



**PDHonline Course C175 (3 PDH)**

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# **Hazardous and Toxic Waste Treatment of Soils & Sludges**

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- (a) Packing density,  $1.5 \text{ m}^2/\text{m}^3$  ( $5 \text{ ft}^2/\text{ft}^3$ ).
- (b) Water flux at a specified pressure and temperature.
- (c) Molecular weight cutoff or rejection.
- (d) Acceptable pH ranges.
- (e) Recommended operating pressure.

(2) Data with regard to specific waste are also required that must be determined or verified experimentally. Manufacturers and suppliers will usually provide assistance in this area. Flux rates and rejection should be determined experimentally.

e. Design Criteria.

(1) The approach to the design of an ultrafiltration system is similar to that for RO. In ultrafiltration design, concentration polarization effects are magnified, and care must be exercised to alleviate this problem. Typically, channels are designed for minimum height, and the unit is operated at a high parallel surface velocity.

(2) Operating pressures for ultrafiltration systems are in the range of 68.9 to 689 kPa (10 to 100 pounds per square inch) with 413 to 551 kPa (60 to 80 pounds per square inch) being typical. As is the case with RO, temperature plays a significant role in the flux rate of ultrafiltration membranes. Fluxes are expected to double for a  $15^\circ$  to  $25^\circ\text{C}$  rise in temperature. Operating temperatures are limited by economics and the material from which the membrane is constructed. Membranes produced from cellulose are limited to the  $50^\circ$  to  $60^\circ\text{C}$  range, while other membranes may be operated at temperatures as high as  $100^\circ\text{C}$ .

(3) Ultrafiltration membranes are specified in terms of molecular weight cutoff or a rejection of a specific molecular weight compound. This is not an absolute measure of rejection. In actuality, rejection is a function of molecular shape, size, and flexibility as well as the operating conditions.

Section II. Treatment of Sludges and Soils

4-18. Biological Treatment.

a. Bioslurry Reactors.

- (1) Process description.

(a) Bioslurry reactors (BSRs) (also referred to as liquid/solids reactors) are an innovative biological technology for rapid treatment of sludges and excavated soils. BSRs offer treatment conditions that are conducive to the optimal biotreatment of contaminated soils by slurring contaminated soils in water using liquid-to-solid ratios ranging from 20 to 50 percent. The soil/water slurries are usually kept in suspension using mechanical mixers,

injected air, recirculation pumps, and/or raker arms scraping the reactor bottom. Typically, BSRs are operated under aerobic conditions; however, BSRs can be configured for anaerobic treatment if warranted. BSRs can be operated in batch or continuous modes. Continuous flow systems are usually operated using multiple reactors in series. Figure 4-19 shows a typical schematic of a BSR system.

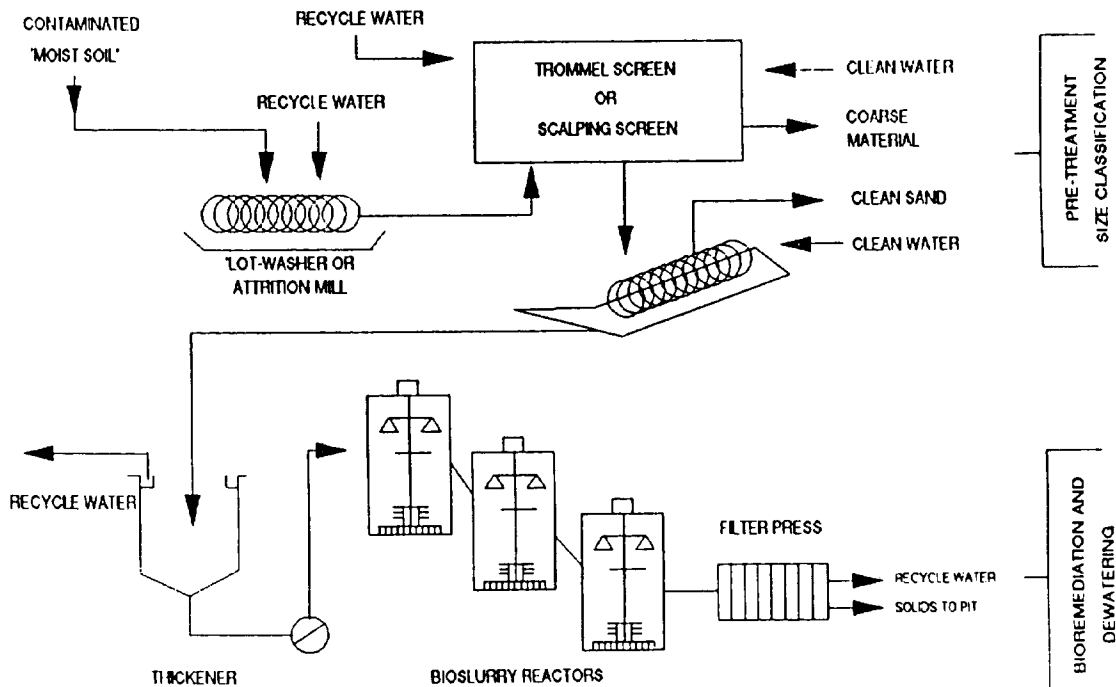


Figure 4-19. Typical Bioslurry Treatment System

(b) Many of the limiting conditions associated with other soil biotreatment technologies are substantially reduced in the BSRs. Oxygen transfer, usually a major limiting factor with the other soil treatment biotechnologies, especially in situ treatment, is improved due to increased mixing efficiency. Oxygen is supplied by the addition of air or oxygen via submerged gas spargers. Nutrients and co-metabolites may also be added depending on the required treatment conditions, usually determined through bench treatability studies. BSRs usually contain both attached and suspended growth consortia allowing for contaminant destruction in both phases. Microbial populations in BSRs are much higher than those found in other soil biotreatment systems due to the improved treatment conditions, thereby maximizing the degradation rate of contaminants due to improved microbe/contaminant contact and increased contaminant desorption rates.

(2) Applications.

(a) BSRs have proven effective in treating soils contaminated with petroleum hydrocarbon and wood preserving wastes. Some systems incorporate soil screening techniques prior to BSR treatment because the majority of the contaminants are sorbed to the finer fraction of the soils. BSR technology

can be applied in custom fabricated, stock commercially available, or earthen reactor units. Soil residence times will vary greatly depending on the contaminant type, concentration, and sorption characteristics.

(b) Various additives can be provided to improve process performance. Surfactants have been proposed to increase the desorption rate of contaminants. Nutrient additive requirements, typically presented as the carbon:nitrogen:phosphate ratio (C:N:P), are usually on the order of 100:20:5; however, recent research indicates that increased ratios may increase contaminant degradation rates. Most contaminated soils contain native microorganisms capable of degrading the target contaminants that simply require stimulation by the addition of a limiting chemical species such as oxygen and/or nutrients. Treatment of sludges and soils which are devoid of native microbial populations may require the addition of a microbial inoculum.

(c) Residuals from BSRs are the soil/water slurry that may require separation (i.e., dewatering). The amount of dewatering required will be dictated by disposal plans for the treated soils. Aqueous solutions usually do not contain organic constituents due to the ease of degradation of the contaminants in solution.

(d) Potential waste streams from a BSR are off-gasing of volatile compounds and heavy-metals-contaminated soil/water slurries if the soil was also contaminated with heavy metals. Gas streams from a BSR can be either eliminated or reduced by use of pure oxygen or possibly an alternate electron acceptor. Gas streams can also be treated using activated carbon canisters.

(3) Advantages/disadvantages. The advantages and disadvantages of BSRs are summarized in below:

<u>Advantages</u>	<u>Disadvantages</u>
Rapid decontamination of contaminants.	Fairly energy intensive.
Numerous process variations which allow for high degree of flexibility.	Capital costs can be high.
Contaminated off-gasing can be easily controlled for complete elimination of contaminant release into the environment.	O&M intensive.
Higher contaminant concentrations compared to other soil biotreatment technologies can be treated due to higher microbial populations.	Requires soil excavation.
Process can be implemented in a variety of reactor systems.	May require soil dewatering.
	Few full-scale implementation verification data available.

(4) Data requirements. Principal data requirements for design of BSRs are determined through bench scale studies due to the lack of empirically based design formulas. The following factors should be evaluated in a properly planned bench study:

- (a) Whether the target contaminants are best degraded under aerobic or anaerobic conditions.
- (b) Benefits of co-metabolite addition.
- (c) Benefits of surfactant addition.
- (d) Optimum C:N:P ratios
- (e) Potential for production of toxic chemical intermediates.
- (f) Effect of addition of an exotic microbial inoculum.
- (g) Retention time required to reach target contaminant levels.
- (h) Optimum soil/water ratio.
- (i) Potential for excessive foaming.

(5) Design criteria. Since there are few design criteria due to the limited evaluation and usage of this technology, the following design considerations must be addressed:

(a) Reactor volume - Reactor volume is dependent on soil retention time and required process flow.

(b) Soil screening - Required for soils containing either large coarse fractions or large debris that may damage the reactor.

(c) Mixing efficiency - High mixing efficiencies must be supplied to optimize the degradation rate of the target compound(s).

(d) Soil dewatering - May be required depending on soil disposal requirements.

(e) Oxygen requirements - Dependent upon the oxygen demands of the system determined during the bench study.

b. Composting.

(1) Composting is a biological treatment method which takes advantage of the heat of reaction during metabolism of organic carbon to sustain rapid decomposition. It is primarily used in treatment of sludges. There are three broad classifications of composting systems in use today. They are:

- (a) Windrow system

- (b) Aerated static piles
- (c) In-vessel, mechanically agitated

(2) The windrow system is the simplest of the three and relies on natural aeration or periodic mixing as a means of supplying oxygen to the system and reducing excessive heat buildup. Specially designed windrow forming and turning machines have found application in large-scale operations.

(3) Aerated static piles provide an increased level of process control. Waste to be composted is typically placed in piles on top of channels or piping through which air may be blown or sucked through the piles. In simpler systems, a timer is used to periodically aerate the pile, the cycle of aeration is determined by trial. In more sophisticated systems, temperature feedback control is utilized to aerate the piles, maintaining a preset temperature. In most instances, temperature control through aeration provides greater than the required oxygen for metabolism.

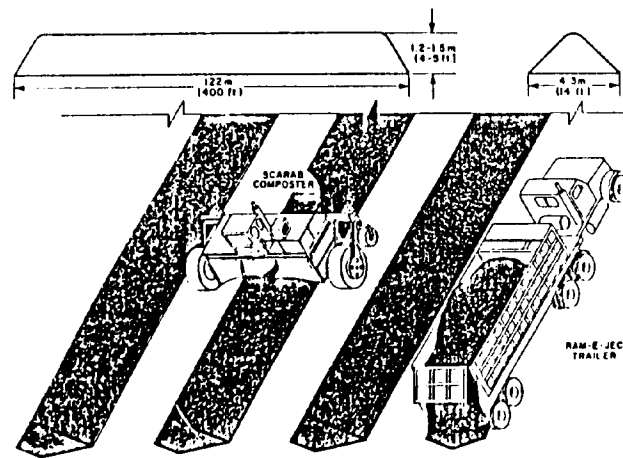
(4) The third system, the in-vessel, mechanically agitated system, is the most complex of the three and provides the highest degree of process control. Various designs have been developed. All allow composting in some form of vessel such as a tank, silo, or trench. Mechanical mixing of the compost through direct agitation or indirect tumbling is performed. Some systems incorporate forced aeration capabilities. As with aerated static piles, temperature is typically the control variable. In-vessel, mechanically agitated systems can be operated on a continuous basis. Figure 4-20 provides an example of the three types of systems.

(5) The primary objectives in sewage sludge treatment with composting are pathogen destruction, dewatering, and volume reduction. In some cases, the final product can be marketed as an agricultural additive. Essentially, the high temperatures achievable in compost systems are sufficient for pathogen destruction. Typically, 3 days at a temperature of 55 °C are required for pathogen destruction. Dewatering occurs as water in the compost mass is evaporated at the increased temperature. In aerated systems, water loss is even greater due to the transport out of the compost by the aeration stream. Volume reduction occurs as metabolism of the organic carbon with subsequent dewatering causes loss in mass and breakdown of internal structure. Addition of an amendment (additional organic carbon, nutrients, or inoculant) as well as bulking agents (wood chips, sawdust, hay, etc.) are often required to allow composting. In addition, water may be required as an additive during composting to maintain active conditions.

