size distribution should not become the sole reason for choosing or eliminating soil washing as a candidate technology for remediation, it can provide an initial means of screening for the potential use of soil washing. Figure 1 presents a simplistic particle size distribution range of curves that illustrate a general screening definition for soil washing technology.

In its simplest application, soil washing is a particle size separation process that can be used to segregate the fine fractions from the coarse fractions. In Regime I of Figure 1, where coarse soils are found, the matrix is very amenable to soil washing using simple particle size separation.

Most contaminated soils will have a distribution that falls within Regime II of Figure 1. The types of contaminants found in the matrix will govern the composition of the washing fluid and the overall efficiency of the soil washing process.

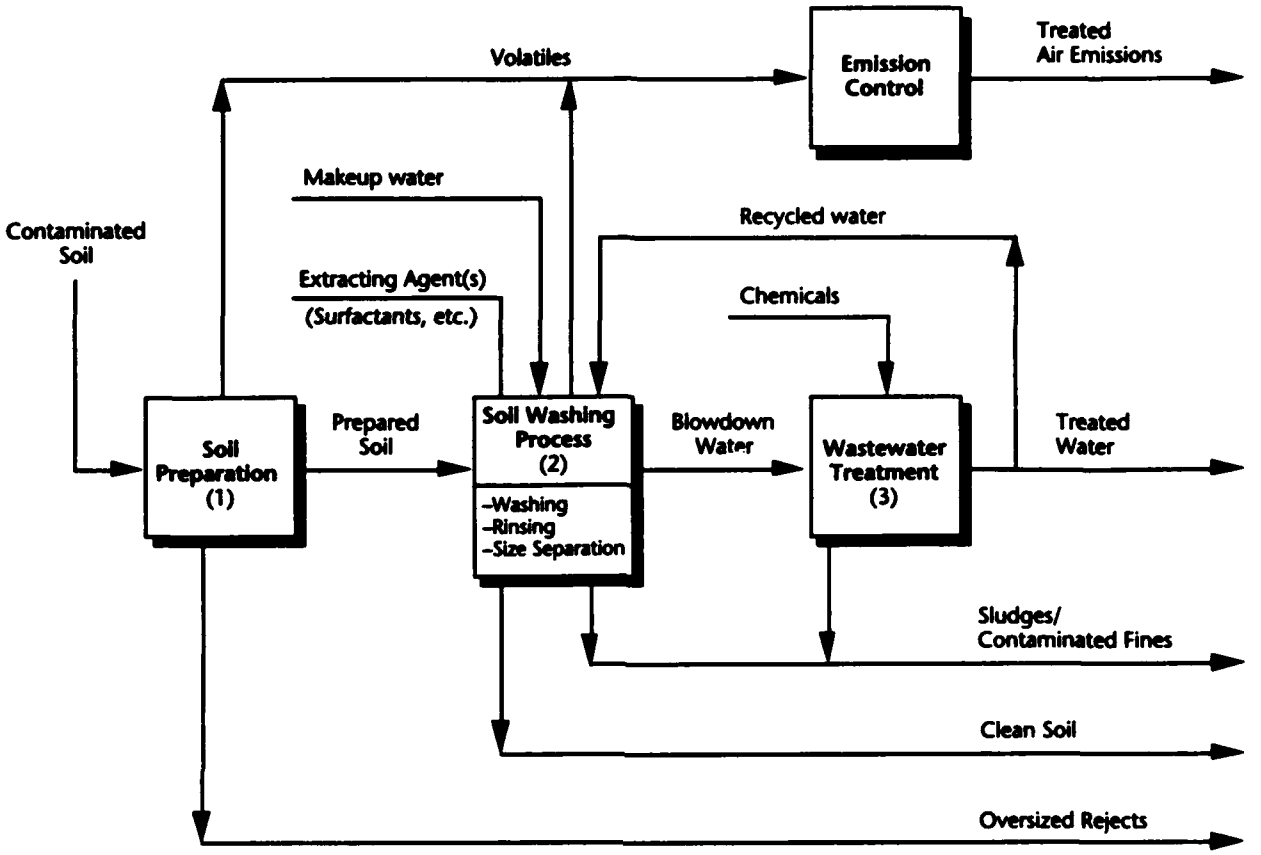
In Regime III of Figure 1, soils consisting largely of finer sand, silt, and clay fractions, and those with high humic content, tend to contain strongly adsorbed organics that generally do not respond favorably to systems that work by only dissolving or suspending contaminants in the wash solution. However, they may respond to soil washing systems that also incorporate a particle size separation step whereby contaminants can be concentrated into a smaller volume.

Limitations

Contaminants in soils containing a high percentage of silt- and clay-sized particles typically are strongly adsorbed and difficult to remove. In such cases, soil washing generally should not be considered as a stand-alone technology.

Hydrophobic contaminants generally require surfactants or organic solvents for their removal from soil. Complex mixtures of contaminants in the soil (such as a mixture of metals, nonvolatile organics, and semivolatile organics) and

Figure 2
Aqueous Soil Washing Process



frequent changes in the contaminant composition in the soil matrix make it difficult to formulate a single suitable washing fluid that will consistently and reliably remove all of the different types of contaminants from the soil particles. Sequential washing steps may be needed. Frequent changes in the wash formulation and/or the soil/wash fluid ratio may be required [3, p. 76][14, p. 7].

While washwater additives such as surfactants and chelants may enhance some contaminant removal efficiencies in the soil washing portion of the process, they also tend to interfere with the downstream wastewater treatment segments of the process. The presence of these additives in the washed soil and in the wastewater treatment sludge may cause some difficulty in their disposal [14, p. 7][15, p. 1]. Costs associated with handling the additives and managing them as part of the residuals/wastewater streams must be carefully weighed against the incremental improvements in soil washing performance that they may provide.

Technology Description

Figure 2 is a general schematic of the soil washing process [1, p. 657][3, p. 72][15, p. 1].

Soil preparation (1) includes the excavation and/or moving of contaminated soil to the process where it is normally screened to remove debris and large objects. Depending upon the technology and whether the process is semibatch or continuous, the soil may be made pumpable by the addition of water.

A number of unit processes occur in the soil washing process (2). Soil is mixed with washwater and possibly extraction agent(s) to remove contaminants from soil and transfer them to the extraction fluid. The soil and washwater are then separated, and the soil is rinsed with clean water. Clean soil is then removed from the process as product. Suspended soil particles are recovered directly from the spent washwater, as sludge, by gravity means, or they may be removed by flocculation with a selected polymer or chemical, and then separated by gravity. These solids will most likely be a smaller quantity but carry higher levels of contamination than the original soil and, therefore, should be targeted for either further treatment or secure disposal. Residual solids from recycle water cleanup may require post-treatment to ensure safe disposal or release. Water used in the soil washing process is treated by conventional wastewater treatment processes to enable it to be recycled for further use.

Wastewater treatment (3) processes the blowdown or discharge water to meet regulatory requirements for heavy metal content, organics, total suspended solids, and other parameters. Whenever possible, treated water should be recycled to the soil washing process. Residual solids, such as spent ion exchange resin and carbon, and sludges from biological treatment may require post-treatment to ensure safe disposal or release.

Vapor treatment may be needed to control air emissions from excavation, feed preparation, and extraction; these emissions are collected and treated, normally by carbon adsorption or incineration, before being released to the atmosphere.

Process Residuals

There are four main waste streams generated during soil washing: contaminated solids from the soil washing unit, wastewater, wastewater treatment sludges and residuals, and air emissions.

Contaminated clay fines and sludges resulting from the process may require further treatment using acceptable treatment technologies (such as incineration, low temperature desorption, solidification and stabilization, biological treatment, and chemical treatment) in order to permit disposal in an environmentally safe manner [16]. Blowdown water may need treatment to meet appropriate discharge standards prior to release to a local, publicly owned wastewater treatment works or receiving stream. To the maximum extent practical, this water should be recovered and reused in the washing process. The wastewater treatment process sludges and residual solids, such as spent carbon and spent ion exchange resin, must be appropriately treated before disposal. Any air emissions from the waste preparation area or the washing unit should be collected and treated, as appropriate to meet applicable regulatory standards.

Site Requirements

Access roads are required for transport of vehicles to and from the site. Typically, mobile soil washing process systems are located onsite and may occupy up to 4 acres for a 20 ton/hour unit; the exact area will depend on the vendor system selected, the amount of soil storage space, and/or the number of tanks or ponds needed for washwater preparation and wastewater treatment.

Typical utilities required are water, electricity, steam, and compressed air. An estimate of the net (consumed) quantity of local water required for soil washing, assuming water cleanup and recirculation, is 130,000-800,000 gallons per 1,000 cubic yards (2,500,000 lbs.) of soil (approximately 0.05-0.3 gallons per pound).

Because contaminated soils are usually considered hazardous, their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures during soil washing operations.

Moisture content of soil must be controlled for consistent handling and treatment; this can be accomplished, in part, by covering excavation, storage, and treatment areas.

Fire hazard and explosion considerations should be minimal, since the soil washing fluid is predominantly water. Generally, soil washing does not require storing explosive, highly reactive materials.

Climatic conditions such as annual or seasonal precipitation cause surface runoff and water infiltration. Berms, dikes, or other runoff control methods may be required. Cold weather freezing must also be considered for aqueous systems and soil excavation operations.

Proximity to a residential neighborhood will affect plant noise requirements and emissions permitted in order to minimize their impact on the population and meet existing rules and regulations.

If all or part of the processed soil is to be redeposited at the site, storage areas must be provided until analytical data are obtained that verifies that treatment standards have been achieved. Onsite analytical capability could expedite the storage/final disposition process. However, soil washing might be applied to many different contaminant groups. Therefore, the analytes that would have to be determined are site specific, and the analytical equipment that must be available will vary from site to site.

Performance Data

The performances of soil washing processes currently shown to be effective in specific applications are listed in Table 3 [1][2][4][7 through 13]. Also listed are the range of particle size treated, contaminants successfully extracted, byproduct wastes generated, extraction agents used, major extraction equipment for each system, and general process comments.

The data presented for specific contaminant removal effectiveness were obtained from publications developed by the respective soil washing system vendors. The quality of this information has not been determined.

RCRA Land Disposal Restrictions (LDRs) that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements (ARARs) for CERCLA response actions. The soil washing technology can produce a treated waste that meets treatment levels set by BDAT, but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where soil washing does not meet these levels, it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. EPA has made the treatability variance process available in order to ensure that LDRs do not unnecessarily restrict the use of alternative and innovative treatment technologies. Treatability variances may be justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil

and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.3-06FS) [16], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-07FS) [17]. Another approach could be to use other treatment techniques in series with soil washing to obtain desired treatment levels.

Technology Status

During 1986-1989, soil washing technology was selected as one of the source control remedies at eight Superfund sites: Vineland Chemical, New Jersey; Koppers Oroville Plant, California; Cape Fear Wood Preserving, North Carolina; Ewan Property, New Jersey; Tinkam Garage, New Hampshire; United Scrap, Ohio; Koppers/Texarkana, Texas; and South Cavalcade, Texas [18].

A large number of vendors provide a soil washing technology. Table 3 shows the current status of the technology for 14 vendors. The front portion of the table indicates the scale of equipment available from the vendor and gives some indication of the vendor's experience by showing the year it began operation.

Processes evaluated or used for site cleanups by the EPA are identified separately by asterisks in the Proprietary Vendor Process/EPA column in Table 3.

The following soil washing processes that are under development have not been evaluated by the EPA or included in Table 3. Environmental Group, Inc. of Webster, Texas, has a process that reportedly removes metals and oil from soil. Process efficiency is stated as greater than 99 percent for lead removal from soils cleaned in Concord, California; greater than 99 percent for copper, lead, and zinc at a site in Racine, Wisconsin; and 94 percent for PCB removal on a Morrison-Knudsen Company project. The process does not appear to separate soil into different size fractions. Detailed information on the process is not available. Consolidated Sludge Company of Cleveland, Ohio, has a soil washing system planned that incorporates their Mega-sludge Press at the end of the process for dewatering solids. The system has not yet been built.

Vendor-supplied treatment costs of the processes reviewed ranged from $50 to $205 per ton of feed soil. The upper end of the cost range includes costs for soil residue disposal.

EPA Contact

Technology-specific questions regarding soil washing may be directed to:

Michael Gruenfeld
U.S. EPA, Releases Control Branch
Risk Reduction Engineering Laboratory
Woodbridge Avenue, Building 10
Edison, New Jersey 08837
Telephone FTS 340-6625 or (201) 321-6625.

Table 3. Summary of Performance Data and Technology Status - Part I

Proprietary Vendor Process/EPA	Highest Scale of Operation	Year Operation Began	Range of Particle Size Treated	Contaminants Extracted From Soil	Extraction Agent(s)
U.S. Processes					
(1) SOIL CLEANING COMPANY OF AMERICA [5][15, p. 2]	Full scale 15 tons/hr	1988	Bulk soil	Oil and grease	Hot water with surfactant
(2)* BIOTROL SOIL TREATMENT SYSTEM (BSTS) [4, p. 6][12]	Pilot scale 500 lbs/hr	Fall, 1987	Above clay size and below 0.5 in. Some cleaning of fine particles in bio-reactor	Organics - pentachlorophenol, creosote, naphthalene, pyrene, fluorene, etc.	Proprietary conditioning chemicals
(3) EPA'S MOBILE COUNTER-CURRENT EXTRACTOR [9][5, p. 5]	Pilot scale 4.1 tons/hr	Modified with drum washer and shakedown-1982 Full Scale-1986	2-25 mm in drum washer <2 mm in four-stage extractor	Soluble organics (phenol, etc.) Heavy metals (Pb, etc.)	Various solvents, additives, surfactants, redox acids and bases Chelating agent (EDTA)
(4)* EPA'S FIRST GENERATION PILOT DRUM SCREEN WASHER [10, p. 8]	Pilot scale	1988	Oversize (>2 mm) removed prior to treatment	Petroleum hydrocarbons	Biodegradable surfactant (aqueous slurry)
(5)* MTA REMEDIAL RESOURCES [11][15, p. 2]	Bench scale	N/A	Oversize removed prior to treatment	Organics (oil) Heavy metals (inorganics) removed using counter-current decantation with leaching	Surfactants and alkaline chemicals added upstream of froth flotation cells. Acid for leaching.
Non-U.S. Processes					
(6) ECOTECHNIEK BV [2, p. 17]	Commercial 100 ton/hr max	1982	Sandy soil	Crude oil	None. Water-sand slurry heated to 90°C max. with steam.
(7) BODEMSANERING NEDERLAND BV (BSN) [2, p. 17]	Commercial 20 ton/hr	1982	>100 mm removed No more than 20% <63 µm Sludge <30 µm not cleaned	Oil from sandy soil	None. Uses high pressure water jet for soils washing.
(8) HARBAUER [2, p. 20][7, p. 5]	Commercial 15-20 tons/hr	Lab - 1985 Commercial -1986 With fines removal - 1987	15 µm - 5mm Pre-treatment: coarse screens, electromagnet blade washer	Mostly organics Limited heavy metals removal experience	Hydraulically produced oscillation/ vibration Surfactants Acid/base
(9) HWZ BODEMSANERING BV [2, p. 17]	Commercial 20-25 tons/hr	1984	<10 mm and >63 µm	Cyanide, Chlorinated HC, some heavy metals, PNA	Sodium Hydroxide to adjust pH Surfactants
(10) HEIJMAN MILIEUTECHNIEK BV [2,p.17][7, p. 6]	Pilot scale 10-15 tons/hr	1985	<10 mm and no more than 30% <63 µm	Cyanide, heavy metals, mineral oil (water immiscible hydro-carbons)	Proprietary extraction agents. Hydrogen Peroxide (H_2O_2) added to react with extracted CN to form CO_2 and NH_3
(11) HEIDEMIJ FROTH FLOTATION [7, p. 8]	Full scale	N/A	<4 mm and no more than 20% <50 µm	Cyanide, heavy metals, chlorinated HCs, oil, toluene, benzene, pesticides, etc.	Proprietary Surfactants and other proprietary chemicals

*Process evaluated or used for site cleanup by the EPA. N/A = Not available.

Table 3. Summary of Performance Data and Technology Status - Part I (continued)

Proprietary Vendor Process/EPA	Highest Scale of Operation	Year Operation Began	Range of Particle Size Treated	Contaminants Extracted From Soil	Extraction Agent(s)
Non U.S. Processes (continued)					
(12) EWH ALSEN - BREITENBURG Dekomat System [2, p. 20]	Pilot scale 8-10 cu. m/hr	N/A	<80 mm Clays treated offsite	Oil from sandy soil	Proprietary
(13) TBSG INDUSTRIEVEITIETUNGEN Oil Crep I System [7, p. 7]	Pilot scale	1986	Sand <50 mm Particles <100 µm treated offsite	Hydrocarbon and oil	Proprietary combination of surfactants, solvents, and aromatic hydrocarbons
(14) KLOCKNER UMWELTECHNIK Jet-Modified BSN [2, p. 20]	Pilot scale	N/A	No more than 20% <63 µm	Aliphatics and aromatics with densities < water, volatile organics, some other hydrocarbons	None. Soil blasted with a water jet (at 5,075 psi)

Table 3. Summary of Performance Data and Technology Status - Part II

Proprietary Vendor Process/EPA	Byproduct Wastes Generated	Extraction Equipment	Efficiency of Contaminant Removal	Additional Process Comments
U.S. Processes				
(1) SOIL CLEANING OF AMERICA	Wet oil	Screw conveyors	Contaminant: Oil and grease; Removal Efficiency %: 50-83; Residual ppm: 250-600	Three screw conveyors operated in series, hot water with surfactant injected into each stage. Final soil rinse on a fourth screw conveyor.
(2) * BIOTROL SOIL TREATMENT SYSTEM (BSTS)	Oil and grease Sludge from biological treatment	Agitated conditioning tank Froth flotation Slurry bioreactor	For the case presented: 90-95% for Pentachlorophenol; to residuals <115 ppm. 85-95% for most other organics; to residuals <1 ppm.	Dewatered clays and organics to be treated offsite by incineration, solidification, etc. Washed soil was approx. 78% of feed. Therefore, significant volume reduction was achieved.
(3) EPA's MOBILE COUNTER-CURRENT EXTRACTOR	Clay fraction Recovered organics (extractor skimmings) Spent carbon (oversize)	Drum screen Water knife Soil scrubber 4-Stage Counter-current chemical extractor	Contaminant: Phenol; Removal Efficiency %: 90 from in. soil, 80 from or. soil; Residual ppm: 1, 96 Contaminant: AS_2O_3; Removal Efficiency %: 50-80; Residual ppm: 0.5-1.3	Clay fraction treated elsewhere.
(4) * EPA's FIRST GENERATION PILOT DRUM SCREEN WASHER (PDSW)	Sludge Flocculated fines	Drum screen washer	Contaminant: Oil and grease; Soil Size Fraction mm: 0.25-2, <0.25; Removal Effic.%: 99, 90; Residual ppm: <5, 2400	Process removal efficiency increases if extracting medium is heated. Install wet classifiers beneath the PDSW to remove waste water from treated soil. Auger classifiers are required to to discharge particles effectively.
(5)* MTA REMEDIAL RESOURCES (MTARRI) Froth Flotation	Flocculation froth	Reagent blend tank Flotation cells Counter-current decantation	Contaminant: Volatile organics; Removal Efficiency %: 98-99+; Residual ppm: < 50 Contaminant: Semivolatile organics; Removal Efficiency %: 98-99+; Residual ppm: < 250 Contaminant: Most fuel products; Removal Efficiency %: 98-99+; Residual ppm: < 2200	Flotation cells linked by underflow weir gates. Induced air blown down a center shaft in each cell. Continuous flow operation. Froth contains 5-10 wt% of feed soil.

*Process evaluated or used for site cleanup by the EPA. N/A = Not available.

Table 3. Summary of Performance Data and Technology Status - Part II (continued)

Proprietary Vendor Process/EPA	Byproduct Wastes Generated	Extraction Equipment	Efficiency of Contaminant Removal	Additional Process Comments
Non U.S. Processes				
(6) ECOTECHNIEK BV	Wet oil	Jacketed, agitated tank	About 90% 20,000 ppm residual oil	Effectiveness of process dependent on soil particle size and type of oil to be separated.
(7) BODEMSANERING NEDERLAND BV (BSN)	Oil/organics recovered from wastewater fines	Water jet	Selected results: Contaminant — Removal Efficiency % — Residual ppm Aromatics — >81 — >45 PNAs — 95 — 15 Crude oil — 97 — 2300	No comments
(8) HARBAUER OF AMERICA	Carbon which may contain contaminants	Conditioning tank Low frequency vibration unit	Contaminant — Removal Efficiency % — Residual ppm Organic-Cl — — ND Tot. organics — 96 — 159-201 Tot. phenol — 86-94 — 7-22.5 PAH — 86-90 — 91.4-97.5 PCB — 84-88 — 0.5-1.3	Vibrating screw conveyor used. Cleaned soil separated from extractant liquor in stages; coarse soil by sedimentation, medium fraction in hydroclone, fines (15-20 µm) by vacuum filter press.
(9) HWZ BODEMSANERING BV	Fines Sludge containing iron cyanide Large particles — carbon, wood, grass	Scrubber (for caustic addition) Upflow classifier	Contaminant — Removal Efficiency % — Residual ppm CN — 95 — 5-15 PNAs — 98 — 15-20 Chlorin-HC — 98 — <1 Heavy metals — 75 — 75-125	When the fines fraction (<63 µm) is greater than 20%, the process is not economical. HWZ has had some problems in extracting PNAs and oily material.
(10) HEIJMAN MILIEUTECHNIEK BV	Flocculated fines sludge Oil (if any) and silt	Mix tank followed by soils fraction equipment — hydroclones, sieves, tilt plate separators	Contaminant — Removal Efficiency % — Residual ppm Cyanide — 93-99 — <15 Heavy metal cations — approx. 70 — <200	Process works best on sandy soils with a minimum of humus-like compounds. Because no sand or charcoal filters are employed by Heijmans, the system does not remove contaminants such as chlorinated hydrocarbons.
(11) HEIDEMIJ FROTH FLOTATION	Contaminated float	Conditioning tank Froth flotation tanks	Contaminant — Removal Efficiency % — Residual ppm Cyanide — >95 — 5 Heavy metals — >90 avg — >150 Chlorin-HC — >99 — 0.5 Oil — >99 — 20	Process has broad application for removing hazardous materials from soil. Most experience has been on a laboratory scale.
(12) EWH ALSEN - BREITENBURG Dekomat System	Recovered oil Flocculated fines (sludge)	High-shear stirred tank	About 95% oil removed	Cleaned soil from high shear stirred tank is separated into fractions using vibrating screens, screw classifiers, hydroclones, and sedimentation tanks.
(13) TBSG INDUSTRIEVERTIET-UNGEN Oil Crep I System	Oil phase containing Oil Crep I	Screw mixer followed by a rotating separation drum for oil recovery	>95% Removal of hydrocarbons has been achieved. Results are influenced by other contaminants present.	Oil Crep system was used successfully in Flansburg, FRG (in 1986) to remove PCBs, PAHs, and other hydrocarbons.
(14) KLOCKNER UMWELTECHNIK High Pressure Water Jet-Modified BSN	Oil/organics recovered from wastewater fines Sludge	Water jet - circular nozzle arrangement	Selected results: Contaminant — Removal Efficiency % — Residual ppm HC — 96.3 — 82.05 Chlorin-HC — >75. — <0.01 Aromatics — 99.8 — <0.02 PAHs — 95.4 — 15.48 Phenol — >99.8 — <0.01	No comments

*Process evaluated or used for site cleanup by the EPA. N/A = Not available.

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EPA

Engineering Bulletin
Solvent Extraction Treatment

Purpose

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

Abstract

Solvent extraction does not destroy wastes, but is a means of separating hazardous contaminants from soils, sludges, and sediments, thereby reducing the volume of the hazardous waste that must be treated. Generally it is used as one in a series of unit operations, and can reduce the overall cost for managing a particular site. It is applicable to organic wastes and is generally not used for treating inorganics and metals [15, p.64].* The technology uses an organic chemical as a solvent [14, p. 30], and differs from soil washing, which generally uses water or water with wash improving additives. During 1989, the technology was one of the selected remedies at six Superfund sites. Commercial-scale units are in operation. There is no clear solvent extraction technology leader by virtue of the solvent employed, type of equipment used, or mode of operation. The final determination of the lowest cost alternative will be more site specific than process equipment dominated. Vendors should be contacted to determine the availability of a unit for a particular site. This bulletin provides information on the technology applicability, the types of residuals produced, the latest performance data, site requirements, the status of the technology, and sources for further information.

Technology Applicability

Solvent extraction has been shown to be effective in treating sediments, sludges, and soils containing primarily organic contaminants such as polychlorinated biphenyls (PCB), volatile organic compounds (VOC), halogenated solvents, and petroleum wastes. The technology is generally not used for extracting inorganics (i.e., acids, bases, salts, heavy metals). Inorganics usually do not have a detrimental effect on the extraction of the organic components, and sometimes metals that pass through the process experience a beneficial effect by changing the chemical compound to a less toxic or leachable form. The process has been shown to be applicable for the separation of the organic contaminants in paint wastes, synthetic rubber process wastes, coal tar wastes, drilling muds, wood treating wastes, separation sludges, pesticide/insecticide wastes, and petroleum refinery oily wastes [3].

Table 1 lists the codes for the specific Resource Conservation and Recovery Act (RCRA) wastes that have been treated by this technology [3][1, p.11]. The effectiveness of solvent extraction on general contaminant groups for various matrices is shown in Table 2 [13, p.1] [15, p.10]. Examples of constituents within contaminant groups are provided in Reference 15, "Technology Screening Guide for Treatment of CERCLA Soils and Sludges." This table is based on the current available information or professional judgment where no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale treatability was tested to show the technology was effective for that particular contaminant and matrix. The ratings of potential effectiveness, or no expected effectiveness are both based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given.

* [reference number, page number]

Limitations

Organically bound metals can co-extract with the target organic pollutants and become a constituent of the concentrated organic waste stream. This is an unfavorable occurrence because the presence of metals can restrict both disposal and recycle options.

Table 1
RCRA Codes for Wastes Treated by Solvent Extraction

Wood Treating Wastes	K001
Water Treatment Sludges	K044
Dissolved Air Flotation (DAF) Float	K048
Slop Oil Emulsion Solids	K049
Heat Exchanger Bundles Cleaning Sludge	K050
American Petroleum Institute (API) Separator Sludge	K051
Tank Bottoms (leaded)	K052
Ammonia Still Sludge	K060
Pharmaceutical Sludge	K084
Decanter Tar Sludge	K089
Distillation Residues	K101

Table 2
Effectiveness of Solvent Extraction on General Contaminant Groups for Soil, Sludge, and Sediments

	Treatability Groups	Effectiveness Soil	Sludge	Sediments
Organic	Halogenated volatiles	▼	▼	▼
	Halogenated semivolatiles	■	▼	▼
	Nonhalogenated volatiles	■	■	▼
	Nonhalogenated semivolatiles	■	■	▼
	PCBs	■	■	■
	Pesticides	■	▼	▼
	Dioxins/Furans	▼	▼	▼
	Organic cyanides	▼	▼	▼
	Organic corrosives	▼	▼	▼
Inorganic	Volatile metals	❑	❑	❑
	Nonvolatile metals	❑	❑	❑
	Asbestos	❑	❑	❑
	Radioactive materials	❑	❑	❑
	Inorganic corrosives	❑	❑	❑
	Inorganic cyanides	❑	❑	❑
Reactive	Oxidizers	❑	❑	❑

■ Demonstrated Effectiveness: Successful treatability test at some scale completed
▼ Potential Effectiveness: Expert opinion that technology will work
❑ No Expected Effectiveness: Expert opinion that technology will not work

The presence of detergents and emulsifiers can unfavorably influence extraction performance and materials throughput. Water-soluble detergents, found in some raw wastes (particularly municipal), will dissolve and retain organic pollutants in competition with the extraction solvent. This can impede a system's ability to achieve low concentration treatment levels. Detergents and emulsifiers can promote the evolution of foam, which hinders separation and settling characteristics and generally decreases materials throughput. Although methods exist to combat these problems, they will add to the process cost.

When treated solids leave the extraction subsystem, traces of extraction solvent will be present [8, p. 125]. The typical extraction solvents used in currently available systems either volatilize quickly from the treated solids or biodegrade easily. Ambient air monitoring can be employed to determine if the volatilizing solvents present a problem.

The types of organic pollutants that can be extracted successfully depends, in part, on the nature of the extraction solvent. Invariably, treatability tests should be conducted to determine which solvent or combination of solvents is best suited to the site-specific vagaries of a particular parameter/matrix mix. In general, solvent extraction is least effective on very high molecular weight organics and very hydrophilic substances.

Some commercially available extraction systems use solvents that are either flammable or mildly toxic or both [20, p. 2]. However, there are long-standing standard procedures used by chemical companies, gasoline stations, etc., that can be used to greatly reduce the potential for accidents.

Technology Description

Figure 1 is a general schematic of the solvent extraction process [3][15, p. 65][4, p. 3].

Waste preparation (1) includes excavation and/or moving the waste material to the process where it is normally screened to remove debris and large objects. Depending upon the process vendor and whether the process is semibatch or continuous, the waste may need to be made pumpable by the addition of solvent or water.

In the extractor (2), the waste and solvent mix, resulting in the organic contaminant dissolving into the solvent. The extraction behavior exhibited by this technology is typical of a mass transfer controlled process, although equilibrium considerations often become limiting factors. It is important to have a competent source conduct a laboratory-scale treatability test to determine whether mass transfer or equilibrium will be controlling. The controlling factor is critical to the design of the unit and to the determination of whether the technology is appropriate for the waste.

The extracted organics are removed from the extractor with the solvent and go to the separator (3), where the pressure

or temperature is changed, causing the organic contaminants to separate from the solvent [9, p. 4-2].

The solvent is recycled (4) to the extractor and the concentrated contaminants (5) are removed from the separator [11, p. 6].

Process Residuals

There are three main product streams generated by this technology: the concentrated contaminants, the treated soil or sludge, and the separated water. The extract contains solvent-free contaminants, concentrated into a smaller volume, for post treatment. The recovered contaminants may require analysis to determine their suitability for recycle, reuse, or further treatment before disposal.

The cleaned soil and solids from treated sludge or sediments may need to be dewatered, forming a dry solid and a separate water stream. The volume of product water depends on the inherent dewatering capability of the individual process, as well as the process-specific requirements for feed slurrying. Since the solvent is an organic material, some residue may remain in the soil matrix. This can be mitigated by solvent selection, and if necessary, an additional separation stage. Depending on the extent of metal or other inorganic contaminants, treatment of the cleaned solids by some other technique (i.e., stabilization) may be necessary. Since the organic component has been separated, additional solids treatment should be simplified. The water produced should be analyzed to determine if treatment is necessary before discharge.

Solvent extraction units are designed to operate without air emissions. However, volatile air emissions could occur during waste preparation.

Site Requirements

Solvent extraction units are transported by trailers. Therefore, adequate access roads are required to get the unit to the site. Typical commercial-scale units, 50-70 tons per day (tpd), require a setup area of up to 3,600 square feet.

Standard 440V three-phase electrical service is needed. Water must be available at the site [3]. The quantity of water needed is vendor and site specific.

Contaminated soils or other waste materials are hazardous and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures. Storage should be provided to hold the process product streams until they have been tested to determine their acceptability for disposal or release. Depending upon the site, a method to store waste that has been prepared for treatment may be necessary. Storage capacity will depend on waste volume.

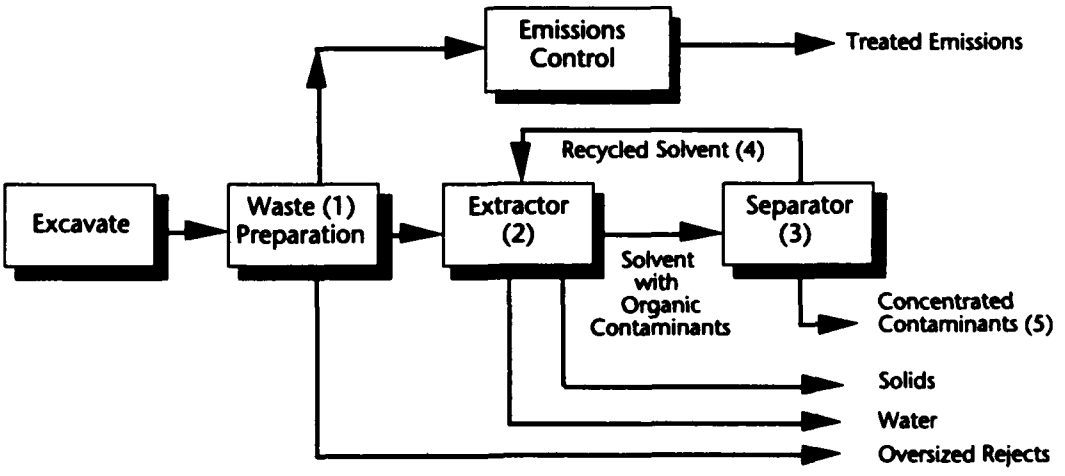
Onsite analytical equipment for conducting oil and grease analyses and a gas chromatograph capable of determining site-specific organic compounds for performance assessment make the operation more efficient and provide better information for process control.

Performance Data

The performance data currently available are mostly from two vendors, CF Systems and Resource Conservation Company (RCC).

CF Systems' full-scale 50-tpd commercial unit (PCU 200), which is treating refinery sludge at Port Arthur, Texas, meets or

Figure 1. Solvent Extraction Process



exceeds the EPA's Best Demonstrated Available Technology (BDAT) standards for a number of organic contaminants (Table 3) [3].

Table 3
API Separator Sludge Results*
(Concentrations in mg/kg)

	Feed Concentrations	*BDAT Target*	*Treated Products for Land Disposal*
Benzene	30.2	9.5	0.18
Toluene	16.6	9.5	0.18
Ethylbenzene	30.4	67.0	0.23
Xylenes (Total)	13.2	Reserved	0.98
Anthracene	28.3	6.2	0.12
Benzo(a)anthracene	BMDL**	1.4	0.18
Benzo(a)pyrene	1.9	0.84	0.33
Bis-(2-ethylhexy)phthalate	4.1	37.0	1.04
Chrysene	6.3	2.2	0.69
Di-n-butyl phthalate	BMDL	4.2	0.11
Naphthalene	42.2	Reserved	0.66
Phenanthrene	28.6	7.7	1.01
Phenol	BMDL	2.7	BMDL
Pyrene	7.7	2.0	1.08

* This information is from vendor-published literature; therefore, quality assurance has not been evaluated.
** Below Minimum Detection Limits (different values in Feed and Treated products).

Source: [3], CF Systems, 50 tpd

Under the Superfund Innovative Technology Evaluation (SITE) program, as shown in Table 4, CF Systems demonstrated an overall PCB reduction of more than 90% for harbor sediments with inlet concentrations up to 2,575 ppm [11, p. 6].

A mobile demonstration unit processed different feed types including clay pit material, ditch skimmer sludge, and drainage basin soil. The wastes were contaminated with oil and grease and aromatic priority pollutants. The oil and grease were separated and their concentrations were reduced to between 89% and 94% of the original amount. For the most part, the aromatic compounds were reduced to nondetectable levels [6, p. 10].

A treatability study completed at the Conroe, Texas, Superfund site with the mobile demonstration unit showed that polynuclear aromatic hydrocarbon (PAH) concentrations in the soil were reduced 95% from 2,879 ppm to 122 ppm [12, p. 3-12].

The only available data for the on-line operational availability were from CF Systems, which they estimated to be 85% (corresponding to a treatment process downtime of 15%). This can be verified and possibly improved with increased operating experience.

The ability of RCC's full-scale B.E.S.T.™ process to separate oily feedstock into product fractions was evaluated by the EPA at the General Refining Superfund site near Savannah, Georgia, in February 1987. It is an abandoned waste oil re-refining facility that contained four acidic oily sludge ponds with high levels of heavy metals (Pb=200-10,000 ppm, Cu=83-190 ppm) and detectable PCBs (2.9-5 ppm). The average composition of the sludge from the four lagoons was 10% oil, 20% solids, and 70% water by weight [16, p. 13]. The transportable 70 tons/day B.E.S.T.™ unit processed approximately 3,700 tons of sludge at the General Refining Site. The treated solids from this unit were back filled to the site, product oil was recycled as a fuel oil blend, and the recovered water was pH adjusted and transported to a local industrial wastewater treatment facility.

Test results (Table 5) showed that the heavy metals were mostly concentrated in the solids product fraction. TCLP test results showed heavy metals to be in stable forms that resisted leaching, illustrating a potential beneficial side effect when metals are treated by the process [1, p. 13].

RCC has bench-scale treatability data on a variety of wastes, including steel mill wastewater treatment sludge and oil refinery sludge (Table 6) [1, p. 12], that will illustrate the degree of separation possible among the oil, water, and solids

Table 4
New Bedford Harbor Sediments Results
(Concentrations in ppm)

Test #	*Initial PCB Concentration*	*Final PCB Concentration*	*Percent Reduction*	*Number of Passes Through Extractor*
1	350	8	98	9
2	288	47	84	1
3	2,575	200	92	6

Source: [11], CF Systems, 1.5 gpm

Table 5
EPA Data from the General Refining Superfund Site, Savannah, GA

Metals	*Initial Concentration (mg/kg)*	*Product Solids Metal (ppm)*	*TCLP Levels (ppm)*
As	<0.6	<5.0	<0.0
Ba	239	410	<0.03
Cr	6.2	21	<0.05
Pb	3,200	23,000	5.2
Se	<4.0	<5.0	0.008

Source: [1], RCC, 100 tpd

components of the waste. The separation of PCBs in contaminated harbor sediments is shown in Table 7 and in a variety of matrices in Table 8. Results of treatment of pesticide-contaminated soils are shown in Table 9.

RCRA Land Disposal Restrictions (LDRs) that require treatment of wastes to BDAT levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements (ARARs) for CERCLA response actions. The solvent extraction technology can produce a treated waste that meets treatment levels set by BDAT, but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where solvent extraction does not meet these levels, it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. EPA has made the treatability variance process available in order to ensure that LDRs do not unnecessarily restrict the use of alternative and innovative treatment technologies. Treatability variances may be justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.3-06FS) [17], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-07FS) [18]. Another approach could be to use other treatment techniques in series with solvent extraction to obtain desired treatment levels.

Table 6
Oil and Grease Removal
Bench Scale

	Steel Mill Sludge	*Refinery Sludge*
Original Sludge Concentration		
Oil %	11	8
Water %	33	77
Solids %	56	15
Product Stream		
Oil		
Water %	<2	<1
Solvent (ppm)	<100	<150
Water		
Oil & Grease (ppm)	<100	<100
Solvent (ppm)	11	12
Solid		
Oil & Grease (ppm)	0.2	0.9
Solvent (ppm)	34	N/A

Source: RCC, 6 kg Batch

Table 7
Harbor Sediments
PCB Extraction — Bench Scale

Original Sediments	4,500 ppm
Product Stream	
Oil	75,000 ppm
Water	10 ppb
Solid	<1 ppm
% Removal	>99%

Source: RCC, 6 kg Batch

Technology Status

During 1989, solvent extraction technology was selected as the remedial action to clean up 2,000-2,200 cubic yards of soil contaminated with PCBs and organics at the Pinette Salvage Superfund site in Washburn, Maine [13, p. 2]. In 1989, solvent extraction was also selected as the source control remedy in the following Records of Decision: F. O'Connor Superfund site in Augusta, Maine; the Norwood PCBs Superfund site in Norwood, Massachusetts; the Ewan Property Superfund site in Shamong, New Jersey; United Creosoting in Conroe, Texas; and Outboard Marine, State of Illinois [19].

The most significant factors influencing costs are the waste volume, the number of extraction stages, and the operating parameters such as labor, maintenance, setup, decontamination, demobilization, and lost time resulting from equipment operating delays. Extraction efficiency can be influenced by process parameters such as solvent used, solvent/waste ratio, throughput rate, extractor residence time, and number of extraction stages. Thus, variation of these parameters in a particular hardware design and/or configuration will influence the treatment unit cost component, but should not be a significant contributor to the overall site costs.

Cost estimates for this technology range from $100 to $500 per ton.

Solvent Extraction Systems

Solvent extraction systems are at various stages of development. The following is a brief discussion of six systems that have been identified.

CF Systems uses liquefied hydrocarbon gases such as propane and butane as solvents for separating organic contaminants from soils, sludges, and sediments. The extraction units are liquid-filled systems that employ pumps to move the material through the system. As such, the feed material is pretreated, through the addition of water, to ensure the "pumpability" of the material [10, p. 12]. The pH of the feed may be adjusted through the addition of lime or a similar material, to maintain the metallurgical integrity of the system. Typically, the feed material is screened to remove particles of greater than 1/8" diameter. Depending upon the nature of the

Table 8
PCB Samples Tested in RCC's Laboratory (1/87 through 7/88)

Client	As Received	Raw Sample Phase Composition			PCBs in Product Fraction			
	PCB (mg/kg)	Oil %	Water %	Solids %	Oil (mg/kg)	Water (mg/kg)	Solids (mg/kg)	% Removal
SLUDGES								
GRI	5.9	27	66	7	9.3	<.005	<.01	99.9%
GRI	4.7	10	58	32	N/A	<.01	0.015	99.9%
GRI	5.3	13	57	30	N/A	<.01	0.14	99.2%
Superfund Site Sh	106	35	44	21	270	N/A	1.0	99.8%
Superfund Site CO "A"	51	49	28	23	80	N/A	0.44	99.8%
Superfund Site CO "B"	21	23	24	53	71	N/A	0.08	99.8%
Superfund Site CO "C"	11	15	16	69	52	N/A	0.06	99.6%
SEDIMENTS								
River Sediment "B"	960	26	17	83	N/A	N/A	40	96.5%
Superfund B (#13)	83	44	40	16	N/A	N/A	1.0	99.8%
Harbor Sediment "B"	20,000	3	22	75	970,000	<.006	27	99.9%
Harbor Sediment "C"	30,000	5.6	62	32	550,000	N/A	94	99.9%
Harbor Sediment "D"	430	0.38	47	53	N/A	N/A	32	96.0%
Harbor Sediment NB-A	5,800	1.9	69	29	280,000	<.005	35	99.4%
Harbor Sediment NB-B	16,500	4.3	51.6	44.1	360,000	<.005	75	99.8%
SOILS								
Industrial Soil A	250	0.06	9.4	91	120,000	N/A	2.2	99.1%
Industrial Soil B	120	0.06	13	87	280,000	N/A	6.4	94.7%
Industrial Soil D	5,300	1.0	19	80	370,000	N/A	11	99.8%
Industrial Soil J	19	.09	16	84	10,000	N/A	0.7	96.3%

Source: RCC, .6 kg Batch

oversize material, the large particles may be reduced in size and then returned to the extraction unit for processing.

CF Systems' extraction technology has been demonstrated in the field at two Superfund sites and approximately 10 refineries and treatment, storage, and disposal (TSD) facilities to date.

CF Systems' solvent extraction technology is available in several commercial sizes and the Mobile Demonstration Unit is available for onsite treatability studies. To date, CF Systems has supplied three commercial-scale extraction units for the treatment of a variety of wastes [12, p. 3-12]. A 60-tpd treatment system was designed to extract organic liquids from a broad range of hazardous waste feeds at ENSCO's El Dorado, Arkansas, incinerator facility. A commercial-scale extraction unit is being installed at a facility in Baltimore, Maryland, to remove organic contaminants from a 20-gpm wastewater stream. A PCU-200 extraction unit is installed and operating at the Star Enterprise (Texaco) refinery in Port Arthur, Texas. This unit is designed to treat listed refinery wastes to meet or exceed the EPA's BDAT standards. Performance data and the technology status are explained in the body of this bulletin.

RCC's B.E.S.T.™ system uses aliphatic amines (typically triethylamine) as the solvent to separate and recover contaminants [1, p. 2]. It is applicable to soils, sludges, and sediments, and in batch mode of operation does not need a pumpable waste. Before the extraction process is begun, feed materials are screened to remove particles of greater than 1" diameter and pH adjusted to an alkaline condition. The process operates at or near ambient temperature and pressure. Triethylamine can be recycled from the recovered liquid phases via steam stripping because of its high vapor pressure and low boiling point azeotrope formation.

RCC has a transportable B.E.S.T.™ pilot-scale unit available to treat soils and sludges. This pilot-scale equipment has been used at a gulf coast refinery treating various refinery waste streams and has treated PCB-contaminated soils at an industrial site in Ohio in November 1989. A full-scale unit with a nominal capacity of 70 tpd was used to clean up 3,700 tons of PCB-contaminated petroleum sludge at the General Refining Superfund Site in Savannah, Georgia, in 1987. Performance data and the technology status are explained in the body of this bulletin.

ENSR is in the process of developing a mobile solvent extraction unit capable of decontaminating soils and sludges at a rate of 5 to 10 cubic yards/hour [5, p. 1]. The ENSR system uses a proprietary reagent and solvent. The company claims that its solvent extraction system is designed to operate without significant pretreatment of the soil/sludge and without the addition or removal of water. Design of a pilot-scale unit is near completion. Thus far, only performance data from earlier bench-scale tests are available.

The **Extraksol™** process was developed in 1984 by Sanivan Group, Montreal, Canada [7, p. 35]. It is applicable to soils, sludges, and sediments. Performance data on contaminated soils and refinery wastes are available for a 1 ton per hour (tph) mobile unit. The process uses a proprietary solvent that reportedly achieved removal efficiencies up to 99% (depending on the number of extraction cycles and the type of soil) on PCBs, oil, grease, PAHs, and pentachlorophenol [7, p. 45]. The 1-tph unit is suitable for small projects with a maximum of 300 tons of material to be treated. The Sanivan group is planning to build a full-scale unit that can process 6-8 tph of waste [7, p. 41].

Harmon Environmental Services and Acurex Corporation are involved in a cooperative joint venture to develop a solvent soil washer/extraction system appropriate for the onsite remediation of Superfund and RCRA sites. They have completed EPA-sponsored bench-scale studies on different types of soils contaminated with #2 fuel oil. The design of a pilot plant unit is being considered.

Table 9
RCC B.E.S.T.™ Treated Pesticide-Contaminated Soil — Bench Scale

Analyte	*Feedstock (ppm)*	*Product Solids (ppm)*	*Removal Efficiency %*
p,p'-DDT	500	0.2	99.96
p,p'-DDE	84	0.5	99.4
p,p'-DDD	190	0.05	99.97
Endosulfan-I	250	<0.02	>99.99
Endosulfan-II	140	<0.02	>99.99
Endrin	140	0.02	99.99
Dieldrin	37	<0.02	>99.95
Toxaphene	2,600	0.9	99.97
BHC-Beta	<30	<0.13	-
BHC-Gamma (Lindane)	<30	<0.07	-
Pentachlorophenol	150	1.9	98.7

Source: RCC, .6 kg Batch

The **Low Energy Extraction Process (LEEP)** is a patented solvent extraction process that can be used onsite for decontaminating soils, sludges, and sediments. LEEP uses common hydrophilic and hydrophobic organic solvents to extract and further concentrate organic pollutants such as PCBs [2, p. 3]. Bench-scale studies are available. The design of the pilot plant is completed, and the plant is scheduled for operation at the beginning of 1990.

EPA Contact

Technology specific questions regarding solvent extraction may be directed to:

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EPA

Engineering Bulletin
Mobile/Transportable Incineration Treatment

Purpose

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

Abstract

Incineration treats organic contaminants in solids and liquids by subjecting them to temperatures typically greater than 1000°F in the presence of oxygen, which causes the volatilization, combustion, and destruction of these compounds. This bulletin describes mobile/transportable incineration systems that can be moved to and subsequently removed from Superfund and other hazardous waste sites. It does not address other thermal processes that operate at lower temperatures or those that operate at very high temperatures, such as a plasma arc. It is applicable to a wide range of organic wastes and is generally not used in treating inorganics and metals. Mobile/transportable incinerators exhibit essentially the same environmental performance as their stationary counterparts. To date, 49 of the 95 records of decision (RODs) designating thermal remedies at Superfund sites have selected onsite incineration as an integral part of a preferred treatment alternative. There are 22 commercial-scale units in operation [5]*. This bulletin provides information on the technology applicability, the types of residuals resulting from the use of the technology, the latest performance data, site requirements, the status of the technology, and where to go for further information.

Technology Applicability

Mobile/transportable incineration has been shown to be effective in treating soils, sediments, sludges, and liquids containing primarily organic contaminants such as halogenated and nonhalogenated volatiles and semivolatiles, polychlorinated biphenyls (PCBs), pesticides, dioxins/furans, organic cyanides, and organic corrosives. The process is applicable for the thermal treatment of a wide range of specific Resource Conservation and Recovery Act (RCRA) wastes and other hazardous waste matrices that include pesticides and herbicides, spent halogenated and nonhalogenated solvents, chlorinated phenol and chlorinated benzene manufacturing wastes, wood preservation and wastewater sludge, organic chemicals production residues, pesticides production residues, explosives manufacturing wastes, petroleum refining wastes, coke industry wastes, and organic chemicals residues [1] [2] [4] [6 through 11] [13].

Information on the physical and chemical characteristics of the waste matrix is necessary to assess the matrix's impact on waste preparation, handling, and feeding; incinerator type, performance, size, and cost; air pollution control (APC) type and size; and residue handling. Key physical parameters include waste matrix physical characteristics (type of matrix, physical form, handling properties, and particle size), moisture content, and heating value. Key chemical parameters include the type and concentration of organic compounds including PCBs and dioxins, inorganics (metals), halogens, sulfur, and phosphorous.

The effectiveness of mobile/transportable incineration on general contaminant groups for various matrices is shown in Table 1 [7, p. 9]. Examples of constituents within contaminant groups are provided in Reference 7, "Technology Screening Guide for Treatment of CERCLA Soils and Sludges." This table

* [reference number, page number]

Table 1
Effectiveness of Incineration on General Contaminant Groups for Soil, Sediment, Sludge, and Liquid

	Contaminant Groups	Soil/ Sediment	Sludge	Liquid
Organic	Halogenated volatiles	■	■	■
	Halogenated semivolatiles	■	■	■
	Nonhalogenated volatiles	■	■	■
	Nonhalogenated semivolatiles	■	■	■
	PCBs	■	■	■
	Pesticides (halogenated)	▼	■	■
	Dioxins/Furans	■	■	■
	Organic cyanides	▼	▼	▼
	Organic corrosives	▼	▼	▼
Inorganic	Volatile metals	❑	❑	❑
	Nonvolatile metals	❑	❑	❑
	Asbestos	❑	❑	❑
	Radioactive materials	❑	❑	❑
	Inorganic corrosives	❑	❑	❑
	Inorganic cyanides	▼	▼	▼
Reactive	Oxidizers	▼	▼	▼
	Reducers	▼	▼	▼

■ Demonstrated Effectiveness: Successful treatability test at some scale completed

▼ Potential Effectiveness: Expert opinion that technology will work

❑ No Expected Effectiveness: Expert opinion that technology will not work

is based on current available information or professional judgment when no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability was tested to show that the technology was effective for a particular contaminant and matrix. The ratings of potential effectiveness or no expected effectiveness are based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given. Other sources of general observations and average removal efficiencies for different treatability groups are the Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS [13], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," (OSWER Directive 9347.3-07FS [14].

Limitations

Toxic metals such as arsenic, lead, mercury, cadmium, and chromium are not destroyed by combustion. As a result, some will be present in the ash while others are volatilized and released into the flue gas [1, pp. 3-6].

Alkali metals, such as sodium and potassium, can cause severe refractory attack and form a sticky, low-melting-point submicron particulate, which causes APC problems. A low feed stream concentration of sodium and potassium may be achieved through feed stock blending [1, pp. 3-11].

When PCBs and dioxins are present, higher temperatures and longer residence times may be required to destroy them to levels necessary to meet regulatory criteria [7, p. 34].

Moisture/water content of waste materials can create the need to co-incinerate these materials with higher BTU streams, or to use auxiliary fuels.

The heating value (BTU content) of the feed material affects feed capacity and fuel usage of the incinerator. In general, as the heating value of the feed increases, the feed capacity and fuel usage of the incinerator will decrease. Solid materials with high calorific values also may cause transient behaviors that further limit feed capacity [9, p. 4].

The matrix characteristics of the waste affect the pretreatment required and the capacity of the incinerator and can cause APC problems. Organic liquid wastes can be pumped to and then atomized in the incinerator combustion chamber. Aqueous liquids may be suitable for incineration if they contain a substantial amount of organic matter. However, because of the large energy demand for evaporation when treating large volumes of aqueous liquids, pretreatment to dewater the waste may be cost effective [1, pp. 3-14]. Also, if the organic content is low, other methods of treatment may be more economical. For the infrared incinerator, only solid and solid-like materials within a specific size and moisture content range can be processed because of the unique conveyor belt feed system within the unit.

Sandy soil is relatively easy to feed and generally requires no special handling procedures. Clay, which may be in large clumps, may require size reduction. Rocky soils usually require screening to remove oversize stones and boulders. The solids can then be fed by gravity, screw feeder, or ram-type feeder into the incinerator. Some types of solid waste may also require crushing, grinding, and/or shredding prior to incineration [1, pp. 3-17].

The form and structure of the waste feed can cause periodic jams in the feed and ash handling systems. Wooden pallets, metal drum closure rings, drum shards, plastics, trash, clothing, and mud can cause blockages if poorly prepared. Muddy soils can stick to waste processing equipment and plug the feed system [9, p. 8].

The particle size distribution of the ash generated from the waste can affect the amount of particulate carry-over from the combustion chamber to the rest of the system [9, p. 16].

Incineration of halogens, such as fluorine and chlorine, generates acid gases that can affect the capacity, the water removal and replacement rates that control total dissolved solids in the process water system, and the particulate emissions [9, p. 12]. The solutions used to neutralize these acid gases add to the cost of operating this technology.

Organic phosphorous compounds form phosphorous pentoxide, which attacks refractory material, causes slagging problems and APC problems. Slagging can be controlled by feed blending or operating at lower temperatures [1, pp. 3-10].

Technology Description

Figure 1 is a schematic of the mobile/transportable incineration process.

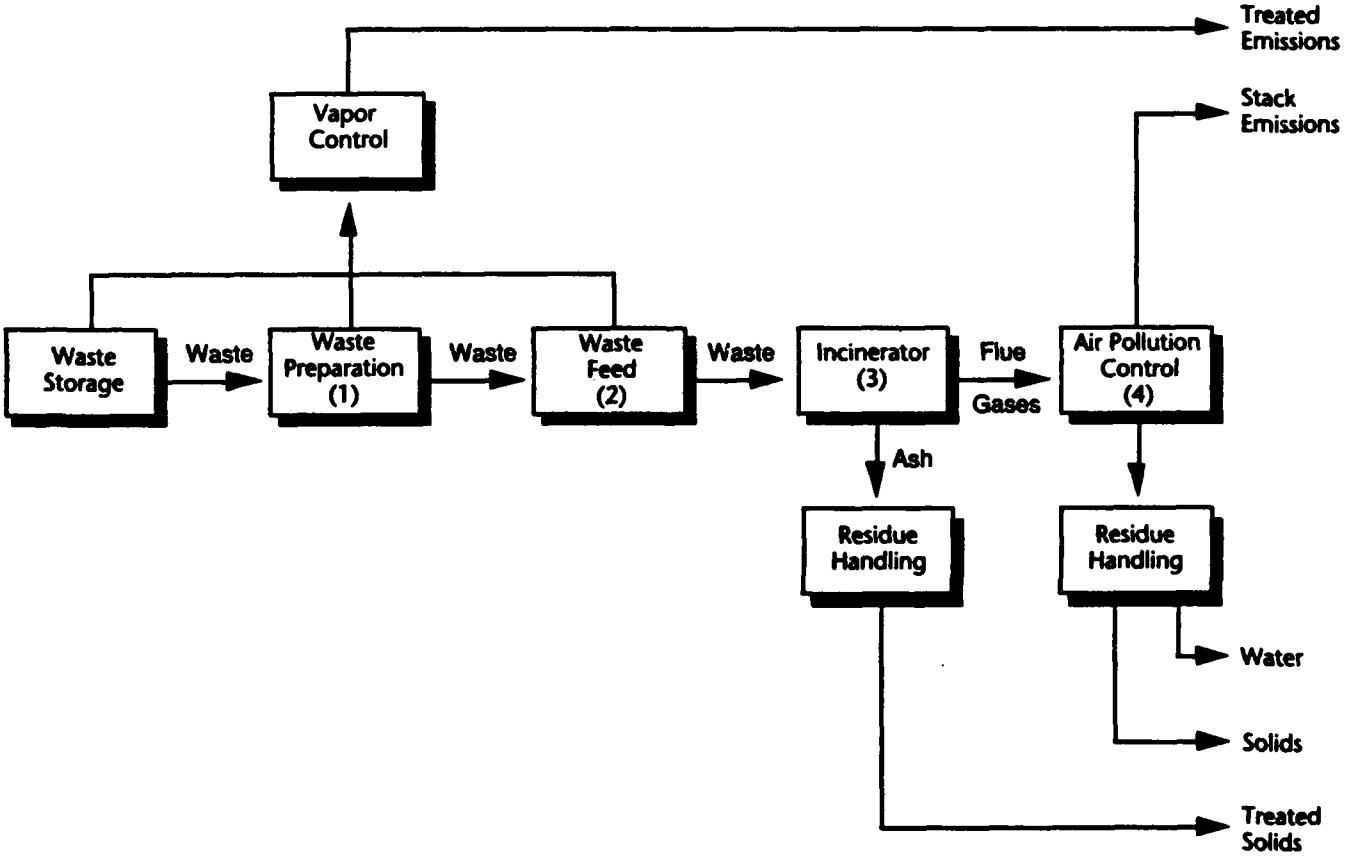
Waste preparation (1) includes excavation and/or moving the waste to the site. Depending on the requirements of the incinerator type for soils and solids, various equipment is used to obtain the necessary feed size. Blending is sometimes required to achieve a uniform feed size and moisture content or to dilute troublesome components [1, pp. 3-19].

The waste feed mechanism (2), which varies with the type of the incinerator, introduces the waste into the combustion system. The feed mechanism sets the requirements for waste preparation and is a potential source of problems in the actual operation of incinerators if not carefully designed [1, pp. 3-19].

Different incinerator designs (3) use different mechanisms to obtain the temperature at which the furnace is operated, the time during which the combustible material is subject to that temperature, and the turbulence required to ensure that all the combustible material is exposed to oxygen to ensure complete combustion. Three common types of incineration systems for treating contaminated soils are rotary kiln, circulating fluidized bed, and infrared.

The rotary kiln is a slightly inclined cylinder that rotates on its horizontal axis. Waste is fed into the high end of the rotary kiln and passes through the combustion chamber by gravity. A secondary combustion chamber (afterburner) further destroys unburned organics in the flue gases [7, p. 40].

Figure 1
Mobile/Transportable Incineration Process



Circulating fluidized bed incinerators use high air velocity to circulate and suspend the fuel/waste particles in a combustor loop. Flue gas is separated from heavier particles in a solids separation cyclone. Circulating fluidized beds do not require an afterburner [7, p. 35].

Infrared processing systems use electrical resistance heating elements or indirect fuel-fired radiant U-tubes to generate thermal radiation [1, pp. 4-5]. Waste is fed into the combustion chamber by a conveyor belt and exposed to the radiant heat. Exhaust gases pass through a secondary combustion chamber.

Offgases from the incinerator are treated by the APC equipment to remove particulates and capture and neutralize acids (4). Rotary kilns and infrared processing systems may require both external particulate control and acid gas scrubbing systems. Circulating fluidized beds do not require scrubbing systems because limestone can be added directly into the combustor loop but may require a system to remove particulates [1, pp. 4-11] [2, p. 32]. APC equipment that can be used include venturi scrubbers, wet electrostatic precipitators, baghouses, and packed scrubbers.

Process Residuals

Three major waste streams are generated by this technology: solids from the incinerator and APC system, water from the APC system, and emissions from the incinerator.

Ash and treated soil/solids from the incinerator combustion chamber may be contaminated with heavy metals. APC system solids, such as fly ash, may contain high concentrations of volatile metals. If these residues fail required leachate toxicity tests, they can be treated by a process such as stabilization/solidification and disposed of onsite or in an approved landfill [7, p. 126].

Liquid waste from the APC system may contain caustic, high chlorides, volatile metals, trace organics, metal particulates, and inorganic particulates. Treatment may require neutralization, chemical precipitation, reverse osmosis, settling, evaporation, filtration, or carbon adsorption before discharge [7, p. 127].

The flue gases from the incinerator are treated by APC systems such as electrostatic precipitators or venturi scrubbers before discharge through a stack.

Site Requirements

The site should be accessible by truck or rail and a graded/gravel area is required for setup of the system. Concrete pads may be required for some equipment (e.g., rotary kiln). For a typical 5 tons per hour commercial-scale unit, 2 to 5 acres are required for the overall system site including ancillary support [10, p. 25].

Standard 440V three-phase electrical service is needed. A continuous water supply must be available at the site. Auxiliary fuel for feed BTU improvement may be required.

Contaminated soils or other waste materials are hazardous and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures.

Various ancillary equipment may be required, such as liquid/sludge transfer and feed pumps, ash collection and solids handling equipment, personnel and maintenance facilities, and process-generated waste treatment equipment. In addition, a feed-materials staging area, a decontamination trailer, an ash handling area, water treatment facilities, and a parking area may be required [10, p. 24].

Proximity to a residential neighborhood will affect plant noise requirements and may result in more stringent emissions limitations on the incineration system.

Storage area and/or tanks for fuel, wastewater, and blending of waste feed materials may be needed.

No specific onsite analytical capabilities are necessary on a routine basis; however, depending on the site characteristics or a specific Federal, State, or local requirement, some analytical capability may be required.

Performance Data

More than any other technology, incineration is subject to a series of technology-specific regulations, including the following Federal requirements: the Clean Air Act 40 CFR 52.21 for air emissions; Toxic Substances Control Act (TSCA) 40 CFR 761.40 for PCB treatment and disposal; National Environmental Policy Act 40 CFR 6; RCRA 40 CFR 261/262/264/270 for hazardous waste generation, treatment performance, storage, and disposal standards; National Pollutant Discharge Elimination System 33 U.S.C. 1251 for discharge to surface waters; and the Noise Control Act P.L. 92-574. RCRA incineration standards have been proposed that address metal emissions and products of incomplete combustion. In addition, State requirements must be met if they are more stringent than the Federal requirements [1, p. 6-1].

All incineration operations conducted at CERCLA sites on hazardous waste must comply with substantive and defined Federal and State applicable or relevant and appropriate requirements (ARARs) at the site. A substantial body of trial burn results and other quality assured data exists to verify that incinerator operations remove and destroy organic contaminants from a variety of waste matrices to the parts per billion or even the parts per trillion level, while meeting stringent stack emission and water discharge requirements. The demonstrated treatment systems that will be discussed in the technology status section, therefore, can meet all the performance standards defined by the applicable Federal and State regulations on waste treatment, air emissions, discharge of process waters, and residue ash disposal [1, p. A-1] [4, p. 4] [10, p. 9].

RCRA Land Disposal Restrictions (LDRs) that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be ARARs for CERCLA response actions. The solid

residuals from the incinerator may not meet required treatment levels in all cases. In cases where residues do not meet BDAT levels, mobile incineration still may be selected, in certain situations, for use at the site if a treatability variance establishing alternative treatment levels is obtained. EPA has made the treatability variance process available in order to ensure that LDRs do not unnecessarily restrict the use of alternative and innovative treatment technologies. Treatability variances may be justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS) [13] and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," (OSWER Directive 9347.3-07FS) [14].

Technology Status

To date, 49 of the 95 RODs designating thermal remedies at Superfund sites have selected onsite incineration as an integral part of a preferred treatment alternative.

Table 2 lists the site experience of the various mobile/transportable incinerator systems. It includes information on the incinerator type/size, the site size, location, and contaminant source or waste type treated [5] [3, p. 80] [8, p. 74].

The cost of incineration includes fixed and operational costs. Fixed costs include site preparation, permitting, and mobilization/demobilization. Operational costs such as labor, utilities, and fuel are dependent on the type of waste treated and the size of the site. Figure 2 gives an estimate of the total cost for incinerator systems based on site size [12, pp. 1-3]. Superfund sites contaminated with only volatile organic compounds can have even lower costs for thermal treatment then the costs shown in Figure 2.

EPA Contact

Technology-specific questions regarding mobile/transportable incineration may be directed to Donald A. Oberacker, U.S. EPA Risk Reduction Engineering Laboratory, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268, telephone: FTS 684-7510 or (513) 569-7510.

Table 2.
Technology Status

Treatment System/ Vendor	*Thermal Capacity (MM BTU/Hr)*	*Experience*		
		Site, Location	*Waste Volume (tons)*	*Contaminant Source or Waste Type*
Rotary Kiln *Ensco*	35	Sydney Mines, Valrico, FL[▲]	10,000	Waste oil
		Lenz Oil NPL Site, Lemont, IL[▲]	26,000	Hydrocarbon - sludge/solid/liquid
		Naval Construction Battalion Center (NCBC), Gulfport, MS	22,000	Dioxin/soil
		Union Carbide, Seadrift, TX*	N/A	Chemical manufacturing
		Smithiville, Canada*	7,000	PCB transformer leaks
	100	Bridgeport Rental, Bridgeport, NJ*[▲]	100,000	Used oil recycling
Rotary Kiln *IT*	56	Cornhusker Army Ammunition Plant (CAAP), Grand Island, NE[▲]	45,000	Munitions plant redwater pits
		Louisiana Army Ammunition Plant (LAAP), Shreveport, LA*[▲]	100,000	Munitions plant redwater lagoon
		Motco, Texas City, TX*[▲]	80,000	Styrene tar disposal pits
Rotary Kiln *Vesta*	8	Fairway Six Site, Aberdeen, NC	50	Pesticide dump
	12	Fort A.P. Hill, Bowling Green, VA	200	Army base
		Nyanza/Nyacol Site, Ashland, MA[▲]	1,000	Dye manufacturing
		Southern Crop Services Site Delray Beach, FL	1,500	Crop dusting operation
		American Crossarm & Conduit Site Chehalis, WA[▲]	900	Wood treatment
		Rocky Boy, Havre, MT*	1,800	Wood treatment

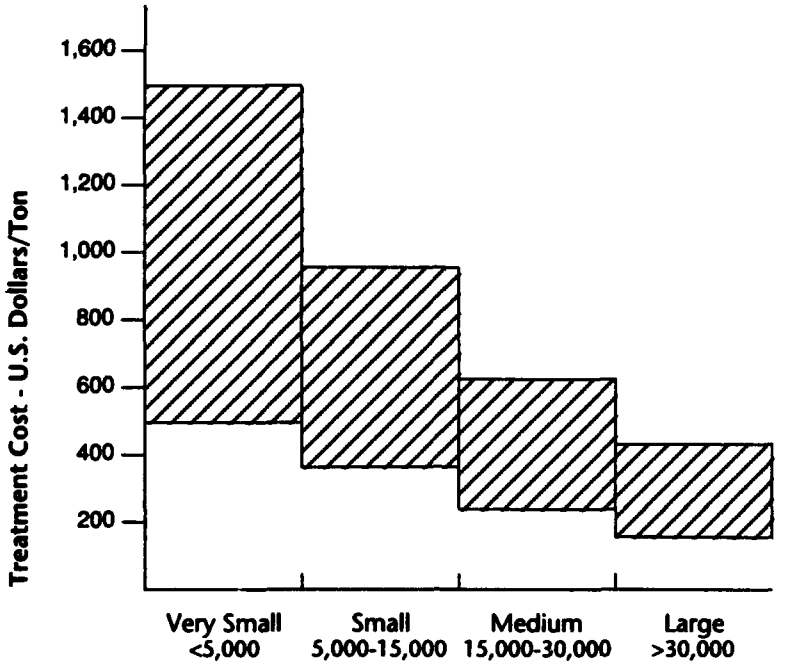
NA - Not available * Contracted, others completed [▲] Superfund Site [Source: References 3, 5, 8]

Table 2
Technology Status (Continued)

Treatment System/ Vendor	*Thermal Capacity (MM BTU/Hr)*	*Experience*		
		Site, Location	*Waste Volume (tons)*	*Contaminant Source or Waste Type*
Rotary Kiln *Weston*	35	Lauder Salvage, Beardstown, IL Paxton Ave., Chicago, IL*	8,500 16,000	Metal scrap salvage Waste lagoon
Rotary Kiln *AET*	20	Valdez, AK	NA	Crude oil spill
Rotary Kiln *Boliden*	40	Oak Creek, WI	50,000	Dye manufacturing
Rotary Kiln *Harmon*	82	Prentis Creosote & Forest Products Prentis, MS Bog Creek, Howell Township, NJ[Δ]	9,200 22,500	Creosote/soil Organics
Rotary Kiln *Bell*	30	Bell Lumber&Pole, New Brighton, MN[Δ]	21,000	Wood treatment
Rotary Kiln *Kimmins*	100	Lasalle, IL*[Δ]	69,000	PCB capacitor manufacturing
Rotary Kiln *USEPA*	10	Denney Farm, MO	6,250	Dioxin Soils
Rotary Kiln *Vertac*	35	Vertac, Jacksonville, AR*[Δ]	6,500	Chemical manufacturing
Shirco Infrared *Haztech*	30	Peak Oil, Tampa, FL[Δ] Lasalle, IL[Δ]	7,000 30,000	Used oil recycling, PCBs/Lead Transformer reconditioning
Shirco Infrared *GDC Engr.*	NA	Rubicon, Geismar, LA*	52,000	Chemical manufacturing
Shirco Infrared *OH Materials*	30	Florida Steel, Indiantown, FL[Δ] Twin City AAP, New Brighton, MN Goosebay, Canada	18,000 2,000 4,000	Steel mill used oils Munitions plant PCBs
	12	Gas Station Site, Cocoa, FL	1,000	Petroleum tank leak
Shirco Infrared *U.S. Waste*	10	Private Site, San Bernadino, CA	5,400	Hydrocarbons
Circulating Bed Combustor *Ogden*	10	Arco Swanson River Field Kenai, AK* Stockton, CA*	80,000 16,000	Oil pipeline compressor oil Underground tank oil leak

NA - Not available * Contracted, others completed [Δ]Superfund Site [Source: References 3, 5, 8]

Figure 2
Effect of Site Size on Incineration Costs



Source: The Hazardous Waste Consultant [12, pp. 1-3]

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EPA

Engineering Bulletin
Pyrolysis Treatment

Purpose

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

Abstract

Pyrolysis is formally defined as chemical decomposition induced in organic materials by heat in the absence of oxygen. In practice, it is not possible to achieve a completely oxygen-free atmosphere; actual pyrolytic systems are operated with less than stoichiometric quantities of oxygen. Because some oxygen will be present in any pyrolytic system, nominal oxidation will occur. If volatile or semivolatile materials are present in the waste, thermal desorption will also occur.

Pyrolysis is a thermal process that transforms hazardous organic materials into gaseous components and a solid residue (coke) containing fixed carbon and ash. Upon cooling, the gaseous components condense, leaving an oil/tar residue. Pyrolysis typically occurs at operating temperatures above 800°F [1, pp. 165, 167] [2, p. 5].* This bulletin does not address other thermal processes that operate at lower temperatures or those that operate at very high temperatures, such as a plasma arc. Pyrolysis is applicable to a wide range of organic wastes and is generally not used in treating wastes consisting primarily of inorganics and metals.

Pyrolysis should be considered an emerging technology. (An emerging technology is a technology for which performance data have not been evaluated according to methods approved by EPA and adhering to EPA quality assurance/quality control standards, although the basic concepts of the process have been validated [3, pp. 1-2].) Performance data are currently available only from vendors. In addition, existing data are limited in scope and quantity and frequently of a proprietary nature.

This bulletin provides information on the technology applicability, the types of residuals resulting from the use of the technology, the latest performance data, site requirements, the status of the technology, and where to go for further information.

Technology Applicability

Pyrolysis systems may be applicable to a number of organic materials that "crack" or undergo a chemical decomposition in the presence of heat. Pyrolysis has shown promise in treating organic contaminants in soils and oily sludges. Chemical contaminants for which treatment data exist include polychlorinated biphenyls (PCBs), dioxins, polycyclic aromatic hydrocarbons, and many other organics. Treatment data discussed in this bulletin were taken from treatability studies conducted by three vendors.

Pyrolysis is not effective in either destroying or physically separating inorganics from the contaminated medium. Volatile metals may be desorbed as a result of the higher temperatures associated with the process but are similarly not destroyed.

The probable effectiveness of pyrolysis on general contaminant groups for various matrices is shown in Table 1. Examples of constituents within contaminant groups are provided in "Technology Screening Guide for Treatment of CERCLA Soils and Sludges" [4, pp. 10-12]. Table 1 is based on current available information or professional judgment where no information was available [1, pp. 165, 168] [2, pp. 9-14] [5, pp. 10-15] [6, p. 9]. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatment results indicated that the technology was effective for

* [reference number, page number]

Table 1
Effectiveness of Pyrolysis on General Contaminant Groups for Soil and Sediment/Sludge

	Contaminant Groups	Effectiveness: Soil	Effectiveness: Sediment/ Sludge
Organic	Halogenated volatiles	▼	▼
	Halogenated semivolatiles	▼	▼
	Nonhalogenated volatiles	▼	■
	Nonhalogenated semivolatiles	■	■
	PCBs	■	■
	Pesticides (halogenated)	▼	▼
	Dioxins/Furans	▼	■
	Organic cyanides	▼	▼
	Organic corrosives	□	□
Inorganic	Volatile metals	□	□
	Nonvolatile metals	□	□
	Asbestos	□	□
	Radioactive materials	□	□
	Inorganic corrosives	□	□
	Inorganic cyanides	□	□
Reactive	Oxidizers	□	□
	Reducers	□	□

■ Demonstrated Effectiveness: Successful treatability test at some scale completed.

▼ Potential Effectiveness: Expert opinion that technology will work.

□ No Expected Effectiveness: Expert opinion that technology will not work.

that particular contaminant and medium. The ratings of potential effectiveness or no expected effectiveness are both based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular medium. When the technology is not applicable or will probably not work for a particular combination of contaminant group and medium, a no-expected-effectiveness rating is given.

Limitations

The primary technical factors affecting pyrolytic performance are the temperature, residence time, and heat transfer rate to the material. There are also several practical limitations which should be considered.

As the medium is heated and passes through a pyrolytic system, energy is consumed in heating moisture contained in the contaminated medium. A very high moisture content would result in lower throughput. High moisture content, therefore, causes increased treatment costs. For some wastes, dewatering prior to pyrolysis may be desirable.

The treated medium will typically contain less than one percent moisture. Dust can easily form in the transfer of the treated medium from the treatment unit, but this problem can be mitigated by water sprays.

A very high pH (greater than 11) or very low pH (less than 5) may corrode the system components. The pyrolysis of halogenated organics will yield hydrogen halides; the pyrolysis of sulfur-containing organics will yield various sulfur compounds including hydrogen sulfide (H_2S). Because hydrogen halides and hydrogen sulfide are corrosive chemicals, corrosion control measures should be taken for any pyrolytic system which will be processing wastes with high concentrations of halogenated or sulfur-containing organics.

Technology Description

Pyrolysis is formally defined as chemical decomposition induced in organic materials by heat in the absence of oxygen. Pyrolysis is a thermal process that transforms organic materials into gaseous components and a solid residue (coke) containing fixed carbon and ash. The pyrolysis of organics yield: combustible gases including carbon monoxide, hydrogen, methane, and other low molecular weight hydrocarbons [7, pp. 252-253]. Pyrolysis occurs to some degree whenever heat is applied to an organic material. The rate at which pyrolysis occurs increases with temperature. At low temperatures and in the presence of oxygen, the rates are typically negligible. In addition, the final percent weight loss for the treated material is directly proportional to the operating temperature. Similarly, the hydrogen fraction in the treated material is inversely proportional to the temperature.

The primary cleanup mechanisms in pyrolytic systems are destruction and removal. Destruction occurs when organics are broken down into lower molecular weight compounds. Removal occurs when pollutants are desorbed from the contaminated material and leave the pyrolysis portion of the system without being destroyed.

Pyrolysis systems typically generate solid, liquid, and gaseous products. Solid products include the treated (and dried) medium and the carbon residue (coke) formed from hydrocarbon decomposition. Various gases are produced during pyrolysis, and certain low-boiling compounds may volatilize rather than decompose. This is not typically a problem. Gases may be condensed, treated, incinerated in an afterburner, flared, or a combination of the above. Depending on the specific components, organic condensate may be reusable. Other liquid streams will include process water used throughout the system. A general schematic of a pyrolytic process is shown in Figure 1.

As shown in Figure 1, the first step in the treatment process is the excavation of the contaminated soil, sludge, or sediment. Oversized rejects such as large rocks or branches are removed and the material is transferred to the pyrolysis unit. The treatment system may include a desorption stage prior to pyrolysis. If so, the desorbed gases flow to the gas treatment system for treatment and/or recovery, and the contaminated matrix (minus any desorbed chemicals) is transferred to the pyrolysis chamber [1, p. 166] [2, pp. 3-6].

The temperature in the pyrolysis chamber is typically between 800 and 2,100° F, and the quantity of the oxygen present is not sufficient for the complete oxidation of all contaminants. In pyrolysis, organic materials are transformed into coke and gaseous components. Gas treatment options include: 1) condensation plus gas cleaning and 2) incineration plus gas cleaning.

Pyrolysis forms new compounds whose presence could impact the design of the offgas management system. For example, compounds such as hydrogen halides and sulfur-containing compounds may be formed. These must be accounted for within the design of the Air Pollution Control (APC) system.

There are three pyrolytic systems which will be discussed in this bulletin. These systems are: the HT-V system marketed by TDI Thermal Dynamics (formerly Southdown Thermal Dynamics), a process developed by Deutsche Babcock Anlagen AG, and an "anaerobic thermal processor" (ATP) marketed by SoilTech, Inc.

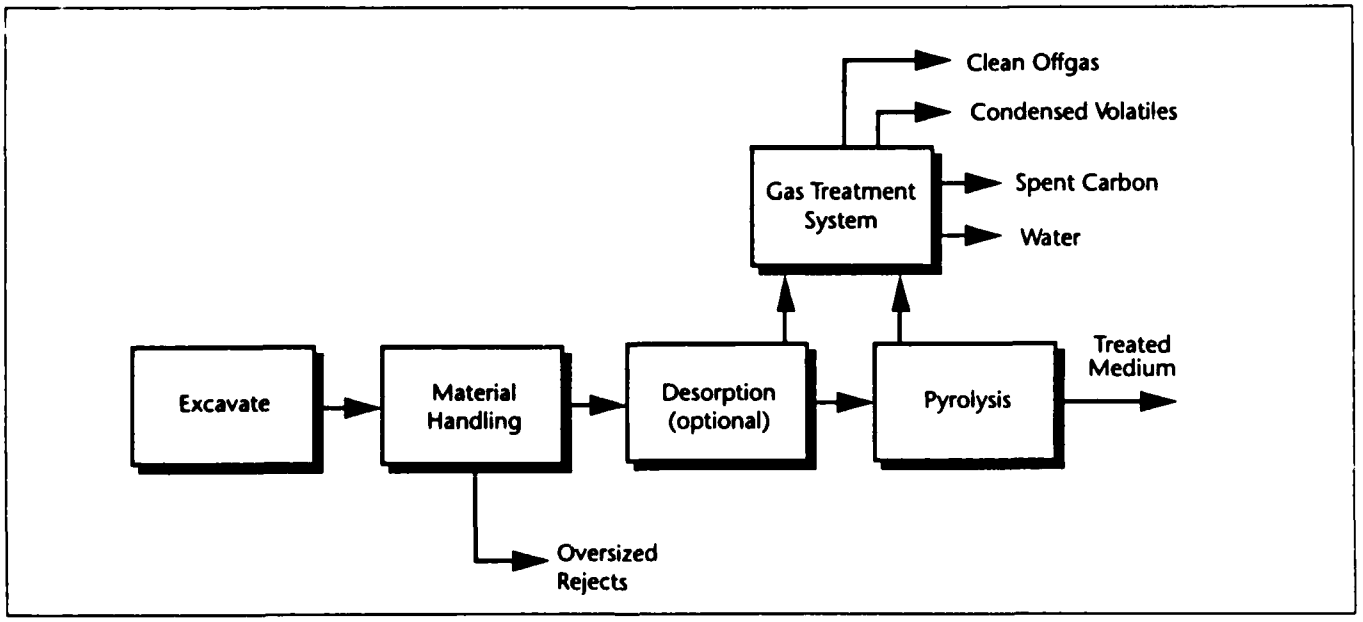
The HT-V Thermal Distillation System is a mobile thermal desorption system which may be operated in a pyrolytic mode. The Thermal Distillation System processes waste by applying heat in a nitrogen atmosphere. Gravity and a system of annular augers are used to transfer waste through a series of three electrically heated distillation chambers. The temperature is ambient at the entrance to the distillation chambers and increases to full operating temperature (up to 2,100°F) as the waste progresses through the chambers. The continuous introduction of a nitrogen sweep gas removes and separates the volatile contaminants [8, p. 3]. The sweep gas must be periodically sent to a flare to reduce the noncondensible combustible portion.

TDI is currently conducting bench-scale tests on the Thermal Degradation System, which was developed for use in conjunction with the Thermal Distillation System. The full-scale design of the system is currently theoretical, but TDI envisions that Thermal Degradation will follow Thermal Distillation and will be used primarily for pyrolysis. In recent bench-scale tests, the Thermal Degradation System was operated at approximately 2,000°F and a copper catalyst was used to enhance the pyrolysis of halogenated organics [2, pp. 3-6] [5, pp. 3-7].

A German company, Deutsche Babcock Anlagen AG, developed a pyrolytic process which utilizes an indirectly heated rotary kiln. In the first step of the Deutsche Babcock system, pyrolysis occurs at a temperature of 1,100 to 1,200°F. If volatile or semivolatile organics are present, they will be desorbed in this step. In the second step, the gases produced by pyrolysis (as well as other volatilized organics) are combusted in an afterburner at a high temperature (1,800 to 2,400°F). Heat produced during the second step may provide at least a portion of the energy for the first step, which is endothermic. Prior to discharge, effluent gases from the second step are scrubbed to remove various pollutants including hydrogen halides and sulfur oxides [1, p. 166].

The pyrolysis systems marketed by Deutsche Babcock are not currently available in mobile or transportable configurations and are therefore not directly applicable to onsite remediation of Superfund sites. These systems were included in this discussion to provide additional data and to indicate the potential viability of pyrolysis. In addition, full-scale applications and testing of the Deutsche Babcock system have included the cleanup of contaminated soils [1, pp. 165-168].

Figure 1. Schematic Diagram of Pyrolysis



Finally, SoilTech, Inc. (Canonie Environmental) markets an anaerobic thermal processor (ATP) which may be operated in a pyrolytic mode. The ATP is also known as the AOSTRA-Taciuk process and is essentially an indirectly-heated rotary kiln. A transportable ATP with a nominal processing rate of 10 tons per hour is available for onsite demonstrations and remediation [9, p. 3].

The ATP unit includes four chambers: preheat, reaction, combustion, and cooling. In the preheat chamber, volatile materials are desorbed at temperatures up to 500°F. Pyrolytic conditions and temperatures between 700 and 1,150°F are maintained in the reaction chamber. The desorption and/or pyrolysis of heavier organics will occur in this chamber. Coke and noncombustible hydrocarbons produced by pyrolysis are transferred to the combustion chamber and burned [9, pp. A-1 to A-2]. Additional fuels such as gas or oil must be available for start-up, for control, and to supplement the pyrolysis products when they do not provide adequate fuel. Solids and gases from the combustion chamber proceed into the cooling zone. The cooling zone and the preheat zone function as a heat exchanger in which heat is transferred from the combustion residuals to the feed [10, p. 3].

Process Residuals

The effluents generated by pyrolytic systems typically include solid, liquid, and gaseous residuals. Solid products include debris, oversized rejects, dust, ash, and the treated medium. Dust collected from particulate control devices may be combined with the treated medium or, depending on analyses for carryover contamination, recycled through the treatment unit.

Depending on the individual system, the flue gases from the pyrolysis unit will generally be treated by wet or dry APC systems before discharge through a stack. In the Deutsche Babcock System, offgases are treated by incineration [1, p. 166].

Ash and treated soil/solids from pyrolysis may be contaminated with heavy metals. APC system solids, such as fly ash, may contain high concentrations of volatile metals. If these residues fail required leachate toxicity tests, they can be treated by a process such as solidification/stabilization and disposed of onsite or in an approved landfill [11, p. 8.97]. If the treated medium and ash pass all required tests, they may be disposed of onsite without further treatment.

Depending on the specific pyrolysis system, liquid streams may include condensed organics or water from the APC system. After organics are removed, condensed water may be used as a dust suppressant for the treated medium. Scrubber purge water can be purified and returned to the site wastewater treatment facility (if available), discharged to the sewer, or used for rehumidification and cooling of the hot, dusty media.

Liquid waste from the APC system may contain excess alkali, high chlorides, volatile metals, organics, metals particulates, and inorganic particulates. Treatment may require neutralization, chemical precipitation, settling, filtration, or carbon adsorption before discharge.

Site Requirements

Pyrolytic treatment processes are not expected to have significantly different site requirements than those for thermal desorption or incineration processes.

Note that the pyrolytic systems marketed by Deutsche Babcock are not currently available in mobile or transportable configurations. The HT-V system and the ATP are transportable, and vendors claim that they can be set up in a matter of days.

Standard site requirements include electric power (440 or 480 V, 3-phase) and water. The quantity of water required is design- and site-specific.

Treatment of contaminated soils or other waste materials require that a site safety plan be developed to provide for personnel protection and special handling measures. Storage should be provided to hold the process product streams until they have been tested to determine their acceptability for disposal or release. Depending upon the site, a method to store waste that has been prepared for treatment may be necessary. Storage capacity will depend on waste volume.

Onsite analytical equipment capable of monitoring site-specific organic compounds for performance assessment make the operation more efficient and provide better information for process control.

Performance Data

Limited performance data are available for pyrolytic systems treating hazardous wastes containing PCBs, dioxins, and other organics [1, pp. 165, 168] [2, pp. 9-14] [5, pp. 10-15] [6, p. 9]. The quality of this information has not been determined. These data are included as a general indication of the performance of pyrolysis equipment and may not be directly transferrable to a specific Superfund site. Good site characterization and treatability studies are essential in further refining and screening the pyrolysis technology.

The HT-V system's performance on oily sludges contaminated with dioxins and PCBs was evaluated in bench-scale treatability tests conducted by Law Environmental on April 25, 1991 [2, pp. 9-14] [5, pp. 10-15]. The simulated waste used in the dioxin test was contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). A decontamination efficiency of over 99.99% was calculated, as no 2,3,7,8-TCDD was detected in the treated residue, offgases, or condensate. In addition, the test report claims that no significant quantities of new toxic compounds were synthesized by the process [2, pp. 9-14].

A second bench-scale treatability study was conducted on a mixture of PCB-contaminated soil, PCB-contaminated oil, and

water. All process streams were sampled and analyses indicated a decontamination efficiency of over 99.99%. PCB levels were below the detection limits in all effluent streams and the test report claims that no significant quantities of new toxic compounds were synthesized by the process [5, pp. 10-15]. Although these results appear promising, complete closures of mass balances are not possible with the information collected during the HT-V treatability tests.

The Deutsche Babcock system was tested in an industrial-scale demonstration in May and June 1988. Prior to this demonstration, the same system was used to treat 35,000 tons of soil. The plant is located in Unna-Bonen, West Germany, at a former coke oven site. The unit had a design rate of 7 tons/hour with a soil moisture content of 21 percent and 5 percent volatile compounds. The destruction of 17 polycyclic aromatics was measured. A system decontamination efficiency of 99.77 percent was achieved. The results are summarized in Table 2 [1, p. 168]. Note that this test was conducted in Germany and that the majority of the applications of the Deutsche Babcock system have been in Germany. German requirements regarding incineration were not researched and may differ significantly from US requirements.

Table 2
Deutsche Babcock Pyrolytic Rotary Kiln
Contaminated Soil Results

Date	March 8, 1989		January 27, 1989	
Pollutant	Input mg/kg	Output mg/kg	Input mg/kg	Output mg/kg
Naphthalene	101.00	1.7	161.60	0.5
2-methylnaphthalene	40.20	0.5	73.80	0.1
1-methylnaphthalene	23.40	0.3	42.90	0.1
Dimethylnaphthalene	n.d.	n.d.	93.20	0.3
Acenaphthylene	n.d.	n.d.	68.20	0.1
Acenaphthene	n.d.	n.d.	42.30	0.1
Fluorene	156.00	0.1	238.00	0.1
Phenanthrene	686.00	0.6	1055.30	1.4
Anthracene	281.00	0.1	226.00	0.3
Fluoranthene	n.d.	n.d.	688.60	1.3
Pyrene	236.00	0.1	398.20	0.6
Benz[a]anthracene	155.00	0.2	2259.20	0.3
Chrysene	214.00	0.5	134.60	0.9
Benzo[e]pyrene	66.60	0.4	111.50	1.1
Benzo[b]fluoranthene	112.00	0.1	168.50	5.2
Benzo[k]fluoranthene	43.70	0.1	81.90	0.3
Benzo[a]pyrene	86.60	0.2	138.10	0.4
Dibenz[a, h]anthracene	16.80	0.1	23.20	0.1
Benzo[g, h, i]perylene	14.00	0.1	60.20	0.1
Indeno[1, 2, 3-cd]pyrene	33.80	0.1	69.50	0.1
Sum	2266.10	5.2	6134.80	13.4
n.d. = not detectable				
Decontamination efficiency in %		99.77		99.78

The Soiltech ATP is being used in conjunction with chemical dehalogenation to remediate the Wide Beach Superfund site. Much of the soil in the small community of Wide Beach, New York is contaminated with PCBs from road oils. PCB levels range from approximately 10 ppm to over 5,000 ppm; the primary cleanup requirement is to reduce PCB concentrations to less than 2 ppm [6, pp. 2-3].

The system used at Wide Beach is similar to the ATP described previously but also includes a reagent mix system. The reagent mix system adds dechlorination chemicals (potassium hydroxide and polyethylene glycol) to a stream of oils recycled from the system effluent [6, p. 4] [12, p. 45].

PCB concentrations in the treated soil were below the reporting limit of 70 ppb, which is significantly below the required level. In addition, the process water contained no more than 1 ppb PCBs, stack gas PCB levels were less than 33 percent of the New York State Department of Environmental Conservation (NYDEC) limits, fugitive emissions were within NYDEC limits, and treated soils passed the toxicity characteristic leaching procedure (TCLP) [6, pp. 2,9]. At the beginning of the cleanup effort, treated soil was returned to local sites. The treated soil, however, does not have the same consistency as untreated soil, and current plans are to landfill the soil rather than returning it to the original sites [12, p. 45].

Technology Status

Pyrolysis has been used to treat various hazardous wastes as documented in the Performance Data section of this bulletin. In particular, pyrolysis has been applied to the remediation of the Wide Beach Superfund site (in conjunction with chemical dehalogenation) [6, pp. 1-2] and to the cleanup of contaminated soils in Germany [1, pp. 165-168].

EPA Contact

Technology-specific questions regarding pyrolysis may be directed to:

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Mr. James Cudahy	Focus Environmental, Inc.
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EPA

Engineering Bulletin
Thermal Desorption Treatment

Purpose

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

Abstract

Thermal desorption is an ex situ means to physically separate volatile and some semivolatile contaminants from soil, sediments, sludges, and filter cakes. For wastes containing up to 10% organics or less, thermal desorption can be used alone for site remediation. It also may find applications in conjunction with other technologies or be appropriate to specific operable units at a site.

Site-specific treatability studies may be necessary to document the applicability and performance of a thermal desorption system. The EPA contact indicated at the end of this bulletin can assist in the definition of other contacts and sources of information necessary for such treatability studies.

Thermal desorption is applicable to organic wastes and generally is not used for treating metals and other inorganics. Depending on the specific thermal desorption vendor selected, the technology heats contaminated media between 200-1000°F, driving off water and volatile contaminants. Offgases may be burned in an afterburner, condensed to reduce the volume to be disposed, or captured by carbon adsorption beds.

Commercial-scale units exist and are in operation. Thermal desorption has been selected at approximately fourteen Superfund sites [1]* [2]. Three Superfund Innovative Technology Evaluation demonstrations are planned for the next year.

The final determination of the lowest cost alternative will be more site-specific than process equipment dominated. This bulletin provides information on the technology applicability, limitations, the types of residuals produced, the latest performance data, site requirements, the status of the technology, and sources for further information.

Technology Applicability

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 primarily volatile organic compounds (VOCs), semivolatiles, and even higher boiling point compounds, such as polychlorinated biphenyls (PCBs) [3][4][5][6]. The technology is not effective in separating inorganics from the contaminated medium. Volatile metals, however, may be removed by higher temperature thermal desorption systems.

Some metals may be volatilized by the thermal desorption process as the contaminated medium is heated. The presence of chlorine in the waste can also significantly affect the volatilization of some metals, such as lead. Normally the temperature of the medium achieved by the process does not oxidize the metals present in the contaminated medium [7, p. 85].

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 [8, p. 2][4][9].

Performance data presented in this bulletin should not be considered directly applicable to other Superfund sites. A number of variables, such as the specific mix and distribution

* [reference number, page number]

Table 1
RCRA Codes for Wastes Treated by Thermal Desorption

Wood Treating Wastes	K001
Dissolved Air Flotation (DAF) Float	K048
Slop Oil Emulsion Solids	K049
Heat Exchanger Bundles Cleaning Sludge	K050
American Petroleum Institute (API) Separator Sludge	K051
Tank Bottoms (leaded)	K052

Table 2
Effectiveness of Thermal Desorption on General Contaminant Groups for Soil, Sludge, Sediments, and Filter Cakes

		Effectiveness			
	Contaminant Groups	*Soil*	*Sludge*	*Sediments*	*Filter Cakes*
Organic	Halogenated volatiles	■	▼	▼	■
	Halogenated semivolatiles	■	▼	▼	■
	Nonhalogenated volatiles	■	▼	▼	■
	Nonhalogenated semivolatiles	■	▼	▼	■
	PCBs	■	▼	▼	▼
	Pesticides	■	▼	▼	▼
	Dioxins/Furans	■	▼	▼	▼
	Organic cyanides	▼	▼	▼	▼
	Organic corrosives	❑	❑	❑	❑
Inorganic	Volatile metals	■	▼	▼	▼
	Nonvolatile metals	❑	❑	❑	❑
	Asbestos	❑	❑	❑	❑
	Radioactive materials	❑	❑	❑	❑
	Inorganic corrosives	❑	❑	❑	❑
	Inorganic cyanides	❑	❑	❑	❑
Reactive	Oxidizers	❑	❑	❑	❑
	Reducers	❑	❑	❑	❑

■ Demonstrated Effectiveness: Successful treatability test at some scale completed
▼ Potential Effectiveness: Expert opinion that technology will work
❑ No Expected Effectiveness: Expert opinion that technology will not work

of contaminants, affect system performance. A thorough characterization of the site and a well-designed and conducted treatability study are highly recommended.

Table 1 lists the codes for the specific Resource Conservation and Recovery Act (RCRA) wastes that have been treated by this technology [8, p. 2][4][9]. The indicated codes were derived from vendor data where the objective was to determine thermal desorption effectiveness for these specific industrial wastes. The effectiveness of thermal desorption on general contaminant groups for various matrices is shown in Table 2. Examples of constituents within contaminant groups are provided in "Technology Screening Guide For Treatment of CERCLA Soils and Sludges" [7, p. 10]. This table is based on the current available information or professional judgment where no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability was tested to show the technology was effective for that particular contaminant and medium. The ratings of potential effectiveness or no expected effectiveness are both based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular medium. When the technology is not applicable or will probably not work for a particular combination of contaminant group and medium, a no expected effectiveness rating is given. Another source of general observations and average removal efficiencies for different treatability groups is contained in the Superfund Land Disposal Restrictions (LDR) Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS, September 1990) [10] and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," (OSWER Directive 9347.3-06BFS, September 1990) [11].

Limitations

The primary technical factor affecting thermal desorption performance is the maximum bed temperature achieved. Since the basis of the process is physical removal from the medium by volatilization, bed temperature directly determines which organics will be removed.

The contaminated medium must contain at least 20 percent solids to facilitate placement of the waste material into the desorption equipment [3, p. 9]. Some systems specify a minimum of 30 percent solids [12, p. 6].

As the medium is heated and passes through the kiln or desorber, energy is lost in heating moisture contained in the contaminated soil. A very high moisture content can result in low contaminant volatilization or a need to recycle the soil through the desorber. High moisture content, therefore, causes increased treatment costs.

Material handling of soils that are tightly aggregated or largely clay, or that contain rock fragments or particles greater than 1-1.5 inches can result in poor processing performance due to caking. Also, if a high fraction of fine silt or clay exists in the matrix, fugitive dusts will be generated [7, p. 83] and a greater dust loading will be placed on the downstream air pollution control equipment [12, p. 6].

The treated medium will typically contain less than 1 percent moisture. Dust can easily form in the transfer of the treated medium from the desorption unit, but can be mitigated by water sprays. Normally, clean water from air pollution control devices can be used for this purpose.

Although volatile organics are the primary target of the thermal desorption technology, the total organic loading is limited by some systems to up to 10 percent or less [13, p. II-

30]. As in most systems that use a reactor or other equipment to process wastes, a medium exhibiting a very high pH (greater than 11) or very low pH (less than 5) may corrode the system components [7, p. 85].

There is evidence with some system configurations that polymers may foul and/or plug heat transfer surfaces [3, p. 9]. Laboratory/field tests of thermal desorption systems have documented the deposition of insoluble brown tars (presumably phenolic tars) on internal system components [14, p. 76].

High concentrations of inorganic constituents and/or metals will likely not be effectively treated by thermal desorption. The maximum bed temperature and the presence of chlorine can result in volatilization of some inorganic constituents in the waste, however.

Technology Description

Thermal desorption is any of a number of processes that use either indirect or direct heat exchange to vaporize organic contaminants from soil or sludge. Air, combustion gas, or inert gas is used as the transfer medium for the vaporized components. Thermal desorption systems are physical separation processes and are not designed to provide high levels of organic destruction, although the higher temperatures of some systems will result in localized oxidation and/or pyrolysis. Thermal desorption is not incineration, since the destruction of organic contaminants is not the desired result. The bed temperatures achieved and residence times designed into thermal desorption systems will volatilize selected contaminants, but typically not oxidize or destroy them. System performance is typically measured by comparison of untreated soil/sludge contaminant levels with those of the processed soil/sludge. Soil/sludge is typically heated to 200 - 1000° F, based on the thermal desorption system selected.

Figure 1 is a general schematic of the thermal desorption process.

Waste material handling (1) requires excavation of the contaminated soil or sludge or delivery of filter cake to the system. Typically, large objects greater than 1.5 inches are screened from the medium and rejected. The medium is then delivered by gravity to the desorber inlet or conveyed by augers to a feed hopper [8, p. 1].

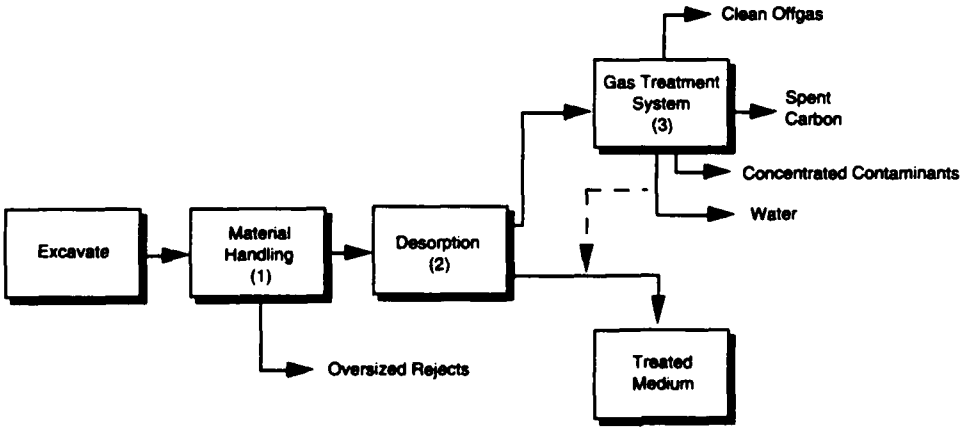
Significant system variation exists in the desorption step (2). The dryer can be an indirectly fired rotary asphalt kiln, a single (or set of) internally heated screw auger(s), or a series of externally heated distillation chambers. The latter process uses annular augers to move the medium from one volatilization zone to the next. Additionally, testing and demonstration data exist for a fluidized-bed desorption system [12].

The waste is intimately contacted with a heat transfer surface, and highly volatile components (including water) are driven off. An inert gas, such as nitrogen, may be injected in a countercurrent sweep stream to prevent contaminant combustion and to vaporize and remove the contaminants [8, p. 1][4]. Other systems simply direct the hot gas stream from the desorption unit [3, p. 5][5].

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 using a series of increasing temperature zones [8, p. 1], 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 [15][16]. Heat transfer fluids used to date include hot combustion gases, hot oil, steam, and molten salts.

Offgas from desorption is typically processed (3) to remove particulates. Volatiles in the offgas may be burned in an afterburner, collected on activated carbon, or recovered in condensation equipment. The selection of the gas treatment system will depend on the concentrations of the contaminants, cleanup standards, and the economics of the offgas treatment system(s) employed.

Figure 1
Schematic Diagram of Thermal Desorption



Process Residuals

Operation of thermal desorption systems typically creates up to six process residual streams: treated medium, oversized medium rejects, condensed contaminants and water, particulate control system dust, clean offgas, and spent carbon (if used). Treated medium, debris, and oversized rejects may be suitable for return onsite.

Condensed water may be used as a dust suppressant for the treated medium. Scrubber purge water can be purified and returned to the site wastewater treatment facility (if available), disposed to the sewer [3, p. 8] [8, p. 2] [4, p. 2], or used for rehumidification and cooling of the hot, dusty media. Concentrated, condensed organic contaminants are containerized for further treatment or recovery.

Dust collected from particulate control devices may be combined with the treated medium or, depending on analyses for carryover contamination, recycled through the desorption unit.

Clean offgas is released to the atmosphere. If used, spent carbon may be recycled by the original supplier or other such processor.

Site Requirements

Thermal desorption systems are transported typically on specifically adapted flatbed semitrailers. Since most systems consist of three components (desorber, particulate control, and gas treatment), space requirements on site are typically less than 50 feet by 150 feet, exclusive of materials handling and decontamination areas.

Standard 440V, three-phase electrical service is needed. Water must be available at the site. The quantity of water needed is vendor and site specific.

Treatment of contaminated soils or other waste materials require that a site safety plan be developed to provide for personnel protection and special handling measures. Storage should be provided to hold the process product streams until they have been tested to determine their acceptability for disposal or release. Depending upon the site, a method to store waste that has been prepared for treatment may be necessary. Storage capacity will depend on waste volume.

Onsite analytical equipment capable of determining site-specific organic compounds for performance assessment make the operation more efficient and provide better information for process control.

Performance Data

Several thermal desorption vendors report performance data for their respective systems ranging from laboratory treatability studies to full-scale operation at designated Superfund sites [17][9][18]. The quality of this information has not been determined. These data are included as a general guideline to the performance of thermal desorption equipment, and may not be directly transferrable to a specific Superfund site. Good site characterization and treatability studies are essential in further refining and screening the thermal desorption technology.

Chem Waste Management's (CWM's) X*TRAX™ System has been tested at laboratory and pilot scale. Pilot tests were performed at CWM's Kettleman Hills facility in California. Twenty tons of PCB- and organic-contaminated soils were processed through the 5 TPD pilot system. Tables 3 and 4 present the results of PCB separation from soil and total hydrocarbon emissions from the system, respectively [4].

During a non-Superfund project for the Department of Defense, thermal desorption was used in a full-scale demonstration at the Tinker Air Force Base in Oklahoma. The success of this project led to the patenting of the process by Weston Services, Inc. Since then, Weston has applied its low-temperature thermal treatment (LT^3) system to various contaminated soils at bench-scale through full-scale projects [19]. Table 5 presents a synopsis of system and performance data for a full-scale treatment of soil contaminated with No. 2 fuel oil and gasoline at a site in Illinois.

Canonie Environmental has extensive performance data for its Low Temperature Thermal Aeration ($LTTA^{SM}$) system at full-scale operation (15-20 cu. yds. per hour). The $LTTA^{SM}$ has been applied at the McKin (Maine), Ottati and Goss (New Hampshire) and Cannon Engineering Corp. (Massachusetts) Superfund sites. Additionally, the $LTTA^{SM}$ has been used at the privately-funded site in South Kearney (New Jersey). Table

Table 3
PCB Contaminated Soils
Pilot X*TRAX™ [4]

Matrix	*Feed (ppm)*	*Product (ppm)*	*Removal (%)*
Clay	5,000	24	99.3
Silty Clay	2,800	19	99.5
Clay	1,600	4.8	99.7
Sandy	1,480	8.7	99.1
Clay	630	17	97.3

Table 4
Pilot X*TRAX™
TSCA Testing - Vent Emissions [4]

Total Hydrocarbons (ppm-V)				
Before Carbon	*After Carbon*	*Removal (%)*	*VOC (lbs/day)*	*PCB* (mg/m^3)*
1,320	57	95.6	0.02	<0.00056
1,031	72	93.0	0.03	<0.00055
530	35	93.3	0.01	<0.00051
2,950	170	94.2	0.07	<0.00058
2,100	180	91.4	0.08	<0.00052

*Note: OSHA permits 0.50 mg/m^3 PCB (1254) for 8-hr exposure.

6 presents a summary of Canonie LTTA℠ data [5]. The Cannon Engineering (Mass) site, which was not included in Table 6, successfully treated a total of 11,330 tons of soil, containing approximately 1803 lbs. of VOC [20].

T.D.I. Services, Inc. has demonstrated its HT-5 Thermal Distillation Process at pilot- and full-scale for a variety of RCRA-listed and other wastes that were prepared to simulate American Petroleum Institute (API) refinery sludge [8]. The company has conducted pilot- and full-scale testing with the API sludge to demonstrate the system's ability to meet Land Ban Disposal requirements for K048 through K052 wastes. Independent evaluation by Law Environmental confirms that the requirements were met, except for TCLP levels of nickel, which were blamed on a need to "wear-in" the HT-5 system [21, p. ii].

Remediation Technologies, Inc. (ReTec) has performed numerous tests on RCRA-listed petroleum refinery wastes. Table 7 presents results from treatment of refinery vacuum

Table 5
Full-Scale Performance Results for the LT³ System [19]

Contaminant	Soil Range (ppb)	Treated Range (ppb)	Range of Removal Efficiency
Benzene	1000	5.2	99.5
Toluene	24000	5.2	99.9
Xylene	110000	<1.0	>99.9
Ethyl benzene	20000	4.8	99.9
Napthalene	4900	<330	>99.3
Carcinogenic			
Priority PNAs	<6000	<330–590	<90.2–94.5
Non-carcinogenic			
Priority PNAs	890–6000	<330–450	<62.9–94.5

Table 6
Summary Results of the LTTA℠ Full-Scale Cleanup Tests [5]

Site	Processed	Contaminant	Soil (ppm)	Treated (ppm)
S. Kearney	16000 tons	VOCs PAHs	177.0 (avg.) 35.31 (avg.)	0.87 (avg.) 10.1 (avg.)
McKin	>9500 cu yds 2000 cu yds	VOCs PAHs	ND-3310	ND-0.04 <10
Ottati & Goss	4500 cu yds	VOCs	1500 (avg.)	<0.2 (avg.)

Table 7
ReTec Treatment Results-Refinery Vacuum Filter Cake (A) [3]

Compound	Original Sample (ppm)	Treated Sample (ppm)	Removal Efficiency (%)
Naphthalene	<0.1	<0.1	---
Acenaphthylene	<0.1	<0.1	---
Acenaphthene	<0.1	<0.1	---
Fluorene	10.49	<0.1	>98.9
Phenanthrene	46.50	<0.1	>99.3
Anthracene	9.80	<0.1	>96.6
Fluoranthrene	73.94	<0.1	>99.8
Pyrene	158.37	<0.1	>99.9
Benzo(b)anthracene	56.33	1.43	97.5
Chrysene	64.71	<0.1	>99.9
Benzo(b)fluoranthene	105.06	2.17	97.9
Benzo(k)fluoranthene	225.37	3.64	98.4
Benzo(a)pyrene	174.58	1.89	98.9
Dibenz(ab)antracene	477.44	10.25	97.8
Benzo(ghi)perylene	163.53	5.09	96.6
Indeno(123-cd)pyrene	122.27	4.16	96.6
Treatment Temperature: 450°F			

Table 8
ReTec Treatment Results-Creosote Contaminated Clay [3]

Compound	Original Sample (ppm)	Treated Sample (ppm)	Removal Efficiency (%)
Naphthalene	1321	<0.1	>99.9
Acenaphthylene	<0.1	<0.1	---
Acenaphthene	293	<0.1	>99.96
Fluorene	297	<0.1	>99.96
Phenanthrene	409	1.6	99.6
Anthracene	113	<0.1	>99.7
Fluoranthrene	553	1.5	99.7
Pyrene	495	2.0	99.6
Benzo(b)anthracene	59	<0.1	>99.99
Chrysene	46	<0.1	>99.8
Benzo(b)fluoranthene	14	2.5	82.3
Benzo(k)fluoranthene	14	<0.1	>99.8
Benzo(a)pyrene	15	<0.1	>99.9
Dibenzo(ab)anthracene	<0.1	<0.1	---
Benzo(ghi)perylene	7	<0.1	>99.4
Indeno(123-cd)pyrene	3	<0.1	>99.3
Treatment Temperature: 500°F			

Table 9
ReTec Treatment Results-Coal Tar Contaminated Soils [3]

Compound	Original Sample (ppm)	Treated Sample (ppm)	Removal Efficiency (%)
Benzene	1.7	<0.1	>94
Toluene	2.3	<0.1	>95
Ethylbenzene	1.6	<0.1	>93
Xylenes	6.3	<0.3	>95
Naphthalene	367	<1.7	>99
Fluorene	114	<0.2	>99
Phenanthrene	223	18	91.9
Anthracene	112	7.0	93.8
Fluoranthrene	214	15	93.0
Pyrene	110	11	90.0
Benzo(b)anthracene	56	<1.4	>97
Chrysene	58	3.7	93.6
Benzo(b)fluoranthene	45	<1.4	>97
Benzo(k)fluoranthene	35	<2.1	>94
Benzo(a)pyrene	47	<0.9	>98
Benzo(ghi)perylene	24	<1.1	>95
Indeno(123-cd)pyrene	27	<6.2	>77
Treatment Temperature: 450°F			

filter cake. Tests with creosote-contaminated clay and coal tar-contaminated soils showed significant removal efficiencies (Tables 8 and 9). All data were obtained through use of ReTec's 100 lb/h pilot scale unit processing actual industrial process wastes [3].

Recycling Sciences International, Inc. (formerly American Toxic Disposal, Inc.) has tested its Desorption and Vaporization Extraction System (DAVES), formerly called the Vaporization Extraction System (VES), at Waukegan Harbor, Illinois. The pilot-scale test demonstrated PCB removal from material containing up to 250 parts per million (ppm) to levels less than 2 ppm [12].

RCRA LDRs that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements for CERCLA response actions. Thermal desorption can produce a treated waste that meets treatment levels set by BDAT but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where thermal desorption does not meet these levels, it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. Treatability variances are justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.3-06FS, September 1990) [10], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-06BFS, September 1990) [11]. Another approach could be to use other treatment techniques in series with thermal desorption to obtain desired treatment levels.

Technology Status

Significant theoretical research is ongoing [22][23], as well as direct demonstration of thermal desorption through both treatability testing and full-scale cleanups.

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 [24].

In this country, thermal desorption technologies are the selected remedies for one or more operable units at fourteen Superfund sites. Table 10 lists each site's location, primary contaminants, and present status [1][2].

Most of the hardware components of thermal desorption are available off the shelf and represent no significant problem of availability. The engineering and configuration of the systems are similarly refined, such that once a system is designed full-scale, little or no prototyping or redesign is required.

On-line availability of the full-scale systems described in this bulletin is not documented. However, since the ex situ system can be operated in batch mode, it is expected that component failure can be identified and spare components fitted quickly for minimal downtime.

Several vendors have documented processing costs per ton of feed processed. The overall range varies from $80 to $350 per ton processed [6][4, p. 12][5][3, p. 9]. Caution is recommended in using costs out of context because the base year of the estimates vary. Costs also are highly variable due to the quantity of waste to be processed, term of the remediation contract, moisture content, organic constituency of the contaminated medium, and cleanup standards to be achieved. Similarly, cost estimates should include such items as preparation of Work Plans, permitting, excavation, processing itself, QA/QC verification of treatment performance, and reporting of data.

EPA Contact

Technology-specific questions regarding thermal desorption may be directed to:

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Table 10
Superfund Sites Specifying Thermal Desorption as the Remedial Action

Site	*Location*	*Primary Contaminants*	*Status*
Cannon Engineering (Bridgewater Site)	Bridgewater, MA (1)	VOCs (Benzene, TCE & Vinyl Chloride)	Project completed 10/90
McKin	McKin, ME (1)	VOCs (TCE, BTX)	Project completed 2/87
Ottati & Goss	New Hampshire (1)	VOCs (TCE; PCE; 1, 2-DCA, and Benzene)	Project completed 9/89
Wide Beach	Brandt, NY (2)	PCBs	In design • pilot study available 5/91
Metaltec/Aerosystems	Franklin Borough, NJ (2)	TCE and VOCs	In design • remedial design complete • remediation starting Fall '91
Caldwell Trucking	Fairfield, NJ (2)	VOCs (TCE, PCE, and TCA)	In design
Outboard Marine/ Waukegan Harbor	Waukegan Harbor, IL (5)	PCBs	In design • treatability studies complete
Reich Farms	Dover Township, NJ (02)	VOCs and Semivolatiles	Pre-design
Re-Solve	North Dartmouth, MA (1)	PCBs	In design • pilot study June/July '91
Waldick Aerospace Devices	New Jersey (2)	TCE and PCE	In design
Wamchem	Burton, SC (4)	BTX and SVOCs (Naphthalene)	In design • pilot study available 5/91
Fulton Terminals	Fulton, NY (2)	VOCs (Xylene, Styrene, TCE, Ethylbenzene, Toluene) and some PAHs	Pre-design
Stauffer Chemical	Cold Creek, AL (4)	VOCs and pesticides	Pre-design
Stauffer Chemical	Le Moyne, AL (4)	VOCs and pesticides	Pre-design

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Mr. James Cummings	EPA-OERR
Dr. Steve Lanier	Energy and Environmental Research Corp.
Ms. Evelyn Meagher-Hartzell	SAIC
Mr. James Rawe	SAIC
Ms. Tish Zimmerman	EPA-OERR

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Catalytic Oxidation of Organics in Vapor Streams at Remediation Sites

Port Hueneme, CA 93043 | NEESA Document No. 20.2-051.5 | January 1993

Introduction

Leaks from underground fuel storage tanks and associated piping have resulted in contamination of soil and ground water. Navy-wide, more than 350 sites are in need of remediation to remove fuel contamination from soil and ground water. These sites are located at about 80 different Navy activities (including Marine Corps installations) (1).

As a result of remedial activities to clean these contaminated soils and ground water, contaminated air streams are often generated. Available alternatives for the treatment of these air streams include carbon adsorption and incineration. This Tech Data Sheet describes catalytic oxidation, a third alternative that has the potential to be effective at a lower cost.

Purpose

The Tech Data Sheets are designed to:

- Disseminate practical, implementation-related information to minimize design and construction problems;
- Help Remedial Project Managers (RPMs) evaluate a technology (recommended in a Feasibility Study [FS], for example) and decide if it is practical and cost-effective;
- Aid RPMs in writing a Remedial Action (RA) Delivery Order;
- Help Engineering Field Division (EFD) Remedial Design personnel write a Statement of Work (SOW) for, and RPMs to review, Remedial Design Plans; and
- Enable field personnel such as Project Superintendents, Engineers in Charge, On-Scene Coordinators (OSCs), and Resident Officers in Charge of Construction (ROICCs) become familiar with a technology at a site they will oversee.

Description of Technology

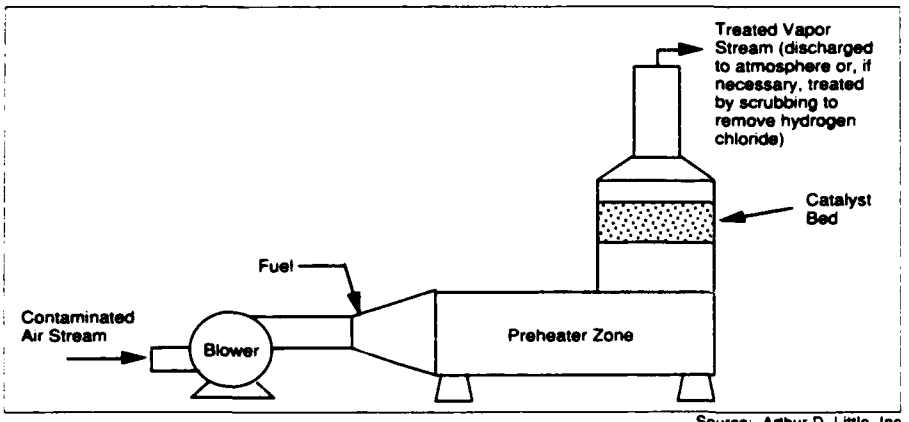
Catalytic oxidation is a relatively new alternative for the treatment of volatile organic compounds (VOCs) in air streams resulting from remedial operations. In catalytic oxidation, VOCs are thermally destroyed at temperatures typically ranging from 600 to 1,000°F by using a solid catalyst. These basic characteristics are responsible for the differences between catalytic oxidation and the more commonly used VOC removal techniques such as carbon adsorption (which does not result in the destruction of the VOCs) and incineration (which destroys the VOCs at much higher temperatures). See "Applications" and "Advantages, Disadvantages, and Limitations" for further discussion of the differences between the technologies.

A schematic of a representative catalytic oxidation system is shown in Figure 1. The catalytic oxidation system consists of two basic components. First, the contaminated air is directly preheated (electrically or, more frequently, using natural gas or propane) to reach a temperature necessary to initiate the catalytic oxidation of the VOCs. Then the preheated VOC-laden air is passed through a bed of solid catalysts where the VOCs are rapidly oxidized.

In most cases, the process can be enhanced to reduce auxiliary fuel costs by using an air-to-air heat exchanger to transfer heat from the exhaust gases to the incoming contaminated air. Typically, about 50% of the heat of the exhaust gases is recovered (2). Depending on VOC concentrations, the recovered heat may be sufficient to sustain oxidation without additional fuel (see "Advantages, Disadvantages, and Limitations").

Catalyst systems used to oxidize VOCs typically use metal oxides such as nickel oxide, copper oxide, or chromium oxide. Noble metals such as platinum and palladium may also be used (3). However, in a majority of remedial applications, non-precious metals (e.g., nickel, copper, or chromium) are used. Most commercially available catalysts are proprietary.

Ideally, the catalytic oxidation process will result in the oxidation of the contaminants to products of complete combustion such as water and carbon dioxide for non-chlorinated VOCs. Complete combustion products of chlorinated VOCs include water, carbon dioxide, and hydrogen chloride. Hydrogen chloride in the gas stream may have to be neutralized (e.g., with a caustic scrubber) prior to final discharge.



Source: Arthur D. Little, Inc.

Figure 1. Schematic of Catalytic Oxidation System

Technology Status

Catalytic oxidation is a proven industrial process used in chemical production as well as in air treatment operations. Specific well-established applications of catalytic oxidation include the treatment of VOC-contaminated air emissions from processes such as spray painting, offset printing, coating operations, and polymer processing (3). In addition, catalytic oxidation is used to oxidize hydrocarbons such as those in automotive exhausts (e.g., an automobile's catalytic converter is a catalytic oxidation system).

Based on its success in industrial applications, catalytic oxidation has been adapted for use in treating off-gases from remedial activities. Catalytic oxidation has been investigated for use in these activities for the past 10 years. The technology has been demonstrated effective and economical for this purpose within the last five years (4).

There is a relatively small number of firms that manufacture catalytic oxidation systems specifically for remedial activities. These firms will generally supply the equipment to remedial action contractors for integration with specific remedial technologies such as in situ vapor extraction of organics from soil or air stripping of organics from ground water (see "Interface with Other Technologies").

Despite its relatively newer application in remedial activities, catalytic oxidation is a mature technology and its status as an implementable technology is well established. Nevertheless, the technology continues to evolve with respect to:

- Enhancement of heat recovery techniques to lower operating costs by reducing fuel requirements;
- Development of new types of catalysts to increase destruction efficiency and/or to extend the operating life of the catalyst bed; and
- Testing of the technology on a wider range of VOCs to extend its areas of proven performance.

Contaminants Mitigated

Recent investigations of catalytic oxidation have indicated that the technology is capable of destroying VOCs that are common contaminants in soil and ground water. These contaminants include those contained in gasoline and lighter fractions of JP-4, JP-5, and diesel fuels (e.g., benzene, toluene, ethylbenzene, and xylene [BTEX] as well as aliphatic hydrocarbons).

Use of catalytic oxidation with chlorinated VOCs such as those found in industrial cleaners and solvents has, until fairly recently, proven difficult due to increased catalyst degradation. However, newer catalysts have been developed that are reportedly capable of effectively destroying halogenated (including chlorinated) hydrocarbons (2, 4). These catalysts are proprietary.

Specific chlorinated hydrocarbons that have been reportedly mitigated include trichloroethylene, trichloroethane, methylene chloride, and 1,1- dichloroethane.

A number of factors may influence the applicability of catalytic oxidation for a given contaminant, including:

- More highly chlorinated VOCs (e.g., trichloroethylene) may resist destruction by catalytic oxidation at normal operating temperatures;
- Mixtures of VOCs may affect the overall effectiveness of catalytic oxidation; and
- The presence of chlorinated hydrocarbons (see comment above) and some heavy metals (e.g., lead) may poison a particular catalyst.

For these reasons, it is important that the contaminated air stream is well characterized. In addition, tests may be necessary to determine treatability by catalytic oxidation.

Applications

Applications of catalytic oxidation include the treatment of contaminated air streams generated during remedial processes. These processes (see "Interface with Other Technologies") include:

- Air stripping to remove VOCs from ground water;
- Soil vapor extraction to remove VOCs from soils in the vadose zone; and

- Dual extraction techniques to simultaneously remove VOCs from contaminated ground water and soils.

In remedial activities such as these it is often necessary to treat the contaminated air stream prior to its discharge. The most commonly used method of treatment is carbon adsorption. Although carbon adsorption is proven effective, it succeeds in merely transferring the contaminant from one medium (air) to another (carbon). To make the carbon adsorption process economical, regeneration of the carbon is required to allow for its reuse. The regeneration process further adds to the complexity and cost of the treatment system.

An alternative to carbon adsorption is the destruction of the VOCs in the air stream by incineration. In general, destruction of a broad range of VOCs can be accomplished by incineration at temperatures of 1,500°F or greater. However, for air streams with relatively low concentrations of VOCs (less than 3,000 ppm, for example), incineration can be very expensive due to supplemental fuel necessary to maintain adequate destruction temperatures. In addition to its high expense, incineration may also result in the generation of unacceptable levels of nitrogen oxides (NOx).

Catalytic oxidation is a third alternative that, in some cases, may provide for effective treatment of remedial technology emissions at a lower cost. In general, catalytic oxidation is used when:

- VOC concentrations in the vapor stream are (roughly) greater than 150 parts per million by volume (ppmv) and less than 3,000 ppmv; and
- Quantity of VOCs to be removed from soil is (roughly) greater than 25 lb/day and less than 50 lb/day.

These applications and a comparison of the three vapor stream treatment alternatives are discussed in "Advantages, Disadvantages, and Limitations."

Advantages, Disadvantages, and Limitations

A summary of advantages and disadvantages of the three primary alternatives for the control of air emissions from the treatment of VOC-contaminated ground water and soil is presented in Figure 2.

The primary advantages to using catalytic oxidation over carbon adsorption to treat VOC-contaminated air emissions are:

- Lower cost for use at sites with greater total quantities of VOCs and/or greater concentrations of VOCs in the air stream resulting from their removal; and
- The contaminant is destroyed on site rather than transferred from one medium to another.

When comparing catalytic oxidation with carbon adsorption, the following factors will generally favor the selection of catalytic oxidation:

- VOCs in the air stream do not adsorb well to activated carbon;
- The air stream is saturated with water, thereby reducing the adsorptive capability of the carbon unless the air stream is heated to drive off the moisture;
- By-products from regeneration of the carbon do not have any value (some solvents removed from carbon can be recovered and reused) and would require further treatment prior to disposal or discharge; and

Control Alternative	Advantages	Disadvantages
Carbon Adsorption	• Proven effective in removing vapor-phase VOCs • Simple technology	• Not a destruction technology • Requires regeneration or disposal of spent carbon • Expensive—roughly doubles the cost of the remedial activity
Incineration	• Destroys contaminants on site • Proven effective with concentrated VOC-contaminated air emissions • Well-established technology	• High temperatures required for effective operation • Expensive—particularly as concentration of organics decreases and more auxiliary fuel is required • Negative public perception • Potential for generation of NOx • Air permit required for operation
Catalytic Oxidation	• Destroys contaminants on site • Provides for thermal destruction of contaminants at relatively low temperatures (600 to 1,000°F) • Proven effective with many dilute VOC-contaminated air emissions • Well-established technology • Less potential for NOx emissions than incineration • Lower operating cost than incineration or carbon adsorption in many applications	• Catalyst activity may be negatively affected by the presence of chlorine or sulfur in air emissions treated • Treatment of chlorinated VOCs will result in the generation of hydrogen chloride—possibly requiring further treatment • Limited to treatment of relatively dilute contaminated air streams to prevent overheating of catalyst • Air permit required for operation • Destruction efficiencies may be lower due to lower temperatures • Spent catalyst must be replaced

Figure 2. Comparison of Air Emission Control Techniques

Source: Arthur D. Little, Inc.

- The quantity of VOCs to be removed from ground water or soil is large (usually greater than 25 lb/day) (4).

One cost comparison of the use of carbon adsorption versus catalytic oxidation indicated that at a throughput of 100 scfm of VOC-contaminated gas, daily operating costs of carbon adsorption exceeded those of catalytic oxidation at VOC concentrations of greater than approximately 150 ppmv (2).

Catalytic oxidation has the potential to be less costly than incineration. This advantage is primarily due to reduced energy requirements as a result of lower-temperature (600 to 1,000 °F) operation and, in some cases, better opportunity for energy recovery. In addition, catalytic oxidation may be more economical than incineration for dilute (less than 3,000 ppm) VOC-contaminated air streams. Incineration, however, may be more economical for the removal of large quantities of VOCs (e.g., greater than 50 lb/day) (4).

Catalytic oxidation is less likely to generate NOx emissions than incineration due to lower-temperature operation. Although both thermal techniques will require an air emission permit to operate, a permit may be easier to obtain for a lower-NOx emission source.

Although catalytic oxidation is typically performed at temperatures below those of high-temperature incineration, these low temperatures may be disadvantageous due to:

- Potentially lower destruction efficiencies; and
- The potential for formation of products of incomplete combustion (PICs) that may be more toxic than the original contaminants.

In general, the catalytic oxidation process is applied to air streams containing about 3,000 ppmv or less of VOCs. At levels approaching 3,000 ppmv VOCs, the recoverable heat from the catalytic oxidation may be sufficient to sustain oxidation without additional fuel. However, there is a risk that these (or greater) concentrations could result in autocombustion of the organics causing temperatures to climb past the design temperature of the catalyst. If confronted with VOC concentrations greater than 3,000 ppmv, alternatives to be considered include incineration of the concentrated air stream or catalytic oxidation preceded by dilution of the air stream.

Selection of an appropriate catalyst is critical. Catalyst performance and overall effectiveness of the catalytic oxidation process can be affected by:

- The presence of chlorinated VOCs or sulfur compounds (5); and
- Mixtures of contaminants (6).

Laboratory or pilot-scale testing may be required to select the optimum catalyst system and appropriate operating parameters.

The replacement of catalysts is a component of the operating cost of a catalytic oxidation system. Although the frequency of catalyst replacement is dependent on application-specific characteristics, the typical lifetime of a catalyst may be approximately one to two years.

An additional consideration with the use of catalytic oxidation is the generation of hydrogen chloride as a result of oxidation of chlorinated VOCs. Such emissions may require further treatment such as scrubbing or neutralization prior to discharge. The additional treatment requirements will add to system complexity and cost.

Interface with Other Technologies

In remedial activities, catalytic oxidation will typically be a final step in a series of processes to remove VOCs from ground water and soil. Processes that have employed catalytic oxidation include:

- *Thermal desorption.* A process in which excavated soil is heated to volatilize VOCs. The volatilized contaminants are then typically drawn from the soil by an air stream that may be treated by catalytic oxidation prior to release.

- *Soil vapor extraction.* An in situ process used to physically remove VOCs from soils in the vadose or unsaturated zone. To recover contaminated air, vapor extraction wells are used to induce air flow through the contaminated soil. The air strips the VOCs from the soil. As with air stripping of ground water, a VOC-laden air stream is generated. This air stream may then be subjected to catalytic oxidation.

- *Dual extraction.* A combination of pump and treat and soil vapor extraction technologies. A vacuum is placed on a ground water extraction well to extract vapors from soil and a pump is used in the well to extract contaminated ground water. The extracted ground water is sprayed into a heated chamber to enhance removal of the VOCs from the water. The VOCs in the contaminated air streams generated by these processes may then be destroyed by catalytic oxidation.

- *Air stripping of ground water.* A means to remove VOCs (and certain semi-volatile organic compounds) from water. This process generates an air stream laden with the organic compounds. This air stream may then be subjected to catalytic oxidation for the destruction of the organics.

An example of the interface of these technologies is shown in Figure 3 (8, 9). This example illustrates a pilot-scale air stripping/catalytic oxidation system used at Wurtsmith Air Force Base to remove and destroy VOCs (primarily trichloroethylene) from contaminated ground water (see "Application Examples"). As shown, only the air from the first stage air stripper that has the highest loading of VOCs is treated by catalytic oxidation. The second air stripper is used to "polish" the ground water by removing small quantities of residual VOCs. The air emissions from this second air stripper are clean enough to discharge without treatment. (Note: Although in a full-scale system, a scrubber would most likely be required to remove hydrogen chloride from the treated air stream, this was not necessary in this pilot application.)

Similarly configured systems may be used for the remediation of ground water contaminated with petroleum products.

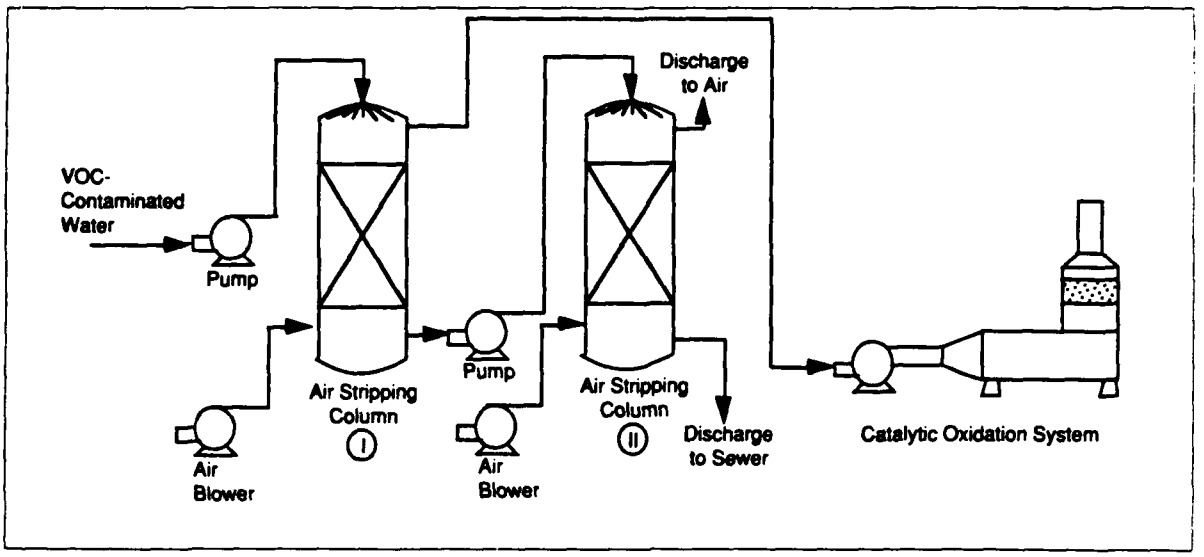


Figure 3. Integrated Air Stripping and Emission Control Treatment System Source: Reference 9

Design Criteria

A number of activities may be required to develop criteria for the design and/or selection of a catalytic oxidation system. These activities include:

- Determination of the quantities and identities of VOCs emitted from the primary treatment process; and
- Laboratory studies, pilot tests, and/or field demonstrations.