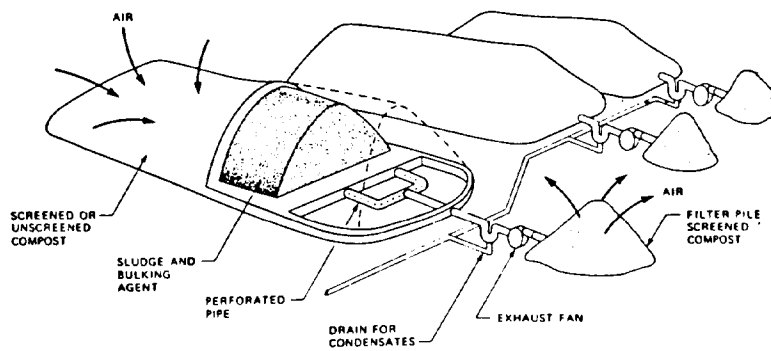
#### c. Applications.

(1) Composting is being used extensively in treatment of sewage sludge at municipal waste treatment plants. As optimum water content in the compost falls between 40 and 60 percent, composting usually does not involve a dewatering step prior to the process.

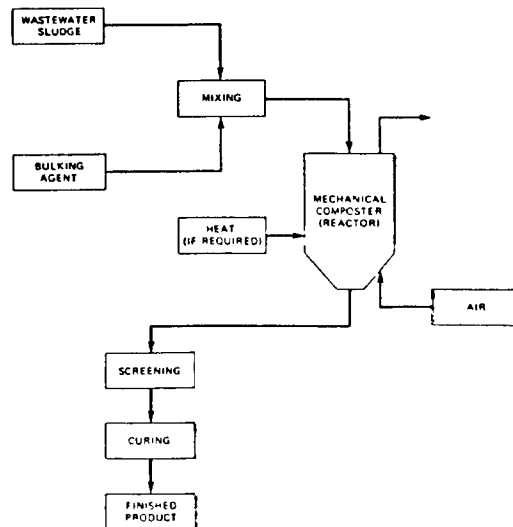
(2) Composting has been applied to a limited extent to process waste streams. Typically, it is more amenable to solid substrate treatment.



a. Typical windrow composting operation.



b. Typical aerated static pile composting system.



c. Typical in-vessel composting operation.

Figure 4-20. Typical Composting Systems

(3) Composting has recently been suggested for use in treatment of hazardous solid wastes. These include contaminated soils and sediments as well as hazardous solid waste from process industries.

d. Advantages/Disadvantages. The advantages/disadvantages of composting are summarized below:

<u>Advantages</u>	<u>Disadvantages</u>
No dewatering required	Treatment levels may be insufficient
Not energy intensive	Odors may present problems
Product may be agriculturally beneficial	Volume increase possible based on amendment requirements
Low capital investment for similar systems	Operation requires experienced personnel
Existing systems demonstrate reliability	

e. Data Requirements.

(1) Principal data requirements for the design of a compost system are very much dependent on the type of operation, either sewage sludge treatment, municipal/process waste treatment, or hazardous waste treatment. The difference comes in the objectives to be obtained. Some parameters required for all types include:

- (a) Throughput (for sizing).
- (b) Nitrogen and phosphorus levels (as nutrients).
- (c) Bulk density (determines need for bulking).
- (d) Water capacity (determines water requirements).
- (e) Ambient temperatures (insulation).
- (f) C:N ratio (amendment selection).

(2) For sewage sludge, the above should allow design estimates to be made as the compost must be maintained at 55 °C for 3 days. Dewatering and volume reduction of the compost mass can then be evaluated as required.

(3) For municipal/process waste treatment, something should be known about the kinetics of the thermophilic degradation of the particular waste stream. Half-life estimates or rate expressions are used to determine length of time required at the controlled temperature for completion.



(4) For hazardous waste treatment, kinetics of degradation must also be known for design. Contaminant availability in terms of desorption characteristics as well as solubility and vapor pressure become important parameters. If the hazardous waste is volatile at compost temperatures, means to control fugitive emissions must be incorporated.

f. Design Criteria.

(1) Key design parameters for composting include bulk density; carbon to nitrogen ratio (C:N ratio); water content; pile formation and shape; and mixing. Bulk densities of 1000 are considered optimum (this is for the composted material, bulking agent, and amendment mixture). Carbon to nitrogen ratios of 30 to 1 are considered optimum. Phosphorus levels are also important but are not felt to be as much an impact as nitrogen levels. A water content of between 40 and 60 percent may be necessary for good composting. The mixing of the compost matrix and subsequent formation into piles can play a large role in the effectiveness of composting. Bringing the ingredients into intimate contact within the solid matrix to allow microbial digestion requires good mixing. Pile design incorporates requirements for aeration and temperature distribution.

(2) Experience plays a large role in compost operations. Often, local recipes are used to construct the compost matrix based on experimentation on site. As composting is typically a longer term process, upsets can often be corrected before system performance degrades substantially.

(3) The pH of the compost material may play a role in operations, however; conflicting reports in the literature concerning the impact of changes in pH make prediction of the effect difficult. Within a range of 6 to 8 there appears to be no problem with pH. Outside this range site-wise determinations would likely have to be made.

(4) The finished compost may have value as an agricultural amendment. Levels of hazardous chemicals and elements play a key role in the final compost products disposal options or retail value.

(5) Selection of the type of system between windrows, static piles, and in-vessel mechanically agitated systems is dependent on many factors. The capital costs increase dramatically from the windrow to the mechanically agitated, in-vessel system. If levels of control are not necessary (including odor control and temperature) then a windrow system would be applicable. The capital cost of the mechanical system should be carefully weighed against the need for this level of process control. Insufficient data on increased reaction rates in these systems make selection difficult. If possible, pilot scale tests of the wastes to be composted should be conducted prior to selecting this form of composting system.

(6) Most compost systems do not require a large amount of specialized equipment. The backhoe and shovel appear as the most frequent equipment item necessary to conduct operations. Solids handling equipment to include conveyors are often used to increase throughput.

4-19. Encapsulation.

a. Process Description.

(1) Encapsulation is the process by which hazardous wastes are physically enclosed by a synthetic encasement to facilitate environmentally sound transport, storage, and disposal of the wastes. As a remedial action, encapsulation may be used to seal particularly toxic or corrosive hazardous wastes that have been removed from disposal sites. Encapsulation processes can be divided into two categories- -thermoplastic microencapsulation, and macroencapsulation (jacketing systems).

(2) Thermoplastic microencapsulation has been successfully employed in nuclear waste disposal and can be adapted to special hazardous wastes. The technique for isolating the waste involves drying and dispersing the material through a heated, plastic matrix. The mixture is then permitted to cool to form a rigid but deformable solid. In most cases it is necessary to use a container such as a fiber or metal drum to give the material a convenient shape for transport. The most common medium for waste incorporation is asphalt; but other materials such as polyethylene, polypropylene, wax, or elemental sulfur have been tried.

(3) Macroencapsulation systems contain potential pollutants by bonding an inert coating or jacket around a mass of cemented waste. This type of waste stabilization is unusual because the jacket or coating of the outside of the waste block is primarily responsible for isolating the waste from its surroundings.

b. Applications.

(1) Waste types that may require encapsulation include the following:

(a) Solid hazardous wastes in bulk or particulate form (e.g., severely contaminated sediments).

(b) Dewatered hazardous sludges.

(c) Containerized hazardous wastes (solids, sludge, or liquid) in damaged or corroded drums.

(d) Hazardous wastes which have been stabilized through solidification/cementation.

(2) TRW Systems Group has successfully developed bench-scale processes to agglomerate and encapsulate toxic and corrosive heavy metal sludges and soluble heavy metal salts, and to encapsulate containerized wastes. The agglomeration/encapsulation process involves mixing dried sludges (containing such hazardous heavy metals as arsenic, lead, mercury, selenium, beryllium, cadmium, zinc, and chromium) with a binder resin (modified 1,2-polybutadiene) and thermosetting the mixture in a special mold, while applying moderate mechanical pressure. The agglomerated material is a hard, tough, solid block. Encapsulating the waste/binder agglomerate with a 1/4-inch seamless jacket of

high density polyethylene (HDPE) is accomplished by packing powdered polyethylene around the block and then fusing the powder in situ with a second metal sleeve mold. A schematic diagram of the apparatus used to encapsulate the agglomerate is shown in Figure 4-21. A commercial-scale encapsulate produced by this method is expected to be a solid cube, 2 feet on edge, weighing 800 to 1,000 pounds. It would require approximately 8 percent (by weight) of polybutadiene resin for its fabrication. Additional jacket sizes will be available in the future.

(3) The second TRW macroencapsulation process is designed to enclose and seal waste containers such as 55-gallon drums (subject to corrosion rupture, leaks, and spills) using the same basic mold and fusion apparatus. To provide load-bearing ability, a 1/8-inch-thick interior casing of fiberglass is used to reinforce the 1/4-inch-thick HDPE jacket that encapsulates the container. A commercial-scale, fiberglass-reinforced HDPE encapsulate is envisioned to provide up to 284 l (75 gallons) of capacity. The cylindrical jacket and casing would comprise about 5.3 percent (by volume) of the total encapsulate volume. Commercially, 7 mm (1/4-inch-thick) HDPE jackets can be fabricated in 30 seconds.

(4) Comprehensive laboratory testing of bench-scale encapsulates has demonstrated their ability to withstand severe mechanical stresses and biological and chemical degradation. Encapsulates containing wastes of various solubility were exposed to leaching solutions of various corrosivity; results indicate that the encapsulated wastes were completely isolated from, and resistant to, simulated disposal environment stresses. The encapsulates were also found extremely resistant to mechanical deformation and rupture. They exhibit high compressive strength and outstanding ability to withstand impact, puncture, and freeze-thaw stresses.

c. Advantages/Disadvantages. The major advantage of encapsulation processes is that the waste material is completely isolated from leaching solutions, and soluble hazardous materials such as heavy metal ions and toxic salts can be successfully encapsulated. The impervious HDPE jacket eliminates all leaching into contacting water (which may infiltrate or flow over disposal sites) and effectively contains hazardous waste substances that might otherwise migrate offsite. The advantages and disadvantages of encapsulation processes are as follows:

<u>Advantages</u>	<u>Disadvantages</u>
Cubic and cylindrical encapsulates allow for efficient space utilization during transport, storage, and disposal	Binding resins required for agglomeration/encapsulation (polybutadiene) are expensive
Hazard of accidental spills during transport is eliminated	Requires large expenditures of energy in fusing the binder and forming the jacket