In some cases, once the waste stream has been fully characterized, vendors and remedial contractors will have sufficient knowledge about the operation of the primary treatment process and catalytic oxidation requirements to proceed with a design without additional studies or tests.

Studies, tests, or demonstrations may be necessary in cases where there are uncertainties associated with the effectiveness of the primary treatment process and/or the applicability of catalytic oxidation. In addition, regulatory requirements may necessitate the performance of some sort of demonstration to prove that specific treatment standards can be met (see "Regulatory Issues"). If required, studies, tests, or demonstrations will usually be performed with the integrated treatment system (including the primary remedial technology and catalytic oxidation) and will typically be conducted by the remedial contractor.

Results of testing and demonstration activities will be used to determine the feasibility of catalytic oxidation with respect to:

- Treatability;
- Potential destruction effectiveness;
- Meeting regulatory permit requirements; and
- Estimate of cost to implement.

Pilot or field demonstrations may be required to optimize operating parameters such as temperature and residence time to achieve desired VOC destruction efficiencies. These tests and demonstrations can have a significant effect on the total cost of the remedial action (see "Key Cost Factors").

Results of the characterization of the air stream to be treated and testing will also be used to develop specific design criteria needed for design, fabrication, and operation of a catalytic oxidation system. Required criteria include:

- Catalyst system to be used;
- Operating temperatures;
- Residence time (or throughput); and
- Auxiliary fuel requirements.

Usually, electrically heated catalytic oxidation systems will be considered for smaller units (operating at 100 scfm or less). Natural gas or propane will be more economical with large systems.

Typically, a vendor under contract to perform the primary remediation (i.e., vacuum extraction, air stripping, etc.) will address the design and operation of a catalytic oxidation system to treat emissions from the primary remediation.

The most experienced vendors will have a good basis for operating a catalytic oxidation system effectively and economically while meeting regulatory requirements. To obtain names of catalytic oxidation system vendors, contact John Fringer (see "Points of Contact").

Implementation Considerations

Overall, procedures for field implementation are relatively easy for most catalytic oxidation units. Portable units are commercially available. These units may be mounted on a single trailer to facilitate mobilization, setup, disassembly, and demobilization.

The size of the system will be dependent on the design capacity. Dimensions of a commercially available 150 scfm unit are 4 feet

in length, 2 feet in width, and 8 feet in height. This unit can be mounted on a trailer with a bed size of 5 feet in width and 10 feet in length (10).

Portable catalytic oxidation systems can typically be set up in a day or two.

A load center for electrical power in the field will be required to power blowers and instrumentation. Additional electrical power will be needed if the catalytic oxidation system itself is to be electrically heated. Since catalytic oxidation systems are used in conjunction with other treatment processes, electrical power will most likely be available. However, the additional load required must be considered.

Unless electrically heated, either natural gas or propane supplies are required to fuel the catalytic oxidation system. Natural gas or propane is used to avoid potential problems due to incompatibilities between the catalyst and components of other fuels. For example, the presence of sulfur may poison the catalyst. In addition, use of "clean" fuels such as natural gas or propane limits the emission of undesirable products of combustion that may result from the use of other fuels.

Manpower requirements for operation are minimal once performance parameters have been established and start-up has been completed. Most systems are automated and equipped with adequate instrumentation so that a daily operational check is adequate.

Control instrumentation will typically include sensors placed in the flue gas to measure excess oxygen, carbon monoxide, and temperature. Operating conditions such as fuel requirements or air flow can be controlled automatically based on the readings of the sensors. Depending on regulatory requirements, opacity meters may be used to monitor flue gas.

Hydrocarbon analyzers may be used to monitor the performance of the catalytic oxidation system. An increase in concentrations of emitted hydrocarbons may indicate performance problems including degradation (or poisoning) of the catalyst or improper operating temperatures.

Residuals Generated

Typically, residuals of catalytic oxidation systems are minimal. However, residuals may be generated if the treated air requires further treatment prior to discharge. For example, if chlorinated hydrocarbons are treated, acidic off-gases may be generated. These off-gases may require neutralization by scrubbing yielding scrubber water. This scrubber water will require management according to the site's discharge permit.

Most Navy applications involve the treatment of petroleum hydrocarbons which will be less likely to generate off-gases that require treatment and therefore eliminate associated treatment residuals.

An additional residual from catalytic oxidation will be the spent catalyst. Spent catalyst management will usually be the responsibility of the remedial contractor. Typically, the spent catalyst will be returned to the catalyst manufacturer in exchange for replacement catalyst. The manufacturer may recover the active metal from spent catalyst for recycling.

Regulatory Issues

Operation of a catalytic oxidation system will require an air quality permit. Depending on local air permitting requirements and prohibitions, it may not be possible to get a permit for any new combustion system. In that case, alternatives such as carbon adsorption would have to be considered in lieu of catalytic oxidation.

Depending on site-specific regulatory requirements, the ability to get an air permit may be contingent on the results of a demonstration of the technology to determine whether system performance meets established criteria.

Feasibility Study (FS) Criteria Ranking

The use of catalytic oxidation has been rated with respect to its response in meeting certain performance and regulatory criteria. The results of this rating are presented in Figure 4.

Long-term effectiveness, reduction of toxicity, and short-term effectiveness are rated favorable for the following reasons:

- Catalytic oxidation is a contaminant destruction technology;
- Typical catalytic oxidation destruction efficiencies are in the range of 95 to 99.8% of influent VOCs (at, or slightly lower than, typical incineration efficiencies);
- The oxidation reactions proceed very rapidly; and
- The oxidation reactions take place at a lower temperature than incineration, thus reducing risks to worker safety and the environment.

Criteria	Ranking
Effect of reducing the overall threat to human health and the environment	
Compliance with Applicable or Relevant and Appropriate Requirements (ARARs)	
Long-term effectiveness and permanence	
Reduction of toxicity, mobility, or volume	
Short-term effectiveness	
Implementability	
Cost	
State and community acceptance	

Favorable ◄——► Unfavorable

Figure 4. FS Criteria Ranking

As with any thermal technology, community acceptance of catalytic oxidation may be a concern. However, the relatively low-temperature oxidation and low-NOx formation rates may be mitigating factors for improved community acceptance.

Key Cost Factors

The primary factors that will impact the overall cost of using catalytic oxidation include:

- Quantity of contaminant(s) to be treated;
- Type of contaminant (as it affects catalyst selection and off-gas treatment requirements);
- Required destruction efficiencies;
- Concentration of contaminant(s);
- Management of residuals; and
- Utility and fuel costs.

If treatability studies, tests, or demonstrations are required, additional costs may include:

- Laboratory treatability studies—$10,000 to $50,000; and
- Pilot tests or field demonstrations—$100,000 to $500,000.

Fuel requirements will depend on required operating temperatures, flow rates, heating value of influent gas stream, and heat recovery (11).

Typically, costs for catalytic oxidation processes are expressed as a part of the entire remedial activity. Typical operating costs for a catalytic oxidation system alone, operating at 100 to 200 scfm, will range from $8 to $15/day (for natural gas or propane-fired systems) to $20 to $40/day (for electrically heated systems).

Capital costs of equipment operating at throughputs of 100 to 200 scfm are estimated to be in a range from $50,000 to $100,000.

A comparison of the capital and operating costs of catalytic oxidation and carbon adsorption as a function of pounds of VOCs treated has been made (10). This 1991 comparison shows that for a range of 5,000 lbs to 50,000 lbs of total VOCs treated, the capital and operating costs of a 200 scfm, gas-fired catalytic oxidation system ranges from about $110,000 to $150,000. Over the same range, capital and operating costs of activated carbon with off-site regeneration ranges from about $80,000 to $550,000.

Points to Remember

The following points are important to consider in the selection or implementation of catalytic oxidation systems for the treatment of off-gases from remedial actions.

√ Regulatory (permitting) requirements should be determined before selecting an off-gas treatment system.

√ Adequate off-gas characterization is required to avoid incompatibilities between catalysts and contaminants.

√ In processes such as vapor extraction, the concentration of VOCs in the primary treatment off-gas will decrease over time as the VOCs are removed from the soil. Even though initial concentrations of VOCs in the off-gas may be high enough to warrant the use of high-temperature incineration, the cost of incineration could significantly increase as the concentrations decrease.

√ In most cases, the final selection of catalytic oxidation over other treatment technologies will be driven by cost. It may be necessary to determine, on a site-specific basis, the concentration and VOC quantity ranges at which catalytic oxidation is more cost-effective than the other alternatives.

√ When procuring the services of a contractor to conduct the overall remediation, the contractor should guarantee the performance of the catalytic oxidation system to ensure that treatment criteria will be met (this will also include the guarantee of catalyst performance).

√ Making use of vendors with experience and proven capabilities will provide assurance that success will be achieved and that regulatory requirements will be met.

Application Examples

Examples of applications using catalytic oxidation to treat off-gases resulting from the treatment of soil and ground water are provided in Figure 5.

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Site	Contamination Profile	Primary Remedial Technology	Description of Catalytic Oxidation Process	Ref.
Wurtsmith Air Force Base	Ground water contaminated with trichloroethylene (TCE)	Air stripping	1,200 scfm catalytic oxidation system operated at a bed temperature of 660°F. Achieved 97-99% destruction of VOCs in the system influent. Catalyst replaced after one year.	8
Former gasoline service station, Santa Monica, CA	Leaking underground storage tank (UST) resulted in contamination of soil and ground water with BTEX	Dual extraction	2,000 scfm catalytic oxidation system operated for 13 months to treat air stream resulting from the remediation of a site containing over 220,000 lb BTEX. Destruction efficiency of 99.9% achieved.	4
Petroleum products terminal, CA	UST, separators, and sumps resulted in the contamination of soil at concentrations as high as 12,000 ppm of total petroleum hydrocarbons	Soil vapor extraction and dual extraction	In 250 days of operation, approximately 52,000 lbs of total hydrocarbons were removed. Off-gases from this extraction were treated in a 1,500 scfm catalytic oxidation unit equipped with a non-precious metal catalyst. A conversion efficiency of 99.8% was achieved meeting California South Coast Air Quality Management District requirements.	12
Former dry cleaner site, San Bernardino, CA	Soil and ground water contaminated with chlorinated hydrocarbons	Dual extraction	500 scfm catalytic oxidation system operated for 2 months to remove over 1,200 lbs of chlorinated hydrocarbons. Destruction efficiency of over 99.9% achieved. Air permit required the use of caustic scrubber for the removal of hydrogen chloride from catalytic oxidation emission prior to final discharge. Residual sodium chloride was generated by the caustic scrubber.	4
Los Angeles, CA	Soil contaminated with TCE	Soil vapor extraction	200 scfm electrically fired catalytic oxidation system operating to treat a stream of chlorinated VOCs at 680°F. Initial influent air stream contained 3,500 ppmv VOCs. After 50 days, influent air stream VOC concentration decreased to approximately 1,600 ppmv. Destruction efficiency of over 90% maintained. Caustic scrubber used to remove hydrogen chloride prior to final discharge of treated air stream. Residual sodium chloride was generated by the caustic scrubber.	2

Figure 5. Application Examples

8. Personal communication with Captain E.G. Marchand, U.S. Air Force Engineering and Services Center, Tyndall Air Force Base, FL, 1992.

9. Hylton, T.D., and Captain E.G. Marchand, *Evaluation of the TCE Catalytic Oxidation Unit at Wurtsmith Air Force Base*, Proceedings of the 1991 AIChE Summer National Meeting, Pittsburgh, PA.

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12. Malot, James J., *Soil Remediation and Free Product Removal Using In Situ Vacuum Extraction with Catalytic Oxidation*, article included in "Statement of Qualification - TerraVac."

Points of Contact

Additional information regarding technical, regulatory, and practical aspects of the use of catalytic oxidation for off-gas treatment may be obtained from:

- Tanwir Chaudhry, Naval Civil Engineering Laboratory, Code L71, Port Hueneme, CA. (805) 982-1609.
- John Fringer, NEESA, Code 112E4, Port Hueneme, CA. (805) 982-4856.
- Captain Edward G. Marchand, U.S. Air Force Engineering and Services Center, Tyndall Air Force Base, FL. (904) 283-6023.
- Dr. Raymond Machacek, Arthur D. Little, Inc., (617) 498-5580.

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EPA

Engineering Bulletin
Chemical Oxidation Treatment

Purpose

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

Abstract

Oxidation destroys hazardous contaminants by chemically converting them to nonhazardous or less toxic compounds that are ideally more stable, less mobile, and/or inert. However, under some conditions, other hazardous compounds may be formed. The oxidizing agents most commonly used for the treatment of hazardous contaminants are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Current research has shown the combination of these reagents or ultraviolet (UV) light and an oxidizing agent(s) makes the process more effective [1] [2] [3, p. 11]. Treatability studies are necessary to document the applicability and performance of chemical oxidation systems technology for a specific site.

Chemical oxidation is a developed technology commonly used to treat liquid mixtures containing amines, chlorophenols, cyanides, halogenated aliphatic compounds, mercaptans, phenols, and certain pesticides [4, p. 7.76] [5, p. 7.42]. In lab-scale tests, chemical oxidation has been shown to be effective for chlorinated organics [6, p. 229].

This bulletin provides information on the technology applicability, limitations, a technology description, the types of residuals produced, site requirements, current performance data, status of the technology, and sources of further information.

Technology Applicability

Chemical oxidation effectively treats liquids that contain oxidizable contaminants; however, it can be used on slurried soils and sludges. Because it is a nonselective treatment, it is most suited to media with low concentrations of contaminants.

The effectiveness of chemical oxidation technology on general contaminant groups is shown in Table 1. Examples of constituents within contaminant groups are provided in "Technology Screening Guide for Treatment of CERCLA Soils and Sludges" [7]. This table is based on the current available information or professional judgement when no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability was tested to show that, for that particular contaminant and matrix, the technology was effective. The ratings of potential effectiveness and no-expected-effectiveness are based upon expert judgement. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given.

Chemical oxidation depends on the chemistry of the oxidizing agent(s) and the chemical contaminants. Table 2 lists selected organic compounds by their relative ability to be oxidized. Chemical oxidation has also been used as part of a treatment process for cynanide-bearing wastes and metals such

* [reference number, page number]

as arsenic, iron, and manganese [8, p. 4.4]. Metal oxides formed in the oxidation process more readily precipitate out of the treated medium.

The oxidation of some compounds will require a combination of oxidizing agents or the use of UV light with an oxidizing agent(s) [1][2] [3, p. 10]. An example of such a situation is polychlorinated biphenyls (PCBs), which do not react with ozone alone, but have been destroyed by combined UV-ozone treatment [5, p. 7.48]. Enhanced chemical oxidation has been used at several Superfund sites [3][9].

Table 1
Effectiveness of Chemical Oxidation on General Contaminant Groups for Liquids, Soils, and Sludges[a]

	Contaminant Groups	Liquids	Soils, Sludges
Organic	Halogenated volatiles	■	▼
	Halogenated semivolatiles	■	▼
	Nonhalogenated volatiles	■	▼
	Nonhalogenated semivolatiles	■	▼
	PCBs	■	❑
	Pesticides	■	▼
	Dioxins/Furans	▼	❑
	Organic cyanides	■	■
	Organic corrosives	▼	▼
Inorganic	Volatile metals	■	▼
	Nonvolatile metals	■	▼
	Asbestos	❑	❑
	Radioactive materials	❑	❑
	Inorganic corrosives	❑	❑
	Inorganic cyanides	■	■
Reactive	Oxidizers	❑	❑
	Reducers	■	▼

■ Demonstrated Effectiveness: Successful treatability test at some scale completed

▼ Potential Effectiveness: Expert opinion that technology will work

❑ No Expected Effectiveness: Expert opinion that technology will not work

a Enhancement of the chemical oxidation process is required for the less easily oxidizable compounds for some contaminant groups.

Table 2
Selected Organic Compounds by Relative Ability to be Oxidized

Ability to be Oxidized	Examples
High	phenols, aldehydes, amines, some sulfur compounds
Medium	alcohols, ketones, organic acids, esters, alkyl-substituted aromatics, nitro-substituted aromatics, carbohydrates
Low	halogenated hydrocarbons, saturated aliphatics, benzene

Limitations

If oxidation reactions are not complete, residual hazardous compounds may remain in the contaminant stream. In addition, intermediate hazardous compounds may be formed (e.g., trihalomethanes, epoxides, and nitrosamines) [10][11, p. 190]. Incomplete oxidation may be caused by insufficient quantity of the oxidizing agent(s), inhibition of oxidation reactions by low or high pH, the strength of the oxidizing agent(s), the presence of interfering compounds that consume reagent, or inadequate mixing or contact time between contaminant and oxidizing agent(s) [12, p. 10.52]. It is important to monitor the concentrations of residual oxidizing agent(s), contaminants, and products to ensure a complete reaction has occurred. It may be necessary to monitor reaction conditions such as pH, temperature, and contact time to optimize the reaction. Determination of potential reactions and rates may be critical to prevent explosions or formation of unwanted compounds.

Oil and grease in the media should be minimized to optimize the efficiency of the oxidation process. Oxidation is not cost-effective for highly concentrated wastes because of the large amounts of oxidizing agent(s) required.

Chemical oxidation can be used on soils and sludges if there is complete mixing of the oxidizing agent(s) and the oxidizable hazardous component in the matrix.

Ozonation systems generally have higher capital costs than those using other oxidizing agents because an ozone generator must be used. They must also have an ozone decomposition unit to prevent emission of excess ozone into the ambient air which futher adds to the cost.

Although hydrogen peroxide is considered a relatively safe oxidant, proper storage and handling is required [5, p. 7.44]. The hydrogen peroxide reaction may be explosive when introduced into high-organic materials [11, p. 190].

The cost of generating UV light and the problem of scaling or coating on the lamps are two of the biggest drawbacks to UV-enhanced chemical oxidation systems. They do not perform as well in turbid waters and slurries because the reduced light transmission lowers the effectiveness [13].

Technology Description

Chemical oxidation is a process in which the oxidation state of a contaminant is increased while the oxidation state of the reactant is lowered. The electrons gained by the oxidizing agent are lost by the contaminant. An example of a common oxidation reaction is:

$$\underset{\text{(sodium cyanide)}}{NaCN} + H_2O_2 \longrightarrow \underset{\text{(sodium cyanate)}}{NaCNO} + H_2O$$

In this reaction, the oxidation state of carbon in the sodium cyanide is increased while the oxidation state of each oxygen in the hydrogen peroxide is decreased.

Chemical oxidation is used when hazardous contaminants can be destroyed by converting them to nontoxic or less hazardous compounds. Contaminants are detoxified by actually changing their chemical forms. The process is nonselective; therefore, any oxidizable material reacts. The oxidizing agent(s) must be well mixed with the contaminants in a reactor to produce effective oxidation. In order for the oxidation reaction to occur, the pH must be maintained at a proper level; therefore, pH adjustment may be necessary [10][14].

Figure 1 shows a process flow diagram for a chemical oxidation system. The main component is the process reactor. Oxidant is fed into the mixing unit (1), then the reactor (2). Reaction products and excess oxidant are scrubbed prior to venting to the ambient air. The pH and the temperature in the reactor are controlled to ensure the reaction goes to completion. The reaction can be enhanced with the addition of UV light.

Common commercially available oxidants include ozone, hydrogen peroxide, hypochlorites, chlorine and chlorine dioxide. Treatment of hazardous contaminants requires a strong oxidizing agent(s), such as ozone or hydrogen peroxide. Ozone and combinations of ozone and hydrogen peroxide react rapidly with a large number of contaminants [3, p. 11]. Ozone has a half-life of 20 to 30 minutes at 20°C (68°F); therefore, it must be produced onsite. This requirement eliminates storage and handling problems associated with other oxidants.

Systems that use ozone in combination with hydrogen peroxide or UV radiation are catalytic ozonation processes. They accelerate ozone decomposition, thereby increasing the hydroxyl radical concentration and promoting the oxidation rate of the compounds of interest [3, p. 10]. Specifically, hydrogen peroxide, hydrogen ion, and UV radiation have been found to initiate ozone decomposition and accelerate the oxidation of refractory organics via the free radical reaction pathway [6, p. 228]. Reaction times can be 100 to 1000 times faster in the presence of UV light [11, p. 195]. Minimal emissions result from the UV-enhanced systems [15, p. 35].

Process Residuals

Residuals produced from chemical oxidation systems can include partially oxidized products (if the reaction does not go to completion) which may require further treatment. In some cases, inorganic salts may be formed [10]. Depending on the oxidizing agent used and the chlorine content of the contaminant, oxidation of organic compounds may result in the formation of HCl and NO_2. Ozone and hydrogen peroxide have an advantage over oxidants containing chlorine because potentially hazardous chlorinated compounds are not formed [11, p. 187].

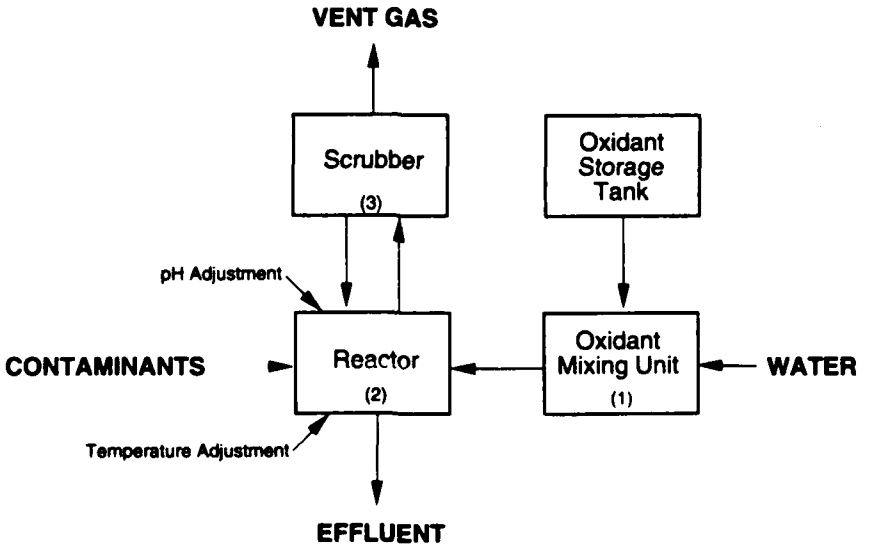
Acid gas control is required for reactions that produce HCl. Any precipitate formed has to be filtered out and may require additional treatment to comply with the appropriate regulations [10].

Site Requirements

Equipment requirements for oxidation processes include storage vessels, metering equipment, and reactor vessels with some type of agitation device. UV light may also be required. All the equipment is readily available and can be skid-mounted and sent to the site.

Ozone must be generated onsite because it is not practical to store. Other oxidizing agents require onsite storage and handling. A site safety plan would have to be developed to

Figure 1
Process Flow Diagram for Chemical Oxidation System



provide for personnel protection and special handling measures. Standard 440V, three-phase electrical service may be required depending on the reactor configuration. Water must be available onsite for cleaning and descaling operations, although the treated effluent might be used for this purpose. Water would also be needed for slurrying soils and sludges. The quantity of water needed is vendor- and site-specific.

Onsite analytical equipment may be needed to conduct pH, oil, and grease analyses. Liquid and gas chromatographs capable of determining site-specific organic compounds may be required for the operation to be more efficient and to provide better information for process control.

Table 3
Lorentz Barrel and Drum SITE Testing Parameters [3]

Run	pH	Time (min)	Ozone dose (mg/l)	H_2O_2 dose (mg/l)	UV Lamps
1	7.2	40	75	25	all on
2	6.2	40	75	25	all on
3	5.2	40	75	25	all on
4	7.2	60	75	25	all on
5	7.2	20	75	25	all on
6	7.2	40	110	25	all on
7	7.2	40	38	25	all on
8	7.2	40	110	38	all on
9	7.2	40	110	13	all on
10	7.2	40	110	13	1/2 on
11	7.2	40	110	13	1/2 on
12	7.2	40	110	13	all on
13	7.2	40	110	13	all on

Performance Data

Performance of full-scale chemical oxidation systems has been reported by several sources, including equipment vendors. Some of the data presented for specific contaminant removal effectiveness were obtained from publications developed by the respective chemical oxidation system vendors. The quality of this information has not been determined; however, it does give an indication of the efficiency of chemical oxidation. Data on chemical oxidation systems at Superfund sites are discussed in the following paragraphs.

Ultrox International installed its system at the Lorentz Barrel and Drum Superfund site in San Jose, California. The system uses ozone and hydrogen peroxide with UV radiation to treat contaminated groundwater whose main contaminants were 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and 1,1-dichloroethane (DCA). Demonstration of this system at the Lorentz site was also part of the Superfund Innovative Technology Evaluation (SITE) program. During the SITE testing, hydraulic retention time (reaction time), ozone dose, hydrogen peroxide dose, UV radiation intensity, and pH level were varied, as shown in Table 3, to assess the system's performance. The results of the testing are listed in Table 4 [3].

The system destruction efficiency averaged more than 90 percent of the TCE in the contaminated groundwater over the range of operating parameters. Destruction efficiencies for 1,1,1-TCA and 1,1-DCA increased when the ozone dosage was increased. During these runs, the destruction efficiency for

Table 4
Lorentz Barrel and Drum SITE Test Results (contaminated groundwater) [3]

	1,1,1-TCA			TCE			1,1-DCA		
Run	Influent[a] (µg/l)	Effluent[a] (µg/l)	% Removed	Influent[a] (µg/l)	Effluent[a] (µg/l)	% Removed	Influent[a] (µg/l)	Effluent[a] (µg/l)	% Removed
1	4.0	1.2	70	86.0	4.6	95	11.5	6.2	46
2	3.7	0.6	83	55.0	2.4	96	10.0	3.2	69
3	3.8	1.3	65	64.0	3.6	94	10.0	6.7	35
4	3.9	1.8	53	56.0	3.4	94	12.0	7.8	32
5	4.1	1.4	66	50.0	6.2	88	10.0	6.4	36
6	3.9	1.0	73	73.0	1.0	98	11.0	5.2	54
7	4.7	3.0	37	70.0	17.0	76	13.0	9.2	30
8	3.5	0.7	80	59.0	0.7	99	9.8	4.7	52
9	4.3	0.8	83	65.0	1.2	98	11.0	5.3	54
10	3.4	0.6	82	57.0	1.6	97	10.0	3.9	62
11	3.8	0.8	80	57.0	1.3	98	11.0	5.4	50
12	3.3	0.4	87	52.0	0.6	99	11.0	3.8	65
13	3.2	0.5	85	49.0	0.6	99	10.0	4.2	60

[a] *Mean Value*

1,1,1-TCA was over 80 percent and almost 60 percent for 1,1-DCA. For a more detailed discussion, the reader should consult reference 3.

The Ultrox® system was also used to treat contaminated groundwater in Muskegon, Michigan. Before treatment, the TCE concentration was reported to be as high as 7 parts per million (ppm). The Ultrox® system has reduced effluent levels to under 2 parts per billion (ppb) [13, p. 90].

Solarchem Environmental Systems installed its Rayox® enhanced oxidation unit at the Oswego, New York, Superfund site. This demonstration system, which uses UV radiation enhancement with ozone and hydrogen peroxide, treated collected leachate from a landfill site. Results of the testing are listed in Table 5 [9].

Peroxidation Systems' **perox-pure™** Organic Destruction process uses hydrogen peroxide and UV light to destroy dissolved organic contaminants. It has been used at a number of sites to reduce contaminants up to 90 percent. The **perox-pure™** has much lower effectiveness on aliphatic compounds, such as TCA, because they are not as reactive [15]. Table 6 is a partial list of contaminants treated and applications where the **perox-pure™** process has been used [16].

Table 7 lists performance data for several sites using the full-scale **perox-pure™** system [17] [18]. Most organics were reduced to extremely low levels by the **perox-pure™** treatment system at every site. At Site 1, the **perox-pure™** system, followed by an air stripper, was able to destroy 4 of the 6 organics below detection limits. It also eliminated over 90 percent of the air emissions as compared to the previous arrangement which used an air stripper followed by the **perox-pure™** system. At Site 5, the system was modified to pretreat the influent to remove iron and calcium. This resulted in no organics being detected in the effluent.

The Purus Inc. enhanced oxidation system was demonstrated on contaminated groundwater at Lawrence Livermore National Laboratory (LLNL). Benzene, toluene, ethylbenzene, and xylene (BTEX) levels were reduced from 5 ppm to as little as 5 ppb [19, p. 9]. The Purus system is also being used to treat

Table 5
Oswego Leachate Test Results [9]

Volatile Organic Compounds (VOCs)	*Inlet (ppb)*	*Outlet (ppb)*	*% Removed*
Methylene chloride (MeCl)	204	1	99.5
1,1-Dichloroethylene (DCE)	118	0	100
1,1-DCA	401	15.7	96
t-1,2-DCE	3690	14.9	99.6
1,2-DCA	701	109	85
1,1,1-TCE	261	3.1	98.9
Benzene	469	1.8	99.6
Methyl isobutyl ketone	47	2.2	95.8
1,1,2,2-Tetrachloroethane	344	4.2	98.8
Toluene	3620	3.9	99.9
Chlorobenzene	704	0	100
Ethylbenzene	2263	1.1	99.9
M-,P-Xylene	4635	1.3	99.9
O-Xylene	6158	2.4	99.9

Table 6
Applications of perox-pure™ System at Selected Sites [16]

Location	*Type*	*Contaminant*
CA	Groundwater	Tetrahydrofuran
CA	Leachate	Mixed organic acids
CA	Groundwater	TCE
CA	Groundwater	TCE, TCA, CCl4, MeCl
MA	Dredge Water	PCBs
NH	Leachate	Ketones, VOCs
MD	Groundwater	TCE, perchloroethylene (PCE), TCA, DCE
MA	Groundwater	MeCl, TCA, dichloromethane (DCM)
CA	Municipal Water	Humic acid/color control
CA	Groundwater	TCE, PCE, TCA, DCE
WA	Groundwater	Pentachlorophenol
CO	Misc. Wastes	Hydrazine, DIMP
CO	Groundwater	Benzene, toluene, xylene (BTX)
CT	Bioeffluent	Chlorobenzene
CA	Groundwater	TCE, TCA, PCE, DCE
NY	Groundwater	TCE, DCE, PCE, TCA
CA	Groundwater	TCA, TCE
NY	Groundwater	TCE, DCE, DCA, TCA
PA	Effluent	Phenol
CA	Groundwater	BTX
PA	Effluent	Nitrated esters
NJ	Groundwater	TCE, DCE, PCE, MeCl
AZ	Groundwater	BTEX
TX	Effluent	Phenols, nitrophenols
MA	Groundwater	BTX
CO	Waste	Hydrazine
CA	Groundwater	TCE, PCE, BTX, TCA
AR	Groundwater	Acrylic acid, butyl acrylate
OH	Recycle	Bacteria, phenol, formaldehyde
LA	Groundwater	TCE, polynuclear aromatic hydrocarbons (PAHs)
AZ	Groundwater	TCE
UT	Effluent	Isopropyl alcohol (IPA), TOC, TCA, DCE, methyl ethyl ketone (MEK)
NJ	Effluent	Phenol
CA	Groundwater	TCE, PCE, DCE, TCA, MeCl, chloroform
CA	Effluent	BTX
CA	Groundwater	BTX
CA	Groundwater	TCE, Freon, MeCl, BTX
NC	Effluent	MeCl, phenol, PAHs

air streams from air stripping of groundwater and vacuum extraction of soils under the SITE emerging technology program at LLNL.

Other case studies have shown greater than 99 percent destruction of the pesticides DDT, PCP, PCB, and Malathion with ozone/UV radiation [4, p. 7.67].

Technology Status

Chemical oxidation is a well-established technology used for disinfection of drinking water and wastewater and is a common treatment for cyanide wastes. Enhanced systems are now being used more frequently to treat hazardous streams. This technology has been applied to Resource Recovery and Conservation Act (RCRA) wastes and has been used on Superfund wastes [7]. In 1988, chemical oxidation was listed in the Record of Decision at Lorentz Barrel & Drum in San Jose, California and Southern Maryland Wood, in Hollywood, MD. In 1989, chemical oxidation was listed at Sullivan's Ledge in New Bedford, Massachusetts; Bog Creek Farm in Howell Twp., New Jersey; Ott/Story/Cordova Chemical in Dalton Twp., Michigan; Burlington Northern in Somers, Montana; and Sacramento Army Depot in Sacramento, California.

Operating costs can be competitive with other treatment technologies such as air stripping and activated carbon. However, oxidation is becoming a more attractive option because the contaminants are destroyed rather than transfered to an-

Table 7
Full-Scale perox-pure™ Performance Data [17][18]

Location	*Contaminant*	*Influent (µg/1)*	*Effluent (µg/1)*
Site 1	MeCl	30	1.5
Source of influent not reported	1,1-DCA	42	BDL
	1,2-DCE	2466	BDL
	1,1,1-TCA	1606	1218
	TCE	1060	BDL
	PCE	3160	BDL
Site 2	Hydrazine	1,200,000	<1
Concentrated Wastewater	Monomethyl Hydrazine	100,000	<10
	Unsymmetrical dimethyl Hydrazine	1,500,000	<10
	Nitrosodimethylamine	1,500	<0.02
	Chlorinated Organics	75,000	<1
	Pesticides/Herbicides	500	<1
Site 3	1,2-DCE	6.2	BDL
Contaminated Groundwater	TCE	66.3	BDL
	Chloroform	2.1	BDL
Site 4	MeCl	600-800	33
Source of influent not reported	1,1,1-TCA	200-400	26
	1,2-DCE	50-250	<1
Site 5	Benzene	7,600	ND*
Contaminated Groundwater	Toluene	24,000	ND*
	Chlorobenzene	8,800	ND*
	Ethylbenzene	3,300	ND*
	Xylenes	46,000	ND*
Site 6	MeCl	903	11
Contaminated Groundwater	1,1,1-TCA	60	6

Detection Limits not Reported
BDL = Below Detection Limit
ND = Nondetected
* With Pretreatment

other media. Operating costs for mobile chemical oxidation systems have ranged from $70 to $150 per 1,000 gallons of water treated [8, p. 4.5]. Operating costs for the Ultrox® enhanced system have varied dramatically from $0.15 to $90/1000 gallons treated, depending on the type of contaminants, their concentration, and the desired cleanup standard. The greatest expense for this system is the cost of electricity to operate the ozone generator and UV lamps [13, p. 92].

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Engineering Bulletin
Supercritical Water Oxidation

Technology Status

Supercritical water oxidation (SCWO) has existed as an emerging waste treatment technology for approximately 10 years [1]. There are currently no full-scale SCWO systems in operation, but considerable bench- and pilot-scale data are available. The largest existing SCWO system can process waste at a rate of approximately 4 gallons per minute (gpm)[2].

Several universities and research institutes are studying SCWO. The U.S. Air Force is investigating SCWO for destruction of rocket fuels and explosives. The U.S. Department of Energy is considering SCWO for treatment of wastes generated at its nuclear plants [3]. SCWO is also being considered by National Aeronautics and Space Administration (NASA) for waste treatment during extended space missions [4][5].

The Defense Advanced Research Projects Agency (DARPA) is also investigating SCWO. Ongoing work under a DARPA contract includes the design and construction of a mobile SCWO unit for the destruction of military wastes. General Atomics is the prime contractor for this project and the University of Texas (UT) Balcones Research Center and Eco Waste Technologies (EWT) are subcontractors [6].

EWT is currently developing a proprietary SCWO system which operates above ground (surface SCWO). Besides its involvement in the DARPA project, EWT is also designing a 5-gpm commercial demonstration unit for a small chemical manufacturing facility [6].

Modell Development Corporation (MODEC) is also developing a proprietary surface SCWO system. MODEC hopes to have a 5 dry ton/day pilot plant completed in 1992 and small commercial units available in 1993 [7].

MODAR, Inc. owns and operates the 4-gpm SCWO system mentioned previously [2]. MODAR conducts surface SCWO research and development in conjunction with its licensor, ABB Lummus Crest [8][9].

GeneSyst International is developing a proprietary SCWO system called a "Gravity Pressure Vessel" which is designed to operate below ground (subsurface SCWO) [10].

Vertech was involved in the development of subsurface SCWO reactors, but it was purchased by Wijnanin N.V., which has Air Products and Chemicals as its U.S. licensee. It is not clear whether Wijnanin N.V. or Air Products and Chemicals plans to pursue SCWO development.

Oxidyne (previously Vertox) was also involved in subsurface SCWO development. Oxidyne developed plans for a full-scale, subsurface subcritical water oxidation reactor in Houston, Texas at Sims Bayou Sewage Treatment Plant. Construction of the reactor was initiated but was not completed due to insufficient funding [11][12][13]. Oxidyne is no longer involved in SCWO research and therefore sold a number of its patents and designs to City Management Corporation (CMC). CMC has no immediate plans to continue SCWO research [14]. The Oxidyne work in Houston is important because the design of that subcritical system may serve as a basis for the design of subsurface systems which operate at supercritical conditions.

Research currently being conducted by various firms and universities focuses on a better understanding of the SCWO process and will be used in the design of full-scale systems. Specific research topics include kinetics, the mechanisms of SCWO, and fluid flow characteristics [15][16].

Technology Description

In SCWO, decomposition occurs in the aqueous phase above the critical point of water (374°C/221 atmospheres or atm). A schematic of a generic SCWO process is provided in Figure 1. As shown in this figure, the feed stream is typically an aqueous waste. An oxidant such as air, oxygen, or hydrogen peroxide must be provided unless the waste itself is an oxidant.

A supplemental fuel source should also be available. Because oxidation is exothermic, SCWO is self-sustaining for a waste stream with an adequate chemical oxygen demand (COD). According to developers, SCWO is self-sustaining provided the waste stream has a COD of approximately 15,000 mg/L or higher [15]. Theoretically, SCWO may be self-sustaining for CODs as low as 5,000 mg/L [10]. At startup and for dilute wastes that will not autogenically sustain combustion, a supplemental fuel such as waste oil is added [17]. Alternatively, some

* [reference number]

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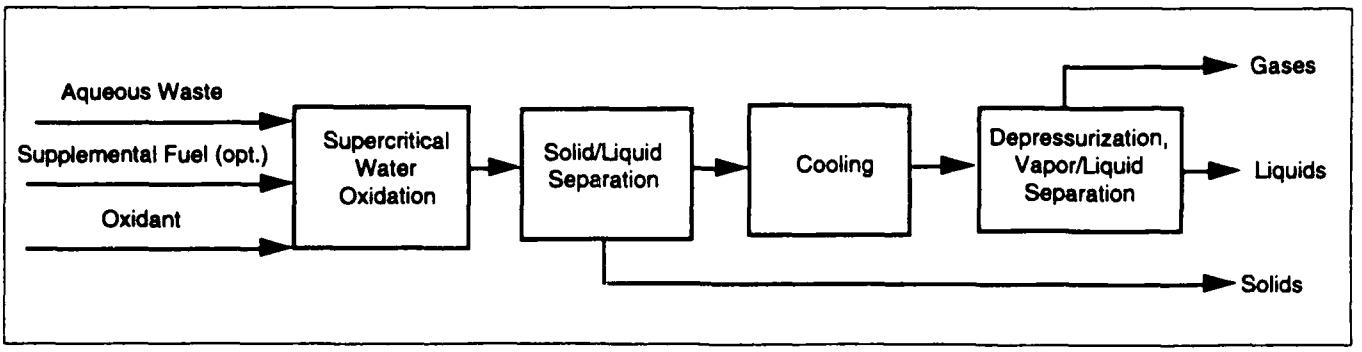
Figure 1
SCWO Schematic



dilute wastes can be dewatered until they are concentrated enough to sustain SCWO without supplemental fuel [18]. Concentrated wastes, on the other hand, must be diluted if the oxidation of the waste will generate more heat than can be readily removed from the SCWO processing vessel [18].

The streams entering an SCWO reactor must be heated and pressurized to supercritical conditions. Influent streams are frequently heated by thermal contact with the hot effluent. Both influent pressure and backpressure (often a restriction of the outlet) must be provided. The influent streams are then combined at supercritical conditions and oxidation occurs.

Certain properties of supercritical water make it an excellent medium for oxidation. Many of the properties of water change drastically near its critical point: the hydrogen bonds disappear and water becomes similar to a moderately polar solvent; oxygen and almost all hydrocarbons become completely miscible in water; mass transfer occurs almost instantaneously; and the solubility of inorganic salts drops to the parts per million (ppm) range [19]. Because inorganic salts (as well as certain other solids) are nearly insoluble in supercritical water, solids removal must be considered in the design of a SCWO reactor [7][20][21].

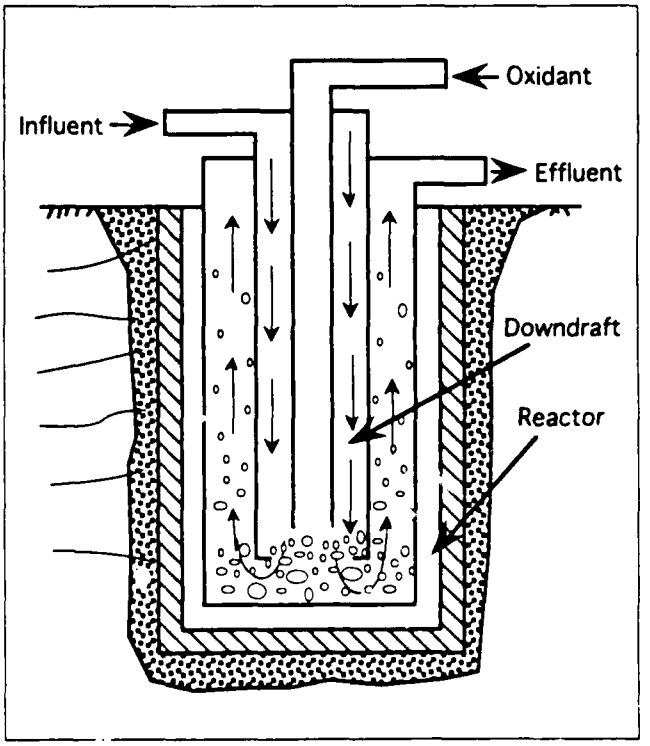
The liquid effluent from SCWO is cooled (often by heat exchange with the influent) and returned to ambient pressure. As the effluent is cooled and depressurized, compounds such as carbon dioxide and oxygen will vaporize. According to SCWO developers, the effluent contains relatively innocuous products. Organic materials produce carbon dioxide and water; additional products depend upon the components of the waste. Nitrogen compounds principally produce ammonia and nitrogen as well as small amounts of nitrogen oxides (NO_x); halogens produce the corresponding halogen acids; phosphorus produces phosphoric acid; and sulfur produces sulfuric acid [18].

Vendors are currently developing both surface and subsurface SCWO systems. Figure 2 is a schematic of a subsurface SCWO reactor. As shown in Figure 2, subsurface SCWO reactors will consist of columns of aqueous waste which are deep enough that the material near the bottom is subjected to a pressure of at least 221 atm [22]. To achieve this pressure solely through hydrostatic head, a water column depth of approximately 12,000 feet will be required [10]. The influent and effluent will flow in opposite directions in concentric vertical tubes [13]. In surface SCWO systems, the majority of the pressure is provided by a source other than gravity, and the reactor is on or above the earth's surface.

Applicability

Surface and subsurface SCWO systems may have slightly different applications. Because subsurface SCWO systems are below ground, developers claim that the earth will provide protection in the event of a catastrophic reactor failure. Subsurface designs have additional advantages over surface SCWO systems, including fewer mechanical parts (which should lead to lower maintenance) and pressure provided by hydrostatic head [13].

Figure 2
Subsurface SCWO Reactor



Surface SCWO systems, however, have several advantages over subsurface systems. Surface systems are much more accessible (and therefore easier to monitor) than subsurface reactors [13]. Developers project that it will not be cost-effective to construct subsurface reactors for small waste streams, as the drilling cost for the well is significant [10].

In general, applications of SCWO processes may include liquid wastes, sludges [13], and slurried solid wastes [18]. Potentially treatable compounds include halogenated and nonhalogenated aliphatic and aromatic hydrocarbons; aldehydes; ketones; esters; carbohydrates; organic nitrogen compounds; polychlorinated biphenyls (PCBs), phenols, and benzenes; aliphatic and aromatic alcohols; pathogens and viruses; mercaptans, sulfides, and other sulfur-containing compounds; dioxins and furans; leachable metals; and propellant components [12][13][18][22][23]. SCWO has been applied to municipal and industrial sludges. Tests performed on pulp mill sludges, for example, showed that SCWO can effectively treat these wastes (a total organic carbon destruction efficiency of 99.3 percent was achieved). Further analysis indicated that treatment of pulp mill sludges by SCWO should be able to compete economically with incineration and, in some regions, with landfilling [7].

SCWO also compares favorably with wet air oxidation (WAO), a commercially available technology which is similar to SCWO. In WAO, thermal decomposition and hydrolysis occur as well as oxidation. WAO is conducted in the aqueous phase and typically utilizes temperatures ranging from 150 to 300°C and pressures up to 200 atm. SCWO provides a number of advantages over WAO, including higher destruction efficiencies (DEs) and lower reaction times [24]. SCWO is also more energy-efficient than WAO [25].

The minimum waste concentration for which SCWO is applicable is waste-specific and can be determined by a cost comparison. The costs associated with dewatering the waste, operating the SCWO system, and purchasing supplemental fuel must be considered. There is also a maximum waste concentration for which SCWO is applicable because the oxidation of the waste must not generate more heat than can be readily removed from the processing vessel [18]. Note, however, that wastes which exceed the maximum concentration can be diluted prior to SCWO. MODAR literature states that its SCWO process is most applicable to wastes with hydrocarbon concentrations of 1 to 30 percent but it does not specify the concentrations of the wastes fed to the SCWO reactor [21].

SCWO developers claim several advantages associated with SCWO as a means of destroying wastes:

- One vendor plans to design a SCWO system which will be transportable and thus applicable to Superfund sites [6].
- One developer claims that the SCWO process is odor-free and extremely quiet [11].
- According to developers, SCWO reactions are self-sustaining provided the waste stream has a COD of approximately 5,000 mg/L or higher [10]. By contrast, self-sustaining incineration requires a minimum COD of approximately 300,000 mg/L [15].
- Because SCWO systems operate in a lower temperature range (400 to 600°C) than typical incineration systems, researchers believe that SCWO will produce lower quantities of NO_x [26].

Developers claim that SCWO is relatively safe because the reaction temperature can be controlled through adjustment of the degree of preheating and/or the concentration of the waste [7]. The high temperatures and pressures necessary for SCWO are potentially dangerous, but designing SCWO reactors with large safety factors should reduce the risk. One developer indicates the failure of a heater tube at approximately 3700 psi and 1400°F produced a loud pop and damage to local insulation, but no injuries and no damage to adjacent equipment or instrumentation. The developer further states that fluid loss from the rupture was minimal [6].

A second danger involves the possibility that the process could be interrupted, causing an incomplete reaction which could produce dangerous offgases. SCWO systems can be designed to provide an emergency shutdown option and it is known that at least one pilot-scale system includes such a provision [6]. Note that the above are only potential dangers, as no safety problems were documented in the literature reviewed.

Limitations

The density of water drops rapidly between 300 and 400°C, and SCWO systems typically operate at or above 400°C. The low densities associated with the supercritical temperatures can result in the deposition of salts and pyrolytic chars. Deposition may result in plugging problems or added cleaning requirements. Some researchers prefer near-critical water oxidation at approximately 300°C, as the density of water is higher and salts and chars are more likely to remain dissolved [27]. Other developers prefer SCWO and are researching solutions to the deposition problem.

Possible problems due to corrosion must be examined when SCWO is considered. Several studies have been conducted regarding the minimization of corrosion in SCWO systems. Titanium, stainless steel 316, Hastelloy C-276, and Monel 400 were considered as alternative materials of construction for SCWO reactors. The results of these studies indicated that titanium had excellent corrosion resistance but its structural properties were unsatisfactory. Stainless steel 316 exhibited adequate corrosion resistance for use at low supercritical temperatures and moderate pH levels and chloride concentrations; a hastelloy (or another nickel-chrome alloy) is recommended for more corrosive conditions (low pH levels or high chloride concentrations). The monel had poor corrosion resistance and is therefore not recommended for SCWO reactor construction [25]. The use of ceramics and ceramic coatings in conjunction with the above metals has also been proposed [10].

High-temperature flames which have been observed during SCWO may present an additional equipment problem in both surface and subsurface SCWO systems. Research is being

conducted to determine what factors influence these "hydrothermal" flames because there is some concern that these flames will cause "hot spots" which could weaken SCWO vessels [1].

Other drawbacks associated with SCWO (as well as other oxidation technologies) include the slow oxidation rate of many polyhalogenated hydrocarbons and the production of dioxins from the oxidation of certain halogenated organics [27]. The production of dioxins may not present a significant problem, however, as the destruction of dioxins by SCWO has been documented [7].

Acetic acid is generally considered one of the most refractory byproducts of the SCWO of industrial wastes [28]. The acetic acid DEs shown in Table 1 reflect a portion of the performance data collected on this compound.

Ammonia, a second refractory compound, is produced by water oxidation of nitrogen-containing wastes at temperatures of 300 to 400°C [19]. Water oxidation does not degrade ammonia at any significant rate at these temperatures. If a water oxidation system is to be operated at or below 400°C, the ammonia may be removed by steam stripping or some other method. Above 425°C, organic nitrogen and ammonia in an SCWO system will decompose at a significant rate [19]. The primary products of this decomposition (below 650°C) are N_2 and N_2O, which further decompose to form N_2 and O_2 [12].

Table 1
SCWO Performance Data

Pollutant	Temp. (deg. C)	Pressure (atm.)	DE (%)	React Time (min.)	Oxidant	Ref.	Feed Conc. (mg/L)
1,1,1 - Trichloroethane	495		99.99	4	Oxygen	13	
1,1,2,2 - Tetrachloroethylene	495		99.99	4	Oxygen	13	
1,2 - Ethylene dichloride	495		99.99	4	Oxygen	13	
2,4 - Dichlorophenol	400		33.7	2	Oxygen	13	2,000
2,4 - Dichlorophenol	400		99.440	1	H_2O_2	13	2,000
2,4 - Dichlorophenol	450		63.3	2	Oxygen	28	2,000
2,4 - Dichlorophenol	450		99.950	1	H_2O_2	28	2,000
2,4 - Dichlorophenol	500		78.2	2	Oxygen	28	2,000
2,4 - Dichlorophenol	500		>99.995	1	H_2O_2	28	2,000
2,4 - Dimethylphenol	580	443	>99	10	$H_2O_2+O_2$	29	135
2,4 - Dinitrotoluene	410	443	83	3	Oxygen	29	84
2,4 - Dinitrotoluene	528	287	>99	3	Oxygen	29	180
2 - Nitrophenol	515	443	90	10	Oxygen	29	104
2 - Nitrophenol	530	430	>99	15	$H_2O_2+O_2$	29	104
Acetic acid	400		3.10	5	Oxygen	13	2,000
Acetic acid	400		61.8	5	H_2O_2	13	2,000
Acetic acid	450		34.3	5	Oxygen	28	2,000
Acetic acid	450		92.0	5	H_2O_2	28	2,000
Acetic acid	500		47.4	5	Oxygen	28	2,000
Acetic acid	500		90.9	5	H_2O_2	28	2,000
Activated sludge (COD)	400	272	90.1	2		30	62,000
Activated sludge (COD)	400	306	94.1	15		30	62,000
Ammonium perchlorate	500	374	99.85	0.2	None	18	12,000
Biphenyl	450		99.97	7	Oxygen	13	
Cyclohexane	445		99.97	7	Oxygen	13	
DDT	505		99.997	4	Oxygen	13	
Dextrose	440		99.6	7	Oxygen	13	
Industrial sludge (TCOD)	425		>99.8	20	Oxygen	19	
Methyl ethyl ketone	505		99.993	4	Oxygen	13	
Nitromethane	400	374	84	3	None	18	10,000
Nitromethane	500	374	>99	0.5	None	18	10,000
Nitromethane	580	374	>99	0.2	None	18	10,000
o - Chlorotoluene	495		99.99	4	Oxygen	13	
o - Xylene	495		99.93	4	Oxygen	13	
PCB 1234	510		99.99	4	Oxygen	13	
PCB 1254	510		99.99	4	Oxygen	13	
Phenol	490	389	92	1	Oxygen	29	1,650
Phenol	535	416	>99	10	Oxygen	29	150

Performance Data

Significant bench- and pilot-scale SCWO performance data are available. Typical DEs for a number of compounds are summarized in Table 1. Although several low DEs are included in this table to illustrate the fact that DE is proportional to both temperature and residence time, DEs in excess of 99 percent can be achieved for nearly all the pollutants studied.

Studies have been conducted to examine the effects of various parameters on SCWO DEs. The operating parameters studied include temperature, residence time, pressure, feed concentration, amount of oxidant (as a multiple of stoichiometric requirements), and type of oxidant [13][16][28].

As noted above, DE was found to increase with operating temperature and residence time. DE also increases with operating pressure, but only slightly [28]. Recent studies also indicate that the addition of catalysts such as potassium permanganate, manganous sulfate, copper, and iron can enhance DEs [13].

In at least one study, DE was found to increase slightly with feed concentration. The relationship between DE and amount of excess oxidant provided has also been examined. DE increases with increasing amounts of oxidant from 100 to 300 percent of the stoichiometric requirements; adding over 300 percent of the stoichiometric amount of oxidant does not significantly affect DEs [16][28].

Early SCWO systems used either oxygen or air as oxidants. Bench-scale studies were conducted to compare the DEs resulting from the use of air and oxygen, but no statistical difference was found [13]. In 1987, Welch and Siegwarth developed and patented a variation of SCWO which uses hydrogen peroxide as the oxidant. In Welch and Siegwarth's system, liquid hydrogen peroxide is mixed with the influent wastewater or slurry [13].

Welch, Siegwarth, and other researchers have shown that the use of hydrogen peroxide as an oxidant in SCWO systems produced DEs which were significantly higher than those obtained from the use of air or oxygen for the compounds tested [13][28]. Oxidation with hydrogen peroxide and oxidation with oxygen or air proceed by different mechanisms. This difference may result in higher DEs for either hydrogen peroxide or oxygen depending on the particular organic compounds being degraded [28]. Several other factors may influence the choice between oxidants. Hydrogen peroxide is significantly more expensive than oxygen but aqueous hydrogen peroxide is easier to pump, requires a less expensive feed system, and may be combined with the influent more readily than oxygen [10][28].

Process Residuals

In general, residuals from SCWO processes include gases, liquids, and solids. The gaseous effluent from the bench-scale treatment of pulp mill sludges was found to primarily consist of oxygen and carbon dioxide, with small concentrations of nitrogen [7]. Gaseous effluent from the bench-scale treatment of propellant components was also analyzed and found to contain nitrous oxide (N_2O) and oxygen. Analysis by mass spectroscopy did not detect the presence of chlorine (Cl_2), nitrosyl chloride (NOCl), or nitrogen dioxide (NO_2). These are positive results because they indicate that SCWO avoided the hazardous products such as Cl_2 and NOCl formed in typical thermal decomposition. In addition, SCWO appears to produce relatively little NO_x [18].

The aqueous effluent from the SCWO of pulp mill sludge had a total organic concentration (TOC) of only 27 ppm. The major inorganics present were calcium, chlorine (as chloride ion), nitrogen (as ammonia), sodium, and sulfur (as sulfate). The minor elements identified were all present at concentrations below Environmental Protection Agency (EPA) groundwater pollution criteria [7]. Liquid effluent from the SCWO of propellant components contained sodium chloride (NaCl), nitrite, and nitrate. The developer believes that the majority of the chlorine from the propellant exists as NaCl, but a chlorine mass balance has not yet been attempted [18].

Limited data describing solid residue from SCWO are available. When a bench-scale SCWO system was used to treat pulp mill sludges, benzene and lead were the only pollutants which the toxicity characteristic leaching procedure (TCLP) detected at concentrations above EPA groundwater limits. Benzo(a) pyrene and PCB, however, had detection limits above the groundwater limit. Based on these results, the developer believes that the solid residue from SCWO should easily qualify for disposal in any sanitary landfill [7]. Before disposal in a sanitary landfill will be allowed, however, the residue must be delisted.

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UV/Oxidation Treatment of Organics in Ground Water

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Introduction

Ultraviolet oxidation (UV/oxidation—also known as photochemical oxidation) is a means of destroying organic compounds in aqueous media such as ground water, drinking water, and wastewater. Unlike commonly used treatment processes such as air stripping and activated carbon adsorption that rely on the transfer of contaminants from one medium (water) to another (air or carbon), UV/oxidation can result in the destruction of the contaminants while generating few, if any, residuals.

This Tech Data Sheet will concentrate on UV/oxidation remediation of contaminated ground water.

Purpose

The Tech Data Sheets are designed to:

- Provide a basic technical overview of the technology;
- Disseminate practical, implementation-related information to minimize design and construction problems;
- Help Remedial Project Managers (RPMs) to evaluate a technology (recommended in a Feasibility Study [FS], for example) and decide if it is practical and cost-effective;
- Help RPMs write a Remedial Action (RA) Delivery Order;
- Help Engineering Field Division (EFD) Remedial Design personnel write a Statement of Work (SOW) for, and RPMs to review, Remedial Design Plans; and
- Enable field personnel such as Project Superintendents, Engineers in Charge, On-Scene Coordinators (OSCs), and Resident Officers in Charge of Construction (ROICCs) to become familiar with a technology at a site they will oversee.

Description of Technology

Reaction Mechanism Overview

UV/oxidation is a method of destroying organic contaminants in water by UV-enhanced reactions with strong oxidizers such as hydrogen peroxide (H_2O_2) and/or ozone (O_3). In ground water remediation, UV/oxidation is a viable alternative to air stripping, activated carbon adsorption, and biotreatment.

Destruction of contaminants by UV/oxidation can occur by a number of mechanisms including:

- Free radical oxidation (the strongest destructive mechanism);
- Direct oxidation by the oxidizer (e.g., O_3 and/or H_2O_2)—although O_3 is a stronger oxidizer than H_2O_2, if H_2O_2 proves to be effective, it is generally the cheaper alternative;
- UV photolysis; and
- The synergistic effect of all three of the above mechanisms.

The combination of chemical oxidation and UV photolysis is responsible for the ability of UV/oxidation systems to destroy a wider variety of organic contaminants at high rates. These destruction characteristics are due to the generation of hydroxyl radicals (OH•) that are powerful and nonselective oxidizers—second only to the fluorine radical in oxidation potential. These hydroxyl radicals will rapidly attack organic contaminants (typically in less than 10^{-6} seconds) (1).

The relative contribution of the above mechanisms (i.e., direct photolysis, direct oxidation with O_3 or H_2O_2, free radical oxidation, or the synergistic effect of all three) varies from contaminant to contaminant and ground water to ground water and continues to be investigated.

UV photolysis of H_2O_2 generates hydroxyl radicals as described by the following:

$$H_2O_2 + h\nu \rightarrow 2\ OH\bullet$$

UV photolysis of O_3 in water yields H_2O_2, which reacts with O_3 and UV to generate hydroxyl radicals as shown (2):

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + h\nu \rightarrow 2\ OH\bullet \text{ and/or}$$

$$2\ O_3 + H_2O_2 \rightarrow 2\ OH\bullet + O_2$$

Although the above equations imply that the mechanism for hydroxyl radical generation is straightforward, it is actually much more complex than can be fully described here.

Effect of UV Intensity and Wavelength

How well these reactions proceed to generate hydroxyl radicals depends, in part, on the wavelengths emitted by the UV light. Typical low-pressure mercury vapor UV lamps (used in disinfectant processes) emit UV radiation predominantly at about 254 nm. However, H_2O_2 absorbs poorly at 254 nm, so other UV absorbers in solution can compete successfully for photons. For this reason, UV/oxidation reactions using H_2O_2 as the sole oxidizer are usually enhanced by using higher-intensity UV lamps that emit partially at wavelengths shorter than 254 nm where H_2O_2 is a better absorber.

Unlike H_2O_2, O_3 absorbs UV radiation well at the emission wavelength of low-pressure UV lamps (254 nm). The photolysis of O_3 at this wavelength will result in the generation of H_2O_2 that must react with O_3 in order for hydroxyl radicals to be formed.

In addition to increasing the rate of hydroxyl radical generation, high-intensity UV lamps may be more effective than low-intensity lamps in the direct photolysis of specific contaminants that absorb well at the shorter wavelengths. For these reasons, the use of high-intensity UV lamps may result in the destruction of more oxidation-resistant contaminants at higher concentrations.

One vendor of UV/oxidation systems uses "pulsed" (i.e., turned on and off regularly) high-intensity UV lamps, supposedly to maximize hydroxyl radical generation efficiency, although such a theory is still speculative (3).

Drawbacks of using high-intensity UV lamps are that they use more power, tend to overheat, and "burn out" faster (particularly when pulsed) than low-pressure mercury vapor lamps.

Effect of Non-Target Solutes

Due to the reactivity of the hydroxyl radical, UV/oxidation is partially nonselective. Oxidizable compounds in the aqueous feed that compete with the target contaminant(s) for hydroxyl radicals are called "scavengers." Scavengers consume hydroxyl radicals and thus increase the load (i.e., energy input) on the treatment system. Scavengers may include humic material; alcohols; and bicarbonate, carbonate, ammonia, and sulfide. In addition, oxidizable forms of metals such as chromium, iron, and manganese may be scavengers. These metals may present further problems. For example, trivalent chromium is oxidized to the more toxic hexavalent chromium. Also, precipitates formed by the oxidation of iron and manganese ions may form deposits (or "scales") on the UV bulbs.

The effect of scavengers, the dosages of H_2O_2 and O_3, and the UV wavelength on the operation of the UV/oxidation system is difficult to predict and is best determined in a treatability study. Results may then be used to determine requirements for pretreatment (see **Interface with Other Technologies** and **Design Criteria**).

End Products of UV Oxidation

The complete oxidation of hydrocarbon contaminants results in the generation of carbon dioxide and water; however, complete oxidation is usually limited to readily oxidizable compounds. In most cases, oxidation ends with the generation of simple carboxylic acids and some carbon dioxide. In the case of chlorinated hydrocarbons, hydrogen chloride will be an additional product of the oxidation reaction. If sulfur-bearing compounds are present, sulfates will be generated by their oxidation. The potential for incomplete oxidation of contaminants must be recognized for appropriate treatment system design (see **Advantages, Disadvantages, and Limitations**).

Available UV/Oxidation Configurations

There are many different configurations of UV/oxidation treatment systems depending on individual vendor design and specific treatment requirements. UV/O_3 and UV/H_2O_2 are the most popular UV/oxidation technologies; the use of high-intensity UV in either configuration varies according to vendor. $UV/O_3/H_2O_2$ is another configuration being investigated. However, due to the necessity and complexity of accurately determining O_3/H_2O_2 ratios prior to application, it is not as common as the use of single oxidizers.

For illustrative purposes, a generalized system consisting of a reactor with several supporting components is shown in Figure 1. Different vendors have taken different approaches to reactor system design. One reactor uses a closed, stainless steel vessel containing multiple UV lamps protected by quartz sleeves. The quartz sleeves are transparent to UV light in a manner similar to clear glass being transparent to visible light. In an alternative configuration, multiple reactors, each containing a single lamp, may be used.

Supporting process components include feed systems for the oxidizer(s) and contaminated water. H_2O_2, usually purchased as a 35% or 50% (by weight) commercial-grade solution, is typically metered into the water stream just before entering the reactor. The combined oxidizer/water stream may pass through a static, in-line mixer to provide for good mixing.

If a UV/O_3 system is used, O_3 is generated on-site (due to its short half-life) by passing compressed air or pure oxygen through a corona discharge. O_3 may be introduced into the bottom of the reactor through diffusers or a sintered metal sparger. O_3 may also be introduced via an in-line mixer prior to entering the reactor.

Off-gases from the reactor may be treated to remove excess O_3 or volatile treatment byproducts. By passing the off-gas stream over a nickel-based catalyst, unreacted O_3 can be decomposed to oxygen. O_3 may also be removed by thermal destruction or carbon adsorption.

Types of Applications

UV/oxidation may be used for the treatment of ground water contaminated with a wide variety of organic compounds including those compounds typically resistant to oxidation using conventional oxidizers. Examples of sites for application of this technology include facilities where petroleum products are (or were) used or stored; facilities using, storing, and/or disposing of chlorinated or non-chlorinated solvents and/or pesticides; and military facilities where ordnance compounds were manufactured, used, stored, or disposed. Although this Tech Data Sheet focuses on ground water remediation, UV/oxidation can

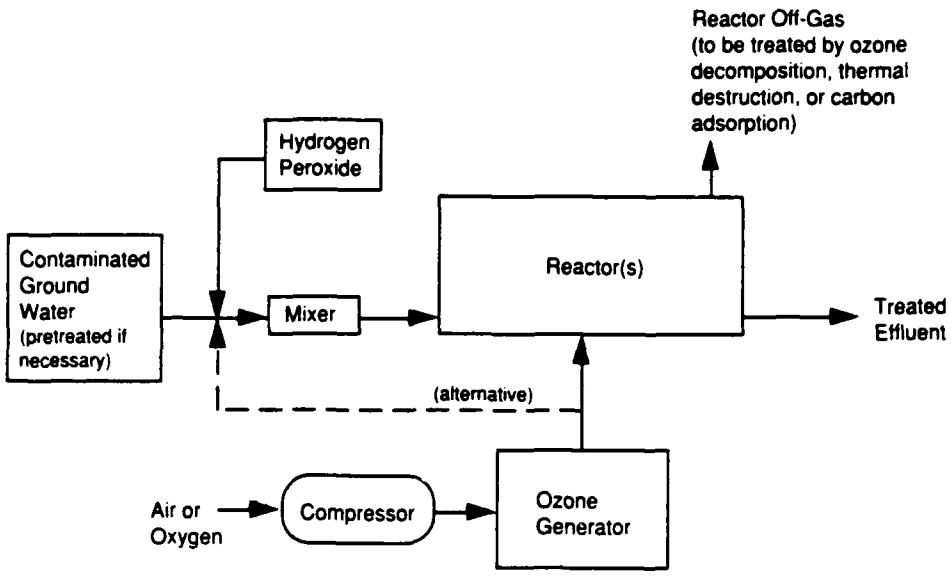

Figure 1. General Schematic of UV/Oxidation Ground Water Treatment System

Source Arthur D Little Inc. and NEESA

also be used on contaminated source waters and municipal and industrial wastewaters.

The technology is most appropriate for aqueous streams with low-level contamination (e.g., less than about 100 mg/L of organics)(2). The feasibility of UV/oxidation for a given waste stream should be determined on a case-by-case basis through the use of treatability studies.