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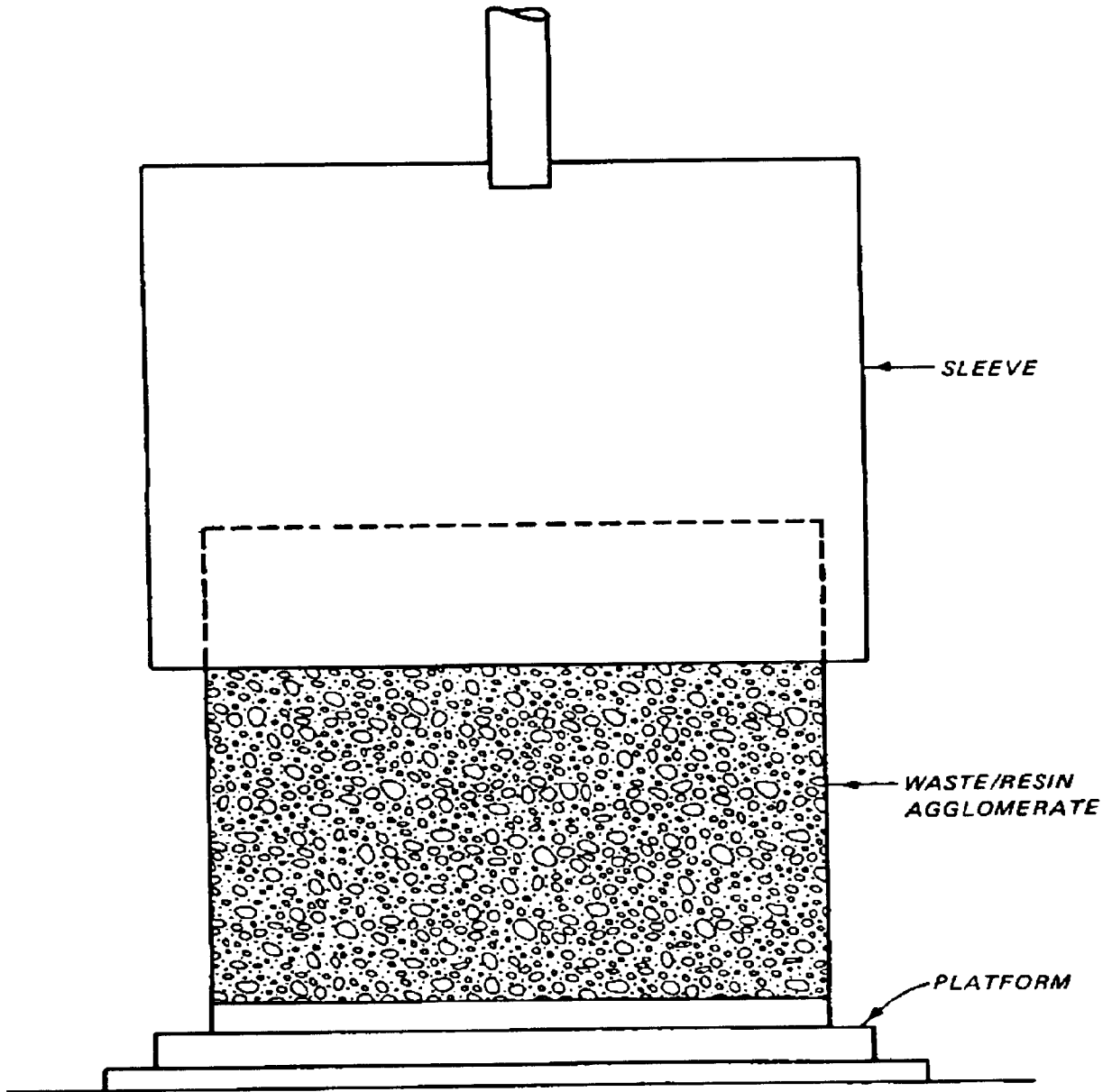


Figure 4-21. Encapsulation Process Concept  
(Source: Lubowitz et al. 1977)

<u>Advantages</u>	<u>Disadvantages</u>
HDPE is low in cost, commercially available, very stable chemically, nonbiodegradable, mechanically tough, and flexible	Requires large capital investments in equipment
Encapsulated waste materials can withstand the mechanical and chemical stresses of a wide range of disposal schemes (e.g., landfill, ocean disposal)	Skilled labor is required to operate molding and fusing equipment
	Drying/dewatering of noncontainerized waste sludges is required for agglomeration/encapsulation
	Process has yet to be applied on a commercial scale under actual field conditions

d. Data Requirements. Data requirements are similar to those required for solidification/stabilization described in paragraph 4-21.

e. Design Criteria.

(1) It is important to emphasize that encapsulation techniques have only recently advanced from the developmental and testing stages, and no large commercial-scale encapsulation facilities have been designed and operated as yet. It is likely that, as a remedial action, encapsulation will not be an economically feasible alternative compared to other direct waste treatment methods. However, a central solidification/encapsulating waste processing facility may be technically and economically feasible as a predisposal operation at hazardous waste storage and disposal facilities in the near future.

(2) The fabrication of commercial-scale encapsulates of containerized wastes under actual field conditions would require an encapsulation unit that is readily transportable to the storage or disposal site where containerized wastes reside. Where containerized wastes are of volumes smaller than the design capacity of the encapsulation unit, sand or soil may be used to fill voids between the container and encapsulate walls. Where very large volume waste containers require encapsulation (greater than 208 l (55 gallons)), it may be necessary to install compaction operations at the site.

4-20. Low Temperature Thermal Desorption.

a. Process Description.

(1) Low temperature thermal treatment is a process of heating contaminated soil only enough to vaporize volatile organic compounds (VOCs). The gases emitted from the soil are then treated by a subsequent unit operation. The process described here as an example (Patent No. 4,738,206) uses indirect heat to separate the VOCs from the soil and incineration to destroy the VOCs in the gas phase. Maximum soil temperature for this process is 150 °C. The process was developed by the U.S. Army Environmental Center to treat soils at

military installations contaminated with trichloroethylene, dichloroethylene, tetrachloroethylene, xylene, and other components of solvents and petroleum fuels.

(2) The thermal processor for this system is a Holo-Flite screw conveyor heated by Dowtherm HT hot oil circulating through the shaft, blades, and jacket of the conveyor. A schematic diagram of the system is illustrated in Figure 4-22. Larger scale models may include two thermal processors operated in series with the first processor mounted on top of the second. Maximum temperature for the oil is 350 °C.

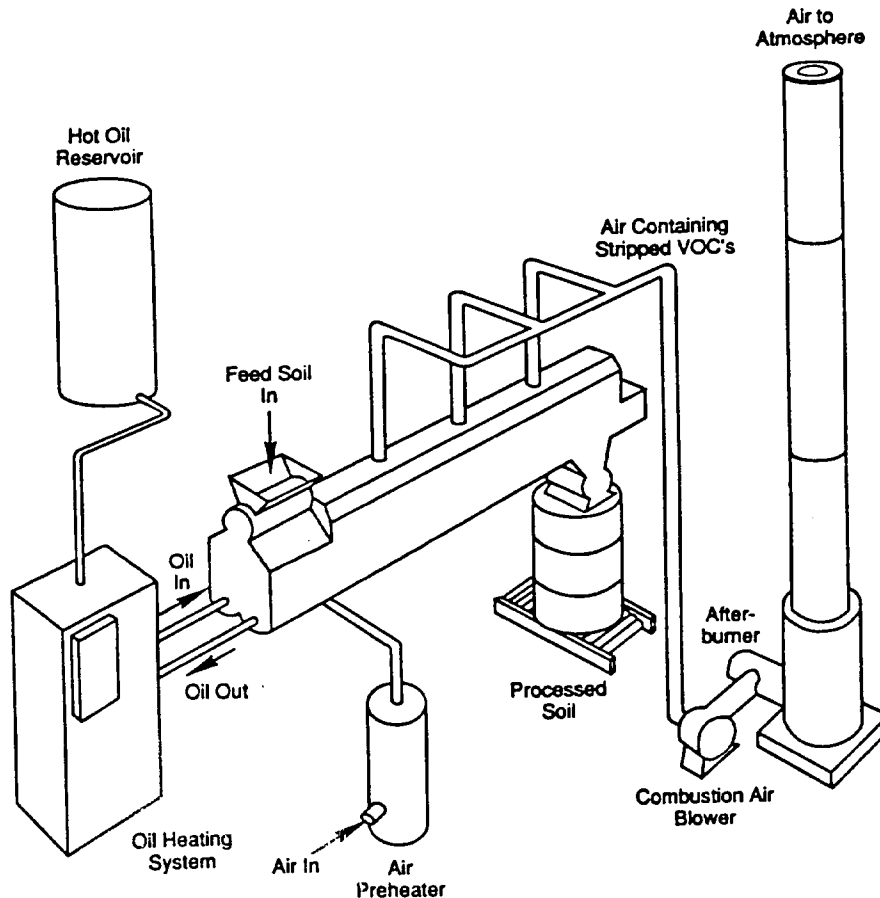


Figure 4-22. Schematic Diagram of a Low Temperature Thermal Treatment System

(3) The vapor stream from the thermal processor consists of the contaminants being removed, water vapor from the soil, and exhaust gases from the hot oil heater. This stream exits at approximately 150 °C (maximum) and flows through a fabric filter, condenser, afterburner, and caustic scrubber system. The fabric filter removes particulate carried over from the processor. The vapor stream then passes through an air-cooled condenser which reduces the temperature to approximately 52 °C. Water and organics condensed reduce the load on the afterburner. The afterburner is a gas-fired, vertical, fume incinerator operating at 980 °C. The afterburner is operated at a minimum of 3 percent excess oxygen. Exhaust from the afterburner is quenched

to approximately 80 °C. It then passes through a packed bed absorber where acid gases produced in the afterburner are neutralized with a caustic solution.

(4) A liquid stream is produced by the condenser which is water rich but does contain some hydrocarbons. The aqueous phase is separated from the organic phase in an oil-water separator. The aqueous phase is processed through a water treatment system consisting of fabric filters followed by granular activated carbon. This water is then used as makeup water for the scrubber and for dust control on processed soil. The organic phase from the separator may be either drummed for off-site disposal or injected into the afterburner.

(5) A system capable of processing 10 metric tons of soil per hour is mobile and can be transported to a site and assembled. Utilities required for operation are propane or natural gas, electricity, and process water. Discharges from the system include the scrubber stack exhaust, the processed soil, the granular activated carbon, and filter cake, and the organic phase from the water separator. Operation requires eight persons for continuous operation, including a site manager and an instrumentation technician.

b. Applications. Low temperature thermal treatment is capable of remediating soils contaminated with volatile and semivolatile compounds. Greater than 99 percent removal from soils has been demonstrated for trichloroethylene, dichloroethylene, and tetrachloroethylene, 1, 2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, toluene, naphthalene, and xylene. It has potential for application to a number of other volatile and semivolatile organic contaminants in soil.

c. Advantages and Disadvantages. Advantages of low temperature thermal treatment are summarized below:

<u>Advantages</u>	<u>Disadvantages</u>
Fully mobile system for on-site treatment	Limited applicability to higher boiling point organic compounds such as PCBs
Indirect heating provides greater thermal efficiency and reduced emission control requirements	Increased moisture content of soil increases costs
Afterburner destroys contaminants	Particle size reduction and debris removal may be required

d. Data Requirements. Design experience for application of this process to a wide range of soil types and contaminants is limited because of its recent development. Laboratory testing to determine optimum temperatures and retention times for the thermal processor should be conducted to develop the process design for the system. Important soil characteristics are grain size, moisture content, and contaminant concentrations.

4-21. Solidification/Stabilization.

a. Process Description.

(1) Solidification/stabilization technology as applied to wastes uses physical and chemical processes to produce chemically stable solids with improved contaminant containment and handling characteristics (Figure 4-23). Waste solidification is the term used to describe the process of sorbing a liquid or semiliquid waste onto a solid medium, such as fly ash, cement, kiln dust, or clay, or otherwise incorporating the waste in a solid matrix. This partial treatment eliminates any free liquid and reduces the risk of spillage or escape of contaminants in any liquid phase.

(2) Solidification may involve the addition of cementing agents so that the solid material (with the sorbed liquid) can be formed into a free-standing impermeable monolith. This part of the waste treatment process reduces the surface area across which transfer or loss of pollutants can occur. Stabilization of waste refers to chemical alteration of the waste so as to reduce the potential for escape of contaminants or to lower the toxicity of specific waste components. Both solidification and chemical stabilization result in transformation of liquid or semisolid wastes to an environmentally safer form. For example, metal-rich sludge would be considered solidified if it were mixed with a dry absorber such as fly ash or dry soil. The benefits of solidification could be carried further if the sorbent and waste were cemented into a permeable, monolithic block. The waste would be considered chemically stabilized if the chemical composition of the sludge were altered by the addition of lime ( $\text{Ca}(\text{OH})_2$ ) to raise the pH so that the potential contaminants (toxic metals) were less soluble and hence less easily leached. An absorbing medium can be formulated to take up free liquid and maintain conditions of lowered solubility for the potential contaminants. Cementing agents (organic polymers, pozzolanic materials, or portland cement) can be added to bind the stable, solid waste into a free-standing, relatively impermeable monolith that represents a substantially reduced environmental threat.

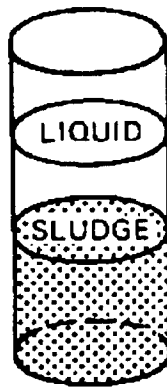
(3) Waste solidification/stabilization systems that have potentially useful application in remedial action activities discussed in this paragraph are: sorption, lime-fly ash pozzolan, and pozzolan-portland cement systems. Encapsulation processes such as thermoplastic microencapsulation and macroencapsulation were addressed in paragraph 4-19.

(a) Sorption. Most waste materials considered for solidification/stabilization are liquids or sludges (semisolids). In order to prevent the loss of drainable liquid and improve the handling characteristics of the waste, a dry, solid sorbent is generally added to the waste. The sorbent may interact chemically with waste or may simply be wetted by the liquid part of the waste (usually water) and retain the liquid as part of the capillary liquid. The most common sorbents used with waste include soil and waste products such as bottom ash, fly ash, or kiln dust from cement manufacture.



**STABILIZATION**

**TREATMENT TO REDUCE SOLUBILITY**



← EX. pH ADJUSTMENT, CHEMICAL OXIDATION, OR REDUCTION

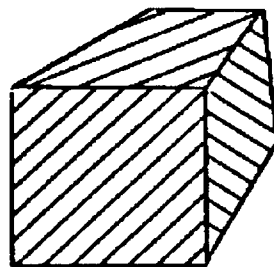
**SOLIDIFICATION**

**SORPTION TO PRODUCE A SOLID WITH NO FREE LIQUID**



← EX. MIXING WITH FLY ASH OR CLAY SORBENTS

**FORMATION OF MONOLITH WITH REDUCED SURFACE AREA**



← EX. ADDITION OF PORTLAND CEMENT (MAY BE ADDED ALONG WITH SORBENTS)

Figure 4-23. Steps in Stabilization/Solidification of Hazardous Wastes

In general, selection of sorbent materials involves tradeoffs between chemical effects, costs, and amounts required to produce a solid product suitable for burial. Table 4-18 summarizes chemical binding properties of natural sorbents for selected waste leach liquids. Where the ability of a sorbent to bind particular contaminants is important to containment, sorbents with specific chemical affinities can be selected. The pH of the waste strongly affects sorption/waste interactions, and pH control is an important part of any sorption process.

Table 4-18. Natural Sorbents and their Capacity for Removal of Specific Contaminants from Liquid Phases of Neutral, Basic, and Acidic Wastes

Contaminant	Neutral waste (calcium fluoride)		Basic waste (metal finishing sludge)		Acidic waste (petroleum sludge)	
Ca	Zeolite	(5054)*	Illite	(1280)	Zeolite	(1390)
	Kaolinite	(857)	Zeolite	(1240)	Illite	(721)
			Kaolinite	(733)	Kaolinite	(10.5)
Cu	Zeolite	(8.2)	Zeolite	(85)	Zeolite	(5.2)
	Kaolinite	(6.7)	Kaolinite	(24)	Acidic F.A.	(2.4)
	Acidic F.A.**	(2.1)	Acidic F.A.	(13)	Kaolinite	(0)
Mg	Basic F.A.	(155)	Zeolite	(1328)	Zeolite	(746)
			Illite	(1122)	Illite	(110)
			Basic F.A.	(176)	Basic F.A.	(1.7)
Zn					Zeolite	(10.8)
					Vermiculite	(4.5)
					Basic F.A.	(1.7)
Ni			Zeolite	(13.5)		
			Illite	(5.1)		
			Acidic F.A.	(3.8)		
F	Illite	(175)	Kaolinite	(2.6)	Illite	(9.3)
	Kaolinite	(132)	Illite	(2.2)	Acidic F.A.	(8.7)
	Acidic F.A.	(102)			Kaolinite	(3.5)
Total CN					Illite	(12.1)
					Vermiculite	(7.6)
					Acidic F.A.	(2.7)
COD	Acidic F.A.	(690)	Illite	(1744)	Vermiculite	(6654)
	Illite	(180)	Acidic F.A.	(1080)	Illite	(4807)
			Vermiculite	(244)	Acidic F.A.	(3818)

\* Values represent sorbent capacity in micrograms of contaminant removed per gram of sorbent used.

\*\* F. A. = fly ash. Acidic F.A. = Class F; Basic F.A. = Class C.

(b) Lime-fly ash pozzolan. Solidification/stabilization of waste using lime and pozzolanic material requires that the waste be mixed with a carefully selected, reactive fly ash (or other pozzolanic material) to a pasty consistency. Lime (calcium hydroxide) is blended into the waste-fly ash mixture. Typically 20 to 30 percent lime is needed to produce a strong pozzolan. The resulting moist material is packed or compressed into a mold to cure or is placed in the landfill and compacted.

(c) Pozzolan-portland cement. There are a wide variety of treatment processes that incorporate portland cement as a binding agent. Pozzolan products (materials with fine-grained, noncrystalline, reactive silica) are frequently added to portland cement to react with any free calcium hydroxide and thus improve the strength and chemical resistance of the concrete-like product. In waste solidification, the pozzolan materials (such as fly ash) are often used as sorbents. Much of the pozzolan in waste processing may be waste coated and relatively unreactive. Any reaction that does occur between the portland cement and free silica from the pozzolan adds to the product strength and durability. Waste solidifying formulations based on portland and pozzolan-portland systems vary widely, and a variety of materials have been added to change performance characteristics. These include soluble silicates, hydrated silica gels, and clays such as, bentonite, illite, or attapulgite. Approximate reagent requirements for some example applications are given in Table 4-19.

Table 4-19. Approximate Reagent Requirements for Various Waste Types Using a Portland Cement/Fly Ash Solidification<sup>1</sup>

Waste	Kilograms of reagent per liter of waste
Spent brine	3.8
Metal hydroxide sludge	2.4
Copper pickle liquor sludge	1.9
FeCl <sub>2</sub> pickle liquor sludge (1.5 percent HCl)	3.5
Sulfuric acid plating waste (15 percent (H <sub>2</sub> SO <sub>4</sub> ))	3.8
Oily metal sludge	0.96

<sup>1</sup>After Stanczyk, Senefelder, and Clarke (1982). The proportion of portland cement to fly ash was not given.

b. Applications.

(1) Most large, hazardous waste landfills are currently employing sorption to satisfy requirements prohibiting burial of liquids. Nineteen million liters (five million gallons) of oil sludge from a former refinery site was landfilled onsite after treatment with cement kiln dust. The process required  $3.71 \times 10^7$  kg (40,939 tons) of kiln dust.

(2) Lime-fly ash solidification/stabilization systems have been successfully used in managing hazardous waste, but generally the containment performance is such that a hazardous waste after processing would still be classed as hazardous. Lime-fly-ash-pozzolan-based landfills have been established using liner and monitoring systems to ensure safe disposal. There have been cases where lead wastes were judged nonhazardous after treatment, but in most cases a pozzolan-treated waste is not delisted.

(3) Pozzolan-portland-cement-based systems are among the most versatile. They can neutralize and seal acids and can handle strong oxidizers such as chlorates and nitrates. These methods are also good for solidifying many toxic metals, since at the pH of the cement (pH 9-11), many metals are insoluble carbonates and hydroxides.

c. Advantages/Disadvantages.

(1) Sorption has been widely used to eliminate free water and improve handling. Some sorbents have been employed to limit the escape of volatile organic compounds. Sorbents may also be useful in waste containment when they modify the chemical environment and maintain the pH and redox potential to limit the solubility of the waste. Although sorption eliminates the bulk flow of wastes from the site, in many cases leaching of waste constituents from the sorbent can be a significant source of pollution.

(2) The major advantages of the lime-fly ash solidification/stabilization technique include the ready availability and low cost of materials, and the familiarity of commonly used equipment. A disadvantage is that the solid mass resulting from lime-based solidification is porous. As such, it must either be sealed or placed in a secure landfill to prevent leaching of contained wastes. Another major disadvantage is that sludge or wastes containing organics cannot be treated.

(3) Provided pozzolan-portland cement based systems are used on compatible wastes, the short-term effectiveness can be expected to be quite good. The equipment for cement mixing is commonplace and the process is quite tolerant of chemical variations. However, because cement is a porous solid, contaminants can be leached out of the matrix over time and, therefore, these systems are usually not effective for organic wastes. Although it is possible to seal the outside of a block of cement-solidified wastes using styrene, vinyl, or asphalt to prevent leaching, no commercial systems are available to do this.

d. Data Requirements. The principal data requirements for solidification/stabilization techniques include:

- (1) Waste characteristics (binding agent selection).
  - (a) pH.
  - (b) Buffer capacity.
  - (c) Water content.
  - (d) Total organic carbon.
  - (e) Inorganic and organic constituents.
- (2) Treatability tests (cure time, mix).
  - (a) Leachability.
  - (b) Strength.

e. Design Criteria. The key design parameters for solidification/stabilization techniques include:

- (1) Solidification mixing ratios.
- (2) Curing time.
- (3) Volume increase of solidified product.

f. Evaluation. The evaluation of these factors is dependent on the solidification technology and the specific waste being treated.

#### 4-22. Thermal Destruction.

a. Process Description. Incineration combusts or oxidizes organic material at very high temperatures. The end products of complete incineration are CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, NO<sub>1</sub>, and HCl gases. Emission control equipment (scrubbers, electrostatic precipitators) for particulates, SO<sub>2</sub>, NO<sub>x</sub>, and products of incomplete oxidation are needed to control emissions of regulated air pollutants. Common types of incinerators most applicable to hazardous waste include:

- (1) Rotary kilns.
- (2) Multiple hearth.
- (3) Fluidized bed.
- (4) Liquid injection.

The key features of incineration methods cited previously are summarized in Table 4-20.

Table 4-20. Key Features of Major Types of Incinerators

Type	Process principle	Application	Combustion temp.	Residence time
Rotary kiln	Slowly rotating cylinder mounted at slight incline to horizontal. Tumbling action improves efficiency of combustion	Most organic wastes; well suited for solids and sludges; liquids and gases	810-1,640 °C (1,500-3,000 °F)	Several seconds to several hours
Multiple hearth	Solid feed slowly moves through vertically stacked hearths; gases and liquids feed through side ports and nozzles	Most organic wastes, largely in sewage sludge; well suited for solids and sludges; also handles liquids and gases	760-980 °C (1,400-1,800 °F)	Up to several hours
Liquid injection	Vertical or horizontal vessels; wastes atomized through nozzles to increase rate of vaporization	Limited to pumpable liquids and slurries (750 SSU Saybolt Seconds Universal) or less for proper atomization)	650-1,650 °C (1,200-3,000 °F)	0.1 to 1 sec
Fluidized bed	Wastes are injected into a hot agitated bed of inert granular particles; heat is transferred between the bed material and the water during combustion	Most organic wastes; ideal for liquids, also handles solids and gases	750-870 °C (1,400-1,600 °F)	Seconds for gases and liquids; longer for solids

b. Applications.

(1) Incineration is used for reduction of sludge volume, thereby reducing land requirements for disposal. Incineration can also be used to destroy most organic wastes whether they be gas, liquid, or solid.

(2) Mobile incineration systems have been considered for onsite treatment at hazardous waste sites. The EPA's Office of Research and Development has completed construction and is in the testing phase of a mobile incineration system. The system was designed to EPA's PCB destruction specifications to provide state-of-the-art thermal detoxification of long-lived, refractory organic compounds, as well as debris from cleanup operations. Hazardous substances that could be incinerated include compounds containing chlorine and phosphorous--for example, PCB's, kepone, dioxins, and organophosphate pesticides, which may be in pure form, in sludges, or in soils. A typical mobile incinerator is illustrated in Figure 4-24.

c. Advantages/Disadvantages. The advantages and disadvantages of hazardous waste treatment with incineration are summarized below:

<u>Advantages</u>	<u>Disadvantages</u>
Can destroy a wide range of organic wastes	Thickening and dewatering pretreatment may be required
Can handle gaseous, liquid, and solid wastes	May not be economical for small plants
	Air pollution control measures are required

d. Data Requirements. The principal data requirements for the design of an incineration system are:

- (1) Waste constituents and characteristics.
  - (a) Moisture content.
  - (b) Volatile materials content.
  - (c) Ash content.
  - (d) Ash specific level, specific gravity, or bulk density.
  - (e) Ash particle size range.
  - (f) Carbon, hydrogen, oxygen, halide, sulfur, nitrogen, phosphorus content.
  - (g) Waste specific gravity, viscosity, and melting point.