Technology Status

The UV/oxidation is an innovative ground water treatment technology compared to the well-established techniques of air stripping or activated carbon adsorption. UV/oxidation has been used in full-scale ground water treatment applications for over five years. Since 1988, UV/oxidation has been proposed as the remediation method in Superfund Records of Decision for several sites. Currently, UV/oxidation processes are in operation in over 15 full-scale remedial applications (4). A majority of these applications are for ground water contaminated with petroleum products or with a variety of industrial solvent-related organics such as trichloroethylene (TCE), dichloromethylene (DCE), trichloroethane (TCA), and vinyl chloride.

As part of the Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) Program, a demonstration of a UV/oxidation system was conducted at a Superfund site. At this site, the UV/oxidation system was used to treat ground water contaminated with various chlorinated solvents (see **Application Examples**).

Bench-scale tests of UV/oxidation processes have been conducted at military sites for the remediation of ground water containing ordnance compounds (see **Application Examples**).

There are a number of vendors of UV/oxidation systems and equipment. There are at least three vendors that specialize in equipment for the treatment of hazardous waste-related streams. Each vendor of UV/oxidation systems specializes in different system types and configurations. For example, systems are available that use low-intensity, standard germicidal wavelength (254 nm) UV light in conjunction with O_3 (and, in some circumstances, H_2O_2). Alternate systems use shorter wavelengths and much higher-intensity UV light with H_2O_2 as the predominant oxidizer.

A wide range of sizes of UV/oxidation systems are commercially available. Single-lamp benchtop reactors that can be operated in batch or continuous modes are available for the performance of treatability studies. Pilot and full-scale systems are available to handle higher throughput (e.g., 1,000 to 1,000,000 gal per day).

Contaminants Mitigated

A wide variety of organic contaminants are susceptible to destruction by UV/oxidation including: petroleum hydrocarbons; chlorinated hydrocarbons used as industrial solvents and cleaners; and ordnance compounds such as trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylenetetranitramine (HMX). Practically any organic contaminant that is reactive with the hydroxyl radical can potentially be successfully treated using UV/oxidation.

Reported results from laboratory through field applications of UV/oxidation treatment indicate that the technology is applicable to many types of contaminants as summarized in Figure 2.

Generally, organic contaminants that are soluble in water are most suitable to treatment by UV/oxidation. In many cases, chlorinated hydrocarbons that are resistant to biodegradation may be effectively treated by UV/oxidation. Typically, easily oxidized organic compounds such as those with double bonds (e.g., TCE, PCE, and vinyl chloride) and aromatic compounds (e.g., toluene, benzene, xylene, and phenol) are rapidly destroyed in UV/oxidation processes (2).

Contaminant Type	Examples
Aromatic hydrocarbons	benzene, toluene, ethylbenzene, xylene
Pesticides	dichlorodiphenyltrichloroethane (DDT), [o- (2,4-dichlorophenoxy)phenyl]acetic acid (2,4-D)
Wood-preserving compounds	pentachlorophenol, phenol
Chlorinated solvents	methylene chloride, dichloroethylene, trichloroethylene (TCE), chloroform, perchloroethylene (PCE)
Ordnance compounds	TNT, RDX, HMX, nitroglycerine, dinitrotoluene
Other	hydrazine, vinyl chloride, polychlorinated biphenyls (PCBs)

Source: References 6 and 7

Figure 2. Types of Contaminants Reportedly Treatable by UV/Oxidation

Contaminants that are resistant to chemical oxidation alone (i.e., methyl ethyl ketone, PCBs, and cyanide complexes) have been found to be destroyed when the treatment is enhanced by UV light (5).

Advantages, Disadvantages, and Limitations

Probably the most important advantage of UV/oxidation in treating contaminated ground water is that the technology destroys the contaminant—and does not transfer it from one medium to another.

In contrast to air stripping, UV/oxidation reduces or eliminates the need for air emission control. Since air stripping transfers the contaminant from the water to an air stream, this air stream must often be treated prior to discharge using carbon adsorption, catalytic oxidation, or thermal treatment. These requirements typically involve regulatory permitting and add to the total cost of treatment.

Activated carbon adsorption results in the concentration of the contaminant on carbon that must then be regenerated or treated and/or disposed. This is a special concern when explosive compounds are being removed. The concentration of explosive compounds on carbon could create a reactive waste and present explosive hazards. Army facilities that have used carbon adsorption for years to treat munition production wastewaters have experienced mixed results with regenerating explosive-laden activated carbon (8). Recent experiments have shown that UV/oxidation is potentially a better way to treat explosive-contaminated wastewater.

Contaminant destruction makes UV/oxidation an attractive technology from the perspective of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). CERCLA states a preference for the selection of remedial technologies in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants, and contaminants..."

Additional advantages of using UV/oxidation to treat contaminated ground water include:

- Application over a broad range of contaminants—it can destroy semi- or non-volatile contaminants resistant to removal by air stripping;
- Effectiveness at removing dilute concentrations or organics through contaminant destruction;
- Process flexibility—maximum effectiveness at the lowest cost can be achieved by optimizing operating parameters such as UV lamp intensity, residence time, oxidizer selection, and oxidizer dosage rate;
- Minimal treatment residues;
- System is easily automated;
- System is easy to transport and set up; and
- Potential for disinfection (important for potable water reuse).

Disadvantages of UV/oxidation include:

- Initial capital costs may be higher than competing technologies;
- Pretreatment of the aqueous stream may be required to minimize ongoing cleaning and maintenance of UV reactor and quartz sleeves;
- Formation of intermediates that may be more toxic than the starting compound;
- Additional time and money may be required to determine the composition of the above intermediates; and
- Handling and storage of oxidizers may present safety problems (see **Implementation Considerations**).

An additional potential disadvantage is that site engineers often (frequently unjustly) consider UV/oxidation a "riskier" technology (for ground water treatment) than more established technologies. As with other innovative treatment technologies, if

immediate action is required, conventional technologies (such as carbon adsorption) may be more expedient, easier to implement, and more acceptable to regulators. However, if time and resources permit, the unique capability of UV/oxidation to destroy contaminants may be an overwhelming advantage in selecting a ground water remediation technology.

Limitations of UV/oxidation include:

- The aqueous stream being treated must provide for good transmission of UV light (high turbidity causes interference). This factor is more important for UV/H_2O_2 than UV/O_3. (Turbidity does not affect direct chemical oxidation of the contaminant by H_2O_2 or O_3);
- Free radical scavengers can inhibit contaminant destruction efficiency (see **Description of Technology**);
- The aqueous stream to be treated by UV/oxidation should be relatively free of metal ions (less than 10 mg/L) and insoluble oil or grease to minimize the potential for fouling of the quartz sleeves; and
- When UV/O_3 is used on volatile organics such as TCA, the contaminants may be volatilized (e.g., "stripped") rather than destroyed. They would then have to be removed from the off-gas by activated carbon adsorption or catalytic oxidation.

Pretreatment methods that have been used to overcome limitations include: 1) filtration to remove suspended solids (that cause turbidity); and 2) metals precipitation to remove dissolved metals prior to UV/oxidation treatment (see **Interface with Other Technologies**). In addition, chemical and mechanical methods can be used to clean the sleeves during treatment operations (see **Design Criteria**).

Once UV/oxidation has been selected as the remedial alternative, the relative advantages and disadvantages of the various process configurations—particularly with respect to the selection of oxidizers and UV lamps—should be considered (see **Design Criteria**).

Interface with Other Technologies

UV/oxidation of contaminated ground water is an ex situ treatment technology used in conjunction with a pump and treat system. In some cases, aquifer injection processes are used after treatment.

With respect to pretreatment, if the ground water contains over 10 mg/L of iron or manganese, these ions should typically be removed from solution. A common means of removing metals from ground water is metals precipitation. Metals precipitation is discussed in the "Precipitation of Metals from Ground Water" Tech Data Sheet. Briefly, precipitation of metals from ground water involves chemically oxidizing the metals, increasing the pH to reduce the solubility of the metal hydroxides in water, and adding a flocculent to encourage precipitation and settling. The settled precipitate is removed and a polishing filter is used to remove most of the remaining suspended solids. Finally, the water is neutralized with an acid prior to treatment in the UV/oxidation process.

With respect to post-treatment, UV/oxidation may be used in conjunction with carbon adsorption to achieve demanding treatment standards. Carbon adsorption may be used after UV/oxidation as a polishing step prior to discharge. UV/oxidation may also be used in combination with biotreatment. By pretreating an aqueous stream with UV/oxidation, compounds may be formed that are more easily biodegraded. UV/oxidation may also be used to provide a final treatment after biotreatment.

Other post-treatment technologies that may interface with UV/O_3 include off-gas treatment techniques such as carbon adsorption and catalytic oxidation (for volatile organics and conversion of O_3 to O_2).

Design Criteria

Prior to the design of UV/oxidation treatment systems, laboratory or pilot-scale treatability tests should be conducted. The initial objectives of these tests are to determine contaminant destruction effectiveness and whether required treatment levels can be achieved at a reasonable cost.

Treatability studies are best conducted using reactor configurations that are representative of those that are commercially available. These representative configurations should consider the type of UV lamps (i.e., intensity and wavelength) to be used in combination with specific oxidizers. It is important to provide a sufficient quantity of representative ground water so that adequate treatability testing can be done to ensure a reliable scale-up. The treatability test personnel will usually specify this quantity (which may be as much as a 55-gal drum). To obtain more information on, or to arrange for, a treatability study, contact Gary Peyton or Mark Zappi (see **Points of Contact**).

After determining the feasibility of UV/oxidation treatment, on-site pilot tests may be performed to develop full-scale implementation design criteria as well as to estimate capital and operating costs. In many cases, adequate design information can be obtained in two weeks of pilot testing (9). To obtain more information on UV/oxidation pilot tests, contact Laura Yeh or Carmen Lebron (see **Points of Contact**).

Issues that may be addressed in treatability and pilot testing include:

- Effectiveness of oxidizers (and/or mixtures of oxidizers);
- Optimum UV intensity and wavelength;
- Reaction times required to achieve adequate contaminant destruction;
- Oxidizer mixture and dosages required to achieve adequate contaminant destruction;
- Presence of scavengers or competing compounds in the water to be treated; and
- Characterization of decomposition products.

These data will allow for the development of specific design criteria for a full-scale UV/oxidation treatment system. These design criteria include:

Application Factor	Design Element
Nature of contaminant	• Choice of oxidizer(s) • Intensity and wavelength of UV light • Off-gas treatment • Use and selection of catalysts
Concentration of contaminant	• Oxidizer dosage • Intensity of UV light • Hydraulic retention time
Composition of feed (pH, competing compounds, metal ions)	• Pretreatment • Oxidizer dosage • Intensity of UV light • Maintenance of quartz sleeves • Off-gas treatment
Degree of contaminant destruction required	• Hydraulic retention time • Reactor size and design • Oxidizer dosage
Flow rate required	• Number, size, and design of reactors

Source: Arthur D. Little, Inc.

Figure 3. Design Factors

- Pretreatment requirements;
- Number, size, and design of reactors;
- Selection of O_3 or H_2O_2;
- Dosage of O_3 or H_2O_2;
- Hydraulic retention time and water flow rate;
- Intensity and wavelength of UV light;
- Power requirements and necessary hookups (for UV light generation and O_3 generation);
- Off-gas treatment requirements; and
- Other post-treatment requirements.

These design components are influenced by site-specific factors. The primary factors and the UV/oxidation design features they influence are illustrated in Figure 3.

It is important to note that even after removing iron and manganese ions, the quartz sleeves may become fouled over time resulting in a decrease in UV light transmission and thus treatment efficiency. To overcome this problem, the design of the UV/oxidation system and operation must include a means of ensuring the quartz sleeves remain clear. The use of a UV light sensor may be beneficial to monitor UV transmission intensity to determine when the sleeves should be cleaned (9).

Techniques used to clean the sleeves include chemical washing and mechanical cleaning. Chemical washing may consist of recirculating a weak acidic solution (e.g., citric or oxalic acid) through the reactor to dissolve metal scale from the sleeves. Mechanical methods, such as passing chemically resistant O-rings over the sleeves, may be used to physically remove scale.

When treating contaminated ground water, it is important that the system be designed to be flexible in response to typical unpredictability in ground water characteristics and extraction. Process flexibility for ground water treatment can be enhanced by the inclusion of recirculation or bypass piping and extra storage capacity in the system design. In addition, ground water feed tanks should be large enough to permit equalization (maximum homogenization of contaminant distribution and concentration).

Vendors will not disclose proprietary information such as the identification of proprietary catalysts and detailed UV lamp specifications.

Implementation Considerations

An electrical load center (typically 440V, three-phase) will be required to power the UV lamps, feed pumps, air compressor, and O_3 generator (if required). (In addition, other parts of the overall treatment system such as the pumps on the ground water extraction wells and equipment used for feed pretreatment or off-gas treatment may require electrical power.)

Overall procedures for mobilization, setup, disassembly, and demobilization are relatively straightforward for most UV/oxidation systems. The systems are typically skid-mounted and relatively portable. Full-scale oxidation systems may be mounted on a single skid containing the reactor(s) and metering equipment for the addition of H_2O_2. If O_3 is used, separate skids are typically included to contain the O_3 generator and the air compressor.

Manpower for operation is minimal—most systems are sufficiently automated that they can be operated with a performance and monitoring check once a day.

In many cases, an approved site safety plan will be required before on-site testing or implementation. This safety plan will include requirements for the storage, handling, and use of oxidizers as well as any contaminant-specific safety concerns. The handling and storage of 35% to 50% solutions of H_2O_2 require that appropriate precautions be taken. As strong oxidizers, these solutions can cause serious burns if they come in contact with skin. In addition, high-strength peroxide solutions can decompose violently at elevated temperatures. It is important to carefully read the Material Safety Data Sheet (MSDS) for H_2O_2 (or any other oxidizer) before handling or storing it. In addition, exposure to O_3 (a gas) can, at high concentrations, cause severe respiratory tract irritation. Despite these hazards, it should be noted that these oxidizers are widely and safely used.

If ground water containing ordnance compounds such as explosives is to be treated, the safety plan will also address any explosive-safety issues that may arise.

Residuals and Wastes Generated

Residuals and wastes generated during ground water remediation using UV/oxidation may include:

- Pretreatment residuals (such as metal precipitates or other solids);

- Incomplete oxidation products that may require additional treatment (e.g., biotreatment, carbon adsorption);
- Chemicals used to clean quartz sleeves;
- Residuals from off-gas treatment, if any (such as activated carbon); and
- Burned out UV lamps containing mercury vapor (these are usually returned to the vendor for recycling).

Regulatory Issues

Regulatory requirements will vary depending on the specific treatment application. Considerations include:

- If the treated effluent is to be discharged to surface water, a National Pollutant Discharge Elimination System (NPDES) permit will be required;
- If the treated effluent is to be discharged to sewers or transported to a Publicly Owned Treatment Works (POTW), the regulations of the receiving POTW will apply;
- If the effluent from ground water treatment is to be reintroduced into the aquifer, proof will be required that the discharge meets established, site-specific treatment standards based on Applicable or Relevant and Appropriate Requirements (ARARs) or risk- and/or hazard-based criteria; and
- The Resource Conservation and Recovery Act (RCRA) may apply if, for example, a hazardous waste is moved outside the area of contamination.

In addition to the above, if any process residuals (e.g., pretreatment or off-gas treatment residuals) are generated, ARARs must be reviewed to identify any that affect their treatment or disposal.

Feasibility Study (FS) Criteria Ranking

The results of a rating of UV/oxidation for use in ground water remedial actions are presented in Figure 4.

UV/oxidation results in the destruction of organic contaminants in water and thus ranks favorably with respect to environmental impacts, long-term effectiveness, reduction of toxicity, and state and local acceptance.

A more neutral ranking is given to UV/oxidation for implementability because its use and success are heavily dependent on water and contaminant characteristics, and treatability studies involving actual contaminated-water samples are required before a full-scale system can be specified.

A neutral ranking is given to UV/oxidation for cost. UV/oxidation costs cover a wide range (see **Key Cost Factors**)—in some cases, it may be very competitive economically; in others, it may be a more expensive alternative.

Criteria	Ranking
Effect of reducing the overall threat to human health and the environment	
Compliance with Applicable or Relevant and Appropriate Requirements (ARARs)	
Long-term effectiveness and permanence	
Reduction of toxicity, mobility, or volume	
Short-term effectiveness	
Implementability	
Cost	
State and community acceptance	
Favorable ◄——► Unfavorable	

Figure 4. FS Criteria Ranking

Key Cost Factors

Factors that influence the cost of implementing UV/oxidation include:

- Types and concentration of contaminants (as they affect oxidizer selection, oxidizer dosage, UV light intensity, and treatment time);
- Degree of contaminant destruction required;
- Desired water flow rates; and
- Requirements for pretreatment and/or post-treatment.

Operating costs for UV/oxidation systems used in the treatment of contaminated ground water may fall within a very large range due to the above variables. Often, the most significant part of operating costs is UV lamp replacement and/or the energy required to power the UV/oxidation system.

UV/oxidation operating costs can vary dramatically according to vendor. For example, three systems (from three different vendors) were compared in treatability tests using the same contaminated ground water at a Superfund site. Projected annual operating costs for the full-scale use of these three different systems at this site ranged from below $500,000 to nearly $2 million (10). Total capital costs were less variable, ranging from $1.325 million to $1.695 million (10).

Other reported or estimated operating costs for specific applications include:

- $1.00 to $1.50 per 1,000 gal for the pilot-scale tests described in **Application Example 1** (below);
- $2.50 to $3.00 per 1,000 gal for the treatment of ground water contaminated with 5 ppm total benzene, toluene, ethylbenzene, and xylene (see **Application Example 3** below);
- $0.73 per 1,000 gal to treat ground water contaminated with 5,500 µg/L TCE to an effluent concentration of 1 µg/L TCE at a flow rate of 210 gpm (11). Treatment involved the use of low-pressure mercury vapor UV lamps and H_2O_2 and O_3 oxidizers;
- $7.50 to $8.10 per 1,000 gal for the treatment of ground water containing a mixture of volatile (48.6 mg/L total) and semi-volatile (3.2 mg/L total) organic compounds to levels of 0.4 mg/L and 0.02 mg/L, respectively (12). These estimates are based on 25 and 65 gpm systems using high-pressure, high-intensity UV lamps with H_2O_2. In this case, O_3 cannot be used because stripping of volatile contaminants is not desired.

As addressed in **Design Criteria**, operation and maintenance costs for a full-scale UV/oxidation system may be significantly optimized by thoroughly characterizing the contaminated ground water and by conducting treatability and pilot-scale tests.

The estimated capital costs to treat contaminated ground water at a Navy site (see **Application Example 1**) range from $900,000 to $1.3 million.

Other costs associated with the implementation of UV/oxidation include the costs of treatability and pilot tests prior to treatment. Ranges for these costs (assumed to be independent of the magnitude of the cleanup effort) are:

- Laboratory treatability studies—$5,000 to $50,000; and
- Pilot tests or field demonstrations—$100,000 to $500,000.

These costs include analytical costs.

Application Examples

A summary of recent examples of applications of UV/oxidation treatment is provided in Figure 5. These examples include bench-, demonstration-, and full-scale applications for a variety of contaminants in ground water.

Example 1. Munitions Washout Lagoon—Site F, Submarine Base, Bangor, Washington (13, 14)

Bench-scale tests were conducted in a 25-liter recirculating reactor to determine the capability of UV/oxidation to treat ground water containing TNT at levels up to 7,000 ppb and RDX at levels up to 600 ppb. Test results indicated that a high-intensity UV lamp (less than 1 kW) with O_3 was the best combination. This combination together with a hydraulic retention time of 25 to 30 minutes resulted in the reduction of TNT levels to below 0.25 ppb and RDX levels to below 0.50 ppb.

Observations during these tests indicated that RDX was rapidly degraded. However, trinitrobenzene (TNB), an intermediate of TNT, proved difficult to degrade.

A pilot study using a 20 gpm UV/O_3 system was completed in March 1993. Additional information regarding this pilot study and plans for full-scale remediation can be obtained from Laura Yeh or Carmen Lebron (See **Points of Contact**).

Example 2. Contaminated Ground Water at Winthrop Superfund Site, Maine (9)

In 1990, an on-site demonstration of the use of UV/oxidation to treat ground water contaminated with the solvent dimethylformamide (DMF) at levels of up to 5,000 ppb was conducted. In addition to the DMF, the ground water contained iron in excess of 300 ppm. Because iron competes with the contaminants for oxidation, it was necessary to pretreat the ground water to reduce the iron to below 10 ppm.

Pretreatment was accomplished by oxidizing the iron to its ferric state followed by increasing the pH to reduce the solubility of the iron hydroxide in the water. A flocculent was added to encourage precipitation and settling. The settled precipitate was removed and the water was sent through a polishing filter to remove the remaining suspended solids. An acid was then added to neutralize the water prior to treatment in the UV/oxidation system.

This test demonstrated the capability of UV/oxidation to reduce DMF from levels of 5,000 ppb to levels below 5 ppb. The treated water flowed to an infiltration lagoon. UV/oxidation was selected as the recommended technology for full-scale implementation at this site.

Additional information may be obtained from Dr. Raymond Machacek of Arthur D. Little, Inc., (617) 498-5580.

Example 3. Ground Water Contaminated by Leaking Underground Storage Tank (6)

In this commercial application, a full-scale application of UV oxidation is treating ground water containing up to 5 ppm of total benzene, toluene, ethylbenzene, and xylene (BTEX) to levels consistently below 5 ppb total BTEX. A 30 kW UV/oxidation system operating at 20 to 25 gpm is being used with H_2O_2 and a proprietary catalyst. The system includes an automated mechanical UV lamp cleaning feature. Operating costs for this complete treatment system range from $2.50 to $3.00 per 1,000 gal.

Example 4. Superfund Innovative Technology Evaluation (SITE) Demonstration—Lorentz Barrel and Drum Site, San Jose, California (11, 15)

As part of the EPA's program to accelerate the development, demonstration, and use of alternative or innovative technologies to provide for permanent, long-term remedial solutions, a UV/oxidation system was demonstrated in 1989. This system was demonstrated at a Superfund site to treat ground water contaminated with a variety of volatile organic compounds (VOCs) including TCE, 1,1-DCA, and 1,1,1-TCA.

Example	Contamination Characterization	Results	Comments	Ref.
1. Navy Munitions Washout Lagoon	Ground water contaminated with TNT (up to 7,000 ppb) and RDX (up to 600 ppb).	Achieved treatment levels for TNT and RDX of less than 0.25 ppb and 0.50 ppb, respectively.	Bench-scale tests. Pilot-scale (5-15 gpm) tests were planned based on these results. High-intensity, short-wavelength lamps used with hydrogen peroxide.	13, 14
2. Ground Water at Superfund Site	Ground water contaminated with DMF (5,000 ppb). Iron present at concentrations greater than 300 ppm.	Reduced level of DMF in discharge to below 5 ppb.	Demonstration test. Pretreatment (metal precipitation) required to remove iron from feed. UV/ oxidation recommended for full-scale remediation. Low-intensity, standard wavelength lamps used with ozone.	9
3. Ground Water Contaminated by Leaking Underground Storage Tank	Ground water contaminated with BTEX (up to 5 ppm).	Total BTEX was consistently reduced to levels below 5 ppb.	Full-scale application (20 to 25 gpm). Operating costs of $2.50 to $3.00 per 1,000 gal of ground water treated. High-intensity, short-wavelength lamps used with hydrogen peroxide.	6
4. SITE Program Demonstration	Ground water contaminated with 44 VOCs (primarily TCE at 48 to 85 ppm).	Total VOC efficiencies as high as 90% were achieved. Removal efficiencies for TCE were greater than 99%.	Innovative technology demonstration. Low-intensity, standard wavelength lamps used with ozone and hydrogen peroxide.	11, 15
5. Rocky Mountain Arsenal Treatability Study	Two ground waters. One contaminated with DIMP at a representative concentration of 806.7 ppb. The other ground water was contaminated with benzene (355,000 ppb) and other volatile organics (total concentration of about 3,640 ppb).	DIMP removals were in excess of 87%. Benzene removals were less than 38%. There was little or no removal of the other organics.	This pilot study used high-intensity, short-wavelength lamps with hydrogen peroxide. Variables included oxidizer dosage and HRT. DIMP removals were best with a high HRT and high oxidizer dosage. Benzene removal generally improved with an increase in HRT.	16, 17

Figure 5. Application Examples

In this demonstration, a 150-gal reactor (3-feet long, 1.5-feet wide, and 5.5-feet high) was used. In addition to the reactor, the system included an O_3 generator, an H_2O_2 feed system, and a catalytic O_3 decomposer to treat reactor off-gas.

Optimum results were achieved at the following operating conditions:

- Hydraulic retention time—40 minutes;
- Influent pH—7.2 (unadjusted);
- O_3 dose—110 mg/L;
- H_2O_2 dose—13 mg/L; and
- UV lamps—24 operating lamps at 64 watts each.

The average electricity consumption was approximately 11 kwh/hour of operation.

At these conditions, discharge from the system met applicable NPDES standards for discharge into a local waterway. Total VOC efficiencies as high as 90% were achieved. Removal efficiencies for TCE (the most predominant VOC) were greater than 99%.

It was observed that with some of the more volatile VOCs, removals were due to both chemical oxidation and stripping. The catalytic O_3 decomposer destroyed the gas phase VOCs to below detection levels.

Example 5. Treatability Study—Contaminated Ground Waters at Rocky Mountain Arsenal (RMA), Colorado (16,17)

The U.S. Army Waterways Experiment Station (WES) conducted a treatability study using UV/oxidation to treat various contaminated waters at RMA. Two of these waters were ground waters designated as North Boundary (NB) ground water and South Plants (SP) ground water.

The UV/oxidation system used in these studies consisted of a 55 gal continuous flow reactor equipped with eight UV lamps inside quartz tubes. The tubes were positioned perpendicularly to flow through the reactor. The UV lamps, capable of operating at low or high intensity, were used at high intensity for these studies. A 40 kW power source was used for the reactor.

The oxidizer used was H_2O_2 as a 50% solution. The H_2O_2 solution was injected into the contaminated water and mixed in a static, in-line mixer prior to entering the reactor.

The test configuration of the treatability studies included runs varying hydraulic retention times (HRT) and H_2O_2 dosages.

HRT evaluated included low (4 minute); medium (6 or 7 minute); and high (11 or 16 minute). Low and high H_2O_2 dosages were tested. The low H_2O_2 dosage was established at a rate that would result in 10 mg/L of H_2O_2 in the reactor effluent (to ensure that the oxidation reactions would not be H_2O_2-limited). The high H_2O_2 dosage was set at an influent rate three times as great as the influent rate of the established low H_2O_2 dosage.

Neither of the ground waters subjected to the treatability studies were pretreated. A representative analysis of the NB ground water indicated a concentration of diisopropyldimethylphosphonate (DIMP) of 806.7 µg/L. An analysis of the SP ground water indicated high concentrations of benzene (355,000 µg/L) and other volatile organics (carbon tetrachloride–155 µg/L; chloroform–2,500 µg/L; toluene–685 µg/L; trichloroethylene–140 µg/L; and xylene–160 µg/L).

Results of the NB ground water test runs indicated that DIMP removals were in excess of 87% for all combinations of HRT and H_2O_2 dosage and thus met target treatment levels. The highest removal (100%) was achieved in the high HRT, high H_2O_2 dose run.

Little or no removal of the organic contaminants in the SP ground water was observed. Improved removals were generally observed during the high HRT runs indicating that the oxidation reactions were rate limited. Benzene removals were less than expected (a maximum of 38%). It was proposed that this phenomenon might be attributed to the partial degradation of the other aromatics present in the ground water into benzene.

Based on the results of these treatability studies, it was recommended that additional measures be investigated to improve the treatment efficiency for these ground waters. Suggested measures include the use of cation-based catalysts and pH adjustment.

In addition to these applications involving ground water treatment, UV/oxidation has been demonstrated in an application involving pretreatment of process wastewater resulting from wood-preserving operations (4). These wastewaters, containing phenols (100 to 150 ppm) and polychlorinated phenols (PCP) at levels of 5 to 10 ppm, must be pretreated to allow for their discharge to a sanitary sewer for subsequent biological treatment in a POTW. Using a low-intensity UV/oxidation system with O_3, concentrations of phenol were reduced to about 10 ppm and PCP levels were reduced to below 0.1 ppm. Operating and maintenance costs for this pretreatment are $1.30 per 1,000 gal of wastewater.

Points to Remember

- The success of UV/oxidation is very dependent on water chemistry (including compounds to be treated). Treatability tests will be required to determine feasibility and optimum operating parameters.
- The presence of oxidizable compounds (organic and inorganic) other than those of concern may decrease effectiveness and increase costs due to consumption of oxidizers and energy to power the UV lamps.
- The presence of metals, insoluble oil or grease, and/or suspended solids in the water to be treated may reduce the effective transmission of UV light throughout the reactor due to turbidity and/or fouling of the quartz sleeves. Pretreatment of the ground water and/or periodic cleaning of the sleeves may be necessary.
- If VOCs are present in ground water, their removal may be by stripping (particularly if O_3 is used) rather than oxidation.
- Design of a UV/oxidation system for ground water treatment should allow for flexibility of operation to account for typical unpredictability in ground water quality and extraction.
- Safety is an important consideration in the handling, storage, and use of oxidizers—particularly H_2O_2. In addition, special safety considerations may be required in the treatment of ground water contaminated with ordnance compounds such as explosives.
- Vendors should demonstrate (for each site-specific set of conditions) that the UV/oxidation system supplied will not generate toxic or other harmful byproducts.

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17. Personal communication with Elizabeth Fleming, U.S. Army Waterways Experiment Station, Vicksburg, MS, 1992.

Points of Contact

Additional information regarding technical, regulatory, and practical aspects of the use of UV/oxidation for the treatment of contaminated ground water may be obtained from:

- Gary R. Peyton, Environmental Chemistry Section, Illinois State Water Survey, Champaign, IL. (217) 333-5905.
- Laura Yeh, NCEL, Code L71, Port Hueneme, CA. (805) 982-1660 [also, Carmen Lebron at (805) 982-1616].
- John Fringer, NEESA, Code 112E4, Port Hueneme, CA. (805) 982-4856.
- Mark E. Zappi, Environmental Laboratory, U.S. Army Engineers Waterways Experiment Station, Vicksburg, MS. (601) 634-2856.

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EPA

Engineering Bulletin
Chemical Dehalogenation Treatment: APEG Treatment

Purpose

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

Abstract

The chemical dehalogenation system discussed in this report is alkaline metal hydroxide/polyethylene glycol (APEG) which is applicable to aromatic halogenated compounds. The metal hydroxide that has been most widely used for this reagent preparation is potassium hydroxide (KOH) in conjunction with polyethylene glycol (PEG)[6, p. 461]* (typically, average molecular weight of 400 Daltons) to form a polymeric alkoxide referred to as KPEG [16, p. 835]. However, sodium hydroxide has also been used in the past and most likely will find increasing use in the future because of patent applications that have been filed for modification to this technology. This new approach will expand the technology's applicability and efficacy and should reduce chemical costs by facilitating the use of less costly sodium hydroxide [18]. A variation of this reagent is the use of potassium hydroxide or sodium hydroxide/tetraethylene glycol, referred to as ATEG, that is more effective on halogenated aliphatic compounds [21]. In some KPEG reagent formulations, dimethyl sulfoxide (DMSO) is added to enhance reaction rate kinetics, presumably by improving rates of extraction of the haloaromatic contaminants [19][22].

Previously developed dehalogenation reagents involved dispersion of metallic sodium in oil or the use of highly reactive organosodium compounds. The reactivity of metallic sodium and these other reagents with water presented a serious limitation to treating many waste matrices; therefore, these other reagents are not discussed in this bulletin and are not considered APEG processes [1, p. 1].

The reagent (APEG) dehalogenates the pollutant to form a glycol ether and/or a hydroxylated compound and an alkali metal salt, which are water soluble byproducts. This treatment process chemically converts toxic materials to non-toxic materials. It is applicable to contaminants in soil [11, p. 1], sludges, sediments, and oils [2, p. 183]. It is mainly used to treat halogenated contaminants including polychlorinated biphenyls (PCBs) [4, p. 137], polychlorinated dibenzo-p-dioxins (PCDDs) [11, p. 1], polychlorinated dibenzofurans (PCDFs), polychlorinated terphenyls (PCTPs), and some halogenated pesticides [8, p. 3][14, p. 2]. This technology has been selected as a component of the remedy for three Superfund sites. Vendors should be contacted to determine the availability of a treatment system for use at a particular site. The estimated costs of treating soils range from $200-$500/ton. This bulletin provides information on the technology applicability, the types of residuals resulting from the use of the technology, the latest performance data, site requirements, the status of the technology, and where to go for further information.

Technology Applicability

This technology is primarily for treating and destroying halogenated aromatic contaminants. The matrix can be soils, sludges, sediments, or oils. If a waste site has contaminants other than halogenated compounds, other alternatives should be considered.

The concentrations of PCBs that have been treated are reported to be as high as 45,000 ppm. Concentrations were

* [reference number, page number]

reduced to less than 2 parts per million per individual PCB congener. Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been treated to nondetectable levels at part per trillion sensitivity. The process has successfully destroyed PCDDs and PCDFs contained in contaminated pentachlorophenol oil. For a contaminated activated carbon matrix, direct treatment was less effective and the reduction of PCDDs/PCDFs to concentrations less than 1 ppb was better achieved by first extracting the carbon matrix with a solvent and then treating the extract [15, p. 1].

All field applications of this technology to date have been in various matrices and not on specific Resource Conservation and Recovery Act (RCRA) listed wastes. The effectiveness of APEG on general contaminant groups for various matrices is shown in Table 1. Examples of constituents within contaminant groups are provided in Reference 23, "Technology Screening Guide for Treatment of CERCLA Soils and Sludges". This table is based on the current available information or professional judgment when no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability was tested to show that, for that particular contaminant and matrix, the technology was effective. The ratings of potential effectiveness and no expected effectiveness are based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given.

Table 1
Effectiveness of APEG Treatment on
General Contaminant Groups for Various Matrices

	Contaminant Groups	Effectiveness			
		Sediments	Oils	Soil	Sludge
Organic	Halogenated volatiles	▼	▼	▼	▼
	Halogenated semivolatiles	▼	▼	▼	▼
	Nonhalogenated volatiles	❑	❑	❑	❑
	Nonhalogenated semivolatiles	❑	❑	❑	❑
	PCBs	■	■	■	■
	Pesticides (halogenated)	▼	■	■	▼
	Dioxins/Furans	■	■	■	■
	Organic cyanides	❑	❑	❑	❑
	Organic corrosives	❑	❑	❑	❑
Inorganic	Volatile metals	❑	❑	❑	❑
	Nonvolatile metals	❑	❑	❑	❑
	Asbestos	❑	❑	❑	❑
	Radioactive materials	❑	❑	❑	❑
	Inorganic corrosives	❑	❑	❑	❑
	Inorganic cyanides	❑	❑	❑	❑
Reactive	Oxidizers	❑	❑	❑	❑
	Reducers	❑	❑	❑	❑

■ Demonstrated Effectiveness: Successful treatability test at some scale completed
▼ Potential Effectiveness: Expert opinion that technology will work
❑ No Expected Effectiveness: Expert opinion that technology will not work

Limitations

The APEG technology is not intended as an in situ treatment. APEG will dehalogenate aliphatic compounds if the mixture is reacted longer and at significantly higher temperatures than for aromatic compounds, it is recommended that a related reagent KTEG be considered for these contaminants. KTEG has been shown at laboratory scale to be effective on halogenated aliphatic compounds such as ethylene dibromide, carbon tetrachloride, ethylene dichloride, chloroform, and dichloromethane (methylene chloride) [18, p. 2]. The necessary treatment time and temperature for KTEG use can be determined from laboratory tests.

Treatability tests should be conducted prior to the final selection of the APEG technology to identify optimum operating factors such as quantity of reagent, temperature, and treatment time. These tests can be used to identify such things as water content, alkaline metals and high humus content in the soils, glycol extractables content, presence of multiple phases, and total organic halides that have the potential to affect processing times and costs [19].

The treated soil may contain enough residual reagent and treatment byproducts that their removal could be required before final disposal. If necessary, such byproducts are usually removed by washing the soil two or three times with water. The soil will have to be neutralized by lowering the pH prior to final disposal.

Specific safety aspects for the operation must be considered. Treatment of certain chlorinated aliphatics in high concentrations with APEG may produce compounds that are potentially explosive (e.g., chloroacetylenes) and/or cause a fire hazard. The use of DMSO or similar reagents may lead to formation of highly flammable volatile organics (e.g., methyl sulfide) [18, §IV C]. Severe corrosivity can be a concern when DSMO is teamed with other APEG reagents. Alkaline reactive materials such as metallic aluminum will compete with the contaminants for the reagent and may produce hydrogen gas (explosive). Vapors from heating oily soils, which are often the matrix in which PCBs are found, can also create such potential problems as fires and noxious fumes. These problems can often be solved by taking appropriate corrective actions during elevated temperature processing.

The operation must also be conducted with care because of the elevated temperatures and production of steam, the use of caustics in the process, and the presence of acids that are used for neutralization. If DMSO is used, care must be taken to prevent its coming into contact with skin, for it enhances transport of PCBs through the skin, thus increasing the risk of exposure.

Technology Description

Figure 1 is a schematic of the APEG treatment process.

Waste preparation includes excavation and/or moving the soil to the process where it is normally screened (1) to remove debris and large objects and to produce particles that are sufficiently small to allow treatment in the reactor without binding the mixer blades.

Typically, the reagent components are mixed with the contaminated soil in the reactor (2). The material must be well mixed with the reagent to allow effective treatment. Treatment proceeds inefficiently without mixing. This mixture is heated to between 100° and 180° C. The reaction proceeds for 1 to 5 hours depending upon the type, quantity, and concentration of the contaminants. The treated material goes from the reactor to a separator (3) where the reagent is removed and can be recycled (4).

During the reaction, water is vaporized in the reactor, condensed (5) and collected for further treatment or recycled through the washing process, if required. Carbon filters (7) are used to trap any volatile organics that are not condensed. In the washer (6), the soil is neutralized by the additions of acid. It is then dewatered (8) before disposal.

Process Residuals

There are three main waste streams generated by this technology: the treated soil, the wash water, and possible air emissions. The treated soil will need to be analyzed to determine if it meets the regulatory requirements for the site before final disposition can be made. The soil's pH must be adjusted before disposal. The chemistry of this technology is specific to halogenated organics and, based upon a test conducted by the EPA in 1985, results in byproduct compounds that appear to be neither toxic nor of concern. In that test the EPA checked for 1) mutagenicity, 2) toxicity, and 3) bioaccumulation/bioconcen-tration of the byproducts of two different contaminants: tetrachlorobenzene and 2,3,7,8 - TCDD that had been treated by the process [3, p. 80]. The individual byproduct chemical compounds were not determined. These compounds and the residual levels of reagent or catalyst did not present a serious health or environmental problem [12, p. 2].

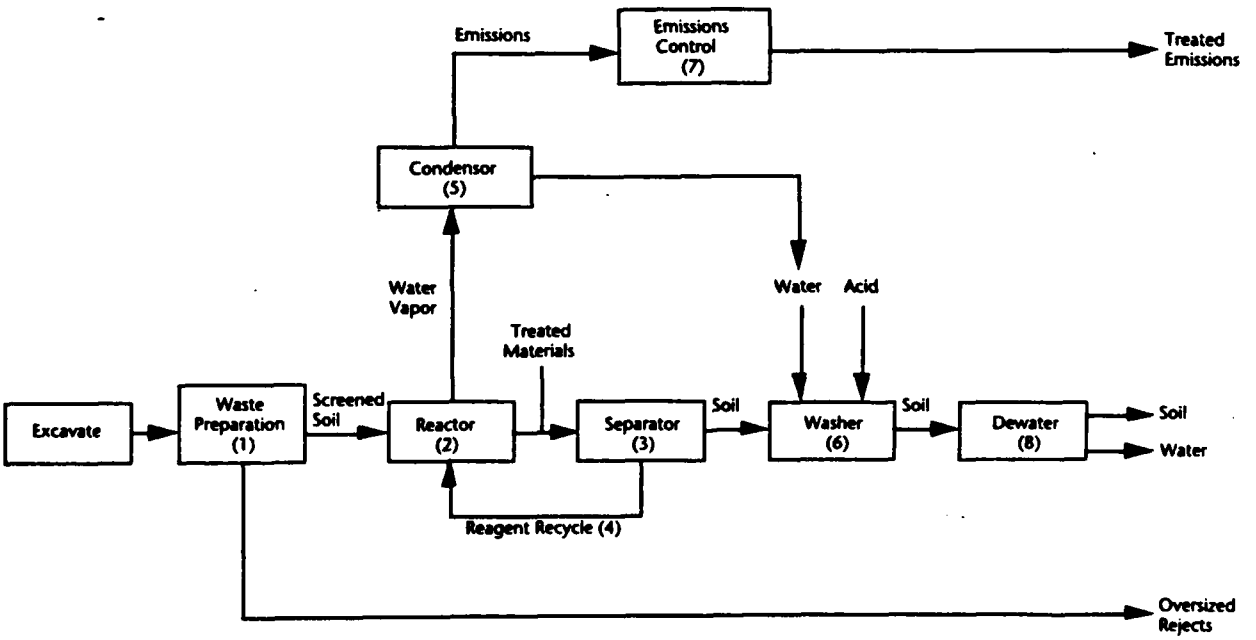
Waste wash water contains only trace amounts of contaminants and reagents and would be expected to meet appropriate discharge standards, enabling it to be discharged to a local, publicly owned treatment works or receiving stream. Volatile air emissions can be released due to the heating and mixing that occurs with the process. They are usually captured by condensation and/or on activated carbon. The contaminated carbon is usually incinerated.

Site Requirements

APEG treatment units are transported by trailers [13,p. 54]. Therefore, adequate access roads are required to get the unit to the site. The system that operated in Guam, which used a 1.5- ton batch reactor, required an area of 100 feet by 100 feet.

Energy requirements involve heating the reactor and removing the water by volatilization. For the reactor used in Guam, a standard 440V, three-phase electrical service was required along with a diesel steam-generating plant rated at

Figure 1
APEG Treatment Process



600 lb/h and 80 psi [13, p. 53]. A standard municipal water supply, or equivalent, is adequate for this process.

Contaminated soils or other waste materials are hazardous and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures.

A means of containing and cleaning up accidental spills must be provided. The reagents (KOH, acids, etc.) should be stored in drums with containment beneath and provisions to pump any spills to a holding area for neutralization [19, p. 2].

The process residuals normally must be stored until their level of contaminants are verified to be below those established for the site. Depending upon the site, a method to store waste may be necessary. Storage capacity will depend on waste volume.

Onsite analytical capabilities are highly desirable. Extraction equipment and gas chromatography/mass spectometer capabilities should be available to measure contaminants of interest and to provide information for process control.

Performance Data

This technology's performance has been evaluated from bench-scale tests to field tests in large reactors. Table 2 summarizes the results of several more important applications of the technology and their results.

RCRA Land Disposal Restrictions (LDRs) that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements (ARARs) for CERCLA response actions. The APEG treatment technology can produce a treated waste that meets treatment levels set by BDAT, but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where APEG treatment does not meet these levels it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. EPA has made the treatability variance process available in order to ensure that LDRs do not unnecessarily restrict the use of alternative and innovative treatment technologies. Treatability variances may be justified for handling complex soil and debris matrices. The following guides describe when

Table 2
APEG Field Performance Data

Site/Date	*Contaminant/ Waste Form*	*Concentration Before*	*Concentration After*	*Volume Treated*
Signo Trading NY/1982	dioxin/liquid	135ppb	<1 ppb	15 gallons
Montana Pole Butte, MT/1986 (16, p. 838) [5, p. 1]	dioxin furans/c	147-83,923 ppb	<1 ppb	10,000 gallons
Western Processing Kent, WA/1986 [16, p. 838]	dioxin/liquid and sludge	120 ppb	<0.3 ppb	7,550 gallons
Wide Beach Erie County, NY/ 1985	PCBs (Aroclor 1254)/soil	120 ppm	<2 ppm	1 ton
Guam U.S.A./1988 793 gal. reactor [13, p. 43]	PCBs/soil	2500[a] ppm with hot spots as high as 45,860 ppm	<1[ab] ppm	22 tons soil 3.4 tons crushed rock
Bengart & Memel Buffalo, NY/1986 55 gal. drum [10, p. 13]	PCBs/soil	51 out of 52 drums, 108 ppm	<27 ppm	52 fifty-five gallon drums
Economy Products Omaha, NE/1987	TCDD, 2, 4-D, 2, 4, 5-T/liquid	1.3 ppm 17,800 ppm 2,800 ppm	ND 334 ppm 55 ppm	20 gallons

a = value is an average value

b = per resolvable PCB cogener

and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS) [20]; and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-07FS) [17]. Another approach could be to use other treatment techniques in series with APEG treatment to obtain desired treatment levels.

Technology Status

The APEG process has been selected for cleanup of PCB-contaminated soils at three Superfund sites: Wide Beach, New York (September 1985), Re-Solve, Massachusetts (September 1987), and Sol Lynn, Texas (March 1988). Wide Beach is expected to start operation in the summer of 1990 [9, p. 99] [19].

This technology has received approval from the EPA's Office of Toxic Substance under the Toxic Substances Control Act for PCB treatment.

Significant advances are currently being made to the APEG technology. These advances employ water rather than costly PEG to wet the soil and require shorter reaction times and less energy. These advances should greatly enhance the economics of the process. Performance information on this modified process is not available at this time for inclusion in this bulletin [18].

This technology uses standard equipment. The reaction vessel must be equipped to mix and heat the soil and reagents. A detailed engineering design for a continuous feed, full-scale system for use in Guam is currently being completed. It is estimated that a full-scale system can be fabricated and placed in operation in 6 to 12 months. Costs to use APEG treatment are expected to be in a range of $200-$500/ton.

EPA Contact

Technology-specific questions regarding APEG technology may be directed to:

Charles J. Rogers
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26 West Martin Luther King Drive
Cincinnati, Ohio 45268
Telephone: FTS 684-7757 or (513) 569-7757

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Precipitation of Metals from Ground Water

Port Hueneme, CA 93043 | NEESA Document No. 20.2–051.6 | March 1993

Introduction

Chemical precipitation of metals has long been the primary method of treating metal-laden industrial wastewaters. Due to the success of metals precipitation in such applications, the technology is being considered and selected for use in remediating ground water containing heavy metals.

In ground water treatment applications, the metal precipitation process is often used as a pretreatment for other treatment technologies (such as chemical oxidation or air stripping) where the presence of metals would interfere with the other treatment processes.

This Tech Data Sheet provides an introduction and summary to the practices of metals precipitation and their potential application to ground water treatment.

Purpose

The Tech Data Sheets are designed to:

- Disseminate practical, implementation-related information to minimize design and construction problems;
- Help Remedial Project Managers (RPMs) to evaluate a technology (recommended in a Feasibility Study [FS], for example) and decide if it is practical and cost-effective;
- Aid RPMs in writing a Remedial Action (RA) Delivery Order;
- Help Engineering Field Division (EFD) Remedial Design personnel to write a Statement of Work (SOW) for, and RPMs to review, Remedial Design Plans; and
- Enable field personnel such as Project Superintendents, Engineers in Charge, On-Scene Coordinators (OSCs), and Resident Officers in Charge of Construction (ROICCs) to become familiar with a technology at a site they will oversee.

Description of Technology

Metals precipitation from contaminated water involves the conversion of soluble heavy metal salts to insoluble salts that will precipitate. The precipitate can then be removed from the treated water by physical methods such as clarification (settling) and/or filtration.

For the metal precipitation process to be effective, it must be coupled with an efficient solids removal process. Otherwise, metal precipitate solids may carry over into the effluent and negatively affect effluent quality and process efficiency.

The heavy metal precipitation step is simple, involving the addition of chemical reagents to adjust the pH of the contaminated water. The desired pH is one in which the metals exhibit low (or minimum) solubilities in water and therefore precipitate. This desired pH is dependent on the specific metal-reagent combination. Common reagents used include:

- Alkalis such as lime, caustic soda, or magnesium hydroxide slurries to precipitate metal hydroxides (hydroxide process); and
- Sulfides such as sodium sulfide or ferrous sulfide slurries to precipitate metal sulfides (sulfide process).

A new process under development is precipitation of metals by xanthates (1). Xanthates are a family of compounds prepared by reacting an alcohol or other organic hydroxyl-containing compound with sodium hydroxide and carbon disulfide. The resulting sodium xanthate reacts with metals to form metal xanthates similar to the way that sodium sulfide forms metal sulfides.

Xanthates were originally used in the mining industry as collector agents in the flotation of sulfide minerals, metallic elements (such as copper, silver, and gold), and oxidized minerals of lead and copper (see **Advantages, Disadvantages, and Limitations**).

The alkali and sulfide or xanthate reagents may be added to the contaminated water by rapid mixing (in a stirred vessel or in-line mixer) followed by mixing in a slowly stirred vessel that allows the precipitate particles to grow and/or flocculate. Alternatively, the slowly stirred vessel may be used for both mixing and flocculation stages. The former process, two-stage precipitation, is generally preferred. In most cases a flocculent aid such as an anionic or cationic polymer is needed to promote flocculation to facilitate subsequent separation.

Once flocculation has occurred, the separation of the precipitate from the water typically takes place by settling in a clarifier. Depending on the point of discharge of the treated water, a final pH adjustment may be required to bring the pH to levels between 6 and 9.

Following its removal by clarification, the precipitate slurry is usually filtered (by a belt press or filter press) to increase the solids content prior to disposal. The filtrate may be returned to the treatment process. The dewatered heavy metal precipitate may be disposed as a hazardous waste. If required, a fixative such as lime/fly ash or portland cement may be added to the precipitate prior to disposal to reduce its permeability and to immobilize the metals.

For hydroxide precipitation of metals from water containing manganese, iron, or chromium, an additional process step is required prior to pH adjustment. These metals must be oxidized or reduced to precipitate them in their least soluble form.

For example, iron and manganese must first be *oxidized* prior to precipitation as hydroxides to produce the least soluble hydroxides of these metals. (Since sulfide precipitating agents also act as reducing agents during the sulfide precipitation step, the iron and manganese need not be oxidized prior to sulfide precipitation.)

On the other hand, chromium (+6), must be *reduced* to chromium (+3) in order for it to be effectively precipitated as the hydroxide in the least soluble form. If sulfide precipitation is used, however, a separate reduction step is not required, since the chromium, like the iron and manganese, is reduced in the process of being precipitated as the sulfide.

As in the case of sulfide precipitation, it may not be necessary to use an oxidation or reduction step prior to the precipitation step if xanthate precipitation is used for chromium, manganese, or iron.

In addition to the hydroxide, sulfide, and xanthate precipitation processes, carbonate precipitation may be advantageous for the precipitation of cadmium and lead (2). The precipitation of these metals by sodium carbonate has proven as effective as hydroxide at a lower pH (7.5 to 8.5 as compared tc 10 or greater) and has been shown to generate a denser, more easily filtered sludge. However, carbonate precipitation is not effective for all metals (a much more limited range than hydroxide) and its use may be limited to ground water containing only lead and/or cadmium. A combination of hydroxide and carbonate precipitation may be effective and allow for a degree of operating pH reduction as well as improve sludge quality. The use of carbonate precipitation would have to be examined in treatability studies (see **Design Criteria**).

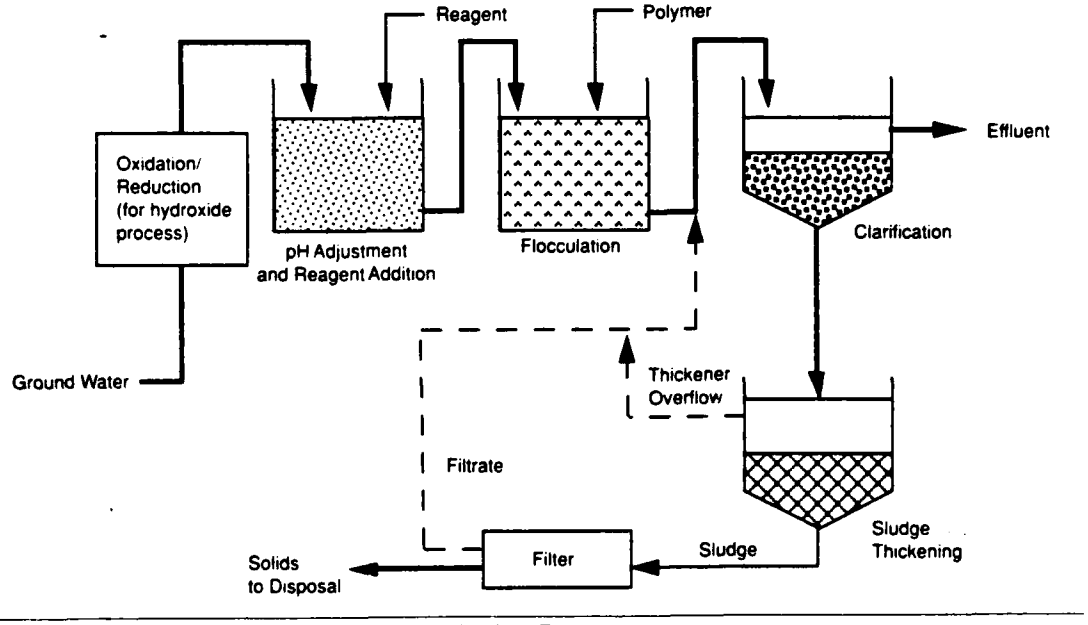


Figure 1. General Schematic of Metals Precipitation Process

Source: Arthur D. Little, Inc.

A schematic of a typical metals precipitation process is provided in Figure 1.

In the 1970s, an electrochemical technology was developed to remove hexavalent chrome and other heavy metals (e.g., arsenic, cadmium, molybdenum, aluminum, zinc, and copper) from water (3). This process uses a flow-through electrochemical cell containing consumable iron electrodes. Insoluble ferrous ions are generated that reduce hexavalent chrome as well as adsorb and coprecipitate heavy metals in the water. This electrochemical process can be used to remove metals at a neutral pH. As with the chemical precipitation processes described above, settling of solids, clarification, and filtration processes may be necessary to remove the solids from the water.

Technology Status

Precipitation of heavy metals as the hydroxide salts of those metals has been practiced as the prime method of treatment for heavy metals in industrial wastewater for many years. More recently, precipitation (usually as the metal hydroxides) has been used in the electronics and electroplating industries as a pretreatment technology for wastewater discharge to a Publicly Owned Treatment Works (POTW).

Within the last 10 years, metal precipitation has been considered for the removal of heavy metals from ground water. In fact, metals precipitation has been selected for treatment of ground water contaminated with heavy metals in many Superfund Records of Decision (ROD) where ground water is to be pumped and treated (see **Application Examples**).

Packaged systems for ground water treatment are available. One vendor of such systems has fabricated and installed about 15 metals precipitation systems (ranging from 3 to 400 gpm) for use in ground water treatment (4).

Types of Contaminants

Chemical precipitation of metals in aqueous waste streams has application to most heavy metals likely to be found in ground water. Examples of metals that have been proven to be effectively removed to less than mg/l concentrations are provided in Figure 2.

The metals shown in Figure 2 have been separated into those metals successfully removed by hydroxide and sulfide precipitation processes, respectively. Xanthate precipitation appears to produce precipitates with roughly the same solubility as sulfides and is therefore likely to have similar results.

In most cases, reduction of the metals listed in Figure 2 to concentrations of less than 1 mg/l would allow for discharge of the treated ground water to a POTW or as a point discharge under a National Pollution Discharge Elimination System (NPDES) permit.

Applications

Metals precipitation is widely used to meet NPDES requirements for the treatment of heavy metal-containing wastewaters. In many cases, metals precipitation may also be used as a pretreatment step prior to discharge of the wastewater to a POTW.

Because of its success in meeting requirements for discharge of treated wastewater, metals precipitation was recognized as having potential for use in remedial activities such as ground water treatment. Precipitation (combined with sedimentation, and/or flocculation and filtration) is becoming the most widely selected means for heavy metals removal from ground water in pump and treat operations. Although there has not yet been extensive experience with this process for ground water treatment, it has been selected as the method of choice for heavy metals removal from ground water in an increasing number of Environmental Protection Agency (EPA) RODs (see **Application Examples**).

In most known applications, metals precipitation is used in conjunction with other technologies to achieve required discharge limitations—particularly with respect to ground water treatment (see **Interface with Other Technologies**).

An additional application of metals precipitation is being explored for the removal of metals (naturally occurring or contaminants) from ground water prior to treatment for removal of organic contaminants. In ground water remediations involving air stripping or ultraviolet-catalyzed oxidation (UV/Ox), it has been found that the presence of iron and/or manganese often

Metals Effectively Removed by Chemical Precipitation to < mg/l Concentrations

Hydroxide Precipitation	Sulfide Precipitation
Cadmium	Arsenic
Chromium (+3)	Cadmium
Nickel	Copper (+1,+2)
Zinc	Chromium (+3, +6)
Manganese	Iron (+2,+3)
Copper (+2)	Lead
Tin (+2)	Mercury
Iron (+3)	Nickel
	Silver
	Tin (+2)
	Zinc

Source: Arthur D. Little, Inc.

Figure 2. Metals Mitigated

causes fouling of process components with precipitated metal scale. In addition, the iron and manganese also increase the oxygen demand in the UV/Ox system. Metals precipitation is being used for pretreatment of ground water to remove the metals prior to further treatment (see **Application Examples**).

Advantages, Disadvantages, and Limitations

Advantages of metals precipitation include:

- The technology is proven—it has long been used for the removal of metals from industrial wastewaters and more recently used (to a much more limited extent) in ground water treatment applications; and
- The metals precipitation process is relatively simple.

Disadvantages of metals precipitation may include:

- As with any pump and treat process, if the source of contamination is not removed (as in metals adsorbed to soil), treatment of the ground water may be superfluous;
- Reagent addition must be carefully controlled to preclude unacceptable concentrations in treatment effluent;
- Efficacy of system relies on adequate solids separation techniques (e.g., clarification, flocculation, and/or filtration);
- Process may generate toxic sludge requiring proper disposal;
- Process can be costly depending on reagents used, required system controls, and required operator involvement in system operation;
- Dissolved salts are added to the ground water as a result of pH adjustment; and
- Polymer may be added to the water to achieve adequate settling of solids. The toxicity of this polymer may need to be addressed.

The latter two issues may require that the ground water be treated further (e.g., by ion exchange, carbon adsorption, or biotreatment) before it can be discharged or reinjected.

Although metals precipitation is widely used with success for wastewater treatment, treating ground water is complicated by:

- Typically lower concentrations of contaminants;
- Potential for presence of naturally occurring compounds (e.g., complexing agents, ligands, and other organic matter) that may interfere with metal precipitation; and
- Variations in metal concentrations over time.

The relative advantages and disadvantages (or limitations) of use of the hydroxide, sulfide, and xanthate processes are summarized in Figure 3.

The solubility of the heavy metal carbonates and hydroxides may be low enough to meet NPDES requirements for p[illegible]t source discharge or for pretreatment for discharge to a POTW

	Hydroxide Precipitation	Sulfide Precipitation	Xanthate Precipitation
Advantages	• Lower capital and operating costs • Much greater industry experience • Fewer safety-related problems in treatment operations than sulfide	• More complete heavy metal removal than hydroxide; higher quality effluent achievable • Lower pH is required for efficient removal compared to hydroxide • Smaller sludge volume than hydroxide • Solids concentration in precipitate sludge usually higher than hydroxide	• More complete heavy metal removal than hydroxide • No residual sulfide in treated water or potential for hydrogen sulfide gas
Disadvantages	• Will not achieve as high of removal efficiency as sulfide or xanthate precipitation • Not all heavy metal hydroxides have the same optimum pH for precipitation • Greater sludge volume than sulfide • Requires careful control of pH to retain minimum metal solubility • Sludge may be difficult to dewater	• Higher capital and operating costs than hydroxide • Potential for toxic hydrogen sulfide gas emissions • Potential for residual sulfide in treatment effluent • Soluble sulfide process may result in odor problem	• Higher capital and operating costs than hydroxide or sulfide • Greater sludge volume than hydroxide or sulfide

Source: References 1 and 5

Figure 3. Relative Advantages and Disadvantages of Precipitation Methods

(generally mg/l concentrations). However, the solubilities of most of these heavy metal carbonates or hydroxides will not allow sufficient heavy metal reduction to meet drinking water standards, which are typically required for ground water recharge (see **Regulatory Issues**).

Precipitation of heavy metals as sulfides or xanthates may be necessary to meet treatment criteria in the µg/l concentration range. Additionally, sulfide or xanthate precipitation may be required for the removal of some heavy metals such as arsenic or mercury to meet even mg/l concentration criteria. This is because of the relatively high solubility of these metals at the high pH (9 to 11) necessary for efficient precipitation of other metals in the hydroxide process.

Where the sulfide or xanthate precipitation process is used for treating higher concentrations of heavy metals (greater than 50 mg/l), it may be advantageous from an operating cost standpoint to use hydroxide precipitation first to reduce the load on the sulfide (or xanthate) precipitation system.

Although sulfide precipitation is more efficient in reducing residual heavy metal concentrations, residual sulfide poses a potential problem. The potential for excess sulfide is greatest when soluble sulfide is used in the precipitation process. Excess soluble sulfide in the treated ground water could result in odor or taste problems, or present health or biotoxic hazards. Such water cannot be recharged.

If an "insoluble" sulfide such as ferrous sulfide is used as the precipitating agent (known as the Sulfex® process), the potential for excess sulfide is limited by the solubility of the ferrous sulfide. Even with the low solubility of ferrous sulfide (at a pH of 10 to 11), however, the residual sulfide would be in the 1 to 10 µg/l range, possibly exceeding water quality criteria for marine organisms or drinking water.

Xanthate precipitation is now being investigated as an alternative to sulfide precipitation for heavy metals precipitation from ground water (6). Depending on the xanthate used, it offers the advantage of no detectable residual sulfide in the treated ground water while still achieving residual heavy metal concentrations comparable to those of sulfide precipitation. The xanthate/metal sludge, however, is greater in volume per unit weight of metal removed.

As stated above, there is currently little information relating to actual experiences with using metals precipitation for ground water treatment. Until more operating experience is acquired, this lack of information and data may be considered a limitation when evaluating the potential of metals precipitation for remedial actions.

Interface with Other Technologies

As discussed above (see **Description of Technology**), the precipitation unit operation must be combined with a solids separation step to be effective. Solids separation may be accomplished by a number of methods.

When the concentration of heavy metals is high and hydroxide precipitation is used, a clarification step is typically used to settle and thicken the precipitate. Depending on the particle size of the precipitate, a flocculent might also be needed to improve the settling or filtration characteristics of the hydroxide sludge. A flocculent is usually required for sulfide or xanthate precipitation. A filter may also be required following clarification and thickening for further removal of particulate.

The slurry of thickened precipitate (sludge) is then dewatered to increase the solids content before disposal. Appropriate dewatering techniques include:

- Vacuum filtration;
- Filter press;
- Belt press; or
- Combination of the above.

A fixative such as lime/fly ash or portland cement may be used to reduce sludge permeability and reduce metal mobility.

Normally, recovery and reuse of metals separated from the sludge will not be economical. This is because of the low commercial value of the metals normally found in ground water (such as iron and manganese) and the costs of separating these metals from the sludge (and from the other metals in the sludge). Exceptions to this may be if precious metals such as silver or gold are present.

Once heavy metal contaminants have been reduced to low concentrations by precipitation (such as by sulfide precipitation to the µg/l levels), other metal polishing techniques such as ultrafiltration, reverse osmosis, activated carbon, or ion exchange may be used to further reduce metal concentrations. These processes can reduce concentrations to the ng/l level for metals such as cadmium, silver, and chromium.

Metals precipitation (coupled with solids removal) may either be used alone as a metals removal process or, more frequently, as a pretreatment step for removing metals prior to subsequent treatment for the removal of other contaminants. In addition, metals precipitation may be used to remove iron (or other

metals species that naturally occur in ground water) to prevent interference in other downstream treatment processes. Examples of these downstream processes are: air stripping or UV/Ox for the removal of volatile organic compounds; or biological treatment for removal of volatile and non-volatile organic compounds.

Design Criteria

To properly size and design a heavy metal precipitation system, the following information is required:

- Chemical analysis of the ground water; and
- Identification of specified treatment requirements (allowable concentrations of heavy metals in effluent).

Bench-scale treatability tests should be conducted to determine operating parameters and characteristics such as:

- Reagent selection;
- Optimum pH for maximum heavy metal removal;
- Retention time (typically 20 to 40 minutes);
- Flow rate;
- Temperature;
- Reagent dosage rates;
- Mixing requirements;
- Flocculent (polymer) selection;
- Suspended solids;
- Filter cloth sizing and selection;
- Precipitate settling and filtration rates;
- Sludge volume; and
- Sludge characteristics.

Depending on the size or capacity of the precipitation system being designed, pilot-scale testing may be desirable for designing and sizing the system with greater accuracy.

The control of pH in hydroxide processes is a critical design element. Minimum metal solubilities are typically obtained in a range from pH 9 to 11. However, once the minimum solubility is reached, changes in the pH (lower *or* higher) may result in dramatic increases in solubility of the metal hydroxide (7).

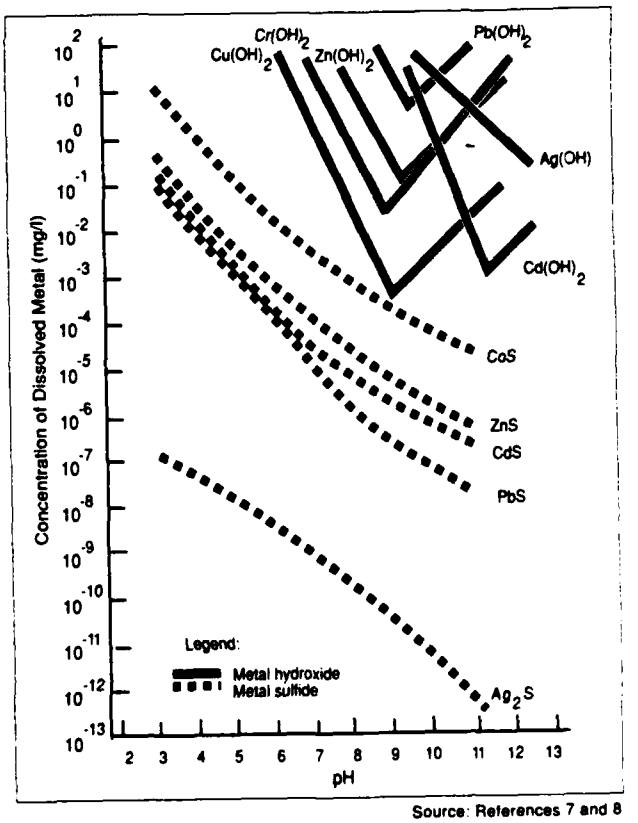
A lower pH (typically 8 to 10) may be used in sulfide or xanthate processes and still achieve lower heavy metal solubilities. In the sulfide and xanthate processes, the metal precipitate solubility will continue to decrease with an increase in pH.