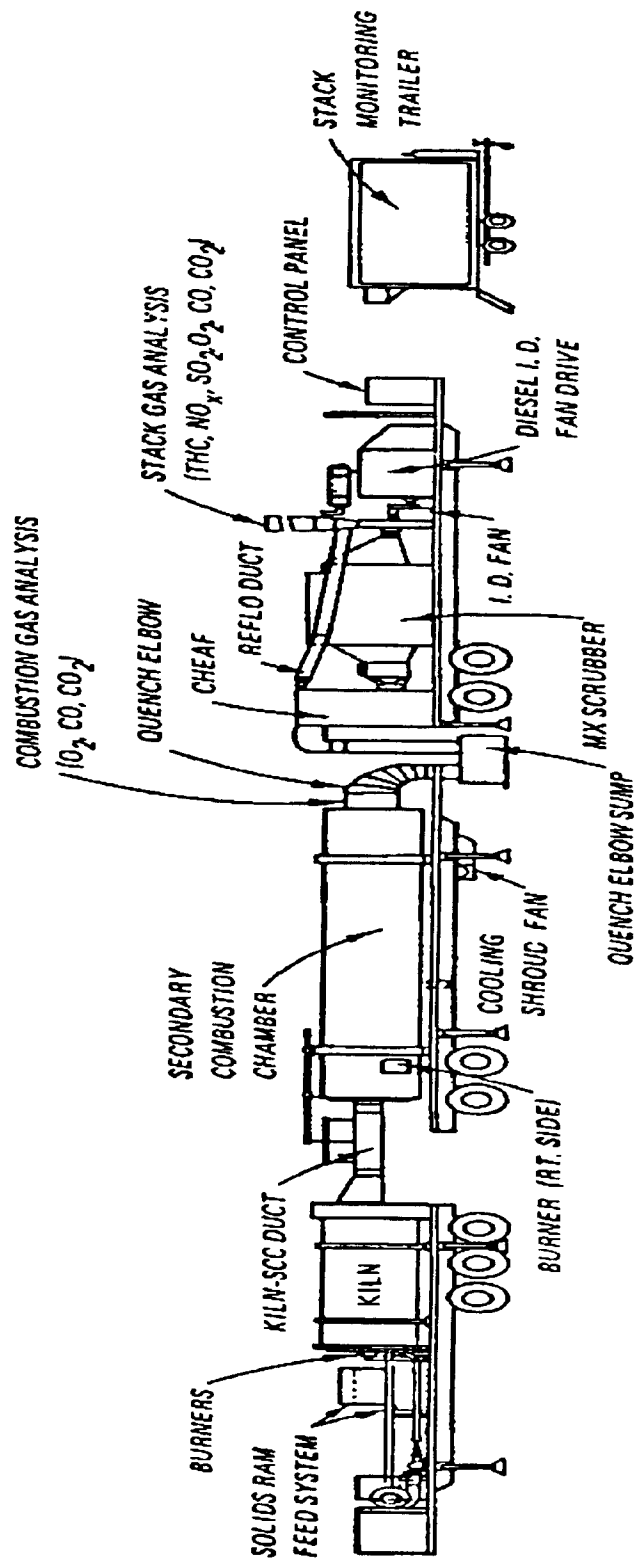


Figure 4-24. EPA Mobile Incineration System



- (h) Metal content.
- (i) Thermogravimetric analysis.
- (j) Suspended and dissolved solids.
- (k) Reactive chemical groups.
- (l) Flammability, stability, detonation.
- (m) Environmental sensitivity.
- (n) Toxicity.
- (2) Process characterization.
- (a) Residence time.
- (b) Temperature.
- (c) Destruction efficiencies.
- (d) Ash residue.
- (e) Gaseous effluent.

e. Design Criteria. The design criteria for a fluidized bed furnace (FBF) and a multiple hearth furnace (MHF) are presented in Tables 4-21 and 4-22, respectively. During actual operations some extensive maintenance problems have occurred with air preheaters. Venture scrubbers have also had scaling problems. Screw feeds and screw pump feeds are both subject to jamming because of either overdrying of the sludge feed at the incinerator or because of silt carried into the feed system with the sludge. Fluidized bed furnace systems have had problems with the burnout of spray nozzles or thermocouples in the bed.

Table 4-21. Design Criteria for Fluidized Bed Furnace

Parameter	Design criteria
Bed loading rate	245 to 294 kg/m <sup>2</sup> /hr (50 to 60 lb wet solids/ft <sup>2</sup> /hr)
Superficial bed velocity	0.12 to 0.18 m/s (0.4 to 0.6 ft/sec)
Sand effective size	0.2 to 0.3 mm (uniformity coefficient = 1.8)
Operating temperature	760 to 816 °C (1,400 to 1,500 °F) (normal); 1204 °C (2,200 °F) (maximum)
Bed expansion	80 to 100 percent
Sand loss	5 percent of bed volume per 300 hr of operation

Table 4-22. Design Criteria for Multiple Hearth Furnace

Parameter	Design criteria
Maximum operating temperature	927 °C (1,700 °F)
Hearth loading rate	29.4 to 49 kg/m <sup>2</sup> /hr ((6 to 10 lb wet solids/ft <sup>2</sup> /hr) with a dry solids concentration of 20-40 percent
Combustion airflow	12 to 13 kg/kg dry (12 to 13 lb/lb dry solids)
Shaft cooling airflow	1/3 to ½ of combustion airflow
Excess air	75 to 100 percent

4-23. Volume Reduction.

a. Process Description.

(1) Volume reduction as applied to sludges can be termed as thickening or dewatering processes. Thickening of sludge consists of the removal of supernatant, thereby reducing the volume of sludge that will require disposal or treatment. Gravity thickening takes advantage of the difference in specific gravity between the solids and water.

(2) Centrifuges are used to dewater sludges using centrifugal force to increase the sedimentation rate of sludge solids. During the process of centrifugation, if a particle is more dense than the fluid, it will tend to migrate in the direction of the centrifugal force, i.e., toward the periphery of the rotating vessel containing the fluid. If the particle is less dense than the fluid, there will be a tendency for the particle to remain near the center of rotation and the fluid to migrate toward the periphery of the vessel. Either way, particles that were uniformly dispersed throughout the fluid prior to centrifugation would now be concentrated in a specific region of the centrifuge where they can be removed as a more concentrated mixture. In centrifugation, the centrifugal force is analogous to gravitational force in the sedimentation process. In centrifugation, however, forces equal to several thousand times the force of gravity are often generated.

(3) Volume reduction will frequently be required to meet regulatory restraints as applied to disposal of hazardous waste. Disposal costs can be reduced through the use of volume reduction techniques by eliminating nonhazardous free liquids from a waste. Before a hazardous waste can be disposed of at a chemical waste landfill, it must be solidified. Typically the solidification process will add to the total weight and volume and therefore the disposal costs. If the same waste can be separated into a reduced volume of hazardous solid waste and a nonhazardous liquid waste, disposal costs can be lowered significantly.

b. Applications. Dewatering and thickening processes have been used primarily to thicken primary, secondary, and digested sludges. Centrifuges may be used for thickening sludges where space limitations or sludge characteristics make other methods unsuitable. However, if a particular sludge can be effectively thickened by gravity without chemicals, centrifuge thickening is not economically feasible. Centrifuges are generally used for dewatering sludge in larger applications where sludge incineration is required.

c. Advantages/Disadvantages. Gravity thickening is highly dependent on the dewaterability of the sludges being treated while centrifugal thickening processes can have significant maintenance and power costs. Adequate electric power must also be provided for the large motors that are required. Depending on the waste, the liquid fraction after centrifugation may be considered hazardous also and require proper disposal. Typically the liquid fraction will be relatively high in suspended nonsettling solids.

d. Data Requirements. The data requirements for gravity thickening or centrifugation include:

- (1) The waste stream daily flow.
- (2) Settling velocity.
- (3) Size distribution.
- (4) Solids specific gravity.
- (5) Liquid specific gravity.

e. Design Criteria.

(1) For gravity thickeners detention times of 1 to 3 days are used, sludge blankets of at least 3 feet are common, side water depths of at least 10 feet are a general practice, and surface loading rates can range from 5 to 25 pounds per day per square foot depending on the sludge type and pretreatment used.

(2) Each installation of a centrifuge is site specific and dependent upon a manufacturer's product line. Maximum capacities of about  $9.1 \times 10^4$  kg (100 tons per hour) of dry solids are available in solid-bowl units with diameters up to 1.4 m (54 inches) and power requirements up to 130 KW (175 horsepower). Disk-type units are available with capacities up to 1.5 m<sup>3</sup>/min (400 gallons per minute) of concentrate.

#### 4-24. Wet Oxidation.

a. Process Description.

(1) Wet air oxidation (WAO) is truly an oxidation process. Thermodynamically, it is similar to chemical oxidation and incineration.

(2) The waste is pumped into the system by the high-pressure pump and mixed with air from the air compressor. The mixture passes through a heat exchanger and then into the reactor where oxygen in the air reacts with organic matter in the waste. This oxidation is accompanied by a temperature rise. The gas and liquid phases are separated after the reactor, and the liquid passes through the heat exchanger heating the incoming material. The gas and liquid streams are discharged from the system through control valves.

(3) As would be expected, the operating temperature is critical. Organic molecules are excited thermally (as opposed to UV light) to a level where a high percentage undergo an oxidation reaction. As expected, various materials require different energy levels for a significant reaction rate to take place. Figure 4-25 shows the relationship between temperature and degree of oxidation for several different materials. At 150 °C, 5 to 10 percent of the COD may be oxidized, whereas at 320 °C, nearly complete oxidation occurs for many substances.

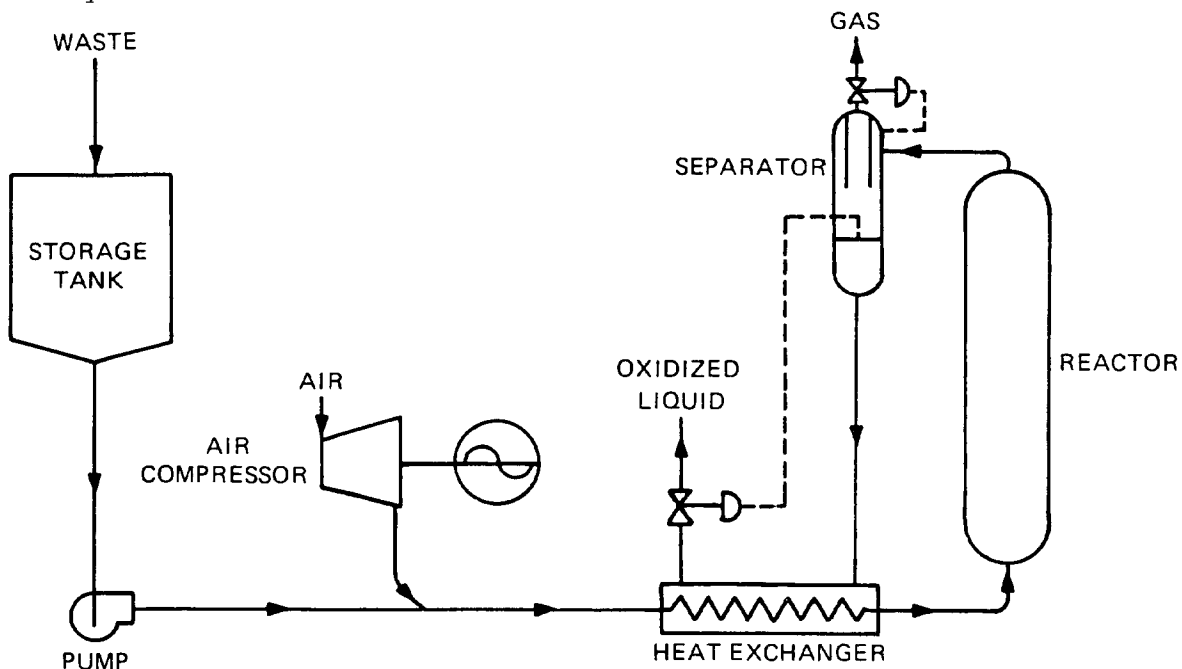


Figure 4-25. Flow Sheet of Wet Air Oxidation

b. Applications.

(1) WAO conditions can be controlled to achieve a desired end product by controlling the temperature and the reaction time. With increased temperature, the degree of oxidation increases as shown in Figure 4-26. As the oxidation condition becomes more severe, more of the nonbiodegradable components of the waste are converted to biodegradable forms. WAO may be used as a treatment to detoxify a waste before biological treatment. This technique has been used to treat acrylonitrile wastewaters that are highly concentrated in cyanide and organic nitrites.