These solubility characteristics are illustrated in Figure 4.

In a sulfide precipitation system, when sufficient sulfide reagent is being added, the major limitations to maximum efficiency are adequate retention time for precipitate formation and adequate precipitate removal. Care must be taken to limit excess soluble sulfide to as low a concentration as possible to preclude its carryover into the effluent.

The separation and physical removal of precipitated solids is critical in achieving desired treatment efficiencies due to the presence of small particles often formed in the precipitation step (particularly with dilute solutions of heavy metals). Adequate physical separation processes such as clarification, flocculation, and filtration will need to be factored into the design.

Variations in feed-water composition (e.g., metal ion concentration) are to be expected when treating ground water. To mini-



Source: References 7 and 8

Figure 4. Solubility Characteristics of Metal Hydroxides and Sulfides

mize the effect of these variations, a feed storage tank should be sized to allow for relatively uniform feed to the metals precipitation system.

Chemicals Required

Chemicals commonly used in the precipitation of metals from water include:

- Sodium, potassium, calcium, or magnesium hydroxides for hydroxide precipitation and pH adjustment;
- Bisulfite solution (e.g., sodium bisulfite) to reduce chromium prior to treatment using hydroxide precipitation;
- Sodium sulfide, hydrogen sulfide, or ferrous sulfide for sulfide precipitation;
- Cellulose or starch xanthates for xanthate precipitation;
- Sodium carbonate for carbonate precipitation of certain metals (e.g., lead and cadmium);
- Aluminum sulfate (alum) or ferrous sulfate to improve flocculation of metal hydroxides and enhance precipitation;
- Organic anionic or cationic polymer (often proprietary) as a flocculating agent to enhance agglomeration and settling of metal precipitates;
- Sulfuric acid to neutralize treated and clarified water; and
- Hydrogen peroxide or potassium permanganate as oxidizing agents (especially for iron and manganese) as well as to kill bacteria.

Implementation Considerations

Standard equipment such as tanks, pumps, mixers, clarifiers, and filters, comprise metals precipitation systems. Relatively simple control systems can be incorporated for reagent addition and flow control. Typically, all equipment is readily commercially available and easily implemented or constructed.

Package metals precipitation systems are available for design flow rates of up to 1,500 gpm (4). These package systems are mounted on skids and contain all system equipment including:

- pH control system;
- Reagent addition systems;
- Treatment tank;
- Mixer;
- Clarification system;
- Sludge thickening system;
- Filter press; and
- Effluent holding tank.

Skids will typically be up to 20 feet long and 5 to 8 feet wide. A packaged system with a design flow rate of 20 gpm will require approximately 400 ft^2 of skid space. A 65 gpm system will require about 1,000 ft^2 of skid space.

Such package systems include plumbing and electrical wiring adequate for connection to on-site water and power supplies. A 480-volt, 3-phase power supply will typically be required.

At higher design flow rates, individual components may become very large. For example, a metals precipitation system designed for 100 gpm operation includes a 12,000-gallon equalization tank; a 6,000-gallon mixing tank; a 20,000-gallon clarifier, and an 800-gallon thickener tank (5). Agitation in the mixing tank will require about 6 hp per 1,000 gallons.

If design flow is such that tanks in excess of 40,000 gallons are required, field erection of the tanks will usually be necessary. This may increase construction time by several months.

The use of chemical reagents (e.g., sodium or magnesium hydroxides, sodium or ferrous sulfides) will require attention to safety issues associated with their use and handling. Safety issues associated with the use of sulfides are especially critical due to the potential for generation of toxic hydrogen sulfide gas.

Quality Control/Operation and Maintenance Considerations

The ultimate effectiveness of the metals precipitation process depends primarily on the design of the system, which, in turn, is based on the heavy metal analysis of the feed water and the required heavy metal effluent limitations. Some correction is possible during operation of the process if necessary, however, to maintain its efficiency.

Flow, chemical addition, and agitation rates must be monitored on a continuing basis. During startup, samples of the influent and effluent should be taken frequently for analysis to confirm removal efficiency and to optimize, if necessary, chemical addition rates and other process conditions. After operating

conditions are established, periodic (i.e., once per shift or once per day) sampling and analysis will be required.

If the heavy metal precipitate solids are being removed effectively with the hydroxide precipitation process, but the dissolved metals concentration is still too high, a sulfide or xanthate precipitation process should be added.

With constant operating conditions (i.e., flow, chemical addition, temperature, etc.) and feed-water composition, the metals precipitation system should provide a constant removal efficiency—only requiring periodic analysis of the effluent to ensure proper heavy metal removal efficiency.

Among the primary metals precipitation operation and maintenance considerations are:

- Metal precipitation systems will typically require a full-time operator to monitor their performance and maintain the optimum feed of reagents. If the metals precipitation system is one of several unit operations (such as UV/oxidation or biological treatment), it may not be necessary that this full-time operator be completely dedicated to the metals precipitation system alone;

- According to one vendor (4), an oxidation-reduction potential (ORP) probe connected to an ORP controller is used to continually monitor iron and manganese ion concentrations. Based on these concentrations, the controller will adjust the rate of hydrogen peroxide (or other oxidant) to ensure that iron and manganese are sufficiently oxidized to form the hydroxide precipitates;

- Probes (ORP and pH) used to monitor the progress of metal oxidation and hydroxide formation should be cleaned periodically (e.g., once per week);

- Provisions for removing the precipitate from the filter press and replenishing treatment chemicals should be made. The frequency of precipitate removal may be once per day (4). Treatment chemicals may be replenished weekly (4);

- Metal ion concentrations will typically not fluctuate significantly in ground water. The concentrations usually drop slowly as the treatment progresses and thus have little or no effect on precipitation efficiency (4) and;

- Normal temperature fluctuations have little effect on precipitation efficiency (4).

Residuals Generated

After initial settling, metals precipitates (sludges) are very high in water content—often having a solids content of only a few percent. After additional settling or thickening, however, the solids concentration will usually increase to about 8 to 10 percent. To reduce the volume of residuals requiring disposal, filtration is usually used to increase the solids content to about 30 percent.

The disposal of sludges resulting from precipitation of metals from ground water may be subject to Land Disposal Restrictions (LDR) (see **Regulatory Issues**). Such sludges may be drummed and disposed of as a hazardous waste or, if required, treated by fixation or stabilization with lime/fly ash or portland cement.

Regulatory Issues

Regulatory requirements will vary depending on the specific application of the metals precipitation process. Generally, NPDES permits will be required if the effluent of the system is discharged to surface water. If the effluent is to be discharged or transported to a POTW, the regulations of the receiving POTW will apply.

Recharge of the treated effluent will require proof that the discharge meets established, site-specific treatment standards based on Applicable or Relevant and Appropriate Requirements (ARARs) or risk and/or hazard-based criteria. Typically, recharge will require that drinking water standards be met. Note that EPA will not allow water containing sulfides or water with a high pH to be reinjected.

Although beyond the scope of this Tech Data Sheet, it should be mentioned that pump and treat methods of ground water remediation are complex from technical and regulatory standpoints. There are a number of EPA documents that address pump and treat issues. A good overview is provided in *Basics of Pump-and-Treat Ground-Water Remediation Technology* (9).

The disposal of metal precipitate sludges will have to adhere to regulations. In some cases, the sludges may be dewatered to the maximum extent possible, drummed and disposed of in a secure landfill. If the residuals exhibit the Resource Conservation and Recovery Act (RCRA) waste toxicity characteristics, they will require treatment in accordance with the appropriate LDR (10).

Sludges may be stabilized or fixed with lime/fly ash or cement. If proven that the fixed sludges do not exhibit the toxicity characteristic through performance of the Toxicity Characteristic Leaching Procedure (TCLP), it may be possible to landfill them as a nonhazardous solid waste.

Feasibility Study (FS) Criteria Ranking

The use of chemical precipitation as a means for removing heavy metals from ground water has been rated with respect to the ability of the process to meet performance criteria. These ratings are relative to other metal removal technologies. The results of this rating are summarized in Figure 5.

Although metals precipitation can remove toxic metals from ground water, a factor that negatively impacts the ranking of the technology is that metal-containing sludges are generated during the process. This factor affects all of the criteria shown in Figure 5 with the exception of cost and implementability. Because many available ground water treatment technologies (e.g., carbon adsorption and ion exchange) do not destroy the contaminant but transfer it to other media, the rankings given to metals precipitation are neutral.

Whether this process can meet efficiency requirements over the long term depends on the residual heavy metal concentrations allowable in the treated ground water. More careful supervision and higher capital and operating costs will be required if treatment to drinking water standards (µg/l concentrations) is necessary than if treatment to mg/l concentrations of heavy metals is required.

The short-term effectiveness of this process is considered medium because while the heavy metals will be removed from the ground water, some of the heavy metals may have been adsorbed to soil and could therefore reenter the ground water. In addition, if the soluble sulfide process is used, there are potential worker safety issues because of the potential for generation of toxic hydrogen sulfide gas.

Criteria	Ranking
Effect of reducing the overall threat to human health and the environment	○
Compliance with Applicable or Relevant and Appropriate Requirements (ARARs)	○
Long-term effectiveness and permanence	○
Reduction of toxicity, mobility, or volume	○
Short-term effectiveness	○
Implementability	◐
Cost	◐
State and community acceptance	◐

Favorable ◀——▶ Unfavorable

Source: Arthur D. Little, Inc.

Figure 5. FS Criteria Ranking

The implementability of metals precipitation is ranked neutral. In terms of equipment availability and simplicity, implementability is favorable compared to ion exchange or reverse osmosis, for example. However, depending on the scale of treatment, if the equipment is too large for a trailer, field erection may be necessary. Such field erection may take weeks or months to complete.

Key Cost Factors

Capital and operating costs vary greatly over the wide range of precipitation systems in use. The primary capital cost factor is design flow rate. The primary factor affecting operating cost is labor.

Capital costs of 20 gpm and 65 gpm packaged metals precipitation systems are approximately $85,000 and $115,000, respectively (4). Operating costs (excluding sludge disposal) are typically in a range from $0.30 to $0.70 per 1,000 gallons of ground water containing up to 100 mg/l of metals (5).

Operating costs for the removal of manganese (initial concentration of 6 mg/l) and iron (initial concentration of 15 mg/l) from ground water to levels of 0.04 mg/l and 0.3 mg/l, respectively, have been estimated at approximately $0.40 per 1,000 gallons of ground water (4). These operating costs assume 2 hours per shift of operating labor.

Costs reported for the removal of hexavalent chrome in ground water (at removals greater than 90%) using the electrochemical process described earlier have been estimated at $0.60 per 1,000 gallons of ground water (3).

For budgetary purposes, sludge disposal may be estimated to increase operating costs by approximately $0.50 per 1,000 gallons of ground water treated (4). Actual sludge disposal costs (including fixation and transportation) have been estimated at approximately $300 per ton of sludge (11).

Costs for performing a laboratory treatability study for metals precipitation may range from $5,000 to $20,000. Depending on the degree of uncertainty or other requirements, a pilot or field demonstration may be needed. Associated costs may range from $50,000 to $250,000 (based on scale, analytical requirements, and duration).

Points to Remember

The following points are essential to consider in the design of a chemical precipitation system to remove heavy metals from ground water:

√ At a minimum, bench-scale precipitation and settling/ filtration tests should be conducted using actual samples of ground water;

√ The system should be designed with sufficient flexibility (e.g., provisions for flocculent, sulfide, or xanthate addition) to correct for any operating deficiencies found in the system; and

√ The *availability* and cost of heavy metal precipitate sludge disposal services must be determined.

Application Examples

Recent examples of the use of metals precipitation in ground water treatment are described in Figure 6.

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14. Personal Communications with Andy Law and Tanwir Chaudhry, NCEL, 1992.

15. Gilson Road Groundwater Treatment Facility, Nashua, NH, 1985, *Operation and Maintenance Manual.*

16. *Pilot-Scale Treatability Study Report for the Winthrop Land-fill Site*, 1990.

Points of Contact

Additional information regarding technical and practical aspects of metals precipitation may be obtained from:

- Tanwir Chaudhry (805)982-1609 or Andy Law (805)982-1650, Naval Civil Engineering Laboratory (NCEL), Code L71, Port Hueneme, CA.

- Mark Bricka, U.S. Army Corps of Engineers Waterways Experiment Station, CEWES-EE-S, 3909 Halls Ferry Rd., Vicksburg, MS 39180-6199, (601)634-3700.

- John Fringer, NEESA, Code 112E4, Port Hueneme, CA. (805)982-3684.

- Armand Balasco, Arthur D. Little, Inc., Cambridge, MA, (617)498-5390.

Site	Contaminants	Discussion	Ref.
Coakley Landfill, New Hampshire	Organics and Metals Selected examples of metals: Cr - 330 ug/l Ni - 122-200 ug/l As - 10-90 ug/l Fe - 21-280 mg/l	A 1990 ROD for this site describes a selected remedial approach for ground water consisting of pretreatment of ground water by hydroxide precipitation with lime. Pretreated ground water would then be air stripped for removal of volatile organic compounds (VOCs). Treated ground water is to be recharged during periods of low ground water. In periods of high ground water, discharge of the treated water will be to surface water. For surface water discharge, additional treatment of activated carbon adsorption or biological degradation may be required to meet ambient water quality criteria for organics. For recharge, treatment criteria include: Cr - 50 ug/l; Ni - 100 ug/l; As - 50 ug/l	12
Stringfellow Acid Pit Site, California	Organics and Metals Selected examples of metals: Cr - 1.5-270 mg/l Cd - 0.32-9.3 mg/l Zn - 2.2-300 mg/l Cu - 1.7-20 mg/l	The alternative recommended (in 1984) for the treatment of this ground water includes pretreatment for the removal of metals and organics followed by transport of the treated water to a local POTW. Pretreatment consists of hydroxide precipitation of the metals with lime. Precipitation and solids separation is followed by activated carbon adsorption for organics removal. Pretreatment criteria for metals include: Cr - 0.5 mg/l; Cd - 0.11 mg/l; Zn - 2.61 mg/l; Cu - 2 mg/l	13
Potential Application for All Metal-Contaminated Ground Water Sites	Iron	NCEL sponsored an investigation by Illinois State Water Survey into the use of potassium hydroxide and air (or oxygen) to precipitate ferric hydroxide. Bench-scale tests conducted at a pH of 8.5 and pilot-scale tests conducted at a pH of 9.5 resulted in reducing levels of iron from 50 to 100 ppm to less than 1 ppm. On the full-scale, this process will be used as a pretreatment step for ground water that will be further treated by UV-catalyzed oxidation for removal of organics. Removal of the iron will result in a reduction of oxygen demand in the catalytic oxidation step and will prevent fouling of the UV reactor system with precipitated iron scale.	14
Gilson Road Ground Water Treatment Facility, Nashua, New Hampshire	Organics and Metals Selected metal influent concentrations: As - 0.04-1.7 mg/l Cd - 0.005-0.1 mg/l Pb - 0.01-0.5 mg/l Fe - 18-640 mg/l Mn - 3-115 mg/l	This sytem was brought on line in 1985–1986. The primary contaminants in ground water are organics. The organics (which average about 7 mg/l) are removed by a combination of processes that include air stripping (with incineration of offgas) and biological treatment. The metals (primarily iron and manganese) are removed by oxidation and precipitation prior to the air stripping to prevent scaling in the air stripper. The system was erected in the field to accommodate flows averaging about 280 gpm. There are no metals treatment criteria for recharge to on-site recharge trenches. Air oxidation (at a pH of about 9.5) plus precipitation, flocculation, settling, and filtration reduce the average influent concentrations of iron and manganese of 20 mg/l to about 0.1 mg/l in the filtered effluent. Lime slurry is used for pH adjustment/metal precipitation.	15
Winthrop Landfill, Winthrop, Maine Pilot Treatability Study/ Demonstration	Organics (Solvents) and Metals Influent concentrations of metals: As - 0.1-0.8 mg/l Ni - 0.04 mg/l Zn - 0.2-0.6 mg/l	In this pilot test (1990), removal of metals from the ground water by precipitaiton was carried out for two purposes. First, it was necessary to reduce the concentration of arsenic, nickel, and zinc in the ground water to meet NPDES limits for discharge to surface water. Secondly, it was necessary to remove iron in the ground water to less than a 1 mg/l residual to improve the effectiveness of the UV/Ox system used for the destruction of the organic contaminants. Potassium permanganate was used to oxidize the iron prior to precipitation using sodium hydroxide at a pH of 11.0 to 11.4. An anionic polymer was used as a flocculant aid prior to solids separation in the clarifier. Pretreatment criteria for metals were met for surface water discharge. Criteria achieved were: 0.05 mg/l arsenic, 0.04 mg/l nickel, and 0.18 mg/l zinc.	16

Figure 6. Application Examples

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In Situ Stabilization/ Solidification

Port Hueneme, CA 93043 NEESA Document No. 20.2–051.2 February 1992

Introduction

NEESA's Remedial Action (RA) Tech Data Sheets are concise, factual, and up-to-date summaries of practical aspects of hazardous waste RA technologies. Where required for clarification, specific technical information is included.

Purpose and Audience

The Tech Data Sheets are designed to:

- Disseminate practical, implementation-related information such as performance criteria, quality control requirements, applications examples, lessons learned, and cost data to minimize the potential for design and construction problems;
- Enable Remedial Project Managers (RPMs) to evaluate technologies recommended in Feasibility Studies (FSs);
- Aid RPMs in writing an RA Delivery Order;
- Help Navy Engineering Field Division (EFD) Remedial Design personnel to write a Statement of Work (SOW) or RPMs to review remedial project design plans; and
- Enable field personnel such as Project Superintendents, Engineers in Charge, On-Scene Coordinators (OSCs), and Resident Officers in Charge of Construction (ROICCs) to become familiar with a technology at a site they will be overseeing.

Description of Technology

Stabilization and solidification waste treatment processes involve the mixing of specialized additives or reagents with waste materials to reduce physically or chemically the solubility or mobility of contaminants in the environmental matrix. The term "stabilization" is used to describe techniques that chemically modify the contaminant to form a less soluble, mobile, or toxic form without necessarily changing the physical characteristics of the waste. Solidification refers to a technique for changing the physical form of the waste to produce a solid structure in which the contaminant is mechanically trapped. Many stabilization and solidification processes overlap, and the common terminology to describe either or both processes is stabilization/solidification (S/S).

Goals of the application of S/S techniques include improving the physical and handling characteristics of liquid or semi-liquid contaminated materials, reducing contaminant solubility, and decreasing the rate of transfer of the contaminant. It is important to emphasize that typically S/S does not provide for contaminant destruction and therefore may not be classified as a permanent solution.

S/S processes have been used for the treatment of heavy metal-containing industrial waste treatment sludges prior to their ultimate disposal to minimize the potential for future leaching of the heavy metals into the environment. More recently, S/S has been evaluated as a lower cost treatment alternative for contaminated soils and sediments. It is the remedial application that is the focus of this Tech Data Sheet.

S/S systems can be used to treat contaminated soil or wastes in place (in situ) or can be employed to treat excavated wastes externally for their subsequent disposal. **This Tech Data Sheet specifically addresses practical implementation considerations relating to in situ treatment with no excavation of untreated or treated materials.**

The primary mechanisms of in situ S/S processes include (1):

- Removal of Free Liquid—involving the addition of a solid to the waste to take up any free liquid. Examples of such solids include activated carbon, sawdust, gypsum, clays, and silicates;
- Lime/Fly Ash Pozzolan Reactions—involving a reaction between non-crystalline silica in fly ash and lime to produce a low-strength solid in which contaminants are physically trapped;

- Pozzolan/Cement Reactions—which employ a pozzolan such as fly ash and cement to produce a relatively high-strength waste/concrete matrix in which contaminants are trapped;
- Vitrification—typically involving the addition of chemicals (silica, borax, soda ash, etc.) and the application of electrical energy to produce a solidified product.

Of these, the processes with the greatest potential effectiveness at the lowest cost are those involving the addition of lime, pozzolans, and/or cement. The remainder of this Tech Data Sheet focuses on these systems.

The quality and type of additive or binder system will be selected based on waste and site characteristics as well as the desired characteristics of the treated material.

Of all the factors that impact the success of in situ S/S in the treatment of contaminated soil, the addition of the reagent and thorough and uniform mixing of the reagent and the soil are the most critical (see "Field Implementation Considerations").

Surface infiltration barriers (caps) and subsurface barriers such as slurry walls may be used in conjunction with in situ S/S (see "Interface with Other Technologies"). An illustrative example of an in situ S/S application with barrier wall and surface cap is provided in Figure 1.

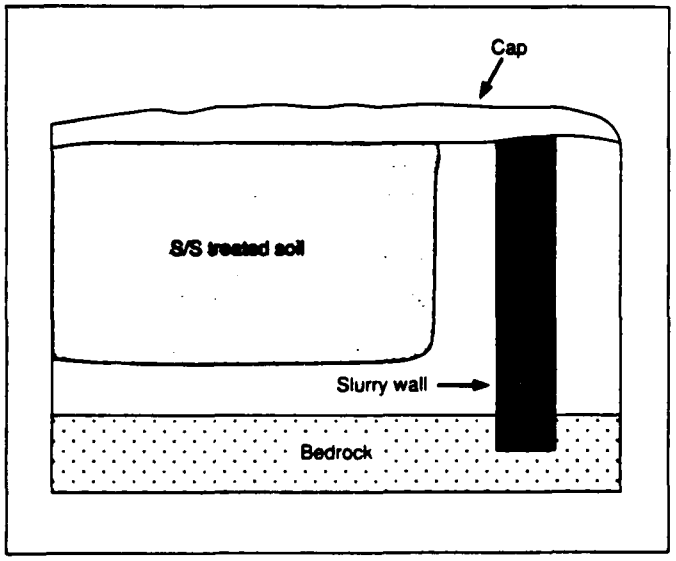

Figure 1. In Situ S/S Application (Cross Section)

Technology Status

S/S technologies have been employed in full-scale surface and in situ applications involving metal-bearing and oily wastewater treatment sludges. The application of S/S for soil and sediment treatment has been a more recent application, par-ticularly with respect to in situ treatment, which is in its relative infancy.

Because of the more recent remedial use of S/S techniques, little is known of long-term effectiveness in terms of fate of the contaminant or integrity of the solid product.

In situ S/S has not yet been employed in remedial actions at Navy sites. Consequently, there have been no statements of work, plans and specifications, or cost estimates prepared for contracting efforts to implement the technology at Navy sites.

An in situ S/S process was selected for participation in the Demonstration Program phase of the Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) Program. This Demonstration Program is designed to develop engineering and cost data on selected technologies to provide for an assessment of technology performance, reliability, and cost. Preliminary results of this demonstration (see "Application Examples") indicate that the technology has the potential to be practically and cost effectively employed.

Contaminants Mitigated

S/S has proven most useful for the treatment of inorganic-containing waste materials including heavy metals. Its utility for the treatment of many organic wastes appears to be limited due to the potential for detrimental chemical interactions, the volatility of the organic compounds, limited success in reducing organic mobility, and competition from other available technologies.

S/S techniques have been demonstrated for use in the control of a variety of contaminants including metals (i.e., chromium, lead, aluminum, nickel), asbestos, polychlorinated biphenyls (PCBs), and radioactive and oily wastes. Specific limitations are described below.

Despite the demonstrated use of S/S techniques, there are few data available to confirm the long-term effectiveness of the technology.

As the technology develops, additives are being used in conjunction with the setting reagents to improve the binding of the contaminant to the solid product and/or to provide for the transformation of the contaminant into a less toxic or mobile form. Use of these additives may extend the S/S application to a wider range of contaminants, including many organics.

Applications, Advantages, and Limitations

In situ S/S may provide a method for the treatment of contaminated soil, which may not be economically or technically feasible to excavate. Examples of such uses include the treatment of:

- Contaminated soils under or adjacent to existing structures;
- Contaminated soils in areas of ongoing industrial activities; and
- Contaminated soils for which excavation would increase the potential for the spread of contamination to groundwater.

Other situations for which in situ S/S may be well-suited include:

- Those that allow for the addition of large amounts of bulk solid reagent(s) to ensure adequate contact between the reagent and the contaminated soil; and
- Contaminated sites with homogeneous chemical and physical characteristics.

The in situ S/S process may represent a quick-to-implement, low-cost remedial alternative. Generally, the additives (reagents or binders) for S/S applications are readily available and relatively inexpensive. In addition, there are no excavation and related material handling costs. Also, fewer associated health and safety measures are required.

Indications are that in situ S/S may provide a short-term remedial solution. Because in situ S/S is a relatively new process, data reflecting the long-term quality of the treated matrix are not available, and therefore definitive conclusions regarding long-term effectiveness cannot be drawn.

Despite the potential favorable applications of in situ S/S, there are several limitations, which are illustrated in Figure 2 and discussed below.

Potential compatibility problems between contaminants and inorganic S/S reagents arise when the contaminants include phenols, halides, cyanides, or sulfates (2). Salts have been shown to cause swelling and cracking in solidified matrices (3). The presence of oil and grease may negatively affect the rate of curing depending on their concentrations in the contaminated soil. Compatibility tests between the reagent and contaminants should be performed to determine potential effects on S/S product structural integrity and the leaching of contaminants out of the treated matrix.

Although S/S techniques (ex situ and in situ) have been employed in the treatment of oily and PCB-contaminated wastes, their use in the treatment of wastes contaminated with other, typically more volatile, organic compounds may be limited. Specific concerns in the application of S/S to these other organics include:

- The organic may act as a solvent for some organic-based S/S reagent systems (3);
- The organics may inhibit the setting or curing reactions necessary to generate an acceptable S/S product (3);
- The potential for generation of air emissions resulting from the volatilization of the organic compounds during reagent and soil mixing and reaction operations; and
- The ability of S/S to reduce the mobility of many organics.

Additional limitations or disadvantages to the use of in situ S/S in remedial activities include: an increase in volume of the

Source	Potential Limitations
Waste characteristics	• Chemical incompatibility between reagent and contaminants • Technology not yet proven effective with a range of organic wastes • Presence of volatile compounds could result in air emissions requiring control • Nonuniform contaminant profiles complicate treatability testing and design
Subsurface characteristics	• Large boulders or debris may preclude the use of available in situ mixing equipment • Soil pH and moisture content may dictate pretreatment and treatment requirements • Inhomogeneities in soil type complicate treatability testing and design
Surface characteristics	• Potential site impact of waste volume increase due to treatment • Application of technology requires considerable site access
Climate	• Potential detrimental effect on product due to wet/dry and freeze/thaw cycling • High and low temperatures (>150°F, <40°F) may affect curing and settling processes
Product management	• Leaving product in place will require increased assurance (i.e., site monitoring) that environmental protection is maintained over the long term • Few established methods to ensure product quality over the long term • Relative newness of technology in remedial applications does not provide for data reflecting long-term performance of the technology

Figure 2. Potential Limitations of In Situ S/S

treated matrix due to the addition of large quantities of reagents and difficulties in assessing and maintaining quality assurance during subsurface reagent delivery and mixing operations (see "Quality Assurance Requirements").

In situ S/S vendors may employ proprietary chemicals or reagent systems. It is difficult for Navy personnel to write specifications for the testing and implementation of remedial actions involving the use of proprietary materials. The Navy discourages the use of proprietary reagents unless their chemical composition is known. It should be stressed to the vendor that the Navy will keep the identity of the proprietary reagent confidential. But, since the Navy is responsible for the long-term liability of the site, it must know what chemicals are to be monitored in the soil and groundwater. Breakdown products of the reagent must also be considered.

One of the primary concerns with the use of in situ S/S is the determination and assurance that effective treatment has taken place. Measures of short-term and long-term effectiveness are difficult since the treated materials remain in place in the subsurface. There are currently no reliable methods to allow for a thorough determination of effectiveness.

Many of the potential limitations may be addressed by conducting treatability and pilot tests prior to design and implementation of the remedial action (see "Design Criteria"). Many of these tests may provide for an assessment of short-term effectiveness, but do not necessarily address long-term effectiveness.

Considerable up-front work needs to be completed prior to design and implementation of in situ S/S techniques. Among the required efforts are:

- Regulatory coordination;
- Conduct of treatability study (see "Design Criteria"); and
- Pilot and/or demonstration testing.

The extent of the actual up-front requirements will be site-specific, but they have the potential to significantly increase both the cost and the time required for the total remedial activity.

Interface with Other Technologies

To ensure the permanence of in situ S/S as a remedial solution, the technology may be used in conjunction with other control methods and technologies. At a minimum, due to the decreased permeability of the treated soil matrix, run-off control at the site may be required. In addition, the use of surface infiltration barriers or caps over the treated wastes may be required to provide for:

- Maintenance of proper levels of moisture in the treated matrix to maintain maximum integrity;
- Protection of the treated wastes from the freeze/thaw cycle; and
- Minimization of rain infiltrating into and through the treated matrix.

Subsurface barriers such as slurry walls or geomembranes may be used to surround the treated site to protect the treated matrix from water infiltration as well as to provide additional long-term protection against the contamination of groundwater.

Design Criteria

Few specific design criteria exist for the implementation of in situ S/S in all situations. Rather, these design criteria are developed throughout the remedial response. A typical pathway required to implement an in situ S/S technology to meet remedial requirements is shown in Figure 3.

Figure 3 and the the following discussion relates to a typical remedial response—site-specific requirements will dictate the exact pathway to be taken in any given situation. It is important to emphasize that regulatory coordination must be maintained throughout the entire process.

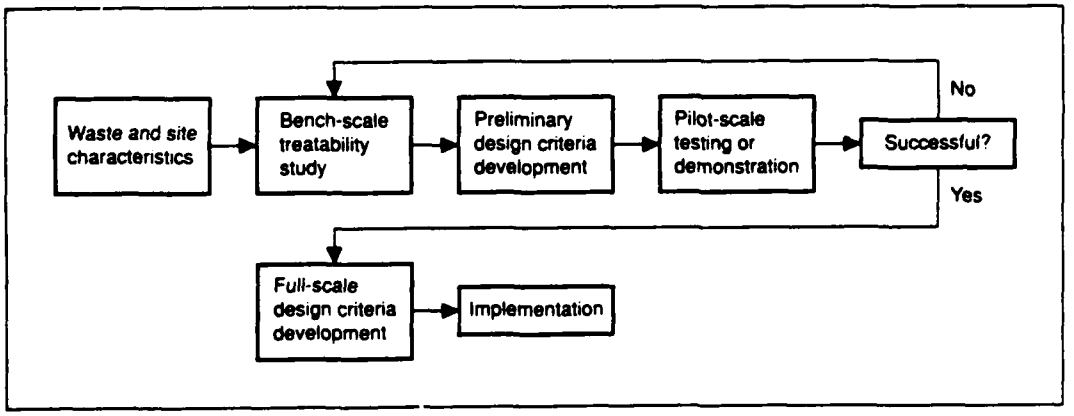

Figure 3. Implementation Pathway

Waste and site characterization will typically entail activities including:

- Sampling;
- Chemical analyses;
- Identification of regulated contaminants;
- Waste volume determination; and
- Physical and geohydrological assessments.

A treatability study will be performed in order to:

- Assess the site-specific feasibility of in situ S/S;
- Select appropriate reagent (binder) systems;
- Optimize process parameters; and
- Provide a basis for pilot-scale design.

Treatability studies will normally include the following activities:

- Process and reagent (binder) screening (literature review);
- Laboratory screening/ bench-scale testing;
- Process and binder selection; and
- Performance optimization.

Based on the results of the treatability study, pilot testing may be performed. As shown in Figure 3, the results of pilot testing may indicate a requirement to repeat some or all of the activities of the treatability study.

If pilot testing is successful, design criteria may be developed for full-scale implementation. At a minimum, the design criteria will reflect elements including:

- Reagent selection;
- Reagent to waste ratio;
- Soil pretreatment requirements (i.e., watering, dewatering, pH adjustment);
- Methods to be employed for reagent addition and optimum mixing;
- Required curing conditions;
- Methods to assess technology performance (leaching potential and durability);
- Requirements for protection of the treated material from wet/dry and freeze/thaw cycles; and
- Long-term monitoring requirements.

Field Implementation Considerations

Because in situ S/S is employed without the excavation of contaminated soil or the placement of treatment materials, field construction activities may be simpler than those associated with ex situ treatment techniques.

Typical S/S construction activities include:

- Mobilization and site preparation;
- Chemical reagent storage and handling;
- Addition of reagent to contaminated soil;
- Mixing of reagent and soil; and
- Cleanup and closure.

Mobilization will include equipment selection based on the methods selected for reagent addition and mixing as well as the breadth and depth of contamination. Area mixing techniques performed by traditional earth-moving equipment such as backhoes, bulldozers, clamshells, and draglines may be used depending on the size and profile of the contaminated site.

Although feasible, mechanical area mixing is unlikely to result in adequate mixing (3). To address mixing concerns, specialized equipment has been developed to provide for subsurface injection of reagent and in-place mixing. These techniques are described below.

It is important that adequate on-site reagent storage is established to prevent delays in remedial operations. Reagent storage is also critical to provide for protection of the reagent from the environment. Handling of the reagent is an important consideration—equipment must be selected to effectively transport dry bulk solids and liquids as necessary. The use of control equipment is critical to provide for the proper metering of reagent to maintain the desired reagent to waste ratio.

The addition of reagent to the contaminated soil may be accomplished by using pneumatic pumps or dump trucks to distribute the reagent over the contaminated surface or by subsurface injection of the additives.

The most critical aspect of the in situ S/S process is the thorough and uniform mixing of the reagent with the soil. Recently, specialized equipment has been developed that provides for reagent addition and mixing.

One in situ S/S process employs a combination of an auger and caisson as shown in Figure 4. In this process, the reagent is fed into the hollow stem of the auger and injected into the waste as the auger is rotated within the caisson into and out of the soil. As the auger rotates, it provides for mixing of the reagent and soil. As shown in Figure 4, columns of treated material are generated. Positioning for the treatment of additional columns is planned so that the columns overlap, providing for complete site coverage (3). The developer reports that the equipment may be used to a depth of 150 feet (2). Use of this addition and mixing process was recently demonstrated as part of the SITE program.

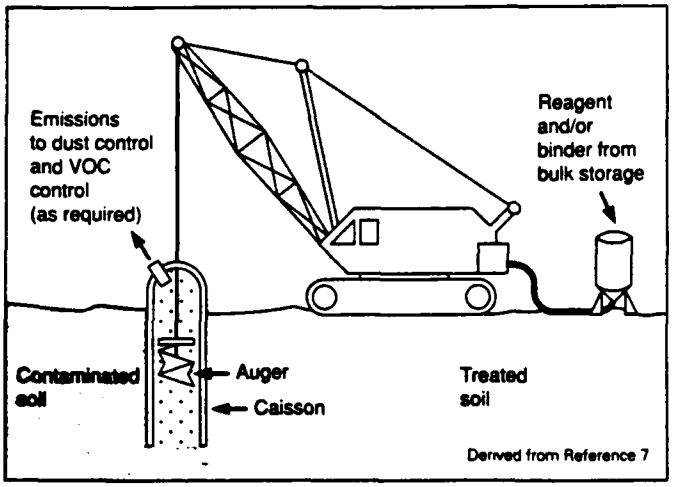

Figure 4. Auger/Caisson In Situ S/S System

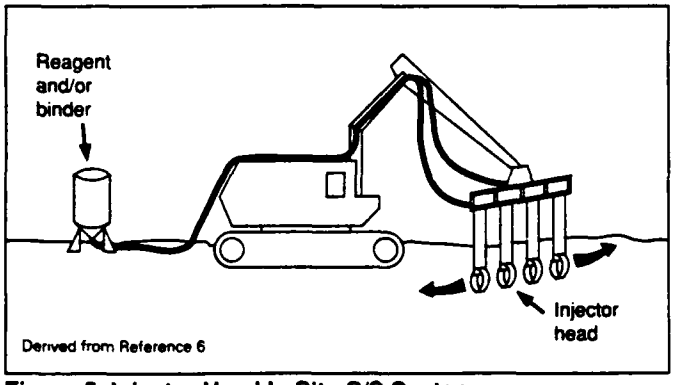

Figure 5. Injector Head In Situ S/S System

A second reagent addition/mixing system, shown in Figure 5, makes use of an injector head installed on a backhoe. The reagent is typically fed pneumatically from a truck to the injector head where it is injected into the soil. Mixing occurs by the back and forth movement of the injector head and the force of the pneumatic delivery (3). Treatment depths are typically less than 18 feet.

Additional demonstrated injector/backhoe techniques include the use of injection and mixing systems employing pneumatic injector tubes outfitted with impellers and augers for mixing (3).

Reagent addition and mixing operations may require the use of air emission control techniques such as dust collectors for particulates and activated carbon adsorption for volatile organic compounds (VOCs). Additional particulate emission control techniques that may be employed include (4):

- Minimization of material handling;
- Erection of portable wind screens;
- Installation of portable surface covers during periods of inactivity; and
- Construction of temporary enclosures.

The most significant post-treatment site cleanup requirements include equipment and personnel decontamination. Specific site closure requirements may vary but will generally include capping of the site with a low permeability (hydraulic conductivity of 10^{-7} or less) layer. In addition, regulatory requirements will dictate activities to monitor air, surface water, and/or groundwater.

Quality Assurance Requirements

Strict quality assurance (QA) measures are critical throughout the process application and most important during addition and subsequent mixing of the reagent with the waste. In ex situ applications, qualitative and quantitative QA measurements can be made during rehandling of the treated waste prior to final disposal. Unfortunately, the ability to make these measurements is difficult during in situ processing. For this reason, QA during in situ S/S applications is best achieved by maintaining a significant level of experienced, on-site inspection and supervision (3).

With respect to on-site activities involved in in situ S/S actions, there are several parameters that can be assessed to maintain QA. For example, parameters that have been shown to affect the mixing of the reagent and waste and thus the ultimate product quality include (5):

- Viscosity of the reagent;
- Permeability of the contaminated soils;
- Porosity of the contaminated soils;
- Distribution of the wastes; and
- Rate of reactions between reagents and wastes.

A number of tests may be used to assess the potential effectiveness of in situ S/S as well as assess the quality of the product. Examples of representative tests, their purpose, and available or applicable criteria are presented in Figure 6. These tests may be conducted during feasibility studies and may be employed with pre- and post-treatment wastes.

The tests listed in Figure 6 represent a small fraction of tests that may be used for in situ S/S applications. The large number of applicable tests presents a significant problem to the remedial designer or engineer. There is no established technical guidance for which tests are best employed in a given situation.

This problem is particularly pronounced in the selection of appropriate leaching tests to determine the degree of contaminant mobility in the untreated and treated materials. Ideally, the leaching procedure selected would simulate field conditions. Realistically, no single procedure can duplicate all poten-

Test	Criteria	Purpose
Particle size analysis	Well-graded 74 m–0.25 in	Determine gradation of untreated soil
Atterberg liquid and plastic limits	Liquid limits: 40–55% water; plastic limits: 20–50% water	Measure of untreated soil compressibility and strength as a function of water content
Moisture content	Application-specific	Determine need for watering or dewatering untreated soil
Density	Application-specific	Measure of porosity of untreated and treated materials; used to indicate volume increase as a result of treatment
Permeability	$<10^{-5}$ cm/s	Measure of resistance of material to passage of water
Unconfined compressive strength	50 psi	Measure of durability of treated material
Freezing/thawing and washing/drying	<15% weight loss (suggested)	Measure of durability of treated material
Leaching tests	Application-specific	Measure of mobility of contaminant
Microstructural analysis	Application-specific	Determination of grading of untreated soil; determination of degree and uniformity of mixing in treated material

Figure 6. Examples of Quality Assurance Measurements

tial field conditions. Therefore, the selection of leaching procedures to be used in treatability studies and in the field is a critical element in QA.

Similar problems are encountered in the selection of physical property tests to establish a measure of durability of the treated materials.

Additional information regarding applicable tests and their selection is provided in references 3 and 6.

Residuals Generated

One of the attractive features of in situ S/S processes is that residuals are minimized due to the absence of excavation and transportation of contaminated materials and placement of treated product.

The primary residuals of concern that may be generated during in situ S/S include:

- Emission control residues such as particulates from dust collectors or spent activated carbon used in volatile organic control;
- Liquid and solid residues resulting from personnel and equipment decontamination and cleaning; and
- Excess reagent.

Special attention must be paid to the management and disposal of the emission control and cleanup/decontamination residues either or both of which may be classified as hazardous.

Regulatory Issues

Regulatory issues affecting the remediation of contaminated sites continue to evolve. A majority of remedial activities may fall under requirements mandated in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act (SARA) of 1986.

Of importance to the use of S/S technologies is the requirement under SARA that remedial actions meet all "applicable or relevant and appropriate requirements" (ARARs) established from federal and more stringent state standards.

When initiating a remedial action, it is necessary to first identify all of the ARARs that may apply. Among the requirements that may apply are those specified in the Resource Conservation and Recovery Act (RCRA), the Clean Water Act (CWA), and the Clean Air Act (CAA). In addition, if the site contains PCBs or PCB-contaminated materials, the Toxic Substances Control Act (TSCA) will apply.

If in situ S/S processes are used to treat hazardous wastes, certain aspects of RCRA may be applicable. Of the requirements, the most likely to be ARARs for in situ S/S are those that are related to the long-term management of the treated site including requirements governing closure and post-closure (2). Potential impacts may include requirements for capping and post-closure care including long-term groundwater monitoring.

One important exception to RCRA requirements may be the apparent exclusion of in situ treatment actions from Land Disposal Restrictions (LDR). *Since in situ treatment does not involve the "placement" of treated wastes, LDR may not apply.*

Specific cleanup standards may affect the selection of S/S. Cleanup standards may be established in terms of permissible levels of specific contaminants in leachate generated from a standard test such as the EPA Toxicity Characteristic Leaching Procedure (TCLP). Cleanup standards may also be expressed in terms of the concentration of the contaminant of interest in the treated waste (not the leachate). This latter standard may present difficulties with respect to S/S due to the fact that generally the S/S technology does not destroy the contaminant but merely places it in a less mobile form.

The most important regulatory consideration in the selection and use of in situ S/S in any situation is the requirement that effective communication between the regulatory agencies and the party responsible for the remediation be maintained. This communication will influence the selection of the remedial technology as well as its design and implementation.

Feasibility Study (FS) Criteria Ranking

The use of in situ S/S processes has been rated by remedial action and engineering experts with respect to the relative ability of the process to meet *performance and regulatory criteria* relevant to FS evaluations. The results of this rating are provided in Figure 7.

There are a number of caveats to the presentation of this rating. One of the concerns is that since a majority of S/S processes do not result in contaminant destruction, it is difficult to compare these processes to those technologies that do destroy the contaminant.

In addition, a rating for long-term effectiveness must be subjective due to the absence of data reflecting this effectiveness.

Implementability of the in situ S/S process is negatively affected by the substantial requirements for treatability studies and tests prior to implementation.

Consideration of the relative costs of employing in situ S/S must also be addressed. Due to the considerable efforts that may be required prior to actual implementation of in situ S/S, preliminary costs may be high. Although the actual costs to conduct in situ S/S in the field may be relatively low, total costs associated with the remedial action may be high (see "Key Cost Factors").

Criteria	Ranking
Effect of reducing the overall threat to human health and the environment	○
Vulnerability to ARARs (Applicable or Relevant and Appropriate Requirements)	◑
Long-term effectiveness (see text)	●
Effectiveness at reducing toxicity, mobility, and volume	◑
Short-term effectiveness	◑
Implementability	◑
Transportability	◑
Up-front cost	◑
Field cost (full-scale)	◑
Readiness of acceptance by the state and community	○

Figure 7. Performance Criteria Rating

Key Cost Factors

Costs associated with in situ S/S remedial activities include the cost of:

- Tasks required prior to field implementation including site characterization, treatability study, and pilot-scale testing or demonstration; and
- Actual field implementation including site preparation, raw materials, treatment activities, and site cleanup and closure.

Total costs associated with in situ S/S remedial applications are very dependent on site-specific conditions and requirements. Issues that have been identified as having the greatest potential for affecting the total cost include:

- Waste characteristics (physical and chemical) and quantity;
- Site hydrogeology;
- Requirements for pretreatment;
- Specific treatment requirements (i.e., cleanup standards and time to complete treatment);

- Selection of reagents and additives to be employed;
- Health and safety considerations;
- Requirements for emission control;
- Regulatory requirements; and
- Site layout.

Ranges of costs (1991 dollars) that may be encountered are:

- *Costs prior to actual treatment:* $50,000 to $1,000,000 (total, assumed to be independent of volume to be treated); and
- *Costs of treatment:* $50 to $250 per cubic yard.

Points to Remember

The following points are important to consider in the selection, design, or implementation of in situ S/S to treat contaminated soil. These points are not intended to be all-inclusive, but represent critical elements as noted by those experienced in the implementation of in situ S/S technologies.

√ In situ S/S does not necessarily represent a permanent remedial solution.

√ The treatability study may be the most significant undertaking of the remedial process (see "Design Criteria").

√ The complete remedial activity may involve the preparation of several specifications for contracting to address treatability study, pilot testing, and implementation phases.

√ Little is known about the long-term effectiveness of in situ S/S.

√ Special consideration must be taken in the selection of QA tests, particularly leaching and durability tests.

√ Adequate site investigation and characterization is required to identify hydrogeological, physical, and chemical conditions or constraints that affect the application of in situ S/S.

√ Ongoing operations at the site must be considered in planning the application.

√ If dust control is required during operations, an on-site source of water may be needed.

√ The future use of the site must be considered in designing the in situ S/S treatment process. In some cases, a significant increase in volume may result from treatment, thereby affecting the local terrain. In addition, future use requirements may dictate the design and construction of caps over the treated materials.

√ The potential for climate effects resulting in frequent wet/dry and freeze/thaw cycling must be considered in feasibility assessments.

√ The use of proprietary reagents or binders may be a concern with respect to preparing contracting specifications as well as potential long-term liability.

√ The maintenance of effective communications with the appropriate regulatory agencies is important in the selection and implementation of in situ S/S. This is especially critical due to the uncertainties involved in assuring short- and long-term treatment effectiveness and long-term monitoring requirements.

Application Examples

Examples of recent (within the last 5 years) applications of in situ S/S for the treatment of contaminated soils and sludges are provided in Figure 8. These examples were selected to provide a representation of the variety of site or contaminant conditions that may be encountered.

The first two examples represent applications in which in situ S/S was employed to treat industrial sludges containing a variety of contaminants, including metals. Although these examples do not address contaminated soil treatment, they

Site	Volume	Contaminant	Reagent	Special Considerations	Ref.
Refinery	100,000 yd^3	oil, Pb, Cr, As	cement, kiln dust	Full-scale treatment of contaminated sludge	5
Electroplating facility	16,000 yd^3	Cu, Cr, Ni	Portland cement	Full-scale treatment of contaminated sludge	5
Electric service shop	7,500 yd^3	PCB, Cr, Cu, Pb, Zn	proprietary reagent/ pozzolan	SITE demonstration. Treated contaminated soil to depths of 25 to 53 feet.	2
Oil refinery	100,000 yd^3	petroleum hydrocarbons	cement	Subsurface application of dry reagent to contaminated soil. Site enclosed by slurry wall and capped with clay.	7

Figure 8. Application Examples

are representative of large-scale in situ S/S applications with a variety of contaminants.

The third example reflects the conduct of a SITE demonstration test employing in situ S/S to treat actual soils contaminated with metals and PCBs. In this EPA-evaluated demonstration, a proprietary reagent was combined with sodium silicate and added by injection to the contaminated soil. Mixing took place by the movement of an auger within a column during injection. A complete demonstration description and presentation of results is provided in Reference 2. Preliminary results indicate that the technology could be practically employed by this method and apparent immobilization of metal and non-volatile organic contaminants may have occurred. One year after the demonstration, the treated product was analyzed and indicated that the permeability of the treated matrix decreased significantly over time (8).

An in situ S/S application to treat a large volume of soil contaminated with petroleum hydrocarbons used cement to generate a strong, solid structure that physically trapped the contaminants. This application represents an integrated treatment system that employed in situ S/S and surface and subsurface barriers (see Figure 1).

References and Sources of Additional Information

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8. Stinson, M.K., 1990, *EPA SITE Demonstration of the International Waste Technologies/Geo-Con In Situ Stabilization Solidification Process*, J. Air Waste Manage. Assoc., Vol. 4, No. 11, Nov. 1990, pp. 1569-1576.

Points of Contact

Additional information regarding technical, regulatory, and practical aspects of in situ S/S in remedial actions may be obtained from:

- Carlton Wiles, Risk Reduction Engineering Laboratory, U.S. EPA, Cincinnati, OH, (513) 569-7795.
- Jeffery C. Heath, Naval Civil Engineering Laboratory, Code L71, Port Hueneme, CA, (805) 982-1657.
- John Fringer, NEESA, Code 112E4, Port Hueneme, CA, (805) 982-4856.
- Itamar Bodek, Arthur D. Little, Inc., Cambridge, MA, (617) 864-5770.

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Superfund | EPA/540/S-92/015 | May 1993

EPA

Engineering Bulletin
Solidification/Stabilization of Organics and Inorganics

Purpose

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

Abstract

Solidification refers to techniques that encapsulate hazardous waste into a solid material of high structural integrity. Encapsulation involves either fine waste particles (microencapsulation) or a large block or container of wastes (macroencapsulation) [1, p. 2]*. Stabilization refers to techniques that treat hazardous waste by converting it into a less soluble, mobile, or toxic form. Solidification/Stabilization (S/S) processes, as referred to in this document, utilize one or both of these techniques.

S/S technologies can immobilize many heavy metals, certain radionuclides, and selected organic compounds while decreasing waste surface area and permeability for many types of sludge, contaminated soils, and solid wastes. Common S/S agents include: Type 1 Portland cement or cement kiln dust; lime, quicklime, or limestone; fly ash; various mixtures of these materials; and various organic binders (e.g., asphalt). The mixing of the waste and the S/S agents can occur outside of the ground (ex situ) in continuous feed or batch operations or in the ground (in situ) in a continuous feed operation. The final product can be a continuous solid mass of any size or of a granular consistency resembling soil. During in situ operations, S/S agents are injected into and mixed with the waste and soil up to depths of 30 to 100 feet using augers.

Treatability studies are the only means of documenting the applicability and performance of a particular S/S system. Determination of the best treatment alternative will be based on multiple site-specific factors and the cost and efficacy of the treatment technology. The EPA contact identified at the end of this bulletin can assist in the location of other contacts and sources of information necessary for such treatability studies.

It may be difficult to evaluate the long-term (>5 year) performance of the technology. Therefore, long-term monitoring may be needed to ensure that the technology continues to function within its design criteria.

This bulletin provides information on technology applicability, the limitations of the technology, the technology description, the types of residuals produced, site requirements, the process performance data, the status of the technology, and sources for further information.

Technology Applicability

The U.S. EPA has established treatment standards under the Resource Conservation and Recovery Act (RCRA), Land Disposal Restrictions (LDRs) based on Best Demonstrated Available Technology (BDAT) rather than on risk-based or health-based standards. There are three types of LDR treatment standards based on the following: achieving a specified concentration level, using a specified technology prior to disposal, and "no land disposal." Achieving a specified concentration level is the most common type of treatment standard. When a concentration level to be achieved is specified for a waste, any technology that can meet the standard may be used unless that technology is otherwise prohibited [2].

The Superfund policy on use of immobilization is as follows: "Immobilization is generally appropriate as a treatment alternative only for material containing inorganics, semi-volatile and/or non-volatile organics. Based on present information, the Agency does not believe that immobilization is an appropriate treatment alternative for volatile organic compounds (VOCs). Selection of immobilization of semi-volatile compounds (SVOCs) and non-volatile organics generally requires the performance of

*[reference number, page number]

a site-specific treatability study or non-site-specific treatability study data generated on waste which is very similar (in terms of type of contaminant, concentration, and waste matrix) to that to be treated and that demonstrates, through Total Waste Analysis (TWA), a significant reduction (e.g., a 90 to 99 percent reduction) in the concentration of chemical constituents of concern. The 90 to 99 percent reduction in contaminant concentration is a general guidance and may be varied within a reasonable range considering the effectiveness of the technology and the cleanup goals for the site. Although this policy represents EPA's strong belief that TWA should be used to demonstrate effectiveness of immobilization for organics, other leachability tests may also be appropriate in addition to TWA to evaluate the protectiveness under a specific management scenario. "To measure the effectiveness on inorganics, the EPA's Toxicity Characteristic Leaching Procedure (TCLP) should be used in conjunction with other tests such as TCLP using distilled water or American Nuclear Society (ANS) 16.1 [3, p. 2].

Factors considered most important in the selection of a technology are design, implementation, and performance of S/S processes and products, including the waste characteristics (chemical and physical), processing requirements, S/S product management objectives, regulatory requirements, and economics. These and other site-specific factors (e.g., location, condition, climate, hydrology, etc.) must be taken into account in determining whether, how, where, and to what extent a particular S/S method should be used at a particular site [4, p. 7.92]. Pozzolanic S/S processes can be formulated to set under water if necessary; however, this may require different proportions of fixing and binding agents to achieve the desired immobilization and is not generally recommended [5, p. 21]. Where non-pumpable sludge or solid wastes are encountered, the site must be able to support the heavy equipment required for excavation or in situ injection and mixing. At some waste disposal sites, this may require site engineering.

A wide range of performance tests may be performed in conjunction with S/S treatability studies to evaluate short- and long-term stability of the treated material. These include total waste analysis for organics, leachability using various methods, permeability, unconfined compressive strength (UCS), treated waste and/or leachate toxicity endpoints, and freeze/thaw and wet/dry weathering cycle tests performed according to specific procedures [6, p. 4.2] [7, p. 4.1]. Treatability studies should be conducted on replicate samples from a representative set of waste batches that span the expected range of physical and chemical properties to be encountered at the site [8, p. 1].

The most common fixing and binding agents for S/S are cement, lime, natural pozzolans, and fly ash, and mixtures of these [4, p. 7.86] [6, p. 2.1]. They have been demonstrated to immobilize many heavy metals and to solidify a wide variety of wastes including spent pickle liquor, contaminated soils, incinerator ash, wastewater treatment filter cake, and waste sludge [7, p. 3.1] [9]. S/S is also effective in immobilizing many radionuclides [10]. In general, S/S is considered an established full-scale technology for nonvolatile heavy metals although the long-term performance of S/S in Superfund applications has yet to be demonstrated [2].

Traditional cement and pozzolanic materials have yet to be shown to be consistently effective in full-scale applications treating wastes high in oil and grease, surfactants, or chelating agents without some form of pretreatment [11] [12, p. 122]. Pretreatment methods include pH adjustment, steam or thermal stripping, solvent extraction, chemical or photochemical reaction, and biodegradation. The addition of sorbents such as modified clay or powdered activated carbon may improve cement-based or pozzolanic process performance [6, p. 2.3].

Regulations promulgated pursuant to the Toxic Substances Control Act (TSCA) do not recognize S/S as an approved treatment for wastes containing polychlorinated biphenyls (PCBs) above 50 ppm. It is EPA policy that soils containing greater than 10 ppm in public/residential areas and 25 ppm in limited access/occupational areas be removed for TSCA-approved treatment/disposal. However, the policy also provides EPA regional offices with the option of requiring more restrictive levels. For example, Region 5 requires a cleanup level of 2 ppm. The proper disposition of high volume sludges, soils, and sediments is not specified in the TSCA regulations, but precedents set in the development of various records of decision (RODs) indicate that stabilization may be approved where PCBs are effectively immobilized and/or destroyed to TSCA-equivalent levels. Some degree of immobilization of PCBs and related polychlorinated polycyclic compounds appears to occur in cement or pozzolans [15, p. 1573]. Some field observations suggest polychlorinated polycyclic organic substances such as PCBs undergo significant levels of dechlorination under the alkaline conditions encountered in pozzolanic processes. Recent tests by the EPA, however, have not confirmed these results although significant desorption and volatilization of the PCBs were documented [13, p. 41] [14, p. 3].

Table 1 summarizes the effectiveness of S/S on general contaminant groups for soils and sludges. Table 1 was prepared based on current available information or on professional judgment when no information was available. In interpreting this table, the reader is cautioned that for some primary constituents, a particular S/S technology performs adequately in some concentration ranges but inadequately in others. For example, copper, lead, and zinc are readily stabilized by cementitious materials at low to moderate concentrations, but interfere with those processes at higher concentrations [12, p. 43]. In general, S/S methods tend to be most effective for immobilizing nonvolatile heavy metals.

The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that treatment efficiencies achieved will be acceptable at other sites. For the ratings used in Table 1, demonstrated effectiveness means that at some scale, treatability tests showed that the technology was effective for that particular contaminant and matrix. The ratings of "Potential Effectiveness" and "No Expected Effectiveness" are both based upon expert judgment. When potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no expected effectiveness rating is given.

Table 1
Effectiveness of S/S on General Contaminant Groups for Soil and Sludges

	Contaminant Groups	Effectiveness Soil/Sludge
Organic	Halogenated volatiles	▫
	Nonhalogenated volatiles	▫
	Halogenated semivolatiles	■
	Nonhalogenated semivolatiles and nonvolatiles	■
	PCBs	▼
	Pesticides	▼
	Dioxins/Furans	▼
	Organic cyanides	▼
	Organic corrosives	▼
Inorganic	Volatile metals	■
	Nonvolatile metals	■
	Asbestos	■
	Radioactive materials	■
	Inorganic corrosives	■
	Inorganic cyanides	■
Reactive	Oxidizers	■
	Reducers	■

KEY:
- ■ Demonstrated Effectiveness: Successful treatability test at some scale completed.
- ▼ Potential Effectiveness: Expert opinion that technology will work.
- ▫ No Expected Effectiveness: Expert opinion that technology will/does not work.

Another source of general observations and average removal efficiencies for different treatability groups is contained in the Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS, September 1990) [16] and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," (OSWER Directive 9347.3-06BFS, September 1990) [17]. Performance data presented in this bulletin should not be considered directly applicable to other Superfund sites. A number of variables such as the specific mix and distribution of contaminants affect system performance. A thorough characterization of the site and a well-designed and conducted treatability study are highly recommended.

Other sources of information include the U.S. EPA's Risk Reduction Engineering Laboratory Treatability Database (accessible via ATTIC) and the U.S. EPA Center Hill Database (contact Patricia Erickson).

Technology Limitations

Tables 2 and 3 summarize factors that may interfere with stabilization and solidification processes respectively.

Physical mechanisms that can interfere with the S/S process include incomplete mixing due to the presence of high moisture or organic chemical content resulting in only partial wetting or coating of the waste particles with the stabilizing and binding agents and the aggregation of untreated waste into lumps [6]. Wastes with a high clay content may clump, interfering with the uniform mixing with the S/S agents, or the clay surface may adsorb key reactants, interrupting the polymerization chemistry of the S/S agents. Wastes with a high hydrophilic organic content may interfere with solidification by disrupting the gel structure of the curing cement or pozzolanic mixture [11, p. 18] [18]. The potential for undermixing is greatest for dry or pasty wastes and least for freely flowing slurries [11, p. 13]. All in situ systems must provide for the introduction and mixing of the S/S agents with the waste in the proper proportions in the surface or subsurface waste site environment. Quality control is inherently more difficult with in situ products than with ex situ products [4, p. 7.95].

Chemical mechanisms that can interfere with S/S of cement-based systems include chemical adsorption, complexation, precipitation, and nucleation [1, p. 82]. Known inorganic chemical interferants in cement-based S/S processes include copper, lead, and zinc, and the sodium salts of arsenate, borate, phosphate, iodate, and sulfide [6, p. 2.13] [12, p. 11]. Sulfate interference can be mitigated by using a cement material with a low tricalcium aluminate content (e.g., Type V Portland cement) [6, p. 2.13]. Problematic organic interferants include oil and grease, phenols [8, p. 19], surfactants, chelating agents [11, p. 22], and ethylene glycol [18]. For thermoplastic micro- and macro-encapsulation, stabilization of a waste containing strong oxidizing agents reactive toward rubber or asphalt must also be avoided [19, p. 10.114]. Pretreating the wastes to chemically or biochemically react or to thermally or chemically extract potential interferants should minimize these problems, but the cost advantage of S/S may be lost, depending on the characteristics and volume of the waste and the type and degree of pretreatment required. Organic polymer additives in various stages of development and field testing may significantly improve the performance of the cementitious and pozzolanic S/S agents with respect to immobilization of organic substances, even without the addition of sorbents.

Volume increases associated with the addition of S/S agents to the waste may prevent returning the waste to the landform from which it was excavated where landfill volume is limited. Where post-closure earthmoving and landscaping are required, the treated waste must be able to support the weight of heavy equipment. The EPA recommends a minimum compressive strength of 50 to 200 psi [7, p. 4.13]; however, this should be a site-specific determination.

Environmental conditions must be considered in determining whether and when to implement an S/S technology. Extremes of heat, cold, and precipitation can adversely affect S/S applications. For example, the viscosity of one or more of the

Table 2.
Summary of Factors that May Interfere with Stabilization Processes *

Characteristics Affecting Processing Feasibility	*Potential Interference*
VOCs	Volatiles not effectively immobilized; driven off by heat of reaction. Sludges and soils containing volatile organics can be treated using a heated extruder evaporator or other means to evaporate free water and VOCs prior to mixing with stabilizing agents.
Use of acidic sorbent with metal hydroxide wastes	Solubilizes metal.
Use of acidic sorbent with cyanide wastes	Releases hydrogen cyanide.
Use of acidic sorbent with waste containing ammonium compounds	Releases ammonia gas.
Use of acidic sorbent with sulfide wastes	Releases hydrogen sulfide.
Use of alkaline sorbent (containing carbonates such as calcite or dolomite) with acid waste	May create pyrophoric waste.
Use of siliceous sorbent (soil, fly ash) with hydrofluoric acid waste	May produce soluble fluorosilicates.
Presence of anions in acidic solutions that form soluble calcium salts (e.g., calcium chloride acetate, and bicarbonate)	Cation exchange reactions - leach calcium from S/S product increases permeability of concrete, increases rate of exchange reactions.
Presence of halides	Easily leached from cement and lime.

* Adapted from reference 2

Table 3.
Summary of Factors that May Interfere with Solidification Processes *

Characteristics Affecting Processing Feasibility	*Potential Interference*
Organic compounds	Organics may interfere with bonding of waste materials with inorganic binders.
Semivolatile organics or poly-aromatic hydrocarbons (PAHs)	Organics may interfere with bonding of waste materials.
Oil and grease	Weaken bonds between waste particles and cement by coating the particles. Decrease in unconfined compressive strength with increased concentrations of oil and grease.
Fine particle size	Insoluble material passing through a No. 200 mesh sieve can delay setting and curing. Small particles can also coat larger particles, weakening bonds between particles and cement or other reagents. Particle size >1/4 inch in diameter not suitable.
Halides	May retard setting, easily leached for cement and pozzolan S/S. May dehydrate thermoplastic solidification.
Soluble salts of manganese, tin, zinc, copper, and lead	Reduced physical strength of final product caused by large variations in setting time and reduced dimensional stability of the cured matrix, thereby increasing leachability potential.
Cyanides	Cyanides interfere with bonding of waste materials.
Sodium arsenate, borates, phosphates, iodates, sulfides, and carbohydrates	Retard setting and curing and weaken strength of final product.
Sulfates	Retard setting and cause swelling and spalling in cement S/S. With thermoplastic solidification may dehydrate and rehydrate, causing splitting.

* Adapted from reference 2

Table 3
Summary of Factors that May Interfere with Solidification Processes * (continued)

Characteristics Affecting Processing Feasibility	*Potential Interference*
Phenols	Marked decreases in compressive strength for high phenol levels.
Presence of coal or lignite	Coals and lignites can cause problems with setting, curing, and strength of the end product.
Sodium borate, calcium sulfate, potassium dichromate, and carbohydrates	Interferes with pozzolanic reactions that depend on formation of calcium silicate and aluminate hydrates.
Nonpolar organics (oil, grease, aromatic hydrocarbons, PCBs)	May impede setting of cement, pozzolan, or organic-polymer S/S. May decrease long-term durability and allow escape of volatiles during mixing. With thermoplastic S/S, organics may vaporize from heat.
Polar organics (alcohols, phenols, organic acids, glycols)	With cement or pozzolan S/S, high concentrations of phenol may retard setting and may decrease short-term durability; all may decrease long-term durability. With thermoplastic S/S, organics may vaporize. Alcohols may retard setting of pozzolans.
Solid organics (plastics, tars, resins)	Ineffective with urea formaldehyde polymers; may retard setting of other polymers.
Oxidizers (sodium hypochlorite, potassium permanganate, nitric acid, or potassium dichromate)	May cause matrix breakdown or fire with thermoplastic or organic polymer S/S.
Metals (lead, chromium, cadmium, arsenic, mercury)	May increase setting time of cements if concentration is high.
Nitrates, cyanides	Increase setting time, decrease durability for cement-based S/S.
Soluble salts of magnesium, tin, zinc, copper and lead	May cause swelling and cracking within inorganic matrix exposing more surface area to leaching.
Environmental/waste conditions that lower the pH of matrix	Eventual matrix deterioration.
Flocculants (e.g., ferric chloride)	Interference with setting of cements and pozzolans.
Soluble sulfates >0.01% in soil or 150 mg/L in water	Endangerment of cement products due to sulfur attack.
Soluble sulfates >0.5% in soil or 2000 mg/L in water	Serious effects on cement products from sulfur attacks.
Oil, grease, lead, copper, zinc, and phenol	Deleterious to strength and durability of cement, lime/fly ash, fly ash/cement binders.
Aliphatic and aromatic hydrocarbons	Increase set time for cement.
Chlorinated organics	May increase set time and decrease durability of cement if concentration is high.
Metal salts and complexes	Increase set time and decrease durability for cement or clay/cement.
Inorganic acids	Decrease durability for cement (Portland Type I) or clay/cement.
Inorganic bases	Decrease durability for clay/cement; KOH and NaOH decrease durability for Portland cement Type III and IV.

* Adapted from reference 2

materials in the mixture may increase rapidly with falling temperatures or the cure rate may be slowed unacceptably [20, p. 27]. In cement-based S/S processes the engineering properties of the concrete mass produced for the treatment of the waste are highly dependent on the water/cement ratio and the degree of hydration of the cement. High water/cement ratios yield large pore sizes and thus higher permeabilities [21, p. 177]. This factor may not be readily controlled in environmental applications of S/S and pretreatment (e.g., drying) of the waste may be required.