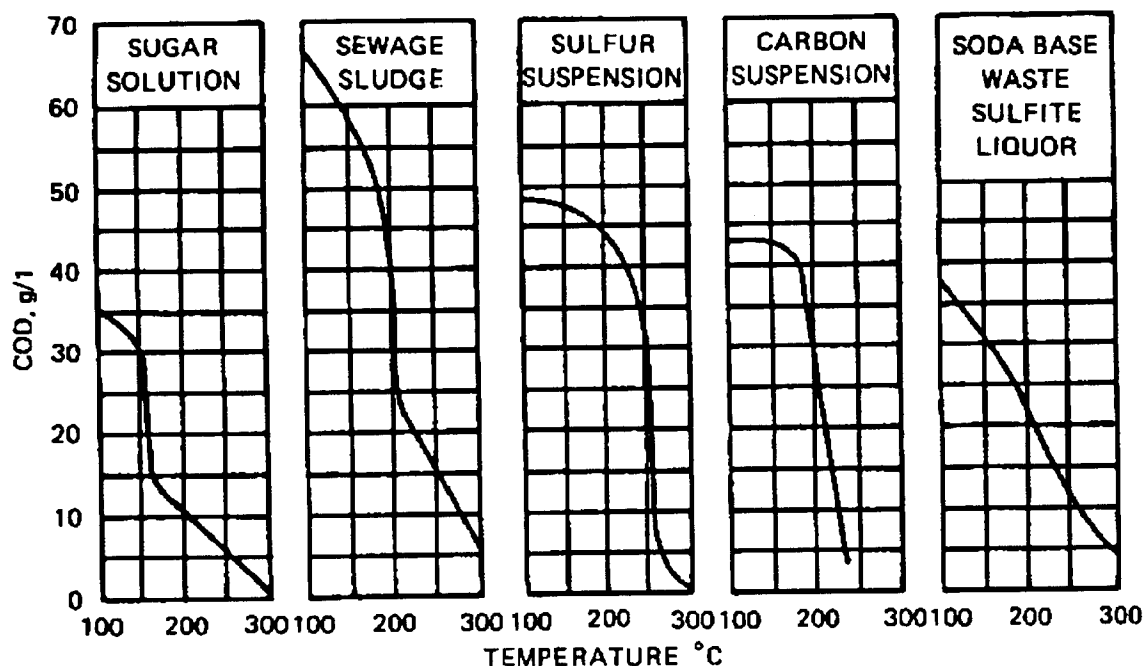


Figure 4-26. Oxidation Curves for Five Aqueous Fuels

(2) WAO may be well suited for treating hazardous waste. Recent studies have focused upon some of the 65 priority pollutants originally proposed by the EPA. Results are shown in Table 4-23. It should be observed that operating conditions were fairly stringent (275 to 320 °C and 6200 to 12,400 KPa (900 to 1800 pounds per square inch) atmosphere (psia)). However, removal percentages are impressive. It is not clear if these reductions represent a conversion to CO<sub>2</sub> or simply a modification to the original molecule. It should be noted that most of the materials in Table 4-23 are aromatic derivatives. In many cases, the toxicity of aromatics is greatly reduced by simply opening the ring structure of the molecules. This would require only fractional oxidation.

c. Advantages/Disadvantages.

(1) WAO is an exciting oxidative process that appears to have wide application along with versatility and flexibility. Almost any combustible materials, organic or inorganic, can be treated by WAO. The question of economics affects selection of this process since it is energy intensive.

(2) Typically WAO should be considered as a step in the overall waste treatment process. It is rarely used as the total treatment. WAO may not be reasonable for waste containing less than 2,000 milligrams per liter COD. Depending upon capital and the nature and treatability of the waste, it may be desirable to treat by another method or to concentrate to reduce the volume prior to WAO treatment.

Table 4-23. Examples of One-Hour Oxidation of Selected Compounds

Compound	Starting Concentration (g/l)	% Starting material destroyed		
		320°C	275°C	275°C/* Cu <sup>++</sup>
Acenaphthene	7.0	99.96	99.99	-
Acrolein	8.41	99.96	99.05	-
Acrylonitrile	8.06	99.91	99.00	99.50
2-Chlorophenol	12.41	99.86	94.96	99.88
2,4-Dimethylphenol	8.22	99.99	99.99	-
2,4-Dinitrotoluene	10.0	99.88	99.74	-
1,2-Diphenylhydrazine	5.0	99.98	99.98	-
4-Nitrophenol	10.00	99.96	99.60	-
Pentachlorophenol	5.0	99.88	81.96	97.30
Phenol	10.0	99.97	99.77	-

\* Cupric sulfate was added as a catalyst.

(3) Primary other advantages and disadvantages are summarized below:

Advantages	Disadvantages
May be controlled to deliver a specific degree of oxidation	Requires operation at high pressure and temperatures
Can be used to detoxify toxic materials	Corrosive inorganics can be a problem at high temperatures
No net heating requirement if the COD is >15,000 mg/l	Initial capital costs are high
	Primarily suited for pretreatment as reductions of 10 to 15% are typical

d. Data Requirements. In general, bench scale and/or pilot scale testing will be required for design. The following parameters should be determined:

- (1) COD of wastes.
- (2) TDS of wastes.
- (3) Operating temperature.
- (4) Retention time.
- (5) Degree of stabilization.
- (6) Degree of detoxification.

e. Design Criteria.

(1) Due to the critical nature of the temperature, the operating system becomes a prime design parameter. Not only will the system require specific design for a specified operating pressure but also the compressor system must be capable of delivering air or oxygen at the maximum operating pressure expected in the system. Table 4-24 presents data on the temperature-pressure relationship of steam.

Table 4-24. Temperature/Pressure Relationship of Saturated Steam

Pressure		Temperature	Temperature
(psia)	(KPa)	(°C)	°(F)
100	689	212	14.7
125	861	257	34
150	1034	302	69
175	1206	347	130
200	1378	392	226
225	1550	437	371
250	1722	482	577
275	1895	527	863
300	2067	572	1248
325	2239	617	1762

(2) As a general rule, the maximum operating temperature will be about 200 °C. Higher temperatures may be reached but at the expense of a large increase in pressure.

(3) If the COD of the waste is less than 15,000 milligrams per liter, consideration should be given to concentrating the waste stream prior to WAO treatment.

4-25. Evaporation.

a. Background.

(1) Evaporation is a technique used for many years in the process industry. It is also used in waste treatment applications. In concept, evaporation is no more complicated than placing a pot on a stove and evaporating the contents. It is not a necessary criterion to carry to dryness.

(2) The objective of evaporation is to reduce the volume of waste to handle by concentrating a solution consisting of a nonvolatile solute and a volatile solvent, In the overwhelming majority of evaporations applicable to

toxic waste sites, the solvent is water. Evaporation is conducted by vaporizing a portion of the solvent to produce a concentrated solution or a thick liquor.

(3) Evaporation differs from drying in that the residue is often a highly viscous liquid, rather than a solid; it differs from distillation in that the vapor is usually a single component, and even when the vapor is a mixture, no attempt is made in the evaporation step to separate the vapor into fractions; it differs from crystallization in that the emphasis is placed on concentrating a solution rather than forming and building crystals. In certain situations, however (for example, in the evaporation of brine to produce salt), the line between evaporation and crystallization is not distinct. Evaporation sometimes produces a slurry of crystals in a saturated mother liquor.

(4) It appears that evaporation will remain a popular unit operation for many years to come even though energy requirements are very significant. As manufacturing facilities push toward zero discharge through various recycling and recovery programs, evaporation will play an important role in closing the loop in many of these operations.

b. Process Description.

(1) There are many types of evaporators currently in use in the industrial scene. The intent here is to introduce only the most likely processes which may be applicable to hazardous waste problems. Evaporator systems may be single or multiple effect. This is analogous to saying they may be single or multiple stages.

(2) Single-effect evaporators are used where the required capacity is small, steam is cheap, the vapors or the liquids are so corrosive that very expensive materials of construction are required, or when the vapor is so contaminated that it cannot be used for steam. Single-effect evaporators may be operated in batch, semibatch, continuous batch, or continuous mode. In any configuration, the single-effect system is the most energy intensive with the least capital expenditure.

(3) Perhaps the most widely used configuration is the multiple-effect scheme. The choice of the number is up to the designer. Most textbooks and references to multiple-effect evaporators will typically show three effects as shown in Figure 4-27. However, a system may theoretically have an infinite number of effects. On the practical side, the number of effects will be limited by a balance between capital cost and operating cost. Vapor from the first effect is used as steam for the second effect and so on. Steam economy of a multiple-effect evaporator will increase in proportion to the number of effects, but will be somewhat less numerically than the number of effects. A system designed for producing pure water from seawater uses a 20-effect system. The steam-to-product ratio is 1 to 19. The increased steam economy is offset by an increase in capital expenditure.



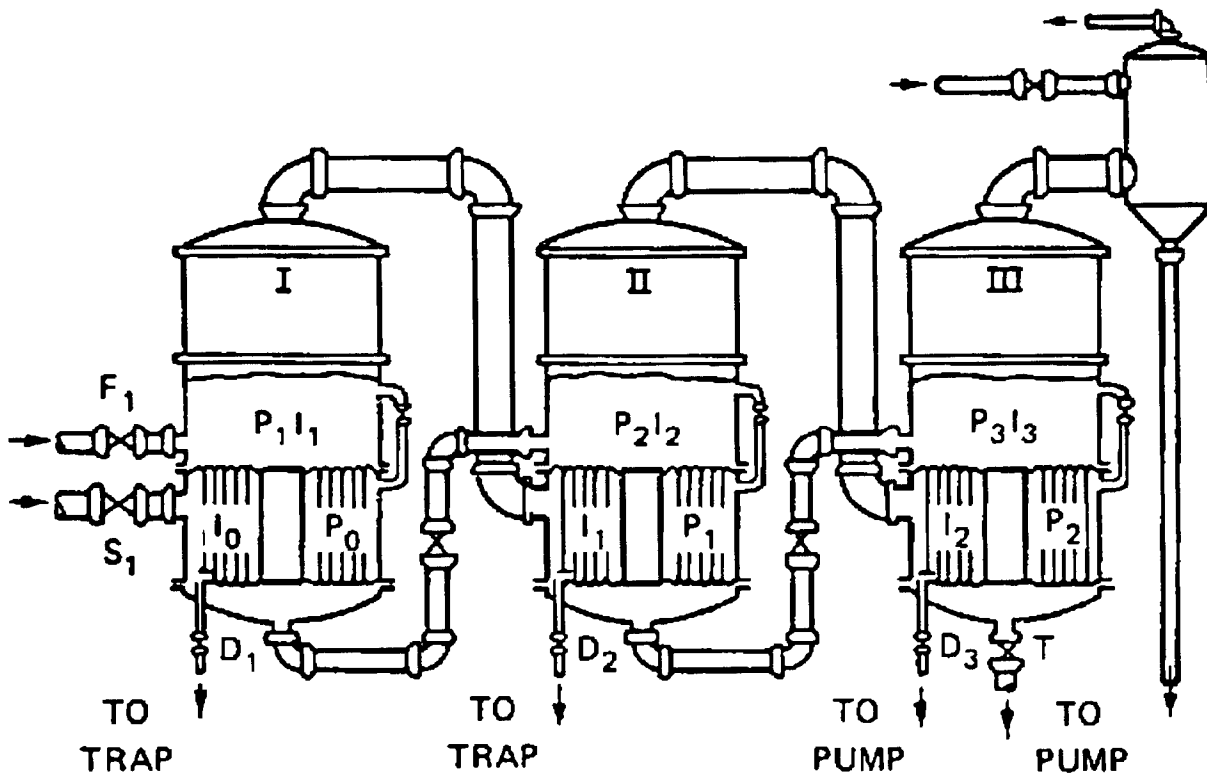


Figure 4-27. Three-Effect Evaporator.