Depending on the waste and binding agents involved, S/S processes can produce hot gases, including vapors that are potentially toxic, irritating, or noxious to workers or communities downwind from the processes [22, p. 4]. Laboratory tests demonstrate that as much as 90 percent of VOCs are volatilized during solidification and as much as 60 percent of the remaining VOCs are lost in the next 30 days of curing [23, p. 6]. In addition, if volatile substances with low flash points are involved, the potential exists for fire and explosions where the fuel-to-air ratio is favorable [22, p. 4]. Where volatization problems are anticipated, many S/S systems now provide for vapor collection and treatment. Under dry and/or windy environmental conditions, both ex situ and in situ S/S processes are likely to generate fugitive dust with potentially harmful impacts on occupational and public health, especially for downwind communities.

Scaleup for S/S processes from bench-scale to full-scale operation involves inherent uncertainties. Variables such as ingredient flow-rate control, materials mass balance, mixing, and materials handling and storage, along with the weather compared to the more controlled environment of a laboratory, all may affect the success of a field operation. These potential engineering difficulties emphasize the need for a field demonstration prior to full-scale implementation [2].

Technology Description

Waste stabilization involves the addition of a binder to a waste to immobilize waste contaminants effectively. Waste solidification involves the addition of a binding agent to the waste to form a solid material. Solidifying waste improves its material handling characteristics and reduces permeability to leaching agents such as water, brine, and inorganic and organic acids by reducing waste porosity and exposed surface area. Solidification also increases the load-bearing capacity of the treated waste, an advantage when heavy equipment is involved. Because of their dilution effect, the addition of binders must be accounted for when determining reductions in concentrations of hazardous constituents in S/S treated waste.

S/S processes are often divided into the following broad categories: inorganic processes (cement and pozzolanic) and organic processes (thermoplastic and thermosetting). Generic S/S processes involve materials that are well known and readily available. Commercial vendors have typically developed generic processes into proprietary processes by adding special additives to provide better control of the S/S process or to enhance specific chemical or physical properties of the treated waste. Less frequently, S/S processes combine organic binders with inorganic binders (e.g., diatomaceous earth and cement with polystyrene, polyurethane with cement, and polymer gels with silicate and lime cement) [2].

The waste can be mixed in a batch or continuous system with the binding agents after removal (ex situ) or in place (in-situ). In ex situ applications, the resultant slurry can be 1) poured into containers (e.g., 55-gallon drums) or molds for curing and then off- or onsite disposal, 2) disposed in onsite waste management cells or trenches, 3) injected into the subsurface environment, or 4) re-used as construction material with the appropriate regulatory approvals. In in situ applications, the S/S agents are injected into the subsurface environment in the proper proportions and mixed with the waste using backhoes for surface mixing or augers for deep mixing [5]. Liquid waste may be pretreated to separate solids from liquids. Solid wastes may also require pretreatment in the form of pH adjustment, steam or thermal stripping, solvent extraction, chemical reaction, or biodegradation to remove excessive VOCs and SVOCs that may react with the S/S process. The type and proportions of binding agents are adjusted to the specific properties of the waste to achieve the desired physical and chemical characteristics of the waste appropriate to the conditions at the site based on bench-scale tests. Although ratios of waste-to-binding agents are typically in the range of 10:1 to 2:1, ratios as low as 1:4 have been reported. However, projects utilizing low waste-to-binder ratios have high costs and large volume expansion.

Figures 1 and 2 depict generic elements of typical ex situ and in situ S/S processes, respectively. Ex situ processing involves: (1) excavation to remove the contaminated waste from the subsurface; (2) classification to remove oversize debris; (3) mixing; and (4) off-gas treatment. In situ processing has only two steps: (1) mixing; and (2) off-gas treatment. Both processes require a system for delivering water, waste, and S/S agents in proper proportions and a mixing device (e.g., rotary drum paddle or auger). Ex situ processing requires a system for delivering the treated waste to molds, surface trenches, or subsurface injection. The need for off-gas treatment using vapor collection and treatment modules is specific to the S/S project.

Process Residuals

Under normal operating conditions neither ex situ nor in situ S/S technologies generate significant quantities of contaminated liquid or solid waste. Certain S/S projects require treatment of the offgas. Prescreening collects debris and materials too large for subsequent treatment.

If the treated waste meets the specified cleanup levels, it could be considered for reuse onsite as backfill or construction material. In some instances, treated waste may have to be disposed of in an approved landfill. Hazardous residuals from some pretreatment technologies must be disposed of according to appropriate procedures.

Figure 1.
Generic Elements of a Typical Ex Situ S/S Process

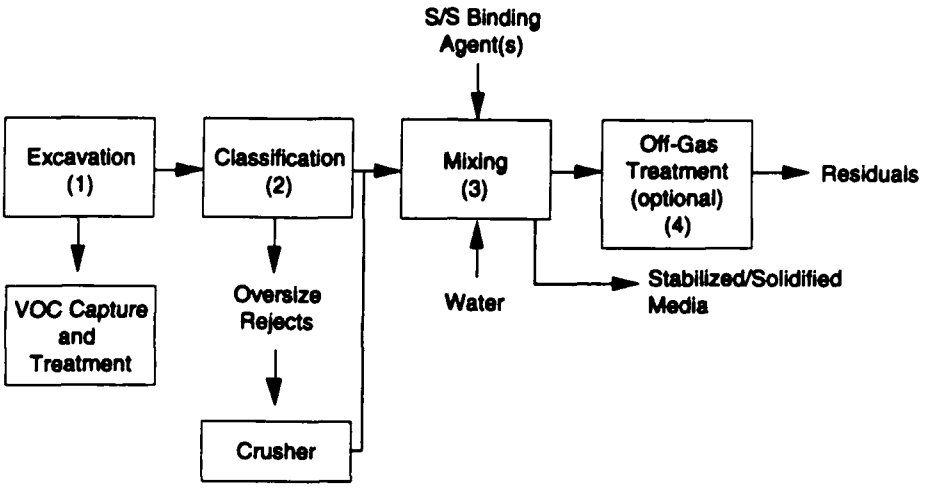
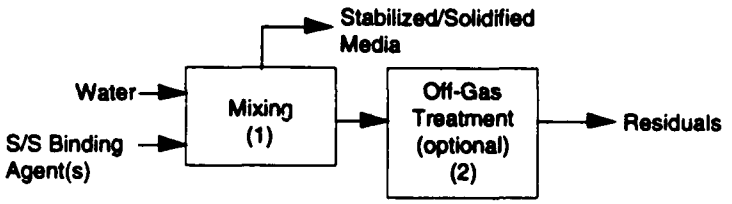


Figure 2.
Generic Elements of a Typical In Situ S/S Process



Site Requirements

The site must be prepared for the construction, operation, maintenance, decontamination, and ultimate decommissioning of the equipment. An area must be cleared for heavy equipment access roads, automobile and truck parking lots, material transfer stations, the S/S process equipment, set up areas, decontamination areas, the electrical generator, equipment sheds, storage tanks, sanitary and process wastewater collection and treatment systems, workers' quarters, and approved disposal facilities (if required). The size of the area required for the process equipment depends on several factors, including the type of S/S process involved, the required treatment capacity of the system, and site characteristics, especially soil topography and load-bearing capacity. A small mobile ex situ unit could occupy a space as small as that taken up by two standard flatbed trailers. An in situ system requires a larger area to accommodate a drilling rig as well as a larger area for auger decontamination.

Process, decontamination, transfer, and storage areas should be constructed on impermeable pads with berms for spill retention and drains for the collection and treatment of stormwater runoff. Stormwater storage and treatment capacity requirements will depend on the size of the bermed area and the local climate. Standard 440V, three-phase electrical service is usually needed. The quantity and quality of process water required for pozzolanic S/S technologies are technology-specific.

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

Performance Data

Most of the data on S/S performance come from studies conducted for EPA's Risk Reduction Engineering Laboratory under the Superfund Innovative Technology Evaluation (SITE) Program. Pilot scale demonstration studies available for review during the preparation of this bulletin included: Soliditech, Inc. at Morganville, New Jersey (petroleum hydrocarbons, PCBs, other organic chemicals, and heavy metals); International Waste Technologies (IWT) process using the Geo-Con, Inc. deep-soil-mixing equipment, at Hialeah, Florida (PCBs, VOCs); Chemfix Technologies, Inc., at Clackamas, Oregon (PCBs, arsenic, heavy metals); Im-Tech (formerly Hazcon) at Douglassville, Pennsylvania (oil and grease, heavy metals including lead, and low levels of VOCs and PCBs); Silicate Technology Corporation (STC), at Selma, California (arsenic, chromium, copper, pentachlorophenol and associated polychlorinated dibenzofurans and dibenzo-p-dioxins). The performance of each technology was evaluated in terms of ease of operation, processing capacity, frequency of process outages, residuals management, cost, and the characteristics of the treated product. Such characteristics

included weight, density, and volume changes; UCS and moisture content of the treated product before and after freeze/thaw and wet/dry weathering cycles; permeability (or permissivity) to water; and leachability following curing and after the weathering test cycles. Leachability was measured using several different standard methods, including EPA's TCLP. Table 4 summarizes the SITE performance data from these sites [20] [24] [25] [26] [27] [28].

A full-scale S/S operation has been implemented at the Northern Engraving Corporation (NEC) site in Sparta, Wisconsin, a manufacturing facility which produces metal name plates and dials for the automotive industry. The following information on the site is taken from the remedial action report. Four areas at the site that have been identified as potential sources of soil, groundwater, and surface water contamination are the sludge lagoon, seepage pit, sludge dump site, and lagoon drainage ditch. The sludge lagoon was contaminated primarily with metal hydroxides consisting of nickel, copper, aluminum, fluoride, iron, and cadmium. The drainage ditch which showed elevated concentrations of copper, aluminum, fluoride, and chromium, was used to convey effluent from the sludge lagoon to a stormwater runoff ditch. The contaminated material in the drainage ditch area and sludge dumpsite was then excavated and transported into the sludge lagoon for stabilization with the sludge present. The vendor, Geo-Con, Inc., achieved stabilization by the addition of hydrated lime to the sludge. Five samples of the solidified sludge were collected for Extraction Procedure (EP) toxicity leaching analyses. Their contaminant concentrations (in mg/l) are as follows: Arsenic (<.01); Barium (.35 - 1.04); Cadmium (<.005); Chromium (<.01); Lead (<.2); Mercury (<.001); Selenium (<.005); Silver (<.01); and Fluoride (2.6 - 4.1). All extracts were not only below the EP toxicity criteria but (with the exception of fluoride) met drinking water standards as well.

Approximately three weeks later UCS tests on the solidified waste were taken. Test results ranged from 2.4 to 10 psi, well below the goal of 25 psi. One explanation for the low UCS could be due to shear failure along the lenses of sandy material and organic peat-like material present in the samples. It was determined that it would not be practical to add additional quantities of lime into the stabilized sludge matrix because of its high solids content. Therefore, the stabilized sludge matrix capacity will be increased to support the clay cap by installing an engineered subgrade for the cap system using a stabilization fabric and aggregate prior to cap placement [29].

The Industrial Waste Control (IWC) Site in Fort Smith, Arkansas, a closed and covered industrial landfill built in an abandoned surface coal mine, has also implemented a full-scale S/S system. Until 1978 painting wastes, solvents, industrial process wastes, and metals were disposed at the site. The primary contaminants of concern were methylene chloride, ethylbenzene, toluene, xylene, trichloroethane, chromium, and lead. Along with S/S of the onsite soils, other technologies used were: excavation, slurry wall, french drains, and a landfill cover. Soils were excavated in the contaminated region (Area C) and a total of seven lifts were stabilized with flyash on mixing pads previously formed. A clay liner was then constructed in Area C to serve as a leachate barrier. After the lifts passed the TCLP test they were taken to Area C for in situ solidification. Portland cement was added to solidify each lift and they obtained the UCS goal of 125 psi. With the combination of the other technologies, the overall system appears to be functioning properly [30].

Other Superfund sites where full scale S/S has been completed to date include Davie Landfill (82,158 yd^3 of sludge containing cyanide, sulfide, and lead treated with Type I Portland cement in 45 days) [31]; Pepper's Steel and Alloy (89,000 yd^3 of soil containing lead, arsenic, and PCBs treated with Portland cement and fly ash) [32]; and Sapp Battery and Salvage (200,000 yd^3 soil fines and washings containing lead and mercury treated with Portland cement and fly ash in roughly 18 months) [33], all in Region 4; and Bio-Ecology, Inc. (about 20,000 yd^3 of soils, sludge, and liquid waste containing heavy metals, VOCs, and cyanide treated with cement kiln flue dust alone or with lime) in Region 6 [34]. All sites required that the waste meet the appropriate leaching test and UCS criteria. At the Sapp Battery site, the waste also met a permeability criterion of 10^{-6} cm/s [33]. Past remediation appraisals by the responsible remedial project managers indicate the S/S technologies are performing as intended.

RCRA LDRs that require treatment of wastes based on BDAT levels prior to land disposal may sometimes be determined to be Applicable or Relevant and Appropriate Requirements (ARARs) for CERCLA response actions. S/S can produce a treated waste that meets treatment levels set by BDAT but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where S/S does not meet these levels, it still may in certain situations be selected for use at a site if a treatability variance establishing alternative treatment levels is obtained. Treatability variances may be justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.3-06FS) [16], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-06BFS) [17]. Another approach could be to use other treatment techniques in conjunction with S/S to obtain desired treatment levels.

Technology Status

In 1990, 24 RODs identified S/S as the proposed remediation technology [35]. To date only about a dozen Superfund sites have proceeded through full-scale S/S implementation to the operation and maintenance (O&M) phase, and many of those were small pits, ponds, and lagoons. Some involved S/S for offsite disposal in RCRA-permitted facilities. Table 5 summarizes these sites where full scale S/S has been implemented under CERCLA or RCRA [7, p. 3-4].

More than 75 percent of the vendors of S/S technologies use cement-based or pozzolanic mixtures [11, p. 2]. Organic polymers have been added to various cement-based systems to enhance performance with respect to one or more physical or

Table 4. Summary of SITE Performance Data

Site	Vendor Technology	Pretreatment	Post Treatment
Imperial Oil Co. / Champion Chemical Co. Morganville, NJ	Soliditech: Urrichem reagent, water, additives, Type II Portland cement	Bulk density: 1.14 to 1.26 g/cm^3 Permeability: Not determined UCS: Not determined Lead-TCLP Extract: 0.46 mg/l	Bulk density: 1.43 to 1.68 g/cm^3 Permeability: 8.9x10^{-9} to 4.5x10^{-7} cm/s UCS: 390 to 860 psi Lead-TCLP extract: <0.05 to <0.20 mg/l
GE Electrical Service Shop Hialeah, FL	IWT-DMS/Geo-Con: In situ injection of silicate additive	Bulk density: 1.55 g/ml Permeability: 1.8x10^{-3} cm/s UCS: 1.2 to 1.85 psi	Bulk density: 1.88 g/ml Permeability: 0.24x10^{-7} to 21x10^{-7} cm/s UCS: 300 to 500 psi
Portable Equipment Salvage Co. Clackamas, OR	Chemfix: polysilicates and dry calcium containing reagents	TCLP-Extractable (Pb, Cu, Zn): 12 to 880 mg/l Hydraulic cond. (CSS-13): 2.4 x10^{-4} to 2.7x10^{-4} cm/s Bulk density: 2.0 to 2.6 g/cm^3	TCLP-Extractable (Pb, Cu, Zn): 0.024 to 47 mg/l Hydraulic cond. (CSS-14): 4.6x10^{-7} to 1.2x10^{-6} cm/s Bulk density: 1.6 to 2.0 g/cm^3 USC (14, 21, 28 days): 131, 136, 143 psi Immersion UCS (30, 60, 90 days): 177, 188, 204 psi
Douglasville Douglasville, PA	Imtech (Hazcon): Chloranan™, water and cement	Bulk density: 1.23 g/ml Permeability: 0.57 cm/s TCLP-Extractable Pb: 52.6 mg/l	Bulk density (7, 28 days): 1.95, 1.99 g/ml Permeability (7, 28 days): 1.6x10^{-9}, 2.3x10^{-9} cm/s TCLP-Extractable Pb (7, 28 days): 0.14, 0.05 mg/l UCS (7,28 days): 1447,113 psi
Selma Pressure Treating Wood Preserving Site Selma, CA	Silicate Tech Corp.: alumino-silicate compounds	Arsenic-TCLP: 1.06 to 3.33 ppm Arsenic-Distilled H_2O TCLP: 0.73 to 1.25 ppm PCP-TWA: 1983 to 8317 ppm Bulk density: 1.42 to 1.54 g/cm	Arsenic-TCLP: 0.086 to 0.875 ppm Arsenic-Distilled H_2O TCLP: < 0.01 to 0.012 ppm PCP-TWA: 14 to 158 ppm Bulk density: 1.57 to 1.62 g/cm Permeability: 0.8x10^{-7} to 1.7x10^{-7} cm/s UCS: 259 to 347 psi

UCS - Unconfined Compressive Strength
TCLP - Toxicity Characteristic Leaching Procedure
TWA - Total Waste Analysis

Table 5. Summary of Full Scale S/S Sites

Site	Contaminant	Physical Form	Binder	Percentage Binder(s) Added	Treatment (batch/ continuous In Situ)
Independent Nail, SC	Zn, Cr, Cd, Ni	Solid/soils	Portland cement	20%	Batch Plant
Midwest, US Plating Company	Cu, Cr, Ni	Sludge	Portland cement	20%	In Situ
Unnamed	Pb/soil 2-100 ppm	Solid/soils	Portland cement and proprietary ingredient	Cement (15-20%) proprietary (5%)	In Situ
Marathon Steel, Phoenix, AZ	Pb, Cd	Dry-landfill	Portland cement and silicates	Varied 7-15% (cement)	Concrete batch plant
Alaska Refinery	Oil/oil sludges	Sludges, variable	Portland cement and proprietary ingredient	Varied 50+	Concrete batch plant
Unnamed, Kentucky	Vinyl chloride Ethylene dichloride	Sludges, variable	Portland cement and proprietary ingredient	Varied 25+	In Situ
NE Refinery	Oil sludges, Pb, Cr, As	Sludges, variable	Kiln dust (high CaO content)	Varied, 15-30%	In Situ
Velsicol Chemical	Pesticides and organics (resins, etc.) up to 45% organic	Sludges, variable	Portland cement and kiln dust, proprietary ingredient	Varied (cement 5-15%)	In Situ
Amoco Wood River	Oil/solids Cd, Cr, Pb	Sludges	Proprietary ingredient	NA, proprietary	Continuous flow (proprietary)
Pepper Steel & Alloy, Miami, FL	Oil saturated soil Pb-1000 ppm PCBs-200 ppm As-1-200 ppm	Soils	Pozzolanic and proprietary ingredient	~30%	Continuous feed (mixer proprietary design)
Vickery, Ohio	Waste acid PCBs (<500 ppm) dioxins	Sludges (viscous)	Lime and kiln dust	~15% CaO ~5% kiln dust	In Situ
Wood Treating, Savannah, GA	Creosote wastes	Sludges	Kiln dust	20%	In Situ
Chem Refinery, TX	Combined metals, sulfur, oil sludges, etc.	Sludges (synthetic oil sludges)	Portland cement and proprietary ingredient	NA	Continuous flow
API Sep. Sludge, Puerto Rico	API separator sludges	Sludges	Portland cement and proprietary ingredient	50% cement ~4 % proprietary	Concrete batch plant
Metaplating, WI	Al-9500 ppm Ni-750 ppm Cr-220 ppm Cu-2000 ppm	Sludges	Lime	10-25%	In Situ

chemical characteristics, but only mixed results have been achieved. For example, tests of standardized wastes treated in a standardized fashion using acrylonitrile, vinyl ester, polymer cement, and water-based epoxy yielded mixed results. Vinyl and plastic cement products achieved superior UCS and leachability to cement-only and cement-fly ash S/S, while the acrylonitrile and epoxy polymers reduced UCS and increased leachable TOC, in several instances by two or three orders of magnitude [36, p. 156].

The estimated cost of treating waste with S/S ranges from $50 to 250 per ton (1992 dollars). Costs are highly variable due to variations in site, soil, and contaminant characteristics that affect the performance of the S/S processes evaluated. Economies of scale likely to be achieved in full-scale operations are not reflected in pilot-scale data.

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EPA

Engineering Bulletin
Air Pathway Analysis

Purpose

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

Abstract

This bulletin presents information on estimating toxic air emissions from Superfund and hazardous waste sites. The focus is on the collection of air emissions data during the site investigation (SI) and remedial investigation/feasibility study (RI/FS). Emissions of volatile compounds and particulate matter during site disturbances, such as excavation, may be several orders of magnitude greater than the emissions levels of an undisturbed site [1]*. The potential air emissions from the undisturbed and disturbed site must be understood before developing a site mitigation strategy.

The USEPA has developed a systematic approach, called an Air Pathway Analysis (APA), for determining what air contaminants are present and at what level these compounds may be released into the atmosphere. The APA method is outlined in a four volume series [2,3,4,5]. The intent of this bulletin is to help Remedial Project Managers (RPMs) and On Site Coordinators (OSCs) conduct adequate APAs to characterize sites and prevent problems during site investigation and remedial action.

This bulletin presents information on how to conduct an APA, equipment and methods for assessing the extent of an air emission problem, and the requirements and limitations of an APA. The emission assessment techniques address all types of air contamination: volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), volatile inorganic compounds (VICs), and particulate matter (PM) including metals, dioxins, etc. Points of contact are provided for further information.

APA Applicability

The protocol for an APA (Figure 1) consists of four major steps: (1) defining the APA objectives; (2) site scoping; (3) site screening; and (4) in depth APA [3, p. 24].

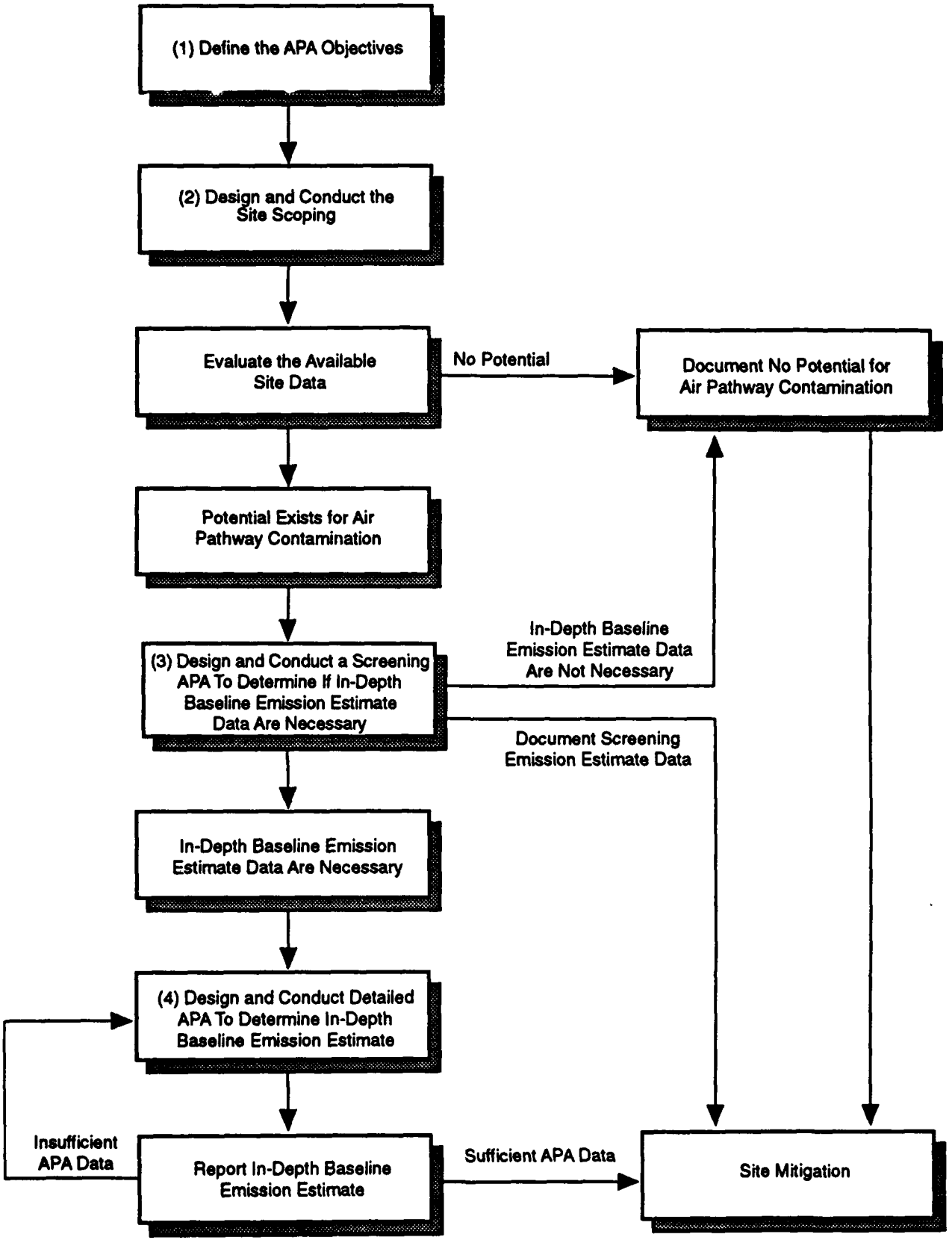
The process is initiated by defining the APA objectives, the most critical step. The objectives should address specific questions or needs (e.g. determine the maximum, short-term exposure levels at the site fenceline) rather than being overly general. The next step is to investigate available file information to determine the level of screening activity appropriate for the site. Site screening is used to determine if the site has the potential to emit air contaminants in its undisturbed or disturbed state. If the site screening indicates that the site does not have the potential to emit significant levels of air contaminants, the RPM can document "no potential" for adverse emissions and the APA is complete. If the potential exists, an in-depth APA should be designed and conducted. In-depth sampling techniques generally are used to collect emission rate data from small areas to estimate what the emissions would be from the entire site.

An initial APA should be conducted as part of the site investigation with a more complete APA performed once the RI/FS data are available. Unfortunately, it is common for air pathway concerns not to be raised until the RI/FS stage of a site. In cases where the RI is complete and insufficient data are available, it may be necessary to return to the site for a limited field study.

Conducting a proper APA also requires that air monitoring be conducted during site remediation to ensure that site activi-

* [reference number, page number]

FIGURE 1. FLOWCHART OF ACTIVITIES FOR DEVELOPING SCREENING AND IN-DEPTH EMISSION ESTIMATES (3, p. 24)



ties, such as excavation or treatment technologies, do not create a short term health risk. Most sites have a significant increase in air emissions when the waste is disturbed.

One important aspect of designing and conducting a successful APA is understanding the pathways by which air contaminants leave the site and factors that influence site emissions. Figures 2 and 3 provide conceptual schematics of likely emission sources for landfills (i.e. any subsurface waste) and lagoons. There are both surface and subsurface pathways. Some pathways are important in the undisturbed state; while others are important in the disturbed state. Most sites have weathered, aged surfaces that inhibit air emissions so the subsurface sources are more dominant for undisturbed sites. Subsurface migration pathways form through the soil and along subsurface conduits. Emissions generally will be dominated by materials handling operations and exposure of freshly disturbed waste (e.g. open pits, stockpiles).

APA Techniques

In general, all screening and in-depth emission assessment techniques fall into one of four basic approaches for obtaining APA data. The techniques include: direct measurement, indirect measurement, fenceline monitoring/modeling and predictive modeling. The variety of available methods allows for cost-effective data collection. Some methods for conducting screening and in-depth air pathway analyses and their applications are shown in Table 1. Selection of the type of the screening or in-depth technology will depend on project resources, schedule, personnel capabilities, emission contaminant type(s) present, site emission potential, and the intended use of the APA data [3].

The direct measurement approach consists of techniques that provide an empirical measurement of emissions. This approach allows for accurate estimates of emissions with known uncertainty but these techniques may be more expensive and time consuming than other techniques. If emission data are needed for health risk assessment, the direct emission measurements may be the most appropriate approach.

Indirect emission measurement techniques involve the collection of ambient concentration data and meteorological information under specific conditions. These data typically are used to develop inputs for a numerical model to estimate the emission rate. These methods are usually less precise than direct methods, but an emission estimate can be calculated without having the specific field data.

The fenceline monitoring/modeling approach requires operation of a monitoring network to tabulate ambient upwind and downwind concentration data with simultaneously collected meteorological data. A dispersion model, based on field study data or published emission factors, can give estimates of downwind concentrations. The model output can be refined by adjusting the hypothetical input until the output matches the actual ambient air monitoring data. The fenceline monitoring/modeling approach is often preferred to other assessment methods when valid, comprehensive ambient air monitoring data are available.

Predictive modeling may be useful in estimating emissions from a site. An appropriate theoretical model is selected to represent the site (i.e., landfill, non-aerated lagoon with oil layer, etc.) and site information is used to estimate gross emissions from the site. Since many variables affect emission rates from a site, this approach is limited by the representativeness of the model and by the input used. This approach is usually used as a screening-level evaluation to support or refute the need for additional APA, but should not be used without site-specific data to support planning or decision-making activities (e.g. health risk assessments).

Screening Level Assessment Techniques

Head space analysis of bottled waste is a simple but effective direct screening measurement technique that involves collecting waste material in a bottle with "significant" head space and allowing the waste/head space to reach equilibrium. The head space gas is then analyzed for volatile compounds with simple real time analyzers. This activity can be conducted in conjunction with a soils investigation. These data are often used to make field decisions regarding which soil/sludge samples should undergo compound specific analyses. If the screening consistently shows little or no volatile emissions from samples across the site, then an in-depth study may not be necessary. Subsurface soils may need to be assessed in addition to surface soils. Little or no volatile emissions are defined as less than three times the analytical detection limit. It is recommended that a few gas samples be collected for a gas chromatograph/mass spectrometry speciation analyses to confirm the emission levels. If these screening level data suggest a strong potential for emissions, then they can be used to help design the in-depth APA.

Particulate matter emissions can also be tested in a screening manner. Collected samples can be analyzed for particle size and soil moisture or tested for "dustiness" [6] or can be estimated via modeling techniques [3]. Experimental waste handling and visual observation can also indicate the emissions potential of PM. These data are used to make the decision as to whether or not further APA activities are needed.

Upwind/downwind survey monitoring is an indirect screening method used to study emissions by monitoring upwind/downwind concentrations of ambient target compounds. A conventional monitoring strategy and air sampling/monitoring approach is used. Often, real time analyzers with flame ionization and photoionization detection are used for organic emission detection. Integrated air samples (e.g., grab samples) are collected using techniques such as evacuated, stainless steel canisters for VOCs and high-volume filter samples for particulate matter. Advanced techniques such as optical remote sensing can also be used to quantify emission potential for the detection of compounds.

A realtime instrument survey is similar to upwind/downwind screening except that the screening usually takes place directly over the waste to obviate modeling by testing the air above the surface. This approach can identify "hot spots" of emissions and zones of similar emissions.

FIGURE 2. CONCEPTUAL SCHEMATIC SHOWING AIR CONTAMINANT PATHWAYS FROM AN UNLINED LANDFILL (3, p. 13)

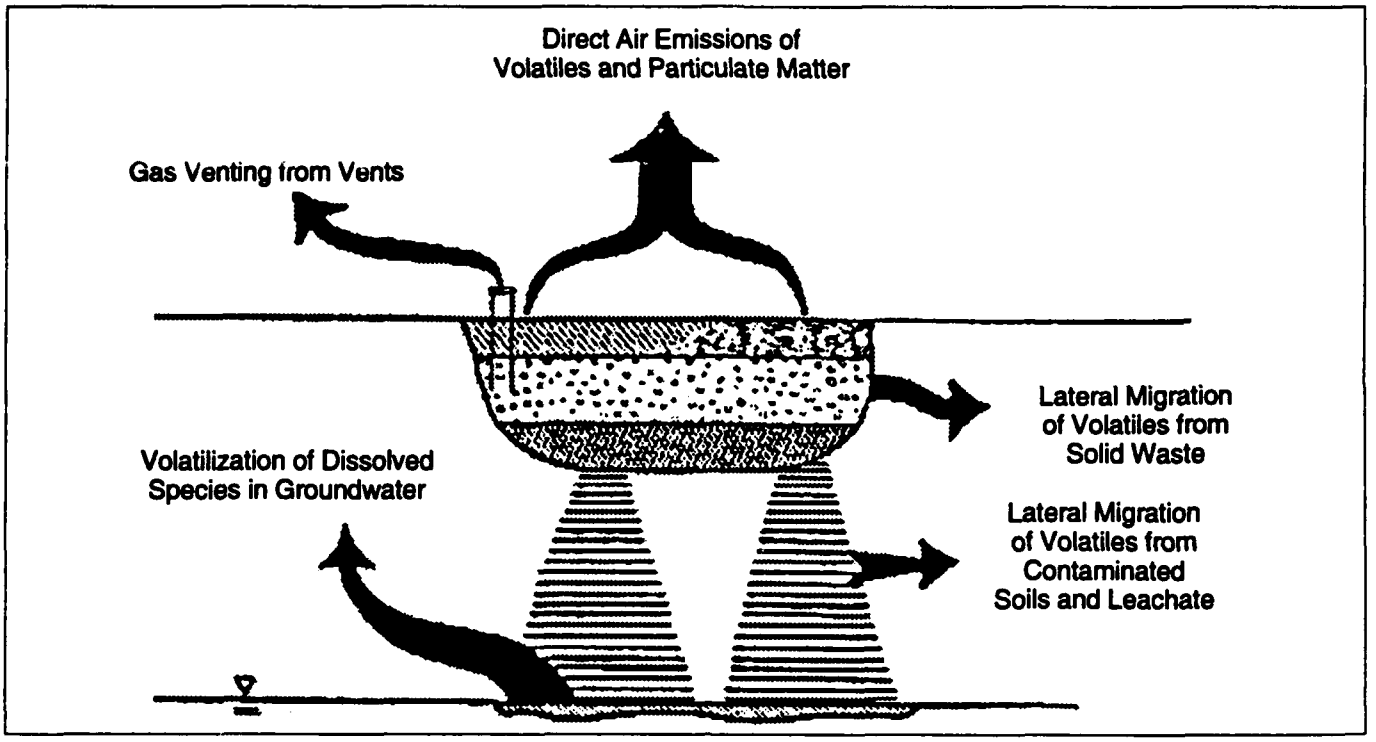


FIGURE 3. CONCEPTUAL SCHEMATIC SHOWING AIR CONTAMINANT PATHWAYS FROM AN UNLINED LAGOON WITH NO COVER (3, p. 14)

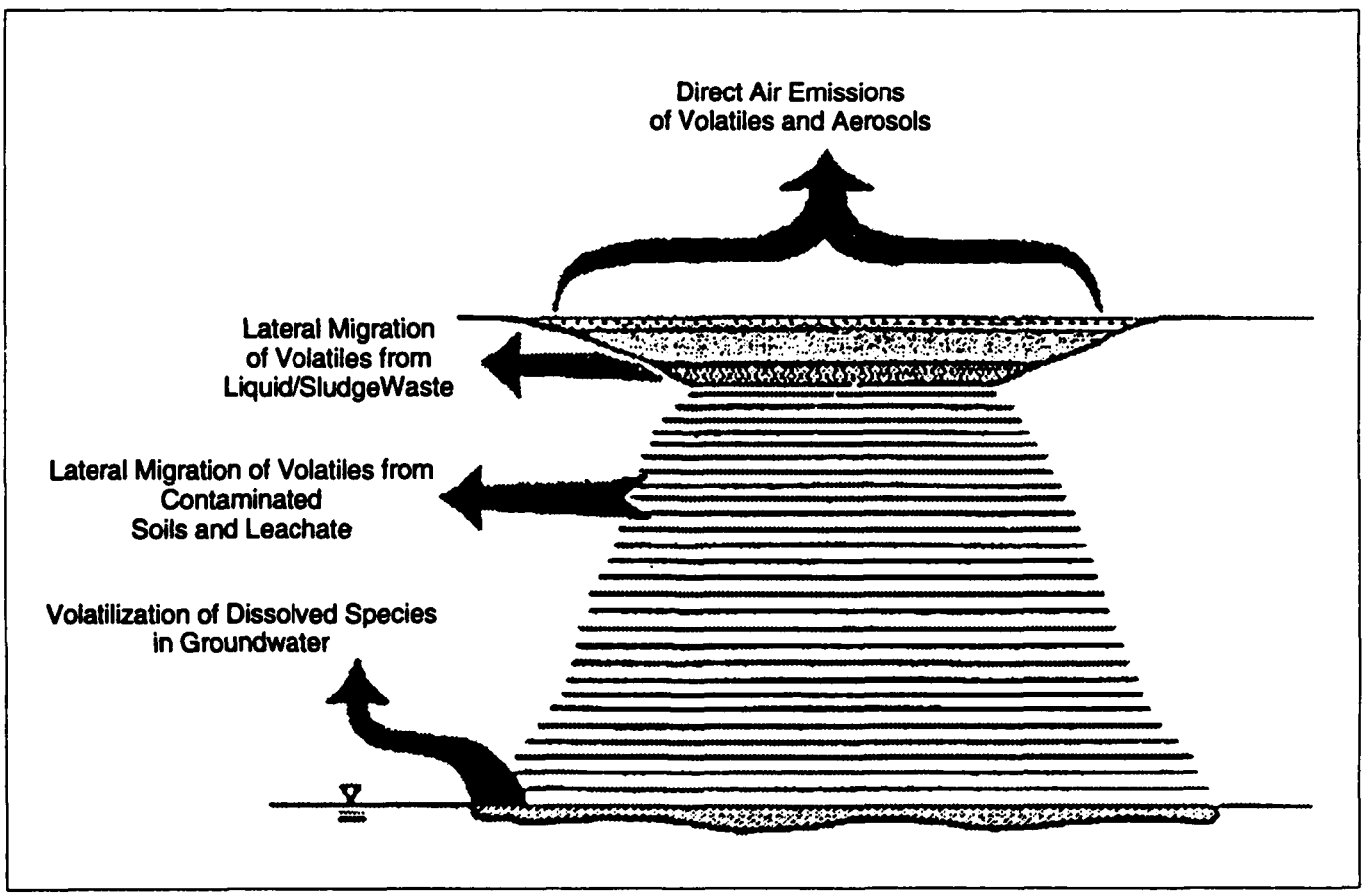


TABLE 1. DATA COLLECTION OPTIONS AND APPLICATIONS

TECHNIQUES	COLLECTION METHOD	LEVEL OF EFFORT	APPLICATION	COMPOUNDS [1]	DETECTORS [2]
Head Space Analysis	Bottle	Screening	Field Measurement	VOC, SVOC; VIC	OVA, PID for VOCs and SVOCs; SD for VICs
Static Chamber	Canisters; Tedlar Bags	Screening/ In-Depth	Field Measurement	VOC, SVOC; VIC	OVA, PID for VOCs and SVOCs; SD for VICs
Realtime Instrument Survey	Instrument on/near Waste Surface	Screening	Field Measurement	VOC, SVOC; VIC; PM	OVA , PID for VOCs and SVOCs;SD, H/S for VICs; DM for PM
Upwind/Downwind Survey	Polyurethane Foam; Solid Sorbent; Filter	Screening	Field Measurement	VOC, SVOC; VIC; PM	OVA , PID for VOCs and SVOCs;SD, H/S for VICs; DM for PM; GC/MS
Modeling	Data Required: Soil Contaminants/Concentrations; Porosity; Moisture	Screening/In-Depth	Field Measurements for Soil Characteristic Data or can use Model Defaults	VOC, SVOC; VIC; PM	N/A
Surface Flux Chamber	Enclosure	In-Depth	Field Measurement;(can use directly on freshly disturbed soil)	VOC, SVOC; VIC; PM	OVA, PID for VOCs and SVOCs; SD, GS/MS
Soil Vapor Probes	Probes	In-Depth	Field Measurement; Conduct Limited Transect (One Upwind, Two or Three Downwind)	VOC, SVOC; VIC; PM	OVA, PID for VOCs and SVOCs; SD, GS/MS
Downhole Flux Chamber	Enclosure	In-Depth	Field Measurement	VOC, SVOC; VIC	OVA, PID for VOCs and SVOCs; SD, GC/MS
Transect	Optical Remote Sensing or Array of Point Samples	In-Depth	Field Measurement	VOC, SVOC; VIC	FTIR, UV-DOAS, GFC, FBPA, Laser, PAS, LIDAR, etc.[3]
Fenceline Monitoring/ Interactive Modeling	Any of Above Methods	In-Depth	Field Measurement	VOC, SVOC; VIC	OVA PID for VOCs and SVOCs; SD

[1] VOC = Volatile Organic Compounds
SVOC = Semivolatile Organic Compounds
VIC = Volatile Inorganic Compounds
PM = Particulate Matter

[2] OVA = Organic Vapor Analyzer
PID = Photoionization Detector
SD = Specific Compound Detector
H/S = Health/Safety Director
DM = Dust Monitor

[3] Optical Remote Sensing Detectors
FTIR = Fourier Transform Infrared
UV-DOAS = Ultraviolet-Differential Optical Absorbance
GFC = Gas Filter Correlation
FBPA = Filtered Band Pass Absorption
Laser = Laser Absorption
PAS = Photoacoustic Spectroscopy
LIDAR = Light Detection And Ranging
ETC = Diode-Laser Spectroscopy

Predictive models can be used to determine if the site has an emissions potential. This is a good screening approach provided that waste composition and concentration data are available. (Since most models are conservative, predictive modeling is generally used to determine if a site does not have a significant emissions potential and that no further APA is required.) This approach can also be used for an in-depth APA, provided that measured and representative model input, including waste composition and physical data, are used with an appropriate model.

In-Depth Level Technologies

Surface flux chamber is a preferred direct measurement approach applicable to many types of waste sites [3] and capable of generating both undisturbed and disturbed emission rate data for volatile and semivolatile compounds. The technology uses a chamber to isolate a surface emitting gas species (organic or inorganic); emission rates are calculated by measuring the gas concentration in the chamber and using the chamber sweep air flowrate and surface area.

Soil vapor probe is a direct measurement method that uses a chamber and sweep air to measure emission rates [3]. The chamber is a small exposed area at the end of a ground probe where sweep air is added at a fixed, known rate and gas samples are collected and analyzed for volatile and semivolatile compounds. While this technology is typically used for plume mapping it is capable of generating emission rate data that represent waste emissions as if the land surface were disturbed and exposed.

Downhole flux chamber, a third direct measurement technology, is similar to the soil vapor probe method in that it obtains subsurface gas emission rates that represent disturbed waste. However, this technology is used with a hollow-stem drilling rig, and emission rates are obtained from subsurface waste up to 100 feet below the surface (or more if necessary). A cylindrical chamber is lowered down the annulus of the hollow-stem auger and the air at the freshly exposed waste at the depth of the borehole is sampled. Both the soil vapor probe and the downhole flux chamber technologies provide useful disturbed waste emission rate data without the need to excavate the waste.

Transect technology is an indirect method that involves the collection of ambient concentration data for gaseous compounds and/or particulate matter using a two-dimensional array of point samplers. These data, along with micro-meteorological data, can be used to estimate the emission rate of the source by using a specific dispersion model. Data can be obtained that represent emissions from a complex or heterogeneous site or an activity that generates fugitive air emissions.

Ambient concentration data can also be collected using path averaged techniques or line integration such as optical remote sensing techniques.

Fenceline monitoring/modeling can be used to develop screening or in-depth emission rate data. Data quality depends on the type of air monitoring conducted, the extent of the data set, the quality of the meteorological data, and the dispersion model used to simulate the emission event. This approach is often used to support emission rate data obtained from other approaches or when fenceline monitoring is conducted for other purposes. It is typically not performed for the sole purpose of providing emission rate data.

Limitations

Screening Level Technologies

Head space analysis of a sample in a bottle is limited by the procedure and instrument used to perform the screen. Typically, a broad-band realtime gas analyzer is used (e.g., an Organic Vapor Analyzer). This type of analyzer provides useful information but is often subject to interferences.

Upwind/downwind survey monitoring is generally limited in its ability to identify properly the emission potential of the site for the following reasons: testing out of the plume; not accounting for upwind interferences; or using survey instruments that are incapable of detecting the compounds emitted.

Realtime instrument survey has the same limitations as upwind/downwind screening except that measurements are generally made over the waste; therefore meteorological conditions have less of an influence on the results.

Predictive models are inherently limited by the assumptions of the model itself. It is important that an appropriate model be selected and site-specific input data are used where possible.

In-Depth Level Technologies

Surface flux chamber is limited by the number of data points that are needed or required to describe the source. If the site is heterogeneous, each area of similar emissions potential requires an assessment. The number of data points needed to describe each unit may be significant. The technology is not applicable to particulate matter and is of limited use for assessing emissions from active processes with fugitive emissions.

Soil vapor probe technology has the same limitations as the surface flux chamber regarding the number of data points required to assess the source and is also limited to gaseous emissions. Further, the depth of the investigation is limited to assessing emissions typically up to 10 feet below the land surface. While the waste source may be deeper, the exposed surface is small, resulting in emission rate estimates of higher uncertainty than other direct technologies.

Downhole flux chamber limitations are similar to those of the soil vapor probe technology, but the maximum depth is generally up to 100 feet below land surface. A drilling rig is required, increasing the costs of the operation. Combining downhole flux chamber measurements with other site assessment activities using hollow-stem augers can substantially reduce costs.

Transect technology is limited by upwind interferences, analytical limits of detection, meteorological influences, and the need to use a model to estimate emission rate. It can be time consuming and expensive to collect the required field data since the meteorological conditions of the model must be met prior to data collection in order for the model to be effective.

Fenceline monitoring/modeling is generally limited by the extent of the monitoring network, the quality of these data, upwind interferences, analytical sensitivity, and the need to use modeling to estimate emission rates. This method has the same limitations as the transect technology and, in addition, is usually considered less accurate because the model used is not specific to the conditions by which the ambient data were collected.

Site Requirements

There are no specific site requirements for an APA assessment other than a secure site, site access, and standard support facilities. As with all site investigation work, a site trailer equipped with 110 volt, 50 or 100 amp electric service, lighting, and a telephone provides a functional work area. Portable field instruments usually are battery powered and require charging overnight. A trailer with 110 volt power permits recharging of the analyzers on the trailer overnight, thereby keeping the equipment onsite. Since many field analyzers require calibration, an area, perhaps along the side of the trailer, can be equipped with a gas bottle rack for safe storage and use of compressed gases (e.g., calibration and support gases). An ambient monitoring network may require weatherproof, AC-powered shelters. Worker support facilities are also recommended but are not required. A facilities trailer equipped with storage and decontamination areas is often useful.

Status of the APA Process

EPA has provided technical guidance for conducting an analysis of the air pathways for air toxic species at waste sites and for conducting air monitoring. This technical guidance is contained in a four-volume series:

VOLUME I Application of Air Pathway Analysis for Superfund Activities

VOLUME II Estimation of Baseline Air Emissions at Superfund Sites

VOLUME III Estimation of Air Emissions from Cleanup Activities at Superfund Sites

VOLUME IV Procedures for Dispersion Modeling and Air Monitoring for Superfund Air Pathway Analysis

These volumes are currently being revised. Any of the EPA contacts will be aware of the current status of the APA documents.

The amended National Contingency Plan expands upon the requirement to conduct and fully document an air pathway analysis. The process is defined as a "systematic approach involving a combination of modeling and monitoring methods to assess actual or potential receptor exposure to air contaminants" [2, p. 2-1]. Volume I explains this approach and how the APA integrates into the site remediation process. Volume II provides the "how to" information needed to conduct an APA including all recommended screening and in-depth technologies for assessing air emissions [3]. Estimating emissions from remedial processes is covered in Volume III [4], and air modeling and air monitoring approaches are presented in Volume IV [5]. This series was written with the EPA RPM as the target audience.

Research efforts are underway to improve these assessment methods and explore further applications. Current research is focused on using these methods to design and then test the effectiveness of various air emission control technologies. Other studies have been proposed to provide correlations for data obtained from screening and in-depth methods so that better estimates of emission rates can be obtained from cost-effective field studies.

EPA Contact

Technology-specific questions regarding air emissions assessment and air monitoring at hazardous waste sites may be directed to:

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EPA

Engineering Bulletin
Control of Air Emissions From Materials Handling During Remediation

Purpose

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

Abstract

This bulletin presents an overview discussion on the importance of and methods for controlling emissions into the air from materials handling processes at Superfund or other hazardous waste sites. It also describes several techniques used for dust and vapor suppression that have been applied at Superfund sites.

Air emission control techniques have been utilized for Superfund cleanups at the McColl site (CA) and at the LaSalle Electric site (IL). Foam suppression has been used at Rocky Mountain Arsenal (CO), Texaco Fillmore (CA), and at a petroleum refinery (CA) site. A number of temporary vapor suppression techniques have also been applied at other sites. Additionally, the experience gained in the mining industry and at hazardous waste treatment, storage, and disposal sites will yield applicable methods for Superfund sites.

This bulletin provides information on the applicability of air emission controls for materials handling at Superfund sites, limitations of the current systems, a description of the control methods that have found application to date, site requirements, a summary of the performance experience, the status of the existing techniques and identification of future development expectations, and sources of additional information.

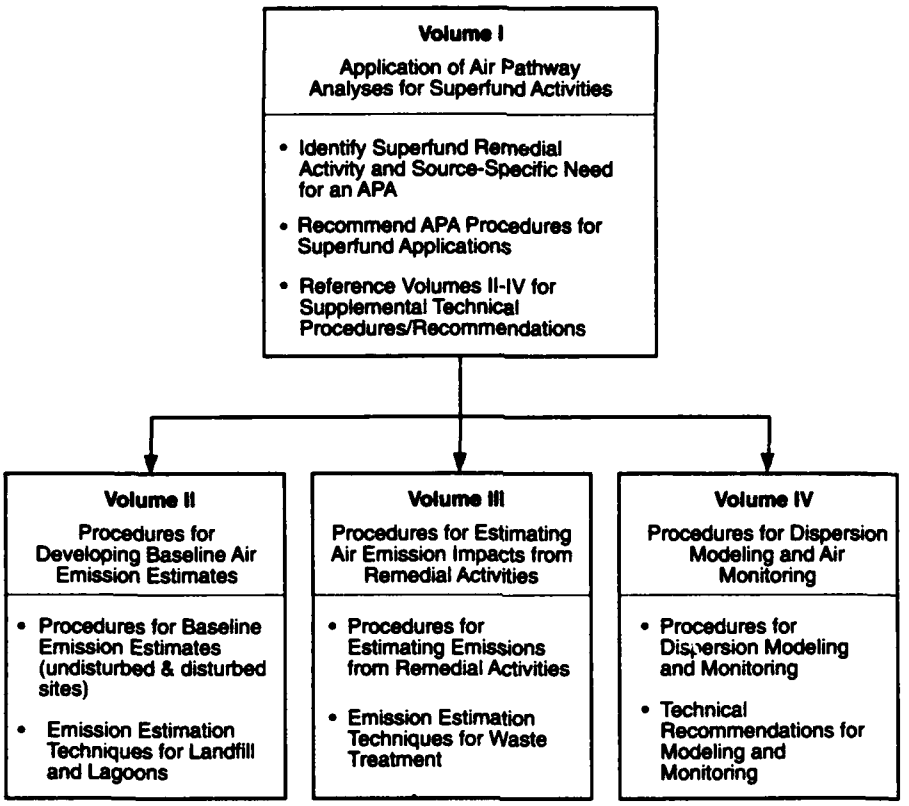
Applicability of Materials Handling Controls

Estimation of the potential releases to the air and an analysis of the impacts to the air pathway are applicable to every activity in the Superfund process. Since nearly every Superfund site has a potential air emissions problem, the focus of this bulletin is to assist RPMs and OSCs in considering the appropriate methods for material handling at Superfund sites. To do that, the first step is to estimate the potential releases using the air pathway analysis (APA) process.

The amended National Contingency Plan expands upon the requirement to conduct and fully document a regimented process called an air pathway analysis (APA). The process is defined as a "systematic approach involving a combination of modeling and monitoring methods to assess actual or potential receptor exposure to air contaminants" [1 p. 1-1]*. When considering removal or remedial responses (i.e., technologies), an APA detailing emission estimates is useful for determining the potential compliance with applicable or relevant and appropriate requirements (ARARs) during remedial action, particularly at a State or local level. Compliance with National Ambient Air Quality Standards during a remediation or the excavation and processing of the contaminated media must be addressed. With the passage of the Clean Air Act Amendments in November 1990 and the advent of numerous state air toxics programs, remediation of Superfund sites must address the

* [reference number, page number]

Figure 1
Procedures for Conducting APA for Superfund Application—Overview [1, p.1-4]



media transfer that excavation and materials handling (before and after treatment) will create, and the ARARs these regulations represent. Figure 1 [1, p. 1-4] indicates the applicability of the guidance study series documents on the air pathway analysis to remedial project managers/on-scene coordinators and to contractors and other technical staff.

The potential for short-term risk (i.e., during the remedial action) is a major criterion when selecting the best remedial alternative. The general classes of contaminants of concern are gaseous and particulate emissions. Particulate matter (PM) becomes airborne via wind erosion, mechanical disturbances (such as excavation and material processing), combustion, and desorption. Gaseous species are primarily volatilized contaminants (VCs), but natural processes such as biodegradation and photo-decomposition can result in releases once the site has been disturbed. Since volatilization is the primary mechanism for gaseous emissions, any volatile contaminant in the soil, a lagoon, a landfill, or even in open containers may be released to the air. The carcinogenic and noncarcinogenic hazards that gases and particulates present in the air pathway must be assessed.

When initially considering remediation technologies applicable to a site, the APA process can play an integral role in estimating the risk that excavation and materials processing pose to the receptors in the area. Any ex situ process that requires such excavation and material sizing, screening, or other pretreatment processing will result in losses of particulate and volatile contaminants.

Similarly, emissions generated during the operation of the technology (i.e., losses from air pollution control equipment or fugitive losses from the treatment process itself) must be estimated in order to complete the air emissions source assessment prior to final selection of the remedial technology. The ambient concentrations of air contaminants may have to be monitored during the remediation process to ensure compliance with local air toxics regulations. All of these considerations should be assessed, a cost estimate prepared, and the results should become an integral input to the selection of alternative technologies according to the National Contingency Plan process. Of these criteria, overall protection of human health and the environment, ARAR compliance, implementability, cost, short-term effectiveness and State and community acceptance become paramount concerns for the air pathway impact.

Results of a recently published study [16] indicate significant VC losses during typical soil excavation, transport, and feed/preparation operations. The contribution of each remedial step to the VC emissions was examined. Table 1 presents the results for each step. Although different chemical constituents and concentrations were present in two different site zones, the contribution of each remedial step to the VC emissions during

Table 1
Remedial Step Fractional Contribution to VCs [16, p. 39]

Remedial Activity	Overall Site
Excavation	0.0509
Bucket	0.0218
Truck Filling	0.0905
Transport	0.3051
Dumping	0.5016
Incinerator	0.0014
Exposed Soil	0287
Total	1.0000

Table 2
Common Control Technologies Available For Materials Handling [*]

Remedial Operation	Control Technology
Excavation	Water sprays of active areas Dust suppressants Surfactants Foam coverings Enclosures Aerodynamic considerations
Transportation	Watersprays of active areas Dust suppressants Surfactants Road carpets Road oiling Speed reduction Coverings for loads
Dumping	Water sprays of active areas Water spray curtains over bed during dumping Dust suppressants Surfactants
Storage (waste/ residuals)	Windscreens Orientation of pile Slope of pile Foam covering and other coverings Dust suppressants Aerodynamic considerations Cover by structure with air displacement and control
Grading	Light water sprays Surfactants
Waste feed/ preparation	Cover by structure with air displacement and control

*Adapted from [1].

the excavation process remained constant. This contribution was dependent on the parameters of the soil and the remedial activity pattern. At this site, dumping and temporary storage at the incinerator accounted for 50 percent of the VC emissions; transport from the excavation zone was the second highest contributor of emissions. All activities were assumed to be uncontrolled. The use of tarps and/or foam suppressants could substantially reduce these emissions from transport and storage.

Limitations

The control methods for dust and vapor suppression rarely remove 100 percent of the contaminants from the air. These releases have to be estimated, along with the cost estimate for application of the control method to properly assess the feasibility of implementating the remediation technology being considered. Site conditions determine the effectiveness of specific control methods.

Some methods have very limited periods of effectiveness, making multiple applications or specialized formulations necessary. The scheduling of media excavation and processing may be impacted, for example, in matching the length of effectiveness of a foam or spray suppression technique being used.

If gaseous emissions are expected to be high, or local fugitive limitations apply, costly areal containment methods may be required. If a very large site is to be excavated and the materials classified or preprocessed, portable versions will have to be designed for local air emission control. The use of such portable containment strategies will affect the overall schedule of the remediation and will mandate unique worker safety plans to ensure that the proper level of protective apparel and monitoring devices are used during the excavation process.

Control Methods

A list of the most commonly used control technologies applicable to VCs and PMs released during soils handling is presented in Table 2 [1, p. 5-31].

Volatilization of contaminants from a hazardous waste site may be controlled by reducing soil vapor pore volume or using physical/chemical barriers [2, p. 116]. The rate of volatilization can be reduced by adding water to reduce the air-filled pore spaces or by reduction of the spaces themselves through compaction techniques. Compaction, however, would displace the volatiles occupying the free spaces (soil venting); water suppression might result in mobilizing the contaminant into a groundwater medium if not properly applied. Wastes amenable to this form of suppression include most volatile organic (e.g., benzene, gasoline, phenols) and inorganic (e.g., hydrogen sulfide, ammonia, radon, methyl mercury) compounds in soil. Contaminants with a high vapor phase mobility and low water phase partition potential are particularly amenable to this vapor control technique. However, the inititial application of water will force VCs from the soil-free spaces.

Physical/chemical barriers have found broad utility in temporary vapor and particulate control from hazardous waste sites [3, p. 4-1 to 4-10]. Evaporation retardants such as foams may be applied, while simpler windscreens, synthetic covers, and water/surfactant sprays have been used during excavation and transportation operations. The most exotic system applied to a Superfund site included a special domed structure erected over the excavation area and equipped with carbon adsorption beds through which the internal vapors were drawn [4]. The domed structure was designed to limit emissions through the structure and was capable of being transported to the next excavation site when required. A similar structure may be necessary at the point of materials processing, prior to a proposed incinerator for the site. This facility might be fixed, provided a centralized location for the incinerator can be established.

Sound engineering practices include a multitude of methods for vapor and dust suppression; these techniques are shown in Table 3 [5, p. vi]. More than a dozen different techniques have been identified. Several of the methods in Table 3 can be used collectively to achieve fugitive emissions control. Application of foams during excavation operations and tarps for overnight storage can achieve a greater overall control efficiency at significantly lower cost than the use of an enclosure with carbon adsorption control. Good engineering practices employing the use of windscreens or other aerodynamic considerations may provide adequate control at some sites; other sites may require application of nearly every method in the list. Cost estimates of many control techniques for VCs are presented in Reference 6 [6, p. 68]. The cost estimates in Reference 6 are not specific to any particular Superfund site. Cost estimates vary significantly according to the site conditions, contaminant type, and ARARs to be met. Table 3 presents a relative cost index for illustrative purposes.

Table 3
Realtive PM/VC Supression Technologies

Suppression technique	Relative Effectiveness Low	Medium	High	Relative Cost
Minimize waste surface area	✖	✖	✖	1
Aerodynamic considerations	✖			1
• Windscreens	✖			1
• Wind blocks	✖			1
• Orientation of activities	✖			1
Covers, mats, membranes, and fill materials	✖	✖		2–3
Water application	✖	✖		2–3
Water/additives	✖	✖		2–3
Inorganic control agents	✖	✖		2–3
Organic dust control		✖		2–3
Foam suppressants		✖	✖	7-10
Enclosures			✖	10

Site Requirements

General site conditions that dictate the estimated magnitude of air emissions are provided in Table 4 [7, p. 16]. The requirements for implementation of the dust/vapor control techniques are a function of the estimated emissions once these site conditions have been assessed. Baseline estimation techniques are available for both undisturbed and disturbed sites, as well as mathematical modeling and actual direct measurement methods to verify estimates. Consideration of the particular weather conditions relative to the proposed remediation schedule is critical to efficient control of air emissions. Tables 3 and 4 should be considered concurrently when structuring an air emissions control strategy for the site and the remediation activities.

Table 4
Important Parameters Affecting Baseline Air Emission Levels [7]

Parameter	Qualitative Effect[a] Volatiles	Particulate Matter
Site Conditions		
Size of landfill or lagoon	Affects overall magnitude of emissions, but not per area.	Affects overall magnitude of emissions, but not per area.
Amount of exposed waste	High	High
Depth of cover on landfills	Medium	High
Presence of oil layer	High	High
Compaction of cover on landfills	Medium	Low
Aeration of lagoons	High	High
Ground cover	Medium	High
Weather Conditions		
Wind speed	Medium	High
Temperature	Medium	Low
Relative humidity	Low	Low
Barometric pressure	Medium	Low
Precipitation	High	High
Solar radiation	Low	Low
Soil/Waste Characteristics		
Physical properties of waste	High	High
Adsorption/absorption properties of soil	Medium	Low
Soil moisture content	High	High
Volatile fraction of waste	High	Low
Semivolatile/nonvolatile fraction of waste	Low	High
Organic content of soil and microbial activity	High	Low

[a]High, medium, and low in this table refer to the qualitative effect that the listed parameter typically has on baseline emissions.

Table 5
Summary of VOC Air Emissions Control Technologies For Landfills [*]

Control	Advantages	Disadvantages
Foams	• Easy to Apply • Effective • Allow for Control of Working Faces • Can Reduce Decontamination	• Moderately Expensive • Requires Trained Operators
Complete Enclosure/ Treatment System	• May Provide the Highest Degree of Control For Some Applications	• High Cost • Air Scrubbing Required • High Potential Risk • Must Work Inside Enclosure
Fill Material	• Inexpensive • Equipment Usually Available	• Hard to Seal Air-Tight • No Control for Working Face • Creates More Contaminated Soil
Synthetic Membrane	• Simple Approach	• Worker Contact with Waste on Application • Hard to Seal Air-Tight
Aerodynamic Modification	• Simple • Lower Cost • Low Maintenance	• Variable Control • Requires Additional Controls
Fugitive VC/PM Collection Systems	• Can Be Used in Active Areas	• Limited Operational Data Exist • Effective Range Limited • Maintenance Required
Minimum Surface Area, Shape	• Inexpensive • Can Be Included in Plan	• Must Maintain • Cannot Always Dictate Shape
Water	• Easy to Apply	• A Potential Exists for Leaching to Groundwater
Inorganic/Organic Control Agents	• Similar to Foams	• Not as Effective as Foams For Working Areas

* Adapted from [14]

Performance Experience

A study of fugitive dust control techniques conducted with test plots at an active cleanup area documented decreasing effectiveness of foam suppressants within 2 to 4 weeks of application. The effectiveness of water sprays on dump trucks and at the loading site was in the 40 to 60 percent range for the site and 60 to 70 percent range for the truck [8, p. 2]. Surfactants increased the effectiveness of the water sprays.

Foam suppressants have been thoroughly studied by at least two vendors: 3M and Rusmar Foam Technology [9][10]. Laboratory data for highly volatile organics, such as benzene and trichloroethylene contaminated sand, indicated more than 99 percent suppression effectiveness for several days. Complementary data indicated better barrier performance of foams over 10-mil polyethylene film in controlling volatilization [11, p. 7 & 8]. A burning landfill was doused and the vapors suppressed by more than 90 percent using foam at a site in Jersey City [12, p. 3]. Similarly, vapors from a petroleum waste site were compared using three different test agents: temporary foam, rigid urea-formaldehyde foam, and a stabilized foam. The temporary foam yielded an average 81 percent control for 20 minutes, rigid foam produced 73 percent control for about 2 hours, and the stabilized foam was 99 percent effective for 24 hours after application [13, p. 4-7].

The performance data reported are specific to the sites and contaminants controlled. There is no direct applicability of the performance data to general Superfund sites or conditions.

Table 5 presents a summary of VC air emissions control technologies for landfills [14, p. 38]. Many of the techniques used can control fugitive particulate emissions as well.

Technology Status

The use of vapor and particulate control techniques has been directly applied to at least three Superfund sites: McColl (California), Purity Oil Site (California), and LaSalle Electric (Illinois). The McColl work is available as a Superfund Innovative Technology Evaluation demonstration of excavation techniques. Although the domed structure used controlled sulfur dioxide and VOC releases to the atmosphere, working conditions within the dome were difficult. High concentrations of dust and contaminants mandated use of a high level of personal protective apparel. Consequently, personnel were able to work within the dome for only short periods of time [15].

A variety of dust and vapor control techniques may be applied at Superfund sites. A systematic approach to estimate the quantities of air emissions to be controlled, the ambient impact, and the selection of the most appropriate control technique requires a thorough understanding of the site, wastes, emissions potential, and the most relevant combinations of control methods.

EPA Contact

Technology-specific questions regarding air emissions may be directed to:

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United States Environmental Protection Agency | Office of Emergency and Remedial Response Washington, DC 20460 | Office of Research and Development Cincinnati, OH 45268

Superfund | EPA/540/S-92/012 | November 1992

Engineering Bulletin
Design Considerations for Ambient Air Monitoring at Superfund Sites

Purpose

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

Abstract

Ambient air monitoring (AAM) may be useful or necessary for determining the air migration of toxic contaminants from Superfund sites. Emissions may be from point or area sources and may be gaseous or particulate in nature.

There are three basic approaches to air monitoring at hazardous waste sites: 1) integrated sample collection using a network of point monitors; 2) monitoring using continuous, realtime instruments or monitors using a network of point monitors; and 3) comprehensive fenceline monitoring using continuous, line source instruments (open-path, optical remote sensing). Selection of an appropriate air monitoring approach will require consideration of relevant project factors in the course of designing the air monitoring program. These basic approaches and the applicable monitoring technologies will be discussed.

This Engineering Bulletin is intended to help the RPM design the site-specific air monitoring program needed before, and during site remediation. The types of AAM activities of interest at Superfund sites are selecting the most appropriate approach, establishing the data quality objectives, and selecting the proper sampling and analytical techniques. Key design considerations, limitations, a procedure for designing the air monitoring program, and other relevant technical information regarding AAM at Superfund sites are presented. This bulletin also provides a point of contact for further information.

Air Monitoring System Design

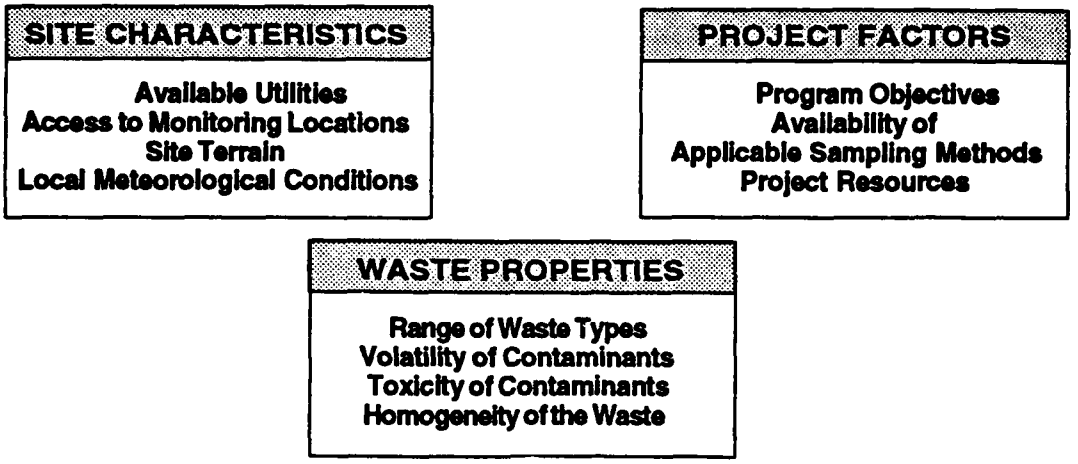
Toxic air emissions may originate from the site: in the undisturbed state; waste handling; or onsite waste treatment and preparation processes (point source) such as solidification, separation activities, waste mixing/shredding, pyrolysis, incineration, stripping, etc. Some of these processes may be in situ treatment processes such as soil flushing, vitrification, etc., which may further be uncontrolled, generating point and fugitive emissions. Due to potential emissions of air toxics, an appropriate air monitoring system must be considered in order to assess harm to the public and environment.

It is essential to conduct a proper Air Pathway Analysis (APA) in order to design a proper air monitoring program [1]*. The APA method is outlined in a four volume series [2, 3, 4, 5]. State and local regulations may require AAM at the fenceline. The air monitoring program used need not be elaborate, technically sophisticated, or require a significant share of the project resources. In fact, if the air monitoring program is properly designed and implemented, the data generated may be used to maintain contractor schedules and even reduce costs of several aspects of the program, such as onsite personnel level of protection (by avoiding shutdown, reducing cost of health/safety supplies and worker break time). The application of air emission control technologies such as area, point, or operational controls can also result in significant net cost savings by avoiding project shutdowns. The primary benefit to the program is the execution of a successful site restoration program that avoids an adverse impact on the local community and air surrounding the site.

The proper design of air monitoring programs at hazardous waste sites is also dependent on the site characteristics, properties of the waste, and other project factors (Figure 1).

* [reference number, page number]

FIGURE 1. KEY SITE FACTORS THAT INFLUENCE OR CONTROL THE DESIGN AND IMPLEMENTATION OF AIR MONITORING PROGRAMS



Site Characteristics

Available utilities may influence the choice of monitors used. Some programs can utilize battery-powered instruments or integrated sample collection techniques; others require line or generator power if many stations are needed or if the program will operate for several months. A water supply is generally needed only for decontamination and worker convenience. Caution needs to be taken in order that emissions from the power generator are not monitored inadvertently.

Access to monitoring locations is also a consideration. Ideally, the perimeter of the property (where most monitoring takes place) will have a road that allows for vehicle access to all fixed and mobile monitoring locations. Access roads save time and effort required to hand-carry equipment and supplies over rough terrain for large sites.

Site terrain directly influences the extent and the design of the air monitoring program. If the site terrain is complex, the migration of contaminants via the air contaminant pathway will be complex and highly variable. In addition, air dispersion modeling for such terrain is difficult and modeled results are often less precise and nonrepresentative. This means that there is an increased likelihood that point source monitors will not measure true site emissions. This situation can be addressed by: 1) increasing the number of point monitor stations and selecting locations to transect the downwind plume, and in some cases 2) using line monitoring techniques such as optical remote sensing (Fourier transform infrared (FTIR) or ultraviolet differential optical adsorption spectroscopy (UV-DOAS)) [3] [6].

Local meteorological conditions also influence the design of the monitoring system. Dominant meteorological conditions should be considered so that monitors are properly located and can provide representative site samples.

Waste Properties

The range of waste types will dictate the number of compounds to be monitored. Although monitoring may be considered for each type of waste, it may be acceptable to select target compounds based on effective risk. This approach is common and can reduce complexity. If individual compounds are of interest, the number of analyses can increase the complexity and cost of the program.

Physical state or volatility of contaminants will affect the air sampling and analysis technique selection. Volatility of contaminants ranges from volatile (found mostly in the gaseous state), semivolatile (found as a gas and solid), to nonvolatile (particulate matter found mostly in the solid state).

The relative toxicity of contaminants will affect the decision as to which compounds will be monitored in the program. It is important to monitor those compounds that dominate the health risk assessment given equivalent receptor exposure.

Homogeneity of the waste will generally reduce the complexity and cost of the air monitoring program. The air monitoring program can be simplified to monitor for one or more indicator compounds.

Project Factors

Program objectives serve to direct and focus the air monitoring program. Available and applicable methods determine if program objectives can be achieved.

The availability of applicable sampling and analytical methods may limit the monitoring effort. There are several sources that provide current reference methods [3] [7] [8] [9] [10]. However, the method available may not be compatible

with the project needs: for example, if the need arises to continuously monitor a contaminant and have realtime data available onsite, but the proposed method is integrated sample collection and analysis with a 36-hour turnaround. This situation is encountered frequently when there is a need to monitor a semivolatile or nonvolatile compound found as particulate matter. The standard approach is to use high- volume collection on filters or foam with offsite laboratory analysis. The appropriate project strategy would be to correlate onsite realtime analysis, such as monitoring with a dust analyzer (screening level monitoring), with high volume sampling and assume a percentage of screening level monitoring response as the contaminant concentration. By combining screening and in-depth approaches and assuming loading, data can be obtained for situations where there are no sampling techniques available to meet the program needs.

Project resources affect what type and level of air monitoring can be conducted at any given site. The amount of resources allotted to the air monitoring program should provide for the selection of methods and how they are to be applied. Resource restrictions may influence the application of methods by limiting frequency (representativeness) or repeatability of the monitoring effort, or it may influence which methods are selected and used.

Limitations

Selection of an air monitoring method involves consideration of both the application of the method and its limitations. Limitations that may affect most air monitoring approaches include:

1) Frequency of monitoring affects data representativeness, regardless of air monitoring approach or method. A well-defined program must monitor at sufficient frequency for the data to be representative.

2) Monitoring of large numbers of specific compounds is costly and time intensive. The requirement for this level of surveillance must be supported at the onset of the program.

3) General class or broad-band monitoring of contaminant species also has advantages and limitations. The advantage of broad-band monitoring is that most of the emissions from the site are monitored. These data can be used with composition data to estimate individual species or types of compounds (i.e., total hydrocarbons as aromatics, or total aromatics as benzene). However, broad-band monitoring is often a conservative estimate and therefore the site may be considered more toxic or to carry a greater risk than is the case.

4) A limited number of monitoring stations affects the coverage at the fenceline. Line source monitoring versus point monitoring should be considered if fenceline coverage is an issue.

5) Meteorological conditions greatly influence the air monitoring program and may affect the design of the program or result in limited data capture. Climate characteristics like a marine environment (i.e., moist, salty air), diurnal wind patterns, and seasonal conditions should be factored into the design to avoid poor data capture.

Design Procedures

The important tasks in designing an air monitoring program for a hazardous waste site restoration activity are: selecting the most appropriate approach, establishing the data quality objectives, and selecting the proper sampling and analytical techniques. Since no two hazardous waste sites are alike, the best way to assist the RPM to design an air monitoring program specific to a site is to develop a protocol that can be applied to any site and to provide useful information that will result in effective air monitoring programs. Figure 2 lists the twelve steps for designing an AAM program. They are described in the following subsections.

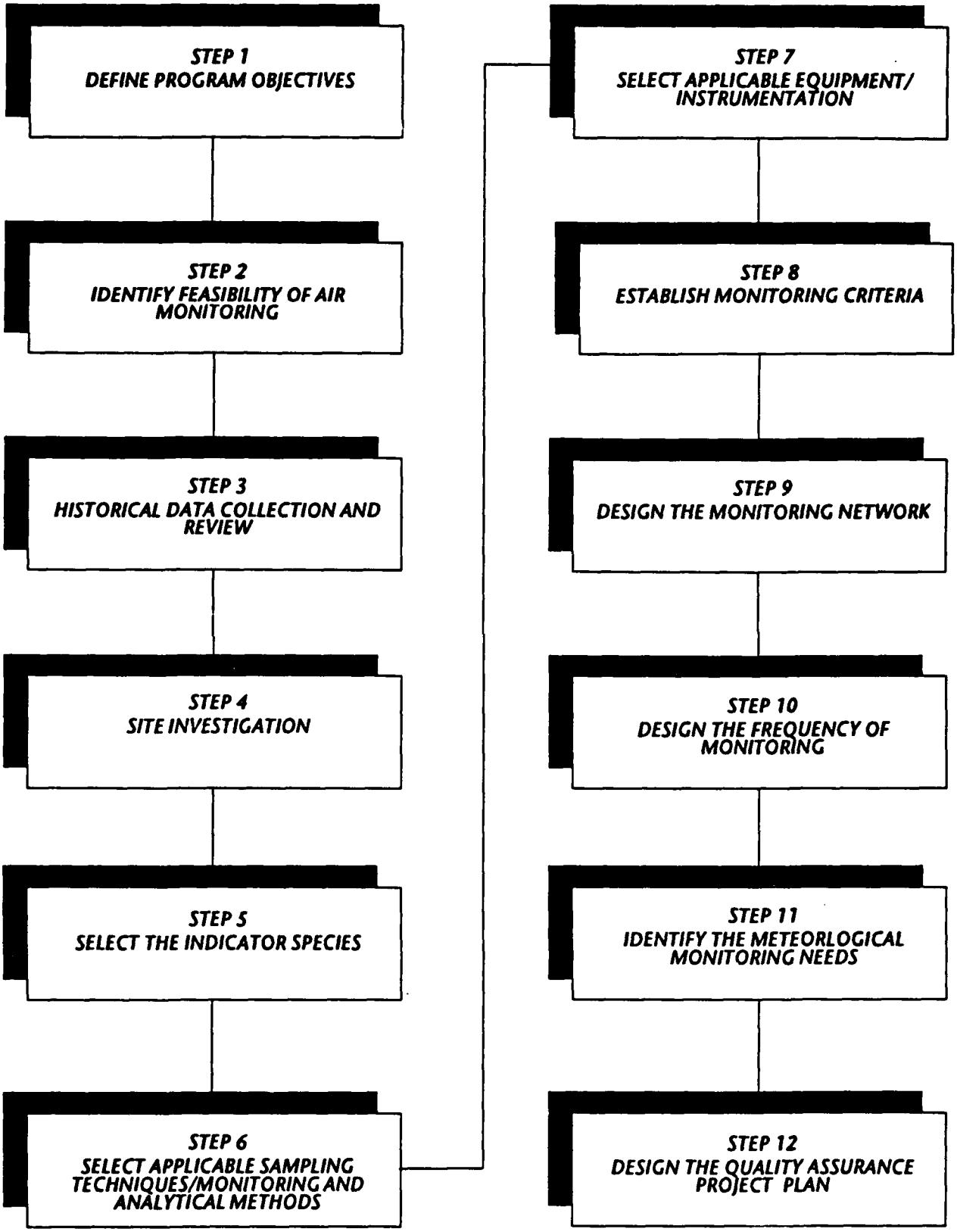
Program objectives must be defined so that they are specific and detailed. A reviewer of these objectives must have a clear understanding of all major aspects of the program. It will be necessary to review these objectives at various times in designing and implementing the program to ensure the program objective will be met. If there is a need to modify the program objective, all parties involved should concur and approve of the program redirection.

Identifying the feasibility of air monitoring is critical at this early stage before significant time and effort is expended pursuing a conceptual program that is not feasible. This should include an analysis of the site characteristics, the properties of the waste, and key project factors. Although this initial analysis does require some prior knowledge of later stages, it is important to take some time to consider what is known and whether or not the project objectives are feasible.

Historical data collection and review will provide some of the information needed for evaluating applicability of air monitoring. Site scoping may include researching the site record, site manifest files, and operating permits; locating regulatory involvement documentation; collecting odor/nuisance complaints; conducting interviews with involved parties; evaluating historical site characterization data; and reviewing historical aerial photography of the site (if available). The objective is to identify the type, physical state, and likely emissions from the site in the undisturbed and disturbed states. Waste composition data and predictive modeling may be used to estimate emission rates of contaminants [3]. These estimates can be used with empirical factors and simple models [4] to estimate emissions from disturbed waste. These data are then used with a dispersion model like the Industrial Source Complex Short Term model (ISCST) to predict contaminant concentration at the fenceline for different meteorological conditions. These estimates of contaminants and their concentrations provide excellent data for planning the air monitoring program.

Site investigation is an opportunity to collect specific and useful data from the site for designing the air monitoring program.

FIGURE 2. FLOWCHART OF ACTIVITIES FOR DESIGNING THE AIR MONITORING PROGRAM



Screening technologies include head space analysis of a sample in a bottle, upwind/downwind air sampling, realtime instrument survey, and the use of predictive models. These technologies are recommended for determining if the waste has the potential for air emissions [3]. In-depth technologies include the surface flux chamber, soil vapor probes, downhole flux chamber, and fenceline monitoring and modeling. The advantages and limitations of these preferred screening and in-depth level technologies are discussed in the APA Engineering Bulletin [1]. These technologies are recommended for determining undisturbed and disturbed waste emission rate estimates from the site and may be useful to emphasize air monitoring techniques if a pretest site screening is needed to support the air monitoring program design. One approach is to preview one or more of the candidate techniques for air monitoring at a "first alert" station so that their performance can be evaluated. Information for identifying candidate sample collection and analytical/monitoring techniques is found in references 1, 3, 9 and 10. Emission rates from the disturbed waste are likely to increase significantly during waste disturbance, and applicable monitoring techniques must be able to detect maximum and minimum concentrations.

The site investigation data are critical in selecting sampling and analytical techniques, establishing contaminants and the likely contaminant concentration range, and evaluating candidate monitoring approaches and/or sampling and analytical technologies.

Selecting the indicator species is important to the selection of air monitoring techniques and will determine the representativeness of the air monitoring data. Indicator species are used to represent the type, range, and concentration of all air contaminant release from the site. The emissions from the waste must be relatively homogeneous for the indicator species concept to be useful. Usually, there are many types of air contaminants released from the site, and it is often not possible to monitor all species. It is often necessary to rely on indicator species monitoring. Further, even if there were resources available to monitor all of the species released, it would probably not be technically feasible, since there are only a handful of valid sampling/analytical methods.

The overall objective of selecting candidate indicator species is to find species that are common to the waste and can be sampled and analyzed using conventional techniques. The ideal indicator species should be found uniformly in the waste and at a relatively constant ratio to other contaminants in the downwind plume; a relatively nonreactive or a stable air contaminant, found in the downwind plume well above the detection limit of the sample collection/analytical technique or air monitoring approach selected; unique to the site and not found in the upwind air at significant levels. Representativeness of the indicator(s) should be demonstrated at the onset and perhaps throughout the program. This is accomplished by collecting samples using techniques that identify and quantify the indicator as well as other dominant and significant compounds. This verification of indicator species is critical for the air monitoring program to properly function.

Selecting applicable sampling and analytical techniques or monitoring methods is the central issue in designing the air monitoring program. The project objective will provide guidance as to the type of contaminant (volatile organic compound (VOC), volatile inorganic compound (VIC), semivolatile organic compound (SVOC), particulate matter (PM)) and which approach is most appropriate (i.e., continuous monitoring, line versus point monitoring, integrated point monitoring, emission measurement and modeling). The project objective should be developed with knowledge of the project needs, site characteristics, waste properties, and project factors. Without this direction, it is not possible to select applicable sampling and analytical techniques or monitoring methods. Table 1 lists general guidance on monitoring, collection, and analysis.

References 8 and 9 contain information that is applicable to many sites and is specific for toxic organic compounds. They provide data on sampling technique, sample collection, and analytical technique for general classifications of compounds commonly found at hazardous waste sites. These approaches are relevant for point monitoring using integrated sample collection and are common for sites that need low level detection, where realtime data is not part of the project objective. Table 2 lists the toxic organic compendium methods.

Selecting applicable equipment/instrumentation follows after the sampling and monitoring method has been selected. Several tables have been assembled to assist in selecting appropriate sampling and analytical methods as well as selecting applicable equipment and instrumentation. These tables provide vendor information, product nomenclature, analyte detection data, and 1991 cost estimate information for field survey and air monitoring techniques and instruments. This information was too extensive to be included in this document, but can be obtained from the EPA contact. This listing is not comprehensive or meant to serve as an endorsement of these products. It is intended as supportive information for the air monitoring design steps that involve identifying, evaluating, and selecting air monitoring approaches and specific technologies.

There are several considerations, however, that will be a part of the selection process: 1) range of detection for the technology in comparison to the project objectives; 2) duration of the sampling period and the capability of the technology; 3) portability of the technology and required support functions; 4) data turnaround time and the project needs; 5) technical expertise needed to operate the technology properly; 6) cost and availability of the technology from the vendor.

Establishing monitoring criteria may happen early in the design process or be part of the program objectives; however, these criteria should be established when air monitoring methods are being evaluated. Project-specific criteria must be established using available health data, site factors such as distance to receptors, exposure criteria such as threshold limit value (TLV) and permissible exposure limit (PEL) data, and a health risk assessment. This process should be used to develop a time-weighted set of criteria that will protect the health of the public and allow for restoration of the site [11] [12].

Designing the air monitoring network and siting monitoring stations involves considering needs for representativeness of these air monitoring data and project resources. In addition to the standard fenceline surveillance, it may be ad-

TABLE 1. GENERAL GUIDANCE FOR INTEGRATED, POINT MONITORING, SAMPLE COLLECTION AND ANALYSIS

CLASSIFICATION	SAMPLING TECHNIQUE	SAMPLE CONDITIONING	ANALYSIS TECHNIQUE
VOLATILES	TENAX ADSORBENT	THERMAL DESORPTION, CYROGENIC TRAPPING AND FOCUSING	GC/MS
	SUMMA CANISTER	NAFION DRYER	GC/MS
		CRYOGENIC TRAPPING (OPTION)	GC/MS
		MODIFIED WATER PURGE TO ADSORBENT TRAP, THEN THERMAL DESORPTION	GC/MS
SEMI-VOLATILES, INCLUDING PESTICIDES AND PCBs	FILTER FOLLOWED BY COMBINATION PUF/XAD-2 ADSORBENT TRAP USING HIGH-VOLUME SAMPLER	10% ETHER/HEXANE SOXHLET EXTRACTION, SILICA GEL CLEAN-UP	GC/MS
METALS	FILTER	MICROWAVE EXTRACTION USING HNO3/HCl ACID SOLUTION	ICAP

GC/MS - GAS CHROMATOGRAPHY/MASS SPECTROMETRY
PUF-XAD-2 - POLYURETHANE FOAM - XAD-2 RESIN
ICAP - INDUCTIVELY COUPLED ARGON PLASMA SPECTROSCOPY

TABLE 2. SUMMARY OF TOXIC ORGANIC (TO) COMPENDIUM METHODS

COMPENDIUM METHOD	TYPE OF COMPOUND	SAMPLE COLLECTION	ANALYTICAL METHOD
TO-1	VOLATILE ORGANIC COMPOUNDS	TENAX SOLID SORBENT	GC/MS
TO-2	VOLATILE ORGANIC COMPOUNDS	MOLECULAR SIEVE SORBENT	GC/MS
TO-3	VOLATILE ORGANIC COMPOUNDS	CRYOTRAP	GC/FID
TO-4	PESTICIDES	POLYURETHANE FOAM	GC/ECD
TO-5	ALDEHYDES/KETONES	IMPINGER	HPLC
TO-6	PHOSGENE	IMPINGER	HPLC
TO-7	AMINES	ADSORBENT	GC/MS
TO-8	PHENOLS	IMPINGER	HPLC
TO-9	DIOXINS	POLYURETHANE FOAM	GC/MS
TO-10	PESTICIDES	POLYURETHANE FOAM	GC/ECD
TO-11	ALDEHYDES/KETONES	SEPELCO-PAK	HPLC
TO-12	NON-METHANE ORGANIC COMPOUNDS	CANISTER	PDFID
TO-13	POLYAROMATIC HYDROCARBONS	POLYURETHANE FOAM	GC/MS,HPLC
TO-14	VOLATILE ORGANIC COMPOUNDS	CANISTER	GC/MS

GC/MS - GAS CHROMATOGRAPHY/MASS SPECTROMETRY
GC/FID - GAS CHROMATOGRAPHY/FLAME IONIZATION DETECTION
GC/ECD - GAS CHROMATOGRAPHY/ELECTROLYTIC CONDUCTIVITY DETECTOR
HPLC - HIGH PRESSURE LIQUID CHROMATGRAPHY
PDFID - PRECONCENTRATION AND DIRECT FLAME IONIZATION DETECTION

vantageous to add a downwind work-zone monitoring station that could serve two purposes: worker protection and adherence to the health and safety plan and a "first-alert" station that could provide rapid response data and valuable information to the site manager regarding site restoration activities. This information could assist in controlling site activities or the source of fugitive emissions and could potentially reduce the threat of impact at the fenceline.

Most air monitoring programs that use point monitoring have at a minimum one station located at the daytime upwind (dominant) position and two or more at downwind positions. The sector approach uses 8 to 12 stations located in each major compass direction for coverage in all dominant wind directions. The selection of number and position of stations will depend on the program objectives and resources. The choice of line monitoring versus point monitoring addresses this issue of

representativeness in the data. Line monitoring using optical remote sensing (FTIR, UV-DOAS) can provide complete fenceline monitoring which would be equivalent to placing point monitors (integrated sample collection or instrumental monitors) side-by-side along the fenceline of concern. The other advantage of line monitoring is that data may be processed onsite and essentially realtime [13]; these two features distinguish line monitoring from all other methods. Project needs, detection limits, and detectability will determine if optical remote sensing is appropriate for the air monitoring approach.

Designing the frequency of AAM can range from limited monitoring on selected days to monitoring at all locations every day. Frequency of sampling may be comprehensive, but analysis of samples of data collected may reflect wind direction or site activities. For instance, sector monitoring with 8 to 12 monitoring locations could involve 24-hour monitoring. However, the dominant upwind and 2 or 3 downwind monitoring station samples may be selected for analysis thus preventing the analysis of useless sample media. Frequency of monitoring will reflect the program AAM objectives.

Identifying the project meteorological monitoring needs usually involves designing a micro-meteorological network for onsite monitoring and/or arranging for data collection from a local airport and/or meteorological monitoring network. Onsite data are recommended so that fenceline concentrations can be evaluated considering site factors such as terrain. Typically, site meteorological monitoring consists of at least one station with a 10-meter tower and sensors for wind speed, wind direction, and temperature. Data are typically collected and stored on a data logger and processed as 5-minute and hourly averages.

Designing the Quality Assurance Project Plan involves defining the type and level of program quality assurance, quality control, and independent auditing. The Quality Assurance Project Plan (QAPP) elements include project description and objectives, all field sampling/monitoring direction, all analytical procedures, data quality objectives, data evaluation procedures, system and performance auditing, and corrective action protocols. This document serves two purposes: 1) provides a complete guidance document for project implementation and execution, and 2) specifies the level of data quality and provides a program for attaining the specified level of data quality. Every air monitoring program needs a site-specific QAPP.

Site Requirements

Site requirements for air monitoring will vary according to the objectives of the air monitoring program and the specific monitoring techniques used. A screening type program may only require minimum support facilities. A more detailed air monitoring program may require weatherproof shelters powered by 110-volt service for each fixed monitoring station and may include data transfer by line or radio to a data processing/ computer center. Support needs including utilities and access to monitoring locations should be considered when designing the air monitoring program.

EPA Contact

Technology-specific questions regarding air monitoring during Superfund remediation may be directed to:

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Immediate Response to Free Product Discovery

Port Hueneme, CA 93043 **NEESA Document No. 20.2–051.4** **November 1992**

Introduction

Underground storage of petroleum products such as gasoline, diesel oil, fuel oil, and aviation fuel can be a significant source of contamination of ground water and soil. Estimates by the Environmental Protection Agency (EPA) indicate that nearly 25% of all steel underground storage tanks (UST) are leaking (1). The need to initiate remedial measures as soon as leaking is detected is of paramount importance. For any migrating fuel plume problem, the first priority must be to gain control of the migrating product to prevent further soil and ground water contamination. Proper immediate response can significantly reduce the ultimate cleanup cost, increase the efficiency of the cleanup, and mitigate further environmental damage.

Purpose and Audience

The purpose of this Tech Data Sheet is to:

- Help plan for response to discovery of free product during UST or other construction activities, which will facilitate future remedial actions and reduce their costs while ensuring regulatory compliance;
- Introduce Project Superintendents, Engineers in Charge, and On-Scene Coordinators to regulatory issues, engineering and hydrogeologic processes, and available remedial technologies; and
- Help Navy Engineering Field Division (EFD) personnel structure contracts and develop scopes of work (SOW) for free product remediation projects, and assist Remedial Project Managers (RPMs) with review of project plans and actions.

Description of the Problem

Petroleum releases from UST are a significant source of contamination to ground water and soil. Releases can originate in the tanks themselves or in supporting piping systems. Subsurface releases can go undetected for relatively long periods of time because the release is below the surface and is not directly observed. While state and federal regulations now require tank owners to have a monitoring system in place to detect releases of petroleum, the regulations do not cover all tanks and have only been in effect for a short period of time. Furthermore, some monitoring systems (inventory reconciliation for example) may not have the ability to detect small releases. Even a relatively small leak, over a period of time, will allow free petroleum product to collect in the ground and come in contact with ground water, given the right conditions.

The potential for accumulation of liquid phase product that is free to move by gravity above the water table is dependent on several factors including:

- Physical and chemical properties of the product released (e.g., viscosity, density, composition, and solubility in water);
- Soil properties (e.g., porosity, moisture content, clay content, hydraulic conductivity, capillary forces, and grain size distribution);
- Nature of the release (e.g., initial date of occurrence, duration, volume, and rate);
- Geology (e.g., stratigraphy that promotes trapped pockets of free product); and
- Hydrogeologic regime (e.g., depth to water table, ground water flow direction, and gradient).

Free product (see "Terminology") can accumulate under a very wide variety of conditions. In general, however, free product is more likely to accumulate in instances where:

- The soil has properties that reduce soil suction (e.g., higher moisture content and larger effective pore radius);
- The petroleum product consists of mostly low density and low solubility components; and
- The ground water is shallow with a relatively low hydraulic gradient.

Free product is often detected directly during UST removals, UST upgrades and investigations, incident response investigations and other activities such as underground utility repair, monitoring well installation, new construction, and demolition. Presence of free product is generally suspected when strong petroleum odors are detected in basements and below-ground structures in areas away from suspected sources.

Potential threats to health, safety, and the environment imposed by the presence of free product include:

- Fire and explosions;
- Exposure to toxic vapors; and
- Damage to surface and ground water drinking water sources and natural habitats.

Terminology

Petroleum products can be contained in the subsurface in several ways. The following terms are commonly used to describe the presence of product:

Free product: Petroleum-based products occurring in the subsurface when the hydraulic pressure of fluid in the ground meets or exceeds ambient soil vapor pressure (one atmosphere). The product is thus "free" to flow in response to gravity.

Floating product: Petroleum-based products having significant fractions of lighter-than-water compounds (e.g., gasoline, diesel fuel, #2 or #4 heating oil, aviation fuel, waste oil, kerosene, lubricating oils) that have accumulated on the water in a well or cavity. Products floating on the water in a well bore are not indicative of the actual conditions in the surrounding subsurface environment. The term "floating" is inadequate to describe fluid processes in the subsurface and should not be used in that context. In addition, the relative amount of product found floating in well bores cannot be used as a direct indicator of the amount of free product available for recovery from wells by gravity methods.

Product can range from a sheen or thin film to an accumulation of pure product several feet thick. The observed thickness of product in a well is generally greater than the actual thickness of free product in the ground, by factors ranging from 2 to 24 (2). Product thickness in the ground is related to many factors—especially grain size distribution (3).

Residual product: Refers to product present in the following forms:

- Liquid product contained in soil pores either bound or migrating in response to capillary forces. This *capillary product* is present at pressures below one atmosphere and will not flow by gravity;
- *Vapor phase* petroleum hydrocarbons contained in soil void space;
- *Dissolved phase* petroleum hydrocarbons in soil moisture and ground water;
- *Solid phase* petroleum hydrocarbons bound by molecular forces to soil particles; and
- *Suspensions*, *emulsions*, and *droplets* of petroleum hydrocarbons within subsurface waters.

Other terms used throughout this Tech Data Sheet include:

Hand bailing: Retrieval of fluid from a well using a bailer (Figure 1a). The bailer is lowered into the well on a rope and allowed to fill from the bottom.

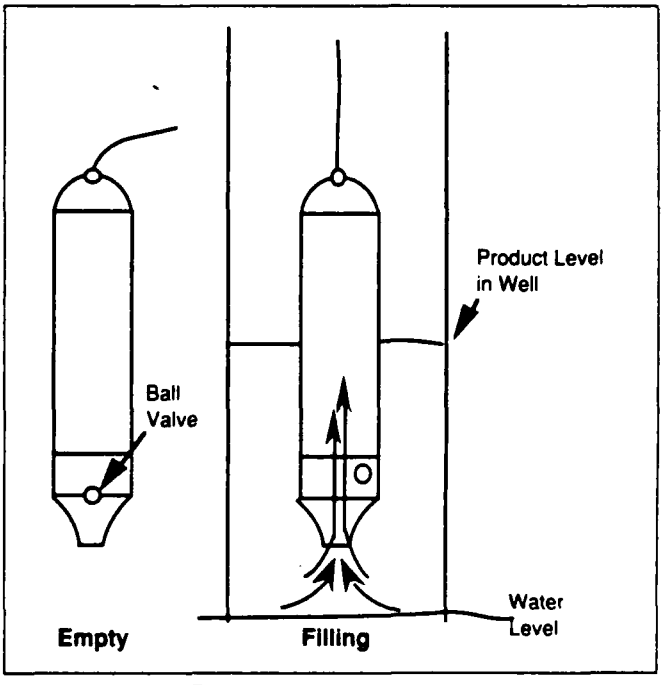

Figure 1a. Hand Bailer (not to scale)

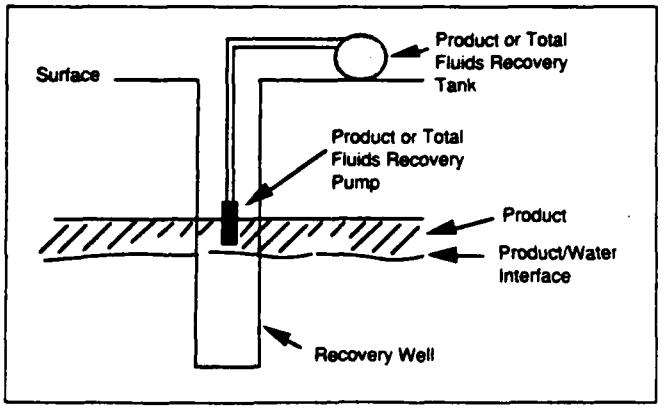

Figure 1b. Skimmer Pump System (not to scale)

Skimmer: A free product removal device used in wells and open pits (Figure 1b). The skimmer is a pump positioned at the oil/water interface to extract product from the water surface. Some skimmers are designed to collect only oil by using hydrophobic filters. Others collect all lower density fluids above the water table.

Dual pumping: A petroleum recovery system in which water in a well is drawn down by pumping to depress the water table and create a high ground water gradient near the well (Figure 1c). A second pump is placed at the top of the water column in the well to collect free product which has accumulated due to gravity.

Stinger truck: Liquid vacuum truck capable of sucking up any liquid including free product and water.

Interceptor trenches: Trenches placed into the water table in the path of ground water flow allowing extraction of contaminated fluids. Free product can then be removed from the collected fluids.

Sparging: A remedial technique in which air is passed (bubbled) through ground water to enhance volatilization and biodegradation of organic contaminants dissolved in the ground water. Volatilized contaminants are generally carried to the ground surface by vapor extraction methods for treatment.

Importance of Rapid Response to Free Product

Using the ARMOS (Areal Multiphase Organic Simulator) model for free product migration and recovery, response times and cleanup efficiencies were analyzed (4). The results, as shown in Figure 2, illustrate the importance of rapid response to free product discovery.

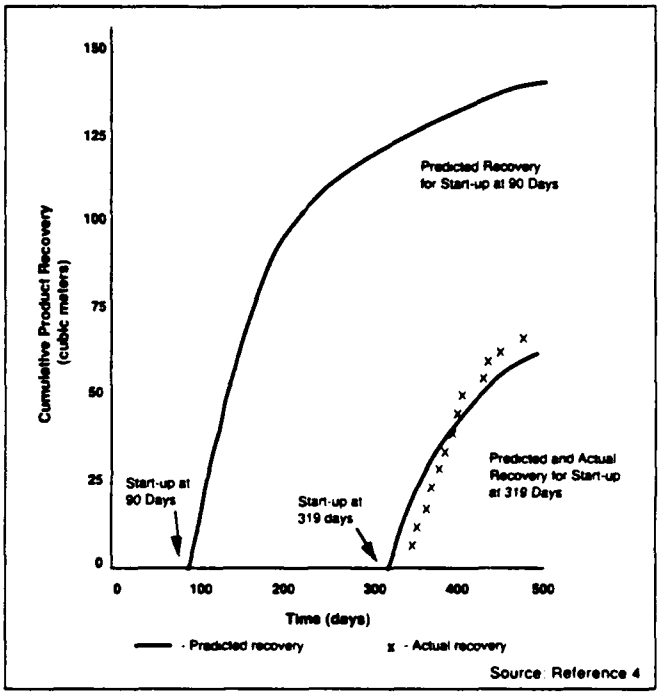

Figure 2. Effects of Start-up Time on Recovery

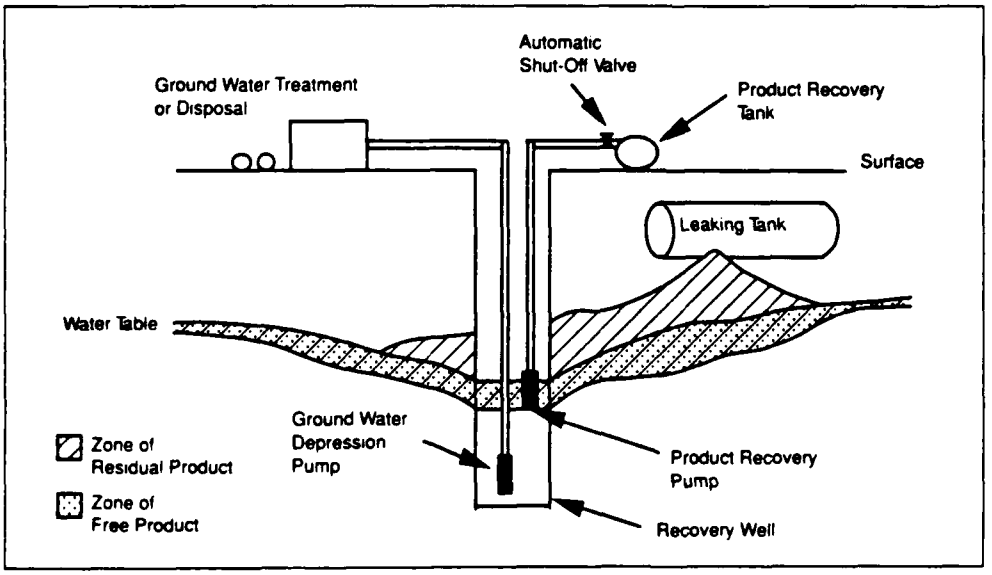

Figure 1c. Dual Pump System (not to scale)

Input to the model included the following actual spill site data:

- Spill volume of 300 cubic meters;
- Redistribution of spill under natural gradient from 0 to 319 days;
- Ground water pumping and oil skimming beginning at day 319 and continuing until day 478; and
- Site-specific soil, product, and hydrogeological properties.

Important results of the model show that if response were initiated after 90 days, by the end of one year nearly 50 percent of the total spill volume would be recovered under the given conditions. In contrast, if response were not initiated until 319 days, the recovery total would begin to level off to approximately 20 percent of the spill volume. This latter observation has been confirmed by actual recovery data obtained in the field.

This model illustrates that the maximum recovery can be achieved by beginning the recovery response as soon as possible after the discovery of free product. The longer one takes to initiate recovery, the more opportunity the plume has to spread. As it spreads, it comes into contact with more and more soil or sediment, thereby rendering more product "tied up" as residual (see "Terminology").

Product lost to residual is no longer available for recovery as pure product but may be present as solid, vapor, or liquid phase contamination in ground water or soil. Remediation of contaminated ground water and soil is generally more expensive than free product recovery. In addition, ground water and soil remediation can take on the order of years (if ever) to reach regulatory cleanup levels. This is in contrast to recovery of free product, which can take on the order of weeks to months to complete.

Failure to react immediately to the identification of free product may result in the need to perform investigation and cleanup efforts over a larger area, as well as requiring additional efforts to treat contaminated ground water and soil. In summary, delays in action increase:

- Environmental, health, and safety risks;
- Overall complexity and time of cleanup; and
- Cost to the Navy.

Approach to Free Product Discovery and Response

An immediate response approach is frequently taken by the private sector and supported by the Environmental Protection Agency (see "Regulatory Issues"). With this approach, mitigation procedures begin immediately upon detection of free product. Effective immediate response can be initiated prior to and during a full site assessment while conforming to EPA policy and maintaining common sense. Interim remedial actions can address contamination as it is discovered. The interface of interim actions with the corrective action is illustrated in Figure 3. It should be noted that specific state or local regulations may impact the course of these actions.

Too often, immediate or interim response measures are not taken to mitigate free product. For example, if free product is found during UST removal or monitoring well installation, the project may be placed on hold to allow for:

- Regulator notification;
- Regulatory approval to take action;
- Preparation and approval of site assessment plan;
- Full site assessment and characterization; and
- Preparation and approval of Corrective Action Plan.

By following this course of action, cleanups may unncecessarily take several years to complete—or may never be completed.

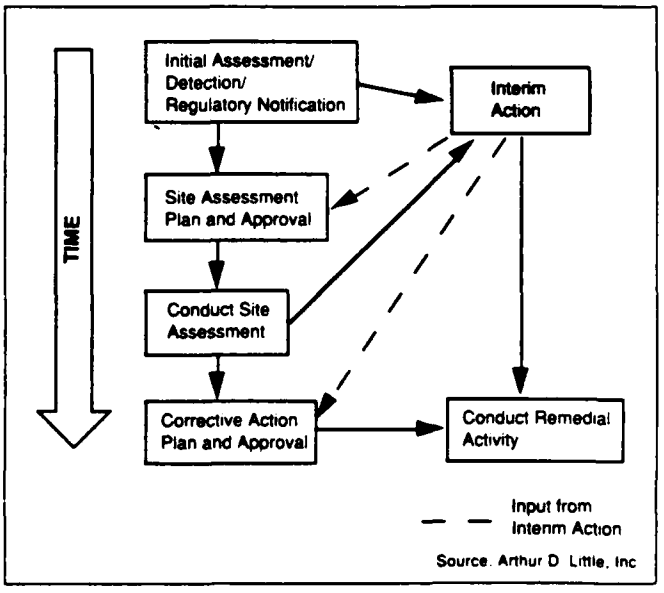

Figure 3. Appoach to Corrective Action

Planning and Response Strategies

Time and resources can be saved by adequate prevention and response planning. This planning should be oriented toward providing the maximum capability for immediate spill response.

One of the primary goals of immediate response is to prevent the spread of the contaminant plume, thus minimizing the potential for increased soil contamination. The greater the extent of soil contamination, the greater the cost and time to remediate. To achieve this goal, the following elements should be key in remedial planning:

- Anticipation of the discovery of free product;
- Knowledge of the actions to be taken upon detection of free product; and
- Immediate implementation of interim remedial action concurrent with regulatory notification.

In general, planning strategies prior to initiating any UST actions should include:

- Ensuring the installation of state-of-the-art leak detectors and alarm systems in new installations or upgrades;
- Educating those responsible for immediate response in procedures and equipment;
- Developing an understanding of the potential for the release and spread of product (based on tank and piping age and history, nature of release, proximity to release, depth to ground water, etc.);
- Establishing actions if product is discovered (including recovery methods and goals, regulatory interaction, and schedules); and
- Developing contingency plans for modification of original project plans after product recovery goals are met.

An additional important feature of planning strategies is notification of appropriate emergency response and construction personnel. If product is discovered, the Resident Officer in Charge of Construction (ROICC) and the Public Works Center (PWC) should be notified immediately. These personnel will ensure that no construction is to be performed in the affected area that could endanger the health and safety of workers or jeopardize environmental remediation activities.

Not all UST investigations and removals warrant the presence of immediate response equipment and personnel; however, advance planning and preparation will help in those situations that require immediate response support to minimize contaminant migration.

For example, if one discovers product while placing a well or boring around an UST under investigation, it would be wise to utilize a stinger truck service during future tank-pulling operations. Typically, a stinger truck should be either placed on standby or available on-site during UST removal and during investigations to remove free product upon discovery. Booms and sorbent pads should be readily available at locations where ground water is likely to be observed in pits or trenches.

Contractual mechanisms should be available to provide immediate response to the discovery of free product. These include:

- Emergency response contracts (established at the EFD level) with local response contractors for petroleum extraction so that actions can be taken immediately with minimum lag time; and
- Contracts with stinger truck services and waste disposal firms established so that trucks can be on-site for each situation in which investigators or workers may encounter free product.

The implementation of proper planning and response strategies will increase the potential for:

- Cost reductions of future remedial actions associated with the site;
- Remedial efficiency; and
- Facilitation of future site characterization and remediation efforts.

Regulatory Issues

Specific regulatory considerations regarding free product detection, response, and recovery relating to UST systems are established under the Resource Conservation and Recovery Act (RCRA). Resulting regulations are published in 40 CFR 280.60 through 280.65. The requirements set forth in these regulations include those actions associated with:

- Initial response (including notification of the implementing regulatory agency) (40 CFR 280.61);
- Initial abatement measures and site assessments and characterization (40 CFR 280.62 and 63);

- Free product removal (40 CFR 280.64); and
- Investigation for soil and ground water cleanup (40 CFR 280.65).

These regulations emphasize the need for immediate response to prevent further release of the regulated substance into the environment. They encourage initiating free product removal as soon as feasible after detection.

As specified in 40 CFR 280.64, free product removal must be conducted so as to minimize the spread of contamination. Techniques selected for the removal or recovery of product must be appropriate to the hydrogeologic conditions at the site. All recovery by-products must be managed in compliance with applicable local, state, and federal regulations. Within 45 days after confirming a release, a free product removal report must be prepared and submitted to the implementing regulatory agency.

These requirements may be supplemented by state and/or local regulations. Federal regulators have attempted to maintain a decentralized posture with respect to UST actions concerning notification, review, and inspection. These activities are carried out on the state or local level to the maximum extent possible (5).

State regulations or policy may affect the response to product discovery. States may require total characterization prior to extraction of product. In some cases, this may not be practical. However, state regulatory issues or policy must be recognized.

In product recovery operations, required permits may include:

- Water permits (for treatment and/or discharge); and
- Air permits (in the event that recovery or water treatment processes create potential sources of emissions).

Product Recovery Techniques

A summary of the applications and limitations of common free product recovery techniques is presented in Figure 4. In addition, relative magnitudes of the levels of sophistication and costs of the techniques are presented.

Technique	Relative Degree of Sophistication	Relative Cost	Advantages	Limitations/ Disadvantages
Booms/Sorbents	Low	Low	Can be employed immediately upon spill detection.	Temporary measure only. Limited to use in open pits or trenches.
Single Phase Extraction (hand bailing, hand pumping)	Low	Low	Important information regarding recovery potential is learned. Can be quickly implemented during UST removals or upon detection of product in wells.	Slow and labor intensive process. Personnel safety equipment required. Ability to remove a significant amount of floating product is limited. Water separation and disposal may be required.
Single Phase Extraction (vacuum pumping, skimming)	Med	Low to Med	Can be employed immediately on product detection. Can be used to remove floating product during UST removals or from wells.	Equipment purchase or rental required. Ability to remove all floating product is limited. Water separation and disposal may be required.
Dual Pump Systems	Med to High	Low to High	Very effective in floating product removal. Useful for long term water treatment.	Water treatment is required. Permits for water treatment may be required thereby adding to response time.
Interceptor Trenches (French Drain)	Low	Med to High	Suitable for long-term product recovery. Capable of collecting large volumes of product.	Long-term action. Not suitable for immediate response if design must be approved by regulators.

Figure 4. Applications and Limitations of Common Recovery Techniques

Source: NEESA and Arthur D. Little, Inc.

Factors to be considered in selecting a particular technology for recovery of free product include:

- The magnitude of the problem;
- Potential impacts of the problem; and
- The nature of the problem.

For example, if large amounts of free product are detected during a tank excavation, a stinger truck can be used to remove the product immediately, and an interceptor trench (French Drain) can be installed for longer term recovery operations.

If tank removals or investigations are performed in areas of standing water, precautionary sorbent booms should be in place to minimize migration of contaminants. If free product is visible in standing water as well as in open pits or trenches, frequent sweeps of the sorbent booms may be appropriate for recovery.

For immediate response, hand bailing or hand pumping can usually be quickly implemented to remove product from a monitoring or extraction well. These techniques may also be useful to determine recharge rates for each well. Increasingly sophisticated techniques such as skimming and dual pumping can be used to increase product removal efficiencies and for longer term recoveries of larger amounts of product.

If recharge of product to the well is slow, use of a hydrophobic oil-selective skimmer may be beneficial. A dual pump system may be required if the estimated product recharge rate is high or the extent of the problem is large.

Free product recovery methods are often limited by the minimum thickness of the product they will recover. Most recovery techniques can remove product to a thickness of less than one-quarter inch without removing water. In order to recover the additional film of free product, some water will need to be removed as well.

Once free product is removed, attention must be paid to the possible presence of residual contaminants. If recovery of residual product is necessary, additional techniques must be employed adding to the overall time and cost required for recovery (see "Interfacing Technologies"). It should be reemphasized at this point that the problems associated with residual product recovery are minimized by an immediate initial response to free product discovery.

Implementation Considerations

Once free product is detected, immediate response should include both removal of the source and recovery of available product by the most expedient means. The use of stinger trucks is expedient; however, these trucks generally do not distinguish product from water and, therefore, the cost of disposal (or recovery) of the free product will increase according to how much water is extracted along with it.

Free product recovery methods will often recover contaminated water with the product. If economically desirable, water and product can be separated by gravity prior to disposal or recycling of the product.

Due to the removal of substantial quantities of water during dual pumping operations, on-site water treatment will normally be required. A typical treatment system may include an initial separation of water and product by gravity (e.g., using an oil/water separator), followed by activated carbon adsorption or air stripping of the water phase.

When treatment of recovered water is required, permits will usually be necessary. These permits will dictate the final disposition of the treated water. Completing permit applications and obtaining approvals may add up to six months to the time required to implement recovery techniques such as dual pumping. For this reason, interim techniques such as single phase extraction will usually be employed as an initial response while concurrently applying for necessary permits.

Most military installations have discharge permits in place for water-using activities. When a contamination problem is discovered, it is advisable to start modifying these permits immediately to accommodate discharge of treated water.

Residuals Generated

Residuals generated from free product recoveries include the product and various amounts of contaminated water. Typically, service contracts with hazardous waste disposal contractors are established to dispose of or recycle recovered product.

Additional residuals may be generated during the treatment of contaminated water resulting from product recoveries. Common treatment residuals include spent activated carbon. This spent carbon may be disposed of or regenerated depending on economics.

Interfacing Technologies

When gathering data during early response and treatment efforts, it is important to recognize the differences between control, treatment, and characterization issues and priorities.

For any migrating fuel plume problem, the first priority goal must be to gain *control* of the migrating product to prevent further soil and ground water contamination.

Treatment of contaminated soil and ground water, while important, must be secondary to control. As control measures are implemented, data must be gathered to identify further control needs and to help select treatment alternatives.

After control measures have been implemented, a full *characterization* of the soil and ground water phases, flow dynamics, and volumes is needed in order to assure complete cleanup.

In this integrated approach, multiple technologies may be interfaced in order to optimize the efficiency and cost of plume control, contaminated media treatment, and ultimate cleanup.

Interfacing remedial technologies available for soil and ground water contaminated with petroleum products include:

- Bioremediation (e.g., naturally aerated, heap pile, or composting—all of which are described in NEESA Tech Data Sheets);
- Soil washing (solvent applications);
- Soil vapor extraction;
- Air sparging (see "Terminology");
- Thermal treatment (e.g., incineration or low temperature thermal desorption); and
- Steam injection.

Product dissolved in ground water may be removed using traditional pump and treat techniques. The most common techniques used are carbon adsorption and air stripping. Both technologies are proven and each has advantages and disadvantages. Carbon adsorption is effective and easy to accomplish; however, the management (regeneration or disposal) of the spent carbon may be a consideration with respect to cost. Air stripping, applicable for volatile contaminants only, may be similarly effective but may generate a contaminated gaseous effluent requiring further control (by carbon adsorption or catalytic oxidation, for example) and/or permitting. Regardless of the technology selected, separation of oil and water after pumping and prior to treatment may be desirable.

A more advanced recovery technique has recently been developed employing a thermal vacuum spray aeration process. This technique is a combination of pump and treat and soil vapor extraction technologies. In this process, a vacuum is placed on the well to extract product vapors from soil, and a pump is installed in the well to extract contaminated ground water. The well is screened above the water table for a sufficient length to ensure effective soil vapor extraction. The extracted water is sprayed into a heated chamber that is also under vacuum. The combination of vacuum and higher than ambient temperature in this chamber enhances the removal of volatile organic contaminants from ground water. This organic-laden stream and the vapors extracted from the well are then thermally oxidized in an internal combustion engine. The engine also drives the vacuum pump for soil vapor extraction and can provide compressed air for pumping ground water from the extraction well. Ideally, the organic contaminants provide sufficient fuel to sustain the engine for thermal oxidation of organic vapors.

The Navy owns one of these multi-phase contaminant removal systems. This system may become available for use by those in need at the installation level (4).

Cost Considerations

Key cost factors for the recovery of free product include:

- Waste disposal (e.g., product, water, sorbent pads, soil);
- Potential for sale of recovered product for recycling;
- On-site equipment rental (stinger trucks, pumps, tanks, treatment systems);
- Installation of permanent equipment (including wells and trenches);
- Engineering and testing costs;
- Operation and maintenance costs (sampling and analyses, activated carbon use, labor, power); and
- Permit application preparation and approval.

Because of the number of variables involved, establishing general costs for free product response is difficult. Some representative costs have been identified based on Navy experience (Figure 5). These costs illustrate the relative magnitudes of the various recovery options available.

It should be emphasized that delays in response can cause costs to increase dramatically. In effective immediate response actions, costs may be limited to those incurred by using simple

Recovery Technique	Estimated Cost ($/month)*	Included in Cost
Single Phase Extraction (Hand bailing)	$500	Bailer, personnel protection equipment, facility report preparation and review, operation and maintenance, product storage
Single Phase Extraction (Skimming)	$1200 to $2000	Equipment rental, operation and maintenance, facility report preparation and review, product storage
Dual Pumping	$2500 to $4000	Recovery and water treatment equipment rental, operation and maintenance, facility report preparation and review, product storage, and permitting.

*Estimated costs are based on use of single recovery system (i.e., one bailer, one skimmer, and one dual pumping system)

Source: NEESA and Arthur D. Little, Inc.

Figure 5. Representative Free Product Recovery Costs

free product recovery methods such as hand bailing and skimming. However, with the progression of time and the resulting loss of recoverable product to residual or migration, costs are likely to increase by orders of magnitude due to:

- Need to remove product over a wider area;
- Employment of more rigorous methods of product recovery;
- Use of pump and treat ground water treatment technologies;
- Soil excavation and cleanup; and
- Additional regulatory interaction, approval, and permitting.

Application Examples

The case studies described below relate the above discussion to real-world experiences.

Case Study 1. Navy Gasoline Station Located in Coastal Area

During an UST investigation in 1986, floating product greater than 0.25 ft in thickness was detected. Regulators were contacted and Navy personnel were instructed to complete a site characterization including construction of monitoring wells. No interim action to remove the floating product was initiated.

Three years after the discovery of the floating product, weekly hand bailing of the wells was initiated. It was observed during hand bailing operations that a few of the wells had relatively rapid product reinfiltration.

Several weeks after initiating hand bailing, skimmer pumps were used for the recovery of floating product in those wells with rapid reinfiltration. After two months of skimming, the more rigorous method of dual pump extraction was employed.

Because of the lag in initiating action, advanced extraction techniques (dual pumping) had to be employed at this site. The spread of contamination over time required the installation of 12 additional monitoring wells bringing the total on-site to 35. Both of these requirements resulted in increased time to treat and increased cost.

Additional results of the lag between discovery and action are the dissolution of product into the ground water and contamination of additional vadose zone soils.

To extract the dissolved hydrocarbons from the water, a thermal vacuum spray aeration system (see "Interfacing Technologies") is being used to treat contaminated ground water at a rate of 60 gallons per minute. Soil vapor extraction will be employed to mitigate contaminated soil.

Lessons learned as a result of this experience include:

- Response lag time of over three years was due to the absence of an interim remedial plan; and
- Cost and time increases were, and continue to be, experienced due to the response lag time.

Additional details regarding this site and planned remedial actions are available from Mark Kram (see "Points of Contact").

Case Study 2. Navy Fuel Farm Located in Coastal Area

Leaks from UST systems at an active fuel farm have occurred over the past 12 years. In response to the detection of free product in on-site subsurface vaults in the 1987/1988 time frame, a pit was dug and 20,000 to 30,000 gallons of free product were pumped from the pit.

Based on observed product thickness in 1990, initial estimates of total product released ranged from 200,000 to 300,000 gallons. However, more recent estimates indicate that the total product volume is less than 100,000 gallons (most likely between 30,000 and 50,000 gallons). The areal extent of contamination is estimated at 50,000 to 87,500 square feet.

In 1990, the local water board issued a Cleanup and Abatement Order in response to the presence of free product at this site. Project engineers prepared a SOW for a treatability study to identify free product recovery systems best suited to the site. Based on results of the treatability study, product-only recovery systems employing skimmer pumps were selected as the recovery systems of choice. Three recovery wells were installed in addition to one French drain/well combination. Current recovery rates of 100 to 120 gallons per month are being achieved. Recovered product is sent off-site for recycling at a slight charge. The reported quality of product is high indicating that the recovery system is achieving a good level of selectivity between product and water.

Current product thicknesses have been observed ranging from 6 inches to 2.5 feet at the plume center and from 1/16-inch to 4 inches at the plume perimeter.

The cost of this response to date is approximately $300,000.

A complete site characterization is planned for 1993 to delineate the extent of contamination. Results of this characterization will be used to enhance product recovery as well as to select techniques for remediation of the site.

An important lesson learned from this experience is the potential for observed product thickness to be misleading when attempts are made to estimate the total volume of product. When initial estimates were made at this site, observed product thickness was significantly greater than later observations indicated. There are many possible reasons for this fluctuation. Project engineers have proposed that the greater thickness was related to greater hydraulic pressure in the surrounding soil as a result of irrigation in an adjacent agricultural field. When this irrigation was stopped, the thickness was observed to decrease—perhaps in response to reduced hydraulic pressure—allowing for the plume to spread, thereby reducing product thickness.

Because of the various factors affecting product thickness, a direct correlation between product thickness and total product volume cannot be assumed (6).

Additional information regarding this site and ongoing and planned actions are available from Mike Radecki (see "Points of Contact").

Case Study 3. Privately-Owned Gasoline Station Near Urban Drinking Water Source (7,8)

In 1990, a catastrophic release of approximately 1500 gallons of gasoline from an UST occurred. The release occurred near a major city drinking water well field. Upon detection of the release, emergency measures were put into force to control contaminant migration and implement interim remedial action to protect drinking water sources.

Within one day of detection, the UST was removed and wells were drilled. Within one week, product recovery involving air stripping of contaminated ground water was initiated. Within three weeks, six recovery wells were in operation and three air stripping columns were used to treat the contaminated ground water. Less than one year after the release, the ground water was cleaned to nondetectable levels and contaminant migration was controlled eliminating potential threat to the drinking water well field.

At the same time ground water was being treated, field screening was done to better define the extent and degree of contamination. As wells were drilled, soil and water were screened in the field using a portable gas chromatograph. This allowed for the fast, optimum placement of additional recovery wells.

Permits for operation of the air strippers were obtained within a week of their installation. Treatability data required by the state for these permits were obtained on-site using field analytical instrumentation.

This Case Study provides a good illustration of the opportunities and benefits of immediate response and the results of adequate planning.

Further information about this case study may be obtained from the State of Connecticut Department of Environmental Protection, (203) 566-4630.

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8. Personal communication with Peter Zack, Senior Environmental Analyst, Connecticut Department of Environmental Protection, 1992.

Points of Contact

Additional information regarding the technical, regulatory, and practical aspects of response to free product discovery may be obtained from:

- Mark Kram, NEESA, Code 112E2, Port Hueneme, CA, (805) 982-2669.
- John Fringer, NEESA, Code 112E4, Port Hueneme, CA, (805) 982-4856.
- John Edkins, NEESA, Code 112E2, Port Hueneme, CA, (805) 982-2631.
- Mike Radecki, SOUTHWESTDIV, San Diego, CA, (619) 532-3874.
- Tom Schruben, EPA Office of Underground Storage Tanks, Washington, D.C., (703) 308-8875.

L.U.S.T. Line, an EPA-funded newsletter addressing UST issues is available. For information, contact Ellen Frey, Editor, (617) 861-8088.

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Engineering Bulletin

EPA

SELECTION OF CONTROL TECHNOLOGIES FOR REMEDIATION OF LEAD BATTERY RECYCLING SITES

Purpose

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

Introduction

The objective of this bulletin is to provide remedial project managers (RPMs), potentially responsible parties (PRPs), and their supporting contractors with information to facilitate the selection of treatment alternatives and cleanup services at lead battery recycling sites (LBRS). This bulletin condenses and updates the information presented in the EPA technical resource document (TRD) entitled; **"Selection of Control Technologies for Remediation of Lead Battery Recycling Sites,"** EPA/540/2-91/014, July 1991 which is available from The National Technical Information Service, Springfield, VA. This bulletin consolidates useful information on LBRS, such as the following:

- Description of types of operations commonly conducted, and wastes generated at LBRS;
- Technologies implemented or selected for LBRS remediation;
- Case studies of treatability studies on LBRS wastes;
- Past experience regarding the recyclability of materials that are found at LBRS; and
- Profiles of potentially applicable innovative treatment technologies.

Batteries account for more than 80% of the lead used in the United States, of which approximately 60% is reclaimed during times of low lead prices and greater percentages are reclaimed during times of high lead prices. In general, 50% of the national lead requirements are satisfied by recycled products. There are 29 Superfund lead battery recycling sites (LBRS). Twenty-two sites are on the National Priority List (NPL), and 10 of these sites have completed RODs. Removal actions are underway or completed at seven other LBRS.

LBRS are likely to contain a variety of wastes (e.g., lead, plastic, hard rubber) that are potentially recyclable. At LBRS, RPMs are typically confronted with metallic lead and lead compounds as the principal contaminants of concern. Other metals (e.g., cadmium, copper, arsenic, antimony, and selenium) are often present at LBRS, but

usually at much lower concentration than lead and often below hazardous concentrations. Also sulfuric acid from batteries may remain in liquid form in pits, ponds, lagoons, storage tanks, or treatment vessels.

Background Information on Lead-Acid Batteries, Battery Breaking and Secondary Lead Smelting Operations

- **Lead-Acid Storage Battery**

While all lead-acid storage batteries are not alike, a description is provided below of a typical lead-acid storage battery (i.e., a car battery) that is likely to have been processed at a defunct LBRS that is now on the Superfund cleanup list.

A lead-acid storage battery consists of two electrodes dipped into partly diluted sulfuric acid. The electrodes consist of metallic lead grids containing either lead dioxide paste (cathode) or spongy lead (anode). The metallic lead grids may contain various elemental additives including antimony, arsenic, cadmium, copper, and tin.

An average automotive battery weighs 17.2 kg, and contains 8.6-9.1 kg of lead (equally divided between anode and cathode), 1.4 kg of polypropylene plastic, and approximately 2 liters of 15-20% sulfuric acid. Although most battery cases are now constructed of polypropylene, they were previously composed primarily of hard rubber-like material that was called ebonite.

- **Battery Breaking and Secondary Lead Smelting Description**

The lead recovery aspects of lead-acid battery recycling operations consist of battery breaking, component separation, lead smelting and refining, as shown in Figure 1. Battery breaking is the first step in the lead recycling process. The flow diagram in Figure 2 depicts the lead-acid battery breaking process. Most breakers are either hammer mills or saw-type breakers.

The smelting process separates the metal from impurities in either blast, reverberatory, or rotary furnaces. Refining is the final step in chemically purifying recycled lead.

Lead Battery Recycling Site Characterization

Lead contaminated media at LBRS can be classified into four main groups:

- Soils, sediments, and sludges - includes soils and particulate matter intermixed with water or other aqueous components.
- Waste piles - by-products from battery recycling operations.
- Water - includes groundwater, surface water and contaminated wash water or process waters from soils, sediments, and sludges treatment processes.
- Buildings, structures and equipment - includes all process structures, buildings and equipment.

An example of a LBRS conceptual model for potential pathways of exposure is presented in Figure 3.

Lead is the primary contaminant found in soils, sediments, and sludges at LBRS. Concentrations ranging up to 7% have been encountered. Lead (Pb), lead sulfate ($PbSO_4$), lead oxide (PbO), and lead dioxide (PbO_2) are the predominant lead species found at a LBRS. Sites with carbonate soils generally contain lead carbonate ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), or lead hillite ($Pb_4SO_4(CO_3)_2(OH)_2$). Other heavy metals such as antimony, arsenic, cadmium, and copper are sometimes present, but normally in relatively low concentrations.

Soil cleanup goals vary depending on site specific factors such as exposure routes and location of humans and sensitive environmental receptors. In spite of this site to site variability, two common cleanup goals do tend to recur. One of these includes reduction of lead concentrations in the soil, sediment, or sludge to the point that the leachate yields less than 5 mg/L of lead when subjected to an EPA-mandated leaching procedure (i.e., EP Toxicity or TCLP tests). Soils with TCLP leachates above 5 mg/L lead are considered to be hazardous waste, which means that the soils generally cannot be landfilled until they have been treated to yield a leachate less than 5 mg/L lead (Federal Register, 1990). A second common cleanup goal is the reduction of the total lead content in residential soil to a level of 500 to 1000 mg/kg. In accordance with EPA Office of Solid Waste and Emergency Response (OSWER) Directive #9355.4-02, an

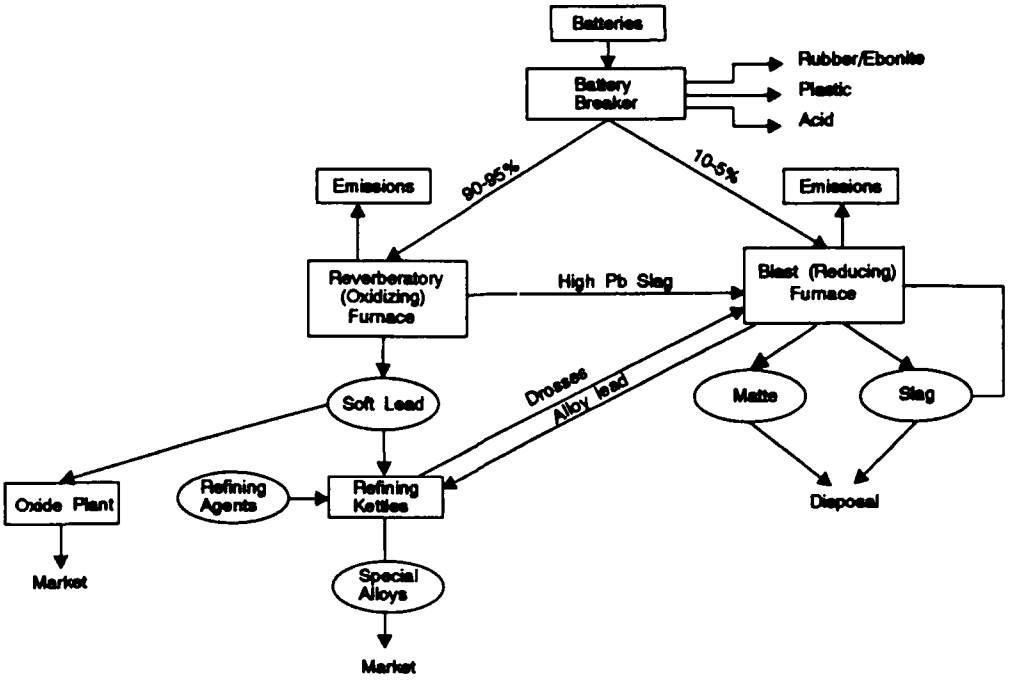

Figure 1. Generalized Secondary Lead Smelting/Refining Process
Source: Exide Corporation, 1992

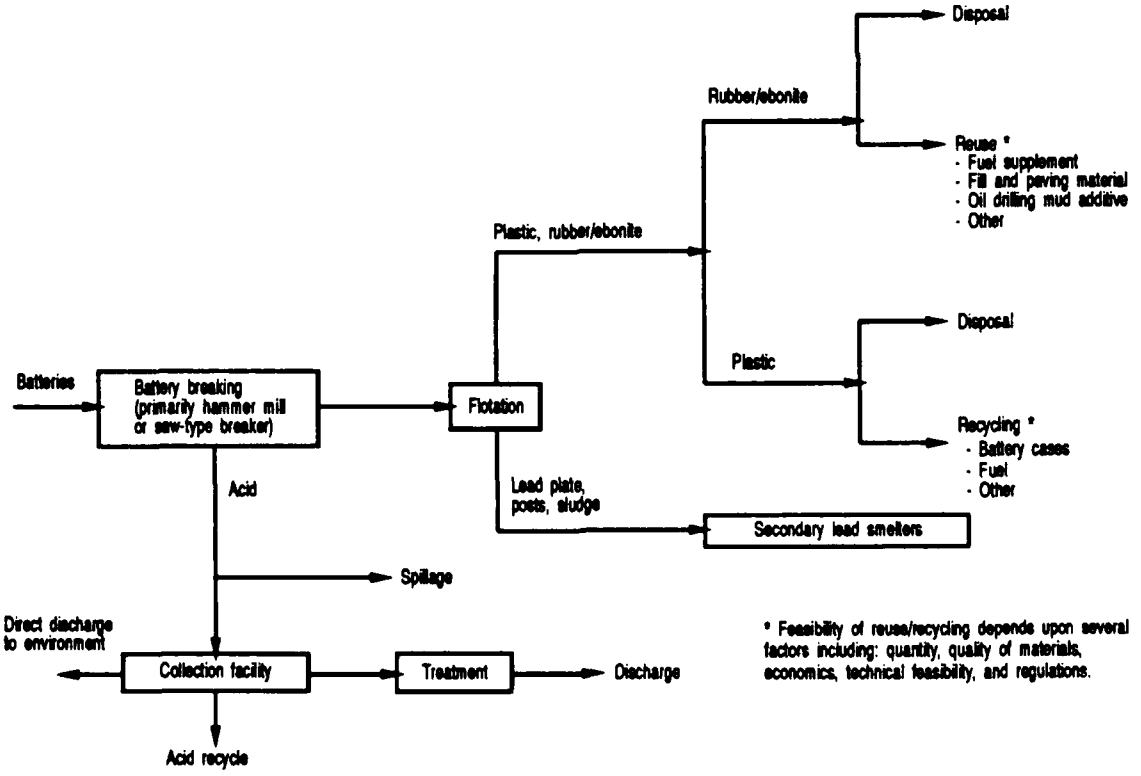

Figure 2. Flow diagram of lead-acid battery breaking.