(4) Energy requirements for evaporation will vary widely depending on the number of effects used as indicated above. Also, the heat transfer coefficients for a particular system will influence the energy requirements. The normal operating range of energy for evaporation is  $6.45 \times 10^{-2}$  to 0.71 KW/hr/Kg  $H_2O$  (100 to 1,100 BTU\*s per pound of water) evaporated. The latter value assumes a single-effect system with little heat recovery.

c. Applications. Evaporation is a well-defined, well-established process that is essentially omnipresent in industry. It is being used currently for the treatment of hazardous waste such as radioactive liquids and sludges, concentrating of plating and paint solvent waste, and in the pulp and paper industry, six-effect evaporators are typically used to concentrate black liquor while producing methanol. It is capable of handling liquids, slurries, and sometimes sludges, both organic and inorganic, containing suspended or dissolved solids or dissolved liquids where one of the components is essentially nonvolatile. It can be used to reduce waste volume prior to incineration or precipitation.

d. Advantages/Disadvantages. A summary of advantages and disadvantages is presented below:

<u>Advantages</u>	<u>Disadvantages</u>
Not a new technology; has been used many years in the chemical process industries	Energy intensive process, offset somewhat by multiple-effect operation
Large volume reductions can be realized	Evaporation tubes are easily fouled, lowering heat transfer coefficients
Effective pretreatment step prior to incineration	Requires a source of steam
Condensate may be marketable	Bottoms and condensate may require further treatment or disposal

e. Data Requirements. Data requirements include:

- (1) Thermodynamic data for stream being evaporated, i.e., sensible heat, heat of vaporization over concentration range, heat of crystallization.
- (2) Feed flow rate and temperature.
- (3) Pressure and/or temperature of available stream.
- (4) Vacuum or boiling temperature of the last stage.
- (5) Suitability of vapor from first stage as steam for the second stage, etc.
- (6) Quality of water to be evaporated, i.e. extent of concentration.
- (7) Number of effects or stages to be used.
- (8) Heat transfer coefficients as a function of boiling temperature and )t.

f. Design Criteria.

(1) Evaporation systems are generally designed to balance the cost between capital and operating costs. As additional effects are added to a system, the more energy efficient the system becomes. This savings in energy will be at the expense of capital cost. At some point, an optimum number of effects will be realized. The number of effects is also constrained by the available steam pressure for the first stage and the vacuum for the last stage. Still another consideration is the quantity of material to be processed. For very small volumes, a single stage may be sufficient.

(2) For waste treatment applications, the number of effects may be established on the basis of the available quantity and quality of steam along with good engineering judgment. Heating surfaces in all effects of a multiple effect system should be equal to obtain economy of construction. Design procedures are presented in Badger and Banchero (1955) and DeRenzo (1978). Metry (1980) should be consulted for heat transfer considerations.

### Section III. In Situ Treatment Technologies

#### 4-26. Biological Treatment.

##### a. Process Description.

(1) Organic materials in contaminated soils may be amenable to biodegradation in place, or in situ. The process consists largely of producing conditions in the soil mass which promote the rate of natural degradation by endogenous organisms. Conditions favoring biodegradation include increased aeration and nutrient concentrations. In some cases, seed cultures may increase the active population and be beneficial.

(2) The biodegradation process is slow relative to other remedial action technologies. Complete degradation of the waste could take several years and may never be complete if refractory compounds such as polynuclear aromatics are present. This is a major disadvantage, since additional migration of contaminants can occur during the treatment and even afterwards.

(3) This technique is generally limited to those situations where the waste material or contaminated soil is naturally aerated or where artificial aeration is feasible. Procedures for the addition of nutrients such as nitrogen and phosphorus may be necessary if the waste material is deficient in these constituents. Lime may be required to maintain proper pH.

##### b. Applications.

(1) Situations where in situ bioremediation could be applied are those where complete mixing and/or aeration can be achieved. A primary application is a chemical spill or landspreading operation where the wastes have not migrated below tilling depth (about 305 to 610 mm (12 to 24 inches)), or a surface impoundment in which the waste is fluid enough to be mechanically aerated and pumped for mixing.

(2) Biodegradation has been used most widely for treatment of oily sludges and refinery waste. Chlorinated solvents such as TCE or PCE are not degraded effectively using current technology; however, work is continuing on these materials. Naturally occurring bacteria and special cultures have been developed which are capable of degrading benzene, phenol, cresol, naphthalene, gasoline, kerosene, and cyanide, and many of their derivatives.

c. Advantages/Disadvantages. In land treatment, if soils are not well aerated, waste degradation will occur only slowly, if at all. Because metals are not degraded, careful attention should be given to the toxic metal load at the site. Since the process can be very slow, additional migration of contaminants may take place during and after treatment. Also, the possibility of forming a toxic byproduct as a result of biodegradation should be considered.

##### d. Data Requirements.

(1) The type, quantity, and distribution of the waste constituents will have to be determined to select a nutrient, and air requirements.

(2) Tests must be made to determine if microorganisms are naturally occurring which will breakdown the target chemicals. If none are present, enriching or seed cultures may be required.

(3) The site topography, hydrogeology, and soil physical, chemical, and biological properties are also necessary to determine the injection and withdrawal system requirements and design.

e. Design Criteria. The key factors for biodegradation include:

- (1) Nutrient balance.
- (2) pH maintenance.
- (3) Soil aeration and/or oxygen availability.
- (4) Degradation rate of waste constituents.
- (5) Waste constituents and location.

#### 4-27. Chemical Oxidation.

a. Process Description. In-situ leachate treatment introduces a reactant into the contaminated region to interact with the leachate plume. Chemical injection entails injecting chemicals into the ground beneath the waste (see Figure 4-28) to neutralize, precipitate, or destroy the leachate constituents of concern.

b. Applications. Sodium hypochlorite has been used to treat leachate containing cyanide (Tolman et al. 1978). Very little field data are available. The areal spread and depth of the leachate plume must be well characterized so that injection wells can be placed properly to intercept all of the contaminated ground water.

c. Advantages/Disadvantages.

(1) Pollutants may be displaced to adjacent areas when chemical solution is added.

(2) Hazardous compounds may be produced by reaction of injected chemical solution with waste constituents other than the treatment target.

d. Data Requirements. The principal data requirements include the contamination plume characteristics: depth to bedrock, plume cross section, leachate or ground-water velocity, and hydraulic gradient. Also the soil permeability, leachate composition, and reaction rates will have to be determined.

e. Design Criteria. Chemical injection systems are in the conceptual stage of development. The permeability of the soil beneath the waste must be known to determine the ground-water flow through the injected waste and the reaction time between the contaminated ground-water and chemicals.

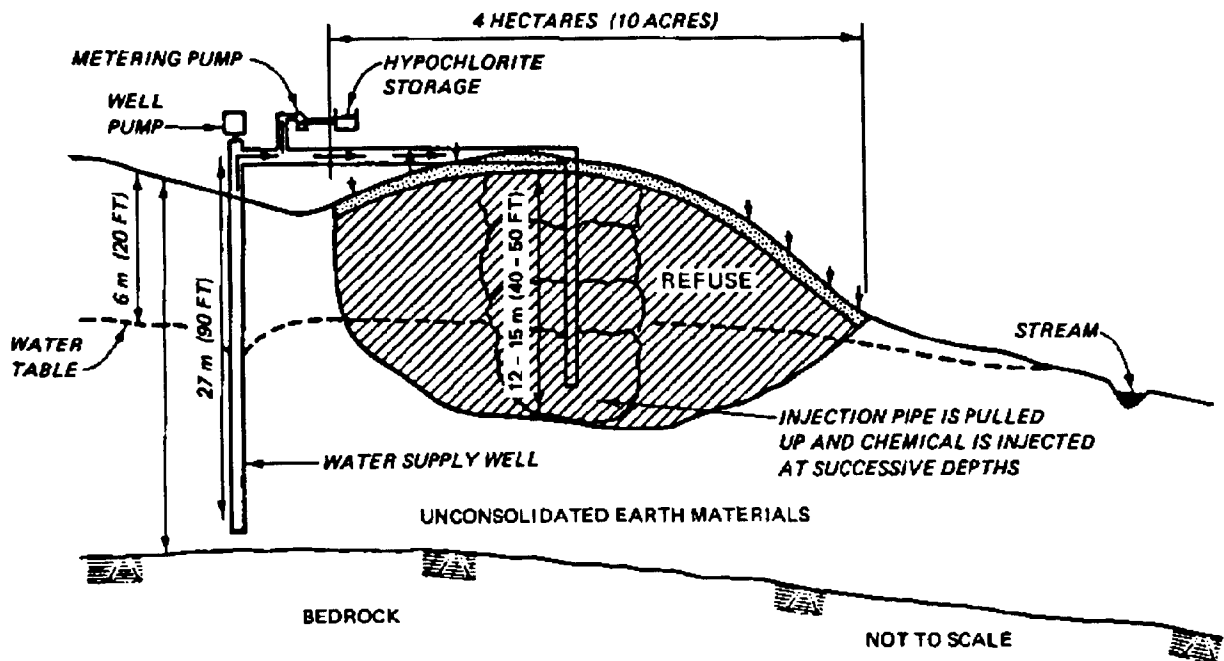


Figure 4-28. Cross Section of Landfill Treated by Chemical Injection

4-28. Permeable Treatment Beds.

a. Process Description. Permeable treatment beds use trenches filled with a reactive permeable medium to act as an underground reactor (see Figure 4-29). Contaminated ground water or leachate entering the bed reacts to produce a nonhazardous soluble product or a solid precipitate.

b. Applications.

(1) Permeable treatment beds are applicable in relatively shallow aquifers since a trench must be constructed down to the level of the bedrock or an impermeable clay. Permeable treatment beds often are effective only for a short time as they may lose reactive capacity or become plugged with solids. Overdesign of the system or replacement of the permeable medium can lengthen the time period over which permeable treatment is effective.

(2) The materials used for this form of treatment are:

(a) Limestone or crushed shell- -Limestone neutralizes acidic ground water and may remove heavy metals such as Cd, Fe, and Cr. Dolomitic limestone ( $MgCO_3$ ) is less effective at removing heavy metals than calcium carbonate limestone. The particle size of the limestone should match a mix of gravel size and sand size. The larger sizes minimize settling of the bed and channeling as the limestone dissolves. The small sizes maximize contact.

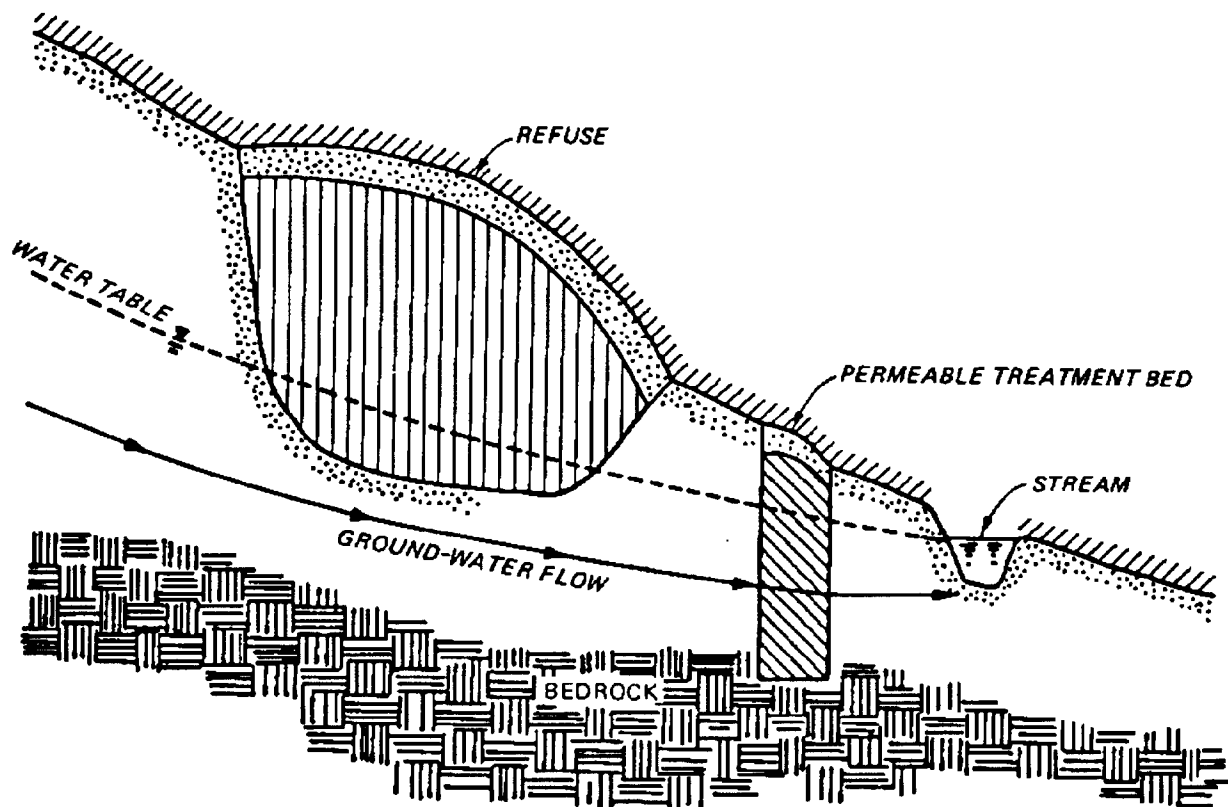


Figure 4-29. Installation of a Permeable Treatment Bed

Extrapolated bench-scale data indicate contact time needed to change 1 pH unit is 8 to 15 days.