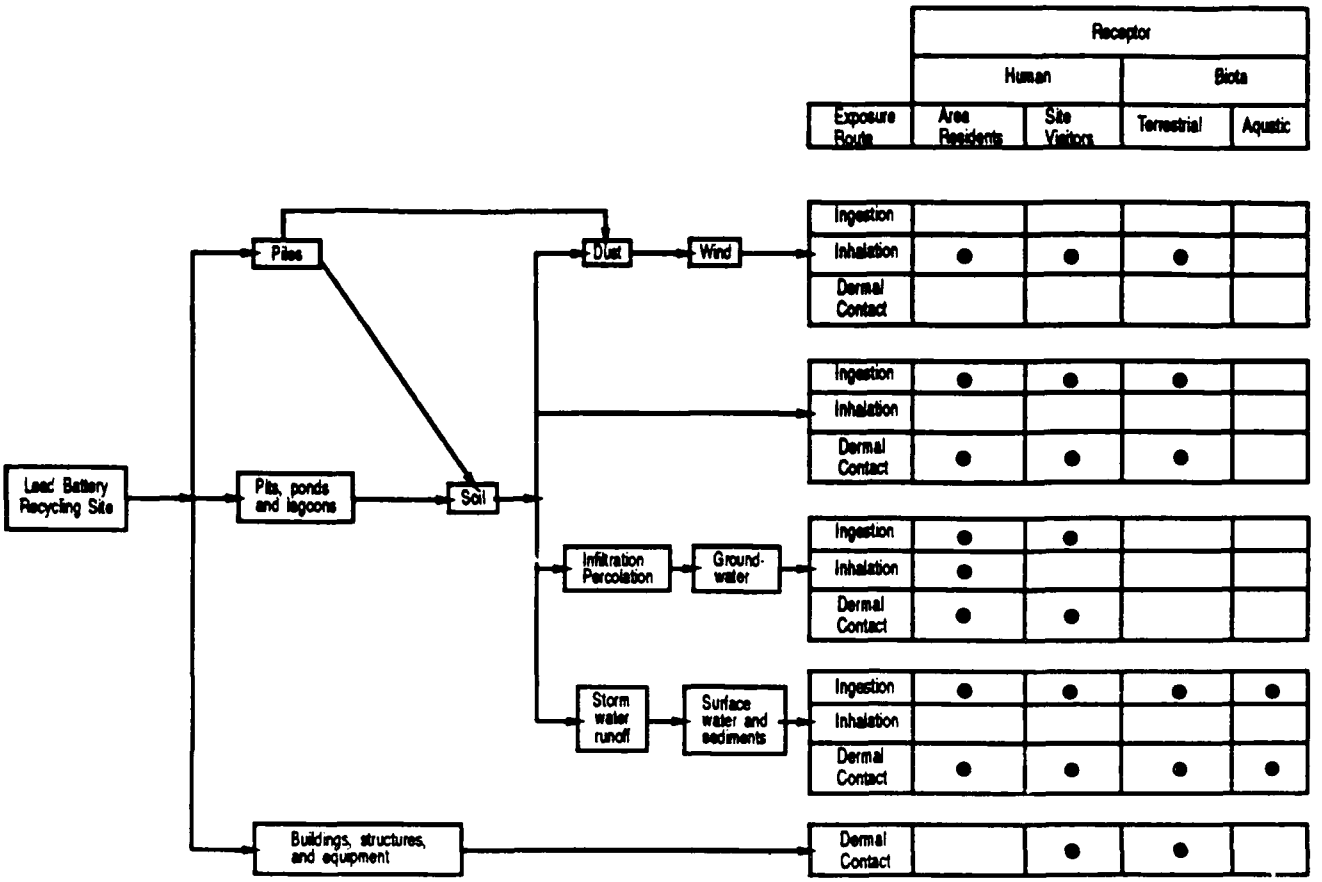

Figure 3. A lead battery recycling site conceptual model.

interim soil cleanup level of 500 to 1,000 mg/kg total lead was adopted for protection from direct contact at residential settings. OSWER is in the process of revising this directive to account for the contribution of various media to total lead exposure and to produce a strong scientific basis for choosing a soil lead cleanup level for a site. OSWER believes that the best available approach is to use the EPA uptake biokinetic model (USEPA, 1991a).

Lead is generally not very mobile in the environment, and tends to remain relatively close to its point of initial deposition following its escape from the recycling process. Soils strongly retain lead in their upper few centimeters. The capacity of soil to adsorb lead increases with increasing pH, cation exchange capacity, organic carbon content, soil/water Eh (redox potential), and phosphate levels. Lead exhibits a high degree of adsorption on clay-rich soil. Lead compounds can also be adsorbed onto hydrous oxides of iron and manganese and be immobilized in double and triple salts. Metallic lead and its compounds are heavier than water and tend to settle out. Some of the compounds are slightly soluble while

others are insoluble in water. Throughout most of the natural environment, the divalent form, Pb^{+2}, is the most stable ionized form.

Geophysical surveys can be used to determine the vertical and lateral variations in both subsurface stratigraphy and subsurface metal contamination. A variety of survey techniques (e.g., ground penetrating radar, electrical resistivity, electromagnetic induction, magnetometry, and seismic profiling) can effectively detect the locations and extent of buried waste deposits. Borehole geophysics investigations can be conducted at selected well locations in order to better characterize subsurface stratigraphy. Field screening techniques such as x-ray fluorescence (XRF) can be used to pinpoint sampling locations at areas of greatest contamination ("hot spots"). To identify the level of risk presented by the site and to evaluate remedial alternatives, soil samples are typically analyzed in the laboratory for the USEPA Target Analyte List (TAL) metals, TCLP toxicity, total cyanide, total organic carbon, sulfate content, pH, acidity/alkalinity, and cation exchange capacity.

Waste piles at LBRS are usually by-products from recycling operations. These waste piles can be broken down into several components: battery casings (made of hard rubber-like composites or polypropylene), battery internal components (e.g., polyvinyl chloride, paper), matte (a metallic sulfide waste containing iron and lead), slag, and contaminated debris. Waste samples are analyzed for the parameters mentioned above.

Groundwater does not normally create a major pathway for lead migration. However, since lead compounds are soluble at low pHs, if battery breaking activities have occurred on-site, and the battery acid was disposed on-site, elevated concentrations of lead and other metals may occur in groundwater. Monitoring wells are installed and sampled upgradient and downgradient from a lead battery recycling site. To identify the level of risk presented by the site and to evaluate remedial alternatives, samples from the wells are analyzed for TAL metals, total cyanide, total organic carbon, total suspended solids, total dissolved solids, pH, alkalinity/acidity, hardness, sulfate, chloride, specific conductance, temperature, and dissolved oxygen. The Office of Emergency and Remedial Response (OERR) has recommended an interim potable groundwater cleanup level of 15 ppb for lead (USEPA, 1990a).

A variety of contaminated structures, buildings, and equipment may be encountered at LBRS. Sampling methods to determine the nature and extent of contamination on buildings, structures, and equipment surfaces have not yet been standardized. Surface-wipe sampling is generally used.

Basic Approaches to the Control of Lead Battery Recycling Sites

Remediation strategies for LBRS may incorporate several distinct technology options assembled into a treatment train to attain specific site goals. These technologies include:

- No action
- Immobilization: preventing contaminant migration through construction of physical barriers (e.g., caps, slurry walls, liners) or utilizing chemical or thermal processes (e.g., solidification/stabilization and vitrification).
- Separation/concentration: includes technologies utilizing chemically or physically induced phase separation processes to concentrate lead contamination for further treatment, partial recycling, or disposal while remediating a major portion of the contaminated material.
- Excavation and off-site disposal: removal of contamination for disposal.

- **Treatment Technologies for Soils, Sediments, and Sludges**

<u>No Action</u>

Two out of 10 Record of Decisions (RODs) for LBRS have selected no action as a remedial alternative, because the results of the Remedial Investigation (RI) showed that the emergency removal processes (excavation and off-site disposal) conducted at sites were effective in removing contaminated soil from the site and the concentrations of contaminants found in the groundwater were below any applicable or relevant and appropriate requirements (ARARs). No action involves environmental monitoring and institutional restrictions such as site fencing, deed restrictions, restrictions on groundwater usage, warning against excavation and a public awareness program.

Immobilization Options

Capping–

To date five out of 10 RODs for LBRS have selected capping as an integral part of a treatment alternative. Capping involves the installation of an impermeable barrier over the contaminated soil to restrict access and reduce infiltration of water into the soil. A variety of cap designs and materials are available. Most designs are multi-layered to conform with the performance standards in 40 CFR 264.310 which addresses RCRA landfill closure requirements. However, single-layered designs are used for special purposes at LBRS, for example, when treated soil is backfilled into an excavated area. Low permeability clays and synthetic membranes are commonly used. They can be covered with top soil and vegetated to protect them from weathering and erosion. Soil materials are readily available, and synthetic materials are widely manufactured and distributed.

The cost of a cap depends on the type and amount of materials selected, the thickness of each layer, and the region. In a recent RCRA Part B permit application for a four acre hazardous waste landfill, the installed cost of a multi-layered cap was estimated at $\$6/ft^2$. The design for this cap included 3 ft of top soil, overlying a 1 ft sand layer, overlying 1 ft of compacted clay, overlying a 30 mil High Density Polyethylene (HDPE) liner, overlying 2 ft of compacted clay (USEPA, 1985).

Table 1 summarizes the data needed to evaluate capping as a remedial alternative for soils, sediments, and sludges.

Solidification/Stabilization (S/S)–

To date, 5 out of 10 RODs for LBRS have selected ex situ S/S as an integral part of a treatment alternative. Solidification processes, either in situ or ex situ, produce monolithic blocks of waste with high structural integrity. The contaminants do not necessarily interact chemically with the solidification reagents (typically cement/lime) but are primarily mechanically locked within the solidified matrix. Stabilization methods usually involve the addition of materials such as fly ash or blast furnace slag which limit the solubility or mobility of waste constituents – even though the physical handling characteristics of the waste may not be changed or improved (USEPA, 1982). Ex situ S/S is widely demonstrated and equipment is readily available. However, long-term reliability of S/S is not yet established.

Ex situ S/S involves mixing the excavated contaminated soil with portland cement and/or lime along with other binders such as fly ash or silicate reagents to produce a strong, monolithic mass. Cement is generally suitable for immobilizing metals (such as lead, antimony, and cadmium) which are found at lead battery recycling sites. Because the pH of the cement mixture is high (approximately 12), most multivalent cations are converted into insoluble hydroxides or carbonates. They are then resistant to leaching.

Costs to use S/S technology are expected to be in a range of $30-$170 per cu yd (USEPA, 1989a). Data needs to evaluate S/S as a remedial alternative are summarized in Table 1.

Three full-scale S/S operations have been implemented at LBRS. Approximately 7,300 tons of soil contaminated with lead (EP Tox >400 mg/L) were treated in a mobile plant with portland cement, fly ash, and water at a rate of 300 tons/day at Norco Battery Site in California. EP Toxicity of the treated soil after 28 days was less than 5 mg/L (USEPA, 1991b). Approximately 11,000 tons of soil (TCLP as high as 422 mg/L) were treated by the proprietary MAECTITE™ process developed by Maecorp, Inc. at the Lee's Farm in Wisconsin. TCLP of the treated soil was less than 1 mg/L. About 20,000 cubic yards of lead-contaminated soil were recently solidified at Cedartown Battery, Inc. in Georgia. Analytical data on this site are currently being processed.

Numerous S/S treatability studies have been completed at LBRS. A pilot-scale treatability test conducted at the Gould Site in Oregon demonstrated that a mix of approximately 14% portland cement Type I-II, 25% cement kiln dust, and 35% water successfully stabilized soils and waste products crushed to 1/8 in. size. Bench-scale treatability studies conducted on soils from three LBRS (C&R Battery Site in Virginia, Sapp Battery Site in Florida, Gould Site in Oregon) demonstrated that cement-based (i.e., cement or cement with additives) blends decreased the leachability of lead and met the EP Toxicity criterion of 5 mg/L.

TABLE 1. DATA NEEDS FOR TREATMENT TECHNOLOGIES FOR SOILS, SEDIMENTS, AND SLUDGES

Technology	Data requirement
Capping (USEPA, 1987a)	• Extent of contamination • Depth to groundwater table • Climate • Waste volume
Solidification/stabilization (USEPA, 1986a and Arniella et al., 1990)	• Metal concentrations • Moisture content • Bulk density • Grain-size distribution • Waste volume • Sulfate content • Organic content • Debris size and type • TCLP
Soil washing/acid leaching (USEPA, 1989c and USEPA, 1990c)	• Soil type and uniformity • Moisture content • Bulk density • Grain-size distribution • Clay content • Metal concentrations/species • pH • Cation exchange capacity • Organic matter content • Waste volume • Mineralogical characteristics • Debris size and type • TCLP
Off-site land disposal (USEPA, 1987b)	• Soil characterization as dictated by the landfill operator and the governing regulatory agency • Waste volume • TCLP

In situ treatment of contaminated soils is innovative. Two specific in situ S/S techniques, under the Superfund Innovative Technology Evaluation (SITE) Program, hold promise for LBRS.

International Waste Technologies/Geo-Con, Inc.– This in situ solidification/stabilization technology immobilizes organic and inorganic compounds in wet or dry soils, using additives to produce a cement-like mass. The basic components of this technology are: a deep soil mixing system (DSM) which delivers and mixes the chemicals with the soil in situ; and a batch mixing plant to supply the International Waste Technologies (IWT) proprietary treatment chemicals. The IWT technology can be applied to soils, sediments, and sludges contaminated with organic compounds and metals. The SITE Demonstration of this technology occurred at a PCB-contaminated site in April, 1988 and the results are summarized in an Applications Analysis Report (USEPA, 1990b).

S.M.W. Seiko, Inc.– The Soil-Cement Mixing Wall (S.M.W.) technology developed by Seiko, Inc. involves the in situ stabilization and solidification of contaminated soils. Multi-axis, overlapping, hollow-stem augers are used to inject solidification/stabilization agents and blend them with contaminated soils in situ. The product is a monolithic block down to the treatment depth. This

technology is potentially applicable to soils contaminated with metals and semi-volatile organic compounds. The search for a demonstration site is currently underway.

Vitrification--

As with solidification, there are both ex situ and in situ procedures for vitrification. In situ vitrification converts contaminated soils into chemically inert, stable glass and crystalline materials by a thermal treatment process. Large electrodes are inserted into soil containing significant levels of silicates. Because soil typically has low conductivity, flaked graphite and glass frit are placed on the soil surface between the electrodes to provide a starter path for electric current. A high current passes through the electrodes and graphite. The heat melts contaminants, gradually working downward through the soil. Volatile compounds are collected at the surface for treatment. After the process ends and the soil has cooled, the waste material remains fused in a chemically inert and crystalline form that has very low leachability rates. This process can be used to remove organics and/or immobilize inorganics in contaminated soils or sludges. It has not yet been applied at a Superfund site. However, it has been field demonstrated on radioactive wastes at the DOE's Hanford Nuclear Reservation by the Geosafe Corporation. Geosafe has also contracted to conduct two superfund site cleanups, one in Spokane, WA, and another in Grand Ledge, MI. Large-scale remediation of this process has been suspended temporarily because of the loss of offgas confinement and control during the recent large-scale testing of its equipment that resulted in fire.

Ex situ vitrification involves heating the excavated soil by a thermal process to form chemically inert materials. Two specific ex situ vitrification techniques under the SITE Program have application to LBRS.

Retech, Inc. Plasma Reactor--This thermal treatment technology uses heat from a plasma torch to create a molten bath that detoxifies contaminants in soil. Organic contaminants vaporize and react at very high temperatures to form innocuous products. Solids melt into the molten bath. Metals remain in this phase, which -- when cooled -- forms a non-leachable matrix. It is most appropriate for soils and sludges contaminated with metals and hard-to-destroy organic compounds. This technology was demonstrated in August 1991 at a Department of Energy research facility in Butte, Montana and the final demonstration report will be completed in August 1992.

Babcock and Wilcox Co. Cyclone Furnace Process--This cyclone furnace technology is designed to decontaminate wastes containing both organic and metal contaminants. The cyclone furnace retains heavy metals in a non-leachable slag and vaporizes organic materials prior to incinerating them. The treated soils resemble natural obsidian (volcanic glass), similar to the final product of vitrification. This technology is applicable to solids and soil contaminated with organic compounds and metals. This technology was demonstrated in November 1991 at Babcock and Wilcox Co. research facility in Alliance, Ohio.

Separation/Concentration Options

Soil Washing and Acid Leaching--

Soil washing is a water-based process for mechanically scrubbing soils ex situ to remove undesirable contaminants. The process removes contaminants from soils in one of two ways: by dissolving or suspending them in the wash solution or by concentrating them into a smaller volume of soil through simple particle size separation techniques. Acid leaching removes lead from soils by first converting the lead to a soluble salt, and then precipitating a lead salt from solution.

Implementation of this technology requires excavating the lead-contaminated soil, washing the lead on-site with a solution (such as nitric acid or EDTA), and returning the treated soil to the site for disposal in the excavation area. One of the limitations of soil washing as a viable alternative concerns the physical nature of the soil. Soils which are high in clay, silt, or fines have been difficult to treat.

Figure 4 is a process flow diagram of an acid leaching process developed by U.S. Bureau of Mines. This process converts lead sulfate and lead dioxide to lead carbonate, which is soluble in nitric acid. Lead is recovered from the leaching solution by precipitating with sulfuric acid (Schmidt, 1989). There is a potential market for lead sulfate. The Bureau of Mines also investigated converting the lead compounds to carbonates followed by leaching with fluosilicic acid. Electrowinning recovers metallic lead from solution while regenerating the acid for

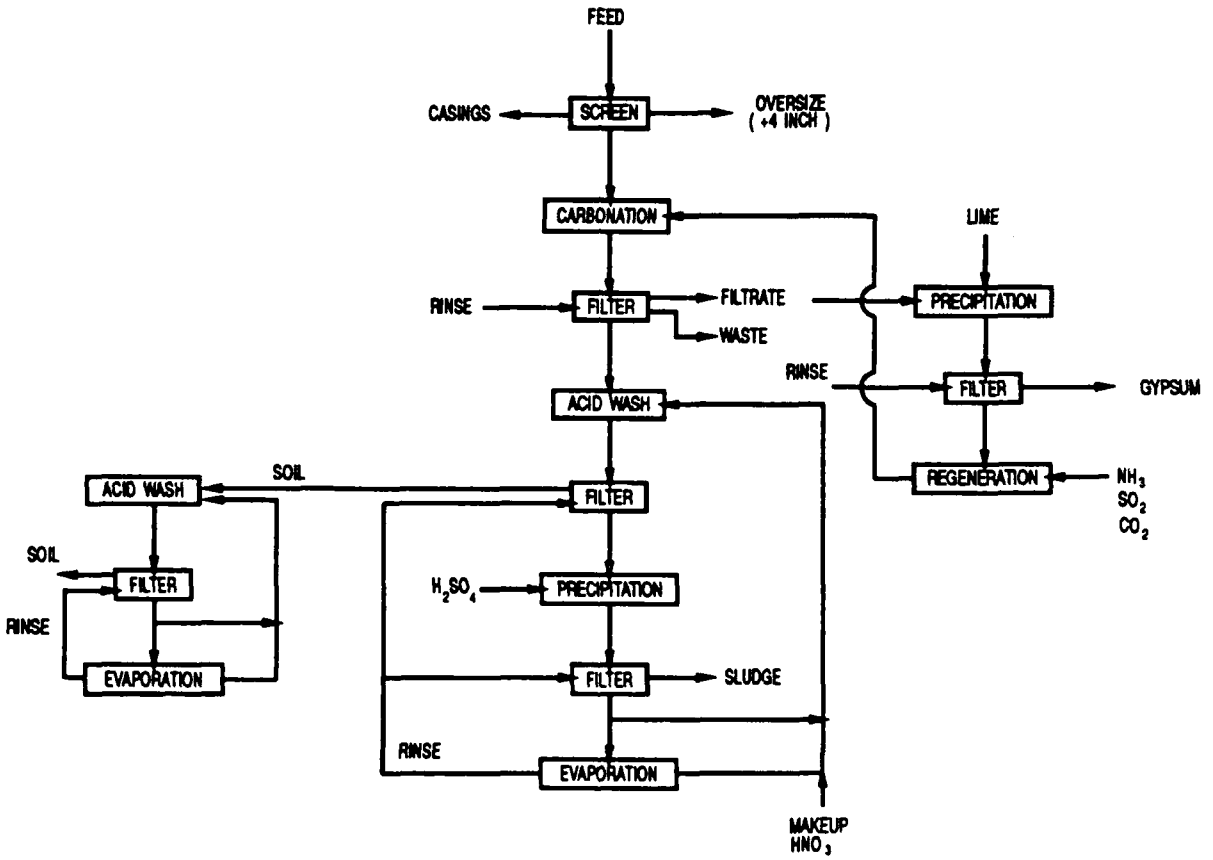

Figure 4. Bureau of Mines acid leaching process.
Source: Schmidt, 1989.

recycle. The clean soil can be returned to the site but waste streams from either soil washing processes require further treatment before final discharge.

Actual field experience of cleaning soil at LBRS is limited. Two sites (Lee's Farm in Woodville, Wisconsin and ILCO site in Leeds, Alabama) have unsuccessfully attempted soil washing of contaminated soil. One ROD (United Scrap Lead Co. Site in Ohio) out of 10 for LBRS has selected acid leaching as an integral part of the treatment alternative but full-scale treatment has not occurred. The Bureau of Mines (BOM) conducted bench-scale studies to evaluate the performance of acid leaching solutions on lead in contaminated soil at battery recycling sites. Table 2 shows some representative results from the Bureau of Mines tests. The results indicated that nitric acid solutions can achieve very high removal efficiencies for soil (greater than 99%) and an EP Toxicity level less than 1 mg/L (Schmidt, 1989). BOM estimates the cost of full-scale operation to be $208 per cu yd of soil.

EPA completed a series of laboratory tests on soil and casing samples from metal recycling sites. The soil samples from these sites were subjected to bench-scale washing cycles using water, EDTA, or a surfactant (Tide detergent), respectively. Soil washing did not remove significant amounts of lead from any of the soil fractions. The lead was not concentrated in any particular soil fraction but rather was distributed among all the fractions. A comparison of lead concentrations in the wash waters indicated that the EDTA wash performed better than the surfactant and water washes (PEI Associates Inc., 1989). While EDTA was reasonably effective in removing lead, Bureau of Mines researchers observed that its effectiveness seemed to vary with the species of lead present (Schmidt, 1989). Additional bench-scale studies are required to verify that site-specific cleanup goals can be achieved employing these techniques. EPA researchers are also in the early stages of investigating the use of milder acids (e.g., acetic acid) than those acids used to date (e.g., nitric, fluosilicic) for leaching of lead from soils (USEPA, 1990d).

TABLE 2. REPRESENTATIVE RESULTS OF THE BUREAU OF MINES TREATABILITY TESTS ON SELECTED SAMPLES OF BATTERY BREAKER SOIL WASTES

Site/waste	Common lead species	Average[a] lead total (ppm)	Leaching method	Total lead (ppm)	EP Toxicity (mg/L)
United Scrap Lead soil	Pb, $PbSO_4$, PbO_x	8,000-18,000	15% HNO_3, 2-hr wash and 1% HNO_3, 24-hr soak	200	<1.0
United Scrap Lead soil	Pb, $PbSO_4$, PbO_x	8,000-18,000	80 g/L F*, 4-hr & 20 g/L F*, 4-hr, 2-stage wash, 1% HNO_3, 24-hr soak	203	<1.0
Arcanum soil	Pb (6.6%), $PbSO_4$	71,000	80 g/L F*, 4-hr, 50°C & 20 g/L F*, 4-hr, 50°C, 2-stage leach and 1% HNO_3, 24-hr wash	334	0.26
Arcanum soil	Pb (6.6%), $PbSO_4$	71,000	15% HNO_3, 2-hr, 50°C leach and 1% HNO_3, 50°C, 24-hr wash	<250	<1.0
C&R Battery Soil Sample B	Pb, $PbSO_4$, $PbCO_3$, PbO_2	17,000	15% HNO_3, 2-hr and 2% HNO_3, 24-hr wash and 1-hr water rinse	29	<0.1

[a]No initial EP Toxicity data available.
F* Fluosilicic acid

Source: Schmidt, 1989

European vendor firms in the soil washing business have been remediating for a number of years sites contaminated with lead. Most of their experience has been with relatively lower lead concentrations (typically less than 500 ppm) from mine tailings and smelter waste materials (bag house dust and slag). No European firms have been found to date who have direct experience in treating soils from lead battery recycling sites (or equivalent) where the lead contamination typically could be around 7,000 ppm total lead. However, in discussions with certain of these vendors, they are of the opinion that soil washing may have application although bench-scale treatability tests would be needed to verify performance.

Soil Excavation and Off-Site Disposal

Excavation and removal of contaminated soil to a RCRA landfill have been performed in the past at LBRS but probably will not continue unless the materials are treated prior to disposal due to land disposal restrictions (LDRs). Excavation and removal are applicable to almost all site conditions, although they may be cost-prohibitive for sites with large volumes, greater depths or complex hydrogeologic environments. Determining the feasibility of off-site disposal requires knowledge of LDRs and other regulations developed by state governments. Without treatment, this technology may not meet RCRA LDRs. The LDRs prohibit the land disposal of certain RCRA hazardous wastes unless they meet specified treatment standards. If lead-contaminated wastes (i.e., soils and fragments of battery cases) fail the Toxicity Characteristic Leaching Procedure (TCLP) test with lead levels equal to or greater than 5.0 mg/L, then, if excavated, their subsequent handling and disposal must comply with RCRA hazardous waste regulations.

Cost estimates for this technology range from $287-$488 per cu yd of soil.

- **Treatment Technologies for Waste Piles**

Waste pile removal and off-site disposal have been practiced in the past but probably will not continue due to LDRs, unless the materials are treated prior to disposal.

Table 3 summarizes the data needs for treatment technologies for waste piles.

Washing of Battery Casings

This technology, developed by the Bureau of Mines (BOM), is similar to acid leaching of soil but somewhat less complicated. Lead contamination is principally in the form of $PbSO_4$ in microcracks in the casing. Casing materials are granulated to less than 3/8 inch to create enough exposed surface area that the $PbSO_4$ could then be successfully removed by the leaching agent such as nitric acid.

There has been no actual field experience to date in the washing of battery casings at lead battery recycling sites. BOM conducted bench-scale treatability studies that showed good removal efficiencies (Table 4). The residual battery casing materials have an EP Toxicity lead concentration less than 5 mg/L (Schmidt, 1989).

Separation and Cleaning of Battery Casings

This alternative comprises excavation of the waste piles, followed by on-site separation of battery casing fragments. Separation is followed by recycling (possibly off-site) of those components that have recycle value; RCRA off-site disposal of hazardous non-recyclable components; and on-site disposal of nonhazardous components.

Canonie Environmental Services Corp. under contract to NL Industries, Inc. has developed a proprietary process for remediating lead battery and smelting wastes at the Gould Site in Portland, Oregon (Canonie Environmental, undated). The process separates the waste materials into recyclable and nonrecyclable products. The recyclable products consist of:

- Materials with a lead content sufficiently high for recycling, and
- Cleaned materials such as plastic and ebonite that will pass the EP Toxicity test for lead.
- The materials that cannot be cleaned to pass the EP Toxicity test for lead and do not contain sufficient lead for recycling are considered "nonrecyclable".

The process is shown schematically in Figure 5. The battery casing is crushed and washed in the first stage. The fines are screened from the washed material, the

TABLE 3. DATA NEEDS FOR TREATMENT TECHNOLOGIES FOR WASTE PILES

Technology	Data requirement
Off-site landfill (USEPA, 1987b)	• Waste pile characterization as dictated by land disposal restrictions • Waste volume • TCLP
Washing of battery casings	• Casing type • Bulk density • Grain-size distribution • Metal concentrations • TCLP
Separation of battery casings	• Composition of battery casings • Metal concentrations • Waste volume • Other information required by recipient • TCLP
Recycling	• Potential buyer/user • Allowable lead content in ebonite/plastic for use as fuels • Lead content for acceptance by smelter

TABLE 4. REPRESENTATIVE RESULTS OF THE BUREAU OF MINES TREATMENT TESTS ON SELECTED CHIP SAMPLES OF BROKEN BATTERY CASING WASTES

Site/waste	Common lead species	Average[a] lead total (ppm)	Leaching method	Total lead (ppm)	EP Toxicity (mg/L)
United Scrap lead granulated chips	$PbSO_4$, Pb	3,000	0.5% HNO_3, 1-hr, 20°C wash	86	<0.2
Arcanum broken chips	$PbSO_4$, Pb	3,000	1% HNO_3, tap water, 50°C, 24-hr, agitated	210	<3.5
C&R Battery casing chips	$PbSO_4$, Pb	175,000	1% HNO_3 4-hr, wash and water rinse	277	0.15
Gould buried casing chips (broken)	$PbCO_3$, $PbSO_4$	193,000	Ammonium carbonate carbonation, 1% HNO_3, 20°C, 4-hr wash	145	0.52
Rhone-Poulenc casing chips (broken)	$PbCO_3$	65,000	Calcium carbonate carbonation, 0.5% HNO_3, 20°C, 1-hr wash	516	3.68

[a]No initial EP Toxicity data available.

Source: Schmidt, 1989

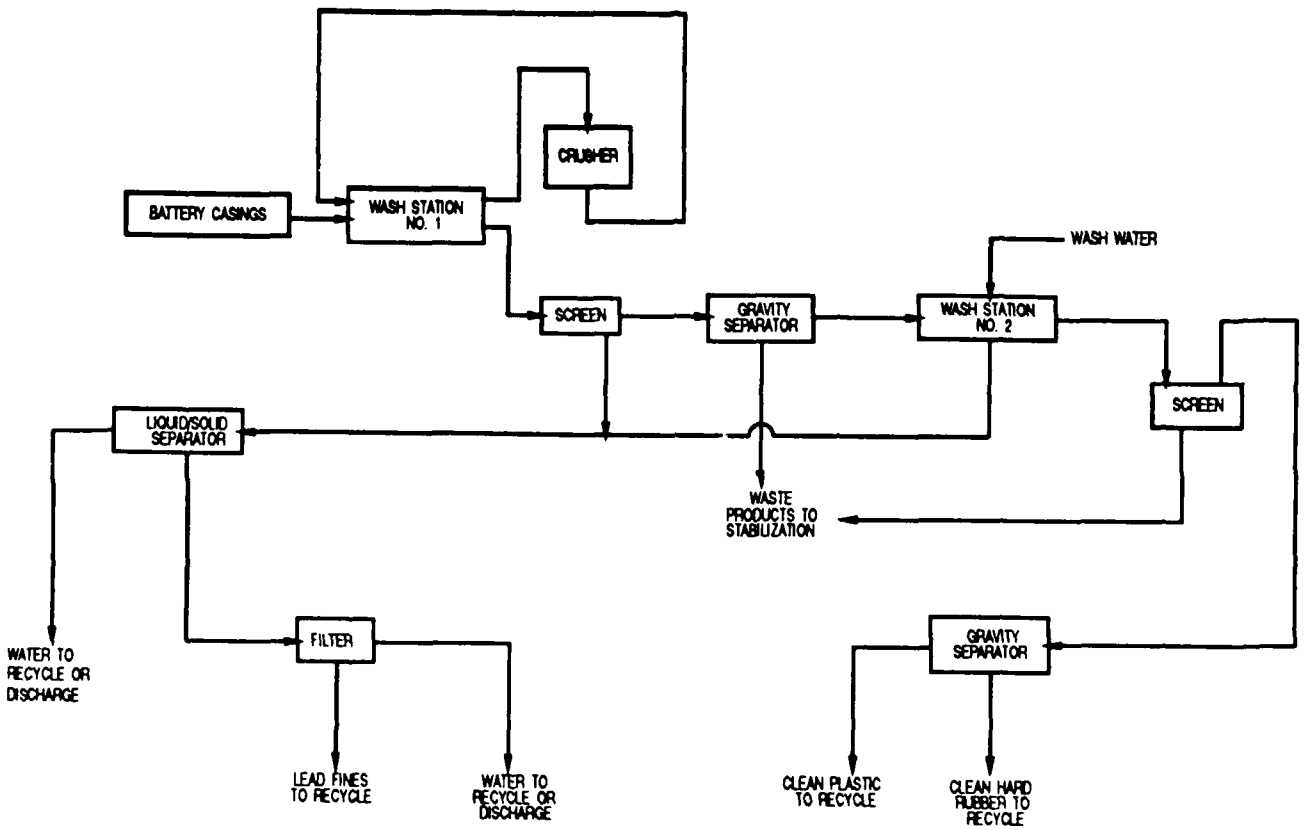

Figure 5. Battery waste treatment process.
Source: Canonie Environmental.

solids are separated from the water in a settling tank, and the settled pulp is filtered from the solution. These materials are the filter cake that will typically contain more than 40% lead and less than 30% moisture. Following the first wash, the screen oversize is fed to a gravity separation device. This system separates the plastic and ebonite in the waste from furnace products, rocks, and trash excavated with the waste. The ebonite and plastic material passes to the second wash stage where the residual amounts of lead contamination are removed.

Performance at the Gould Site--The Gould site contains approximately 117,500 tons of waste. Canonie claims that its separation and washing process there could produce approximately 80,500 tons of recyclable materials and 37,000 tons of material for stabilization and subsequent on-site disposal. At other sites, the amount of recyclable material may vary according to site history and use (Canonie Environmental, undated).

Canonie Environmental conducted a marketing study to identify the markets for the products from the above process. The market suggested for the lead fines are primary and secondary lead smelters. Plastic, if it can be suitably cleaned, appears to have numerous potential users. The most likely market for ebonite from the Gould site appears to be as a fuel supplement for cement kilns or power plants (Canonie Environmental, 1990). Additional market research is planned to assess the effect of the new RCRA boiler and industrial furnace regulations regarding combustion of hazardous wastes. As noted below, secondary lead smelters are potential users of hard rubber-like battery casings, but none are sufficiently close to the Gould site.

Innovative Processes for Waste Piles Treatment

The Horsehead Resource Development Co., Inc. Flame Reactor Process--A patented, hydrocarbon-fueled, flash smelting system that treats residues and wastes containing metals. The reactor processes wastes with a very hot reducing gas >2000°C produced from the combustion of solid or gaseous hydrocarbon fuels in oxygen-enriched air. In a compact, low cost reactor, the feed materials react rapidly, allowing a high waste throughput. The end products are a non-leachable slag (glass-like when cooled) and a recyclable heavy metal-enriched oxide, which may be marketable. This technology has potential application to soils contaminated with heavy metals. A SITE demonstration was performed at the Monaca facility in Pennsylvania in March 1991. The waste material was a secondary lead smelter blast furnace slag from the National Smelting and Refining Site in Atlanta, Georgia. Lead and other metals were removed from the raw waste and concentrated in the bag house dust which may be recycled for its lead content. The process reduced the lead content of the slag from 5.4% to 0.6%. All samples of processed waste slag passed the TCLP test for metals. For lead, the TCLP values fell from approx. 5 mg/L to <0.33 mg/L (USEPA, 1991c).

The Risk Reduction Engineering Laboratory (RREL) Debris Washing System (DWS)--Developed by RREL staff and IT Environmental Programs, Inc., this technology will decontaminate debris found at Superfund sites throughout the country. The DWS can clean various types of debris (e.g., metallic, masonry, or other solids) that are contaminated with hazardous chemicals such as pesticides, PCBs, lead, and other metals. Site demonstration was performed at three Superfund sites (Carter Industrial Superfund Site in Detroit, MT, PCB-Contaminated Site in Hopkinsville, KY, and Shaver's Farm Site in Walker County, GA).

Bench-scale studies conducted on six pieces of debris including plastic spiked with DDT, lindane, PCB and lead sulfate, then washed using surfactant achieved an overall percentage reduction of lead greater than 98%. This technology has potential application to battery casings and other metallic and masonry debris found at LBRS.

As part of the emerging technology portion of the SITE Program, the **Center for Hazardous Materials Research (CHMR)** proposes to research, develop, and evaluate the economics of using secondary lead smelters for the recovery of lead from rubber battery casings. Secondary lead smelting technology is a process which may be able to remove the lead from the battery casings and other waste materials. The net result will be the detoxification of these materials while providing a usable product (i.e., reclaimed lead). A test was conducted in September 1991 with five truckloads of battery casing material at Exide's Reading, PA smelter. The initial results were promising, but the project report has not yet been published.

- **Treatment Technologies for Water**

Treatments using precipitation/flocculation/sedimentation and ion exchange are often considered for remediation of LBRS. Contaminated water from pits, ponds, and lagoons is typically pumped and treated together with groundwater.

Table 5 summarizes the data needs for treatment technologies for water.

Precipitation/Flocculation/Sedimentation

The combination of precipitation/flocculation/sedimentation is a well-established technology with specific operating parameters for metals removal from ground and surface waters. Typical removal of metals employs precipitation with hydroxides, carbonates, or sulfides. Generally lime, soda ash, or sodium sulfide is added to water in a rapid-mixing tank along with flocculating agents such as alum, lime, and various iron salts. This mixture then flows to a flocculation chamber that agglomerates particles, which are then separated from the liquid phase in a sedimentation chamber. Hydroxide precipitation with lime is the most common choice. Metal sulfides exhibit significantly lower solubility than their hydroxide counterparts, achieve more complete precipitation, and provide stability over a broad pH range. At a pH of 4.5, sulfide precipitation can achieve the EPA-recommended standard for final cleanup level for lead in groundwater usable for drinking water (i.e., 15 μg/L). Sulfide precipitation -- often effective -- can be considerably more expensive than hydroxide precipitation, due to higher chemical costs and increased process complexity. The precipitated solids would then be handled in a manner similar to contaminated soils. The supernatant would be discharged to a nearby stream or to a publicly owned treatment works (POTW).

Ion Exchange

Ion exchange is a process whereby the toxic ions are removed from the aqueous phase in an exchange with relatively harmless ions held by the ion exchange material. Modern ion exchange resins consist of synthetic organic materials containing ionic functional groups to which exchangeable ions are attached. These synthetic resins are structurally stable and exhibit a high exchange capacity. They can be tailored to show selectivity towards specific ions. The exchange reaction is reversible and concentration-dependent; the exchange resins are regenerable for reuse. All metallic elements -- when present as soluble species, either anionic or cationic -- can be removed by ion exchange.

TABLE 5. DATA NEEDS FOR TREATMENT TECHNOLOGIES FOR WATER

Technology	Data requirement
Precipitation/flocculation/sedimentation (USEPA, 1989b)	• Total suspended solids • pH • Metal concentrations • Oil and grease • Specific gravity of suspended solids
Ion exchange (USEPA, 1989b)	• Total suspended solids • Total dissolved solids • Inorganic cations and anions • Oil and grease • pH
Pumping via wells	• Depth to water table • Groundwater gradients • Hydraulic conductivity • Specific yield estimate • Porosity • Thickness of aquifers • Storativity

A practical upper concentration limit of toxic ions for ion exchange is about 2,500 to 4,000 mg/L. A higher concentration results in rapid exhaustion of the resin and inordinately high regeneration costs. Suspended solids in the feed stream should contain less than 50 mg/L to prevent plugging the resins (USEPA, 1986b).

Innovative Processes for Water Treatment

The Bio-Recovery Systems, Inc. Biological Sorption Process--Bio-Recovery Systems, Inc. in Las Cruces, New Mexico is testing AlgaSORB®, a new technology for the removal and recovery of heavy metal ions from groundwater. This biological sorption process is based on the affinity of algae cell walls for heavy metal ions. This technology is being tested for the removal of metal ions that are "hard" or contain high levels of dissolved solids from groundwater or surface leachates. This process is being developed under the SITE Emerging Technologies Program.

Colorado School of Mines' Wetlands-Based Treatment--This approach uses natural biological and geochemical processes inherent in man-made wetlands to accumulate and remove metals from contaminated water. The treatment system incorporates principal ecosystem components from wetlands, such as organic soils, microbial fauna, algae, and vascular plants. Waters which contain high metal concentrations and have low pH flow through the aerobic and anaerobic zones of the wetland ecosystem. The metals can be removed by filtration, ion exchange, adsorption, absorption, and precipitation through geochemical and microbial oxidation and reduction.

Conclusion

EPA's recent publication of the document, **Selection of Control Technologies for the Remediation of Lead Battery Recycling Sites**, EPA/540/2-91/014, enables EPA, State, and private sector remediation managers to quickly identify past experience and information that can be applied to site characterization and control technology evaluation activities.

Regarding the remediation of soils, sediments, and sludges, the feasibility of the previously popular remedy of excavation and off-site disposal has been basically eliminated unless a waiver can be obtained or the soil is determined to pose a threat to groundwater, but is not considered a RCRA hazardous waste. Cement-based S/S has been implemented at full-scale on at least three sites (Norco, CA; Lee's Farm,WI; Cedartown Battery, GA) and is scheduled for implementation at several others. S/S of soils can be expected to remain a popular option for lead and other heavy metal contaminated soils, sediments, and sludges due to (a) relative simplicity, (b) ready availability of equipment and vendors, and (c) low cost. Disadvantages include: (a) S/S can cause substantial increases (e.g., 30%) in the volume of material, (b) long-term immobilization of lead is not yet demonstrated, and (c) organic contaminants present in the soil may interfere with the S/S process.

Should S/S of soils, sediments, and sludges become obsolete due to observed leaching failures, then the chances of acceptance of other novel technologies such as in situ and ex situ vitrification, soil washing, and acid leaching may improve. In situ and ex situ vitrification may provide improved permeation and leaching resistance, but tend to be more complicated and expensive than cement-based solidification. Soil washing and acid leaching technologies are more complicated, costly, and novel than solidification, but they have the potentially significant advantage of actually removing the lead from the soil, which should minimize the need for long-term monitoring and would eliminate the potential of any long-term leaching problems. The success or failure of acid leaching technology at the United Scrap Lead Site in Ohio is viewed as critical to the future acceptability of this technology for LBRS remediation.

Recycling of waste piles to reduce the volume of hazardous waste, and to recover lead, lead compounds, plastic, and hard rubber is a challenge that has continued to receive considerable attention. To date, large-scale recycling of defunct LBRS waste materials is not known to occur. A key site regarding recycling is the Gould site, Portland, OR where efforts are underway in separating and recycling of lead fines to a secondary smelter, plastic to a plastics recycler, and hard rubber-like material as a fuel supplement. Also important is the Tonolli site, Nesquehoning, PA where a full-scale treatability study is examining the feasibility of using hard rubber battery scraps as a fuel supplement in a nearby secondary lead smelter. Battery scraps from other defunct LBRS may be tested as well. For sites where lead leaching from slag is posing a health or environmental threat, a process (flame reactor) for recovering lead from slag and simultaneously converting the slag to a non-hazardous material (i.e.,

TCLP leachate < 5 mg/L lead) is undergoing testing in EPA's SITE Program. The flame reactor may also be applicable to lead contaminated soils. Within another several years, the use of acid leaching for cleaning and recovery of lead from battery cases may also be demonstrated at the United Scrap Lead site to be a viable option.

The selection of control technology for LBRS remediation is expected to remain an interesting and important remediation issue for the next several years.

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Engineering Bulletin Technology Preselection Data Requirements

Purpose

Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants, and contaminants as a principal element." The Engineering Bulletins are a series of documents that summarize the latest information available on selected treatment and site remediation technologies and related issues. The summaries and references are designed to help remedial project managers, on-scene coordinators, contractors, and other site cleanup managers understand and select technologies that may have potential applicability to their Superfund or other hazardous waste sites.

This bulletin provides a listing of soil, water, and contaminant data elements needed to evaluate the potential applicability of technologies for treating contaminated soils and water. With this base set of data in hand, experts familiar with the applicability of treatment technologies can better focus the advice and assistance they give to those involved at Superfund sites. The data compiled should permit preselection of applicable treatment methods and the direct elimination of others.

This bulletin emphasizes the site physical and chemical soil and water characteristics for which observations and measurements should be compiled. However, several other kinds of information may be equally helpful in assessing the potential success of a treatment technology including the activity history of the site, how and where wastes were disposed, topographic and hydrologic detail, and site stratigraphy. Gathering and analyzing the information called for in this bulletin prior to extensive field investigations [i.e., the Remedial Investigation and Feasibility Study (RI/FS)] will facilitate streamlining and targeting of the sampling and analytical objectives of the overall program.

Additional information on site data requirements for the selection of specific treatment technologies may be found in several EPA publications [1] [2] [3] [4] [5].* These documents form much of the basis for this Engineering Bulletin. The bulletin may be updated by periodically-issued addenda.

Abstract

A base set of soil and water analytical (measured) data requirements has been developed to enable prescreening of technologies that may have potential applicability at Superfund sites. Data requirements for soils include the traditional engineering properties of soils and data on soil chemistry, including contaminants and oxygen demand. Analytical data requirements for water (usually groundwater) include chemistry, oxygen demand, and pH. Of particular importance in chemical characterization of both soils and water are contaminating metals and organic chemicals, whose presence or absence is often suggested by historical site activities. Sampling and measurements at this stage need not be in great detail, but should be sufficient to preliminarily characterize the site variability in three dimensions. Topography, groundwater flow, stratigraphy of the contaminated zone, and degree of consolidation will also affect the choice of treatment technology.

The relationships between each of the data requirements and specific treatment technologies are briefly summarized. The detailed reasoning may be found in one or more of the references.

The guidance presented in this bulletin is not exhaustive. The data elements are those that have wide technological applicability and those that can be collected in a straightforward manner. Data gaps are still likely to exist. However, an almost certain result is that the additional data needs will be better focused.

Background Information

The background information collected during the Site Screening Investigation and Preliminary Assessment identifies the probable types and locations of contaminants present. Study of the chemicals used or stored at the site and the disposal methods used during the period(s) of operation is essential. When chemical-use records are unavailable for an industrial site, knowledge of the Standard Industrial Classification may indicate the probability of the presence of metals, inorganics, pesticides, dioxins/furans, or other organics. Information on what classes and concentrations of chemicals contaminate the site, where they are distributed, and in what media they appear is essential in beginning the preselection of treatment technologies [2, p. 7].

* [reference number, page number]

The contaminant distribution, types, and concentrations will affect the choice of treatment technology. Other considerations in the selection of treatment options include the proximity of residential areas and the location of buildings and other structures. These aspects should be determined early in the investigation process. Much of the determination of the range and diversity of contamination, as well as likely contaminant sources, may be observational, rather than measurement-based.

Basic Measurement Data Requirements

The discussion of data requirements is divided into two sections, soil and water. For each of the two media, the vertical and horizontal contaminant profiles should be defined as much as possible. Information on the overall range and diversity of contamination across the site is critical to treatment technology selection. This generally means that samples will be taken and their physical and chemical characteristics determined. The following subsections present the characteristics and rationale for collection of preselection data for each of the two media. Other documents present similar data requirements, especially for soils [6].

The minimum set of soil measurement data elements usually necessary for soil treatment technology preselection is presented in Table 1. Table 2 presents the basic set of data necessary for contaminated water treatment technology preselection. It is common for the two media at one site to be contaminated with the same substances, thus many of the required data elements are similar. The information contained in Table 1 and Table 2 is based on professional judgement.

The ratings in Table 1 and Table 2 are related to measured values of the parameters. The values are described as "higher" and "lower" in defining their tendency toward preselecting a technology group. In general, these descriptors are related to the tendency of the parameter to enhance or to inhibit particular processes. Where no symbol is shown for a characteristic in Table 1 and Table 2, the affect on the associated technology is considered inconsequential.

Each characteristic is judged, or rated, as to its effect in preselecting each of the treatment technology groups which represent various treatment processes. A rating applies generally to a technology, but it does not ensure that the rating will be applicable to each specific technology within a technology group. Examples of specific treatments within the technology groups are as follows:

- Physical
  - Soil washing
  - Soil flushing
  - Steam extraction
  - Air stripping
  - Solvent extraction
  - Vapor extraction
  - Carbon adsorption
  - Filtration
  - Gravity separation
- Chemical
  - Oxidation
  - Hydrolysis
  - Polymerization
  - Reduction
  - Precipitation
- Thermal
  - Incineration
  - Plasma Arc
  - Pyrolysis
  - Thermal desorption
- Biological
  - Aerobic
  - Slurry reactor
  - Anaerobic
  - Land treatment
- Solidification/Stabilization
  - Cement-based
  - Fly ash/lime
  - Kiln dust
  - Vitrification
  - Asphalt

Soil

Site soil conditions are frequently process-limiting. Process-limiting characteristics such as pH or moisture content [6] may sometimes be adjusted. In other cases, a treatment technology may be eliminated based upon the soil classification (e.g., particle-size distribution) or other soil characteristics.

Soils are inherently variable in their physical and chemical characteristics. Frequently the variability is much greater vertically than horizontally, resulting from the variability in the sedimentation processes that originally formed the soils. The soil variability, in turn, will result in variability in the distribution of water and contaminants and in the ease with which they can be transported within, and removed from, the soil at a particular site.

Many data elements are relatively easy to obtain, and in some cases, more than one test method exists [6] [7] [8] [9] [10] [11] [12]. Field procedures, usually visual inspection and/or operation of simple hand-held devices (e.g., auger), are performed by trained geologists or soils engineers to determine the classification, moisture content, and permeability of soils across a site. Due to the fact that zones of gross contamination may be directly observed, field reports describing soil variability may lessen the need for large numbers of samples and measurements in describing site characteristics. Common field information-gathering often includes descriptions of natural soil exposures, weathering that may have taken place, trench cross-sections, and subsurface cores. Such an effort can sometimes identify probable areas of past disposal through observation of soil type differences, subsidence, overfill, etc.

While field investigations are important, they cannot eliminate the need for or lessen the importance of soil sampling and measurements sufficient to define those characteristics that are essential to the selection and design of soil treatment technologies.

Soil **particle-size distribution** is an important factor in many soil treatment technologies. In general, sands and fine gravels are easiest to deal with. Soil washing may not be effective where the soil is composed of large percentages of silt and clay because of the difficulty of separating fine particles from each other and from wash fluids [13, p. 1]. Fine particles also can result in high particulate loading in flue gases due to

TABLE 1. SOIL CHARACTERISTICS THAT ASSIST IN TREATMENT TECHNOLOGY PRESELECTION

CHARACTERISTIC	TREATMENT TECHNOLOGY GROUP				
	PHYSICAL	CHEMICAL	BIOLOGICAL	THERMAL	S/S
Particle size	■	▼	▼	■	■
Bulk density	▼			■	
Particle density	■				
Permeability	■		■		
Moisture content	▼		■	❐	❐
pH and Eh		▼	▼	▼	
Humic content	❐	❐	❐	▼	❐
Total organic carbon (TOC)		▼	■	■	▼
Biochemical oxygen demand (BOD)			■		
Chemical oxygen demand (COD)		■	■		
Oil and grease	▼	❐			❐
Organic Contaminants					
Halogenated volatiles	▼	▼	❐	■	❐
Halogenated semivolatiles	▼	▼	❐	■	❐
Nonhalogenated volatiles	▼	▼	▼	■	❐
Nonhalogenated semivolatiles	▼	▼	▼	■	❐
PCBs	▼	▼	▼	■	❐
Pesticides	▼	▼	▼	■	❐
Dioxins/Furans	▼	▼	▼	■	❐
Organic cyanides	▼	▼	▼	■	❐
Organic corrosives	▼	▼	▼	❐	❐
Light Nonaqueous-Phase Liquid	▼		▼	■	❐
Dense Nonaqueous-Phase Liquid	▼		▼	▼	❐
Heating value (Btu content)				■	
Inorganic Contaminants					
Volatile metals		▼		❐	
Nonvolatile metals	■	▼	❐	❐	■
Asbestos				❐	■
Radioactive materials	▼	▼	❐	❐	▼
Inorganic cyanides		▼		▼	▼
Inorganic corrosives		▼		❐	▼
Reactive Contaminants					
Oxidizers		▼			
Reducers		▼			

■ = higher values support preselection of technology group.

❐ = lower values support preselection of technology group.

▼ = Effect is variable among options within a technology group.

Where no symbol is shown, the effect of that characteristic is considered inconsequential

TABLE 2. WATER CHARACTERISTICS THAT ASSIST IN TREATMENT TECHNOLOGY PRESELECTION

CHARACTERISTIC	TREATMENT TECHNOLOGY GROUP			
	PHYSICAL	CHEMICAL	BIOLOGICAL	THERMAL
pH, Eh		▼	▼	▼
Total organic carbon (TOC)		▼	■	■
Biochemical oxygen demand (BOD)			■	
Chemical oxygen demand (COD)		■	■	
Oil and grease	▼	❐		
Suspended solids	▼	▼	▼	
Nitrogen & phosphorus			▼	
Organic Contaminants				
Halogenated volatiles	▼	▼	❐	■
Halogenated semivolatiles	▼	▼	❐	■
Nonhalogenated volatiles	▼	▼	▼	■
Nonhalogenated semivolatiles	▼	▼	▼	■
PCBs	▼	▼	▼	■
Pesticides	▼	▼	▼	■
Dioxins/Furans	▼	▼	❐	■
Organic cyanides	▼	▼	▼	■
Organic corrosives	▼	▼	▼	❐
Light Nonaqueous-Phase Liquid	▼		▼	■
Dense Nonaqueous-Phase Liquid	▼		▼	▼
Inorganic Contaminants				
Asbestos				❐
Radioactive materials	▼	▼	❐	❐
Metals (Drinking Water Stds.)	▼	■	❐	❐

■ = higher values support preselection of technology group.

❐ = lower values support preselection of technology group.

▼ = Effect is variable among options within a technology group.

Where no symbol is shown, the effect of that characteristic is considered inconsequential

turbulence in rotary kilns. Heterogeneities in soil and waste composition may produce non-uniform feed streams for incineration that result in inconsistent removal rates [1][14]. Fine particles may delay setting and curing times and can surround larger particles causing weakened bonds in solidification/stabilization processes. Clays may cause poor performance of the thermal desorption technology due to caking [15, p. 2]. High silt and clay content can cause soil malleability and low permeability during steam extraction, thus lowering the efficiency of the process [16, p. 2]. Bioremediation processes, such as in slurry reactors, are generally facilitated by finer particles that

increase the contact area between the waste and microorganisms [14] [17, p. 1].

In situ technologies dependent on the subsurface flowability of fluids, such as soil flushing, steam extraction, vacuum extraction, and in situ biodegradation, will be negatively influenced by the impeding effects of clay layers [15, p. 2] [18, p. 4]. Undesirable channeling may be created in alternating layers of clay and sand, resulting in inconsistent treatment [2, p. 79]. Larger particles, such as coarse gravel or cobbles, are undesirable for vitrification and chemical extraction processes and also may not be suitable for the stabilization/solidification technology [2, p. 93].

The **bulk density** of soil is the weight of the soil per unit volume including water and voids. It is used in converting weight to volume in materials handling calculations [19, p. 3-3]. Soil bulk density and particle size distribution are interrelated in determining if proper mixing and heat transfer will occur in fluidized bed reactors [2, p. 39].

Particle density is the specific gravity of a soil particle. Differences in particle density are important in heavy mineral/metal separation processes (heavy media separation). Particle density is also important in soil washing and in determining the settling velocity of suspended soil particles in flocculation and sedimentation processes [13, p. 1].

Soil **permeability** is one of the controlling factors in the effectiveness of in situ treatment technologies. The ability of soil-flushing fluids (e.g., water, steam, solvents, etc.) to contact and remove contaminants can be reduced by low soil permeability or by variations in the permeability of different soil layers [16, p. 2] [19, p. 4-9]. Low permeability also hinders the movement of air and vapors through the soil matrix, lessening the volatilization of VOCs in vapor extraction [17, p. 2]. Similarly, nutrient solutions, used to accelerate in situ bioremediation, may not be able to penetrate low-permeability soils in a reasonable time [1]. Low permeability may also limit the effectiveness of in-situ vitrification by slowing vapor releases [2, p. 59].

Soil **moisture** may hinder the movement of air through the soil in vacuum extraction systems [3, p. 90] [17, p. 1]. High soil moisture may cause excavation and material transport problems [20, p. 2] and may negatively impact material feed in many processes [2] [15, p. 2] [19, p. 4] [21]. Moisture affects the application of vitrification and other thermal treatments by increasing energy requirements, thereby increasing costs. On the other hand, increased soil moisture favors in situ biological treatment [22, p. 40].

Many treatment technologies are affected by the **pH** of the waste being treated. For example, low pH can interfere with chemical oxidation and reduction processes. The solubility and speciation of inorganic contaminants are affected by pH. Ion exchange and flocculation processes, applied after various liquid extraction processes, may be negatively influenced by pH [1, p. 5, 16]. Microbial diversity and activity in bioremediation processes can be reduced by extreme pH ranges. High pH in soil normally improves the feasibility of applying chemical extraction and alkaline dehalogenation processes [2, p. 67].

Eh is the oxidation-reduction (redox) potential of the material being considered. For oxidation to occur in soil systems, the Eh of the solid phase must be greater than that of the organic chemical contaminant [22, p. 19]. Maintaining anaerobiosis, and thus a low Eh, in the liquid phase, enhances decomposition of certain halogenated organic compounds [23].

Humic content (humus) is the decomposing part of the naturally occurring organic content of the soil. The effects of high humic content upon treatment technologies are usually negative. It can inhibit soil-vapor extraction, steam extraction, soil washing, and soil flushing due to strong adsorption of the contaminant by the organic material [2, p. 76] [17, p. 2]. Reaction times for chemical dehalogenation processes can be increased by the presence of large amounts of humic materials. High organic content may also exert an excessive oxygen demand, adversely affecting bioremediation and chemical oxidation [24, p. 2] [25, p. 1].

Total organic carbon (TOC) provides an indication of the total organic material present. It is often used as an indicator (but not a measure) of the amount of waste available for biodegradation [2, p. 109]. TOC includes the carbon both from naturally-occurring organic material and organic chemical contaminants. Ordinarily, not all of the organic carbon is contaminating, but all of it may compete in redox reactions, leading to the need for larger amounts of chemical reduction/oxidation reagents than would be required by the organic chemical contaminants alone [2, p. 97].

Biochemical oxygen demand (BOD) provides an estimate of the biological treatability of the soil contaminants by measuring the oxygen consumption of the organic material which is readily biodegraded [3, p. 89]. **Chemical oxygen demand** (COD) is a measure of the oxygen equivalent of organic content in a sample that can be oxidized by a strong chemical oxidant. Sometimes COD and BOD can be correlated, and COD can give another indication of biological treatability or treatability by chemical oxidation [2, p. 97]. COD is also useful in assessing the applicability of wet air oxidation [2, p. 51].

Oil and grease, when present in a soil, will coat the soil particles. The coating tends to weaken the bond between soil and cement in cement-based solidification [14]. Similarly, oil and grease can also interfere with reactant-to-waste contact in chemical reduction/oxidation reactions thus reducing the efficiency of those reactions [2, p. 97].

Identification of the site **organic and inorganic contaminants** is the most important information necessary for technology prescreening. At this stage, it may not be necessary to identify specific contaminants, but the presence or absence of the groups shown in Table 1 should be known. These groups have been presented in the other Engineering Bulletins in order to describe the effectiveness of the particular treatment technology under consideration.

The soil may be contaminated with organic chemicals that

are not miscible with water. Often, they will be lighter than water and float on top of the water table. These are called light nonaqueous-phase liquids (LNAPLs). Those heavier than water are called dense nonaqueous-phase liquids (DNAPLs). Most of these liquids can be physically separated from water within the soil, especially if they are not adsorbed to soil particles.

Volatile, semivolatile, and other organics may be adsorbed in the soil matrix. Volatiles may be in the form of vapors in the pores of non-saturated soil, and may be amenable to soil-vapor extraction. Fuel value, or Btu content, of the contaminated soil is directly related to the organic chemical content. High Btu content favors thermal treatment, or perhaps recovery for fuel use.

High halogen concentrations, as in chlorinated organics, lead to the formation of corrosive acids in incineration systems. Volatile metals produce emissions that are difficult to remove, and nonvolatile metals remain in the ash [14].

Metals may be found sometimes in the elemental form, but more often they are found as salts mixed in the soil. Radioactive materials are not ordinarily found at waste disposal sites. However, where they are found, treatment options are probably limited to volume reduction, and permanent containment is required. Asbestos fibers require special care to prevent their escape during handling and disposal; permanent containment must be provided. Radioactive materials and asbestos require special handling techniques to maintain worker safety.

Often, specific technologies may be ruled out, or the list of potential technologies may be immediately narrowed, on the basis of the presence or absence of one or more of the chemical groups. The relative amounts of each may tend to favor certain technologies. For example, significant amounts of dioxin/furans, regardless of the concentrations of other organics, will ordinarily lead to preselection of thermal treatment as an alternative.

Data available from the preliminary assessment, the site inspection and the National Priorities List (NPL) activities may provide most of the contaminant information needed at the technology prescreening stage. If the data are not sufficient, waste samples may be scanned for selected priority pollutants or contaminants from the CERCLA Hazardous Substances List. During the ensuing RI/FS scoping phase, these data are evaluated to identify additional data which must be gathered during the site characterization. Guidance is available on the RI/FS process and on field methods, sampling procedures, and data quality objectives [4][5][6][12] and therefore is not discussed in this bulletin.

Water

It is common for groundwater and surface water drainage to be contaminated with the same substances found in soils derived from previous activities. At Superfund sites, many of the required data elements are similar, e.g., pH, TOC, BOD, COD, oil and grease, and contaminant identification and quantification. Frequently, many of the water data elements will be available from existing analytical data. Some initial data requirements may even be precluded by the collection of existing regional or local information on surface and groundwater conditions. When data are not available, knowledge of the site conditions and its history may contribute to arriving at a list of contaminants and cost-effective analytical methods.

As with soils, the **pH** of groundwater and surface water is important in determining the applicability of many treatment processes. Often, the pH must be adjusted before or during a treatment process. Low pH can interfere with chemical redox processes. Extreme pH levels can limit microbial diversity and hamper the application of both in situ and above-ground applications of biological treatment [2, p. 97]. Contaminant solubility and toxicity may be affected by changes in pH. The species of metals and inorganics present are influenced by the pH of the water, as are the type of phenolic, and nitrogen-containing compounds present. Processes such as carbon adsorption, ion exchange, and flocculation may be impacted by pH changes [1, p. 5].

Eh helps to define, with pH, the state of oxidation-reduction equilibria in groundwater or aqueous waste streams. The Eh must be below approximately 0.35 volts for significant reductive chlorination to take place, but exact requirements depend on the individual compounds being reduced. As noted earlier in the soils section, maintaining anaerobiosis (low Eh) enhances decomposition of certain halogenated compounds [23].

BOD, COD, and TOC measurements in contaminated water, as in soils, provide indications of the biodegradable, chemically oxidizable, or combustible fractions of the organic contamination, respectively. These measurements are not interchangeable, although correlations may sometimes be made in order to convert the more precise TOC and/or COD measurements to estimates of BOD. Interpretation of these data should be made by an expert in the technologies being considered.

Oil and grease may be present in water to the extent that they are the primary site contaminants. In that case, oil-water separation may be called for as the principal treatment. Even in lower concentrations, oil and grease may still require pretreatment to prevent clogging of ion exchange resins, activated carbon systems, or other treatment system components [3, p. 91].

Suspended solids can cause resin binding in ion exchange systems and clogging of reverse osmosis membranes, filtration systems and carbon adsorption units. Suspended solids above 5 percent indicate that analysis of total and soluble metals should be made [1, p. 14].

Standard analytical methods are used to identify the specific **organic and inorganic contaminants**. Properties of organic chemical contaminants important in treatment processes include solubility in water, specific gravity, boiling point, and vapor pressure. For the identified contaminants, these properties can generally be found in standard references [26] or in EPA/RREL's Treatability Database [27].

Insoluble organic contaminants may be present as non-aqueous phase liquids (NAPLs). DNAPLs will tend to sink to the bottom of surface waters and groundwater aquifers. LNAPLs will float on top of surface water and groundwater. In addition, LNAPLs may adhere to the soil through the capillary fringe and may be found on top of water in temporary or perched aquifers in the vadose zone.

As noted previously, volatile organics may be in the form of vapors in the pores of non-saturated soil, or they may be dissolved in water. Even low-solubility organics may be present at low concentrations dissolved in water. Some organics (e.g. certain halogenated compounds, pesticides, and dioxins/furans in water) resist biological treatment, while others may be amenable to several technologies.

Dissolved metals may be found at toxic levels or levels exceeding drinking water standards. Often they will require chemical treatment. The speciation of metals may be important in determining the solubility, toxicity, and reactivity of metal compounds.

Status of Data Requirements

The data requirements presented in Tables 1 and 2 are based on currently available information. Preselection of new and evolving technologies, or of currently used technologies that have been modified, may require the collection of additional data. New analytical methods may be devised to replace or supplement existing methods. Such improvements in analytical technology also could require additional data to be collected. This bulletin may be updated if major changes occur in data requirements for preselection of treatment technology alternatives.

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