(b) Activated carbon--Activated carbon removes nonpolar organic contaminants such as  $\text{CCl}_4$ , PCBs, and benzene by adsorption. Activated carbon must be wetted and sieved prior to installation to ensure effective surface solution contact.

(c) Glauconitic green sand--This sand, actually a clay, is found predominantly on the coastal plain of the Mid Atlantic states and has a good capacity for adsorbing heavy metals. Bench-scale studies indicate removal efficiencies of greater than 90 percent for As, Cu, Hg, and Ni, and 60 to 89 percent for Al, Cd, Ca, Cr, Co, Fe, Mg, Mn, and Zn, for detention times on the order of several days.

(d) Zeolites and synthetic ion exchange resins--These materials are also effective in removing solubilized heavy metals. Disadvantages such as short lifetime, high costs, and regeneration difficulties make these materials economically unattractive for use in permeable treatment beds.

c. Disadvantages.

(1) Plugging of the bed may divert contaminated ground water and channeling through the bed may occur. Both problems permit passage of untreated wastes.

(2) Changing hydraulic loads and/or contaminant levels may render the detention inadequate to achieve the design removal level.

d. Data Requirements. The principal data requirements include the contamination plume characteristics: depth to bedrock, plume cross section, leachate or ground-water velocity, and hydraulic gradient. Also the soil permeability, leachate composition, and reaction rates will have to be determined.

e. Design Criteria.

(1) A permeable treatment bed is constructed by digging a trench to an impermeable layer (bedrock or clay), filling the trench with the appropriate material, and capping to control infiltration. The width of the trench is determined by the permeability of the material used for treatment, the ground-water flow velocity, and the contact time required for treatment. These parameters are related as:

$$w_b = (v_b) (t_c) \quad (4-8)$$

where

$w_b$  = barrier width, m

$v_b$  = ground-water flow velocity in the barrier, m/sec

$t_c$  = contact time to achieve the desired removal, sec

Ground-water velocity,  $v$ , in turn, is determined by Darcy's law:

$$v = ks \quad (4-9)$$

where

$s$  = the gradient or loss of head per unit length in the direction of flow (unitless)

$k$  = coefficient of permeability, a soil-specific value, m/sec

(2) Since the ground-water velocity through the permeable bed cannot be predetermined, the trench should be designed for the maximum ground-water velocity through the soil. If one assumes the hydraulic gradient is equal for the soil and the permeability bed, the permeability of the barrier must equal that of the soil.

4-29. Soil Flushing.

a. Process Description. Solution mining (extraction) is the application of a solvent to a waste solid or sludge, and collection of the elutriate at well points for the removal and/or treatment of hazardous waste constituents. Typically, solvents used are water, acids (sulfuric, hydrochloric, nitric, phosphoric, carbonic), ammonia, and/or chelating agents such as EDTA which solubilize heavy metals and other inorganic ions. As the solvent is collected, a fraction can be recycled through the landfill with a make-up solution. The remainder can be treated and disposed.

b. Applications. Chemical extraction has been used by the chemical processing and mining industries for many years. The techniques are well understood, but experience with in-situ treatment of hazardous waste is lacking. Therefore, very little data are available on the application of this technology in a remedial action setting. Bench-scale laboratory studies of extraction of heavy metals from sludges and plans to conduct full-scale metal extraction from industrial wastes have been made.

c. Advantages/Disadvantages.

(1) The advantages of the process are that, if the waste is amenable to this technique and distribution, collection, and treatment costs are relatively low, solution mining can present an economical alternative to the excavation and treatment of the wastes. It may be particularly applicable if there is a high safety and health hazard associated with excavation. Also, the effectiveness and completion of the treatment process can be measured via sampling prior to wastewater treatment.

(2) Disadvantages include an uncertainty with respect to adequate contact with wastes; that is, because the wastes are buried, it is difficult to determine whether the solvent has contacted all the waste. Also, containerized waste cannot be treated effectively by this method. Another disadvantage is that the solution mining solvent or elutriate may become a pollutant itself if the system has been poorly designed.

d. Data Requirements. Principal data requirements would include laboratory testing to determine extraction efficiency of the solvents and waste analysis for presence of constituents not compatible with the solvent. Also, field testing and a geohydrologic site survey to establish potential for solvent migration into uncontaminated ground water and to establish well placement sites for collection of the elutriate are required.

e. Design Criteria. The data requirements will determine the selection of an extraction solvent, the well placement for collection of the elutriate, and the injection well locations for the extracting solvent.

4-30. Vapor Extraction.

a. Background. Soils may become contaminated in a number of ways with such volatile organic chemicals as industrial solvents and gasoline components. The sources of contamination at or near the earth's surface include



intentional disposal, leaking underground storage tanks, and accidental spills. Contamination of ground water from these sources can continue even after discharge has stopped because the unsaturated zone above a ground-water aquifer can retain a portion or all of the contaminant discharge. As rain infiltrates, chemicals elute from the contaminated soil and migrate toward ground water.

b. Process Description.

(1) A soil vapor extraction, a forced air venting, or an in situ air stripping system (Figure 4-30) revolves around the extraction of air containing volatile chemicals from unsaturated soil. Fresh air is injected or flows into the subsurface at locations around a spill site, and the vapor-laden air is withdrawn under vacuum from recovery or extraction wells.

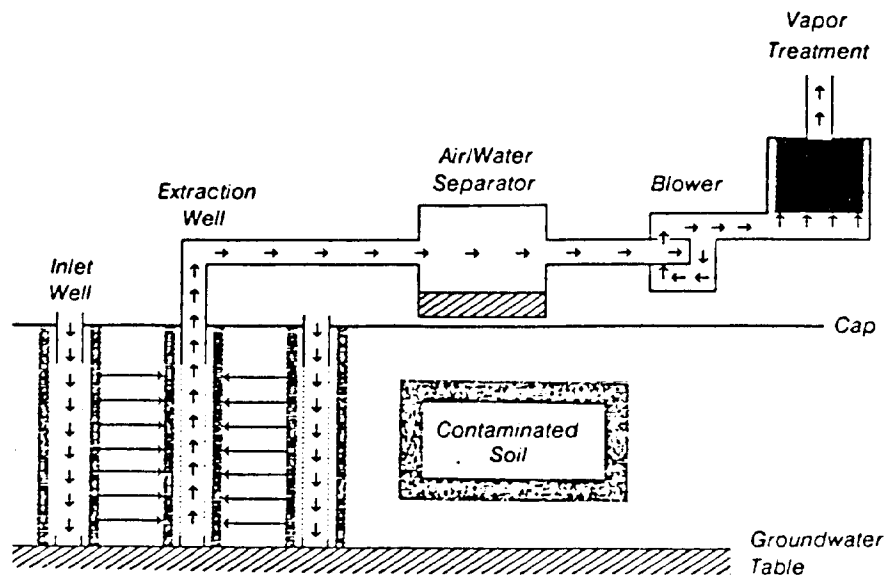


Figure 4-30. Soil Vapor Extraction System (Terravac, Inc.)

(2) In the simplest soil vapor extraction systems, air flows to an extraction well from the ground surface. To enhance air flow through zones of maximum contamination, it may be desirable to include air inlet wells in the installation. These injection wells or air vents, whose function is to control the flow of air into a contaminated zone, may be located at numerous places around the site. Typically, injection wells and air vents are constructed similarly to extraction wells. In some installations, extraction wells have been designed so they can also be used as air inlets. Usually, only a fraction of extracted air comes from air inlets. This indicates that air drawn from the surface is the predominant source of clean air.

(3) Extraction wells are typically designed to fully penetrate the unsaturated zone to the capillary fringe. Extraction wells usually consist of slotted plastic pipe placed in permeable packing and sealed near the surface to avoid "short-circuiting." (See also paragraph 3-13 on wellpoints).

(4) During remediation, the blower is turned on and the air flow through the soil comes to an equilibrium. The flows that are finally established are a function of the equipment, the flow control devices, the geometry of well layout, the site characteristics, and the air permeability of the soil. At the end of operation, the final distribution of VOCs in the soil can be measured to ensure decontamination of the site. Wells may be aligned vertically or horizontally. Vertical alignment is typical for deeper contamination zones and for residue in radial flow patterns. If the depth of the contaminated soil or the depth to the ground-water table is less than 10 to 15 feet, it may be more practical to dig a trench across the area of contamination and install horizontal perforated piping in the trench bottom rather than to install vertical extraction wells. Usually several wells are installed at a site.

(5) The means to verify the success of cleanup is often problematic. Soil sampling is difficult to use because of the uncertainties in replicating the sampling results at a location. Measuring the soil gas concentrations are more repeatable but difficult to relate to regulatory standards, where they exist.

c. Applications. Alternatives for decontaminating unsaturated soil include excavation with onsite or offsite treatment or disposal, biological degradation, and soil flushing. Soil vapor extraction is also an accepted, cost-effective technique to remove volatile organic chemicals from contaminated soils. Soil vapor extraction can be effectively used for removing a wide range of volatile chemicals in a wide range of conditions. The design and operation of these systems is flexible enough to allow for rapid changes in operation, thus, optimizing the removal of chemicals.

d. Advantages/Disadvantages. Advantages and disadvantages of soil vapor extraction are summarized below:

<u>Advantages</u>	<u>Disadvantages</u>
Minimal disturbance of the contaminated soil	There are few guidelines for the optimal design, installation, and operation of soil vapor extraction
Systems can be constructed from standard equipment	Theoretically based design equations defining the limits of this technology are lacking and system designs are mostly empirical
Systems have been demonstrated at pilot- and field-scale	
Systems can be used to treat larger volumes of soil than are practical for excavation	Alternative designs can only be compared by the actual construction, operation, and monitoring of each design
Systems have the potential for product recovery system	

(Continued)

<u>Advantages</u>	<u>Disadvantages</u>
Spills can be cleaned up before the chemicals reach the ground water table	Vapors and condensed liquids collected from the wells may require treatment prior to discharge to the air
Systems can be integrated with other cleanup technologies to provide complete restoration of contaminated sites	Extraction of volatile chemicals from clays and silts may be difficult
Can treat soils at depths greater than in range of excavation	Determining when the site is sufficiently clean to cease operation

e. Data Requirements. A number of variables characterize the successful design and operation of a vapor extraction system:

(1) Site conditions: Distribution of VOCs, depth to ground water, infiltration rate, location of heterogeneities including paved or sealed areas, temperature, atmospheric pressure.

(2) Soil properties: Permeability, porosity, organic carbon content, soil structure, soil moisture characteristics, particle size distribution.

(3) Control variables: Air withdrawal rate, well configuration, extraction well spacing, vent well spacing, ground surface covering, inlet air VOC concentration and moisture content, pumping duration.

(4) Response variables: Pressure gradients, final distribution of VOCs, final moisture content, extracted air concentration, extracted air temperature, extracted air moisture, power usage.

(5) Chemical properties: Henry\*s constant, solubility, adsorption equilibrium, diffusivity (air and water), density, viscosity.

f. Design Criteria. The design and operation of soil vapor extraction systems can be quite flexible; changes can be made during the course of operation with regard to well placement, or blower size, or air flows from individual wells. If the system is not operating effectively, changes in the well placement or capping the surface may improve it. Based on the current state of the technology of soil vapor extraction systems, the following design criteria can be recommended.

(1) Intermittent blower operation is probably more efficient in terms of removing the most chemical with the least energy.

(2) Extraction wells are usually screened from a depth of from 1.5 to 3 m (5 to 10 feet) below the surface to the ground-water table. For thick zones of unsaturated soil, maximum screen lengths of 6.1 to 9.1 m (20 to 30 feet) are specified.

(3) Air/water separators are simple to construct and should probably be installed in every system.

(4) Installation of a cap over the area to be vented reduces the chance of extracting water and extends the path that air follows from the ground surface, thereby increasing the volume of soil treated.

(5) Incremental installation of wells, although probably more expensive, allows for a greater degree of freedom in design. Modular construction where the most contaminated zones are vented first is preferable.

(6) Use of soil vapor probes in conjunction with soil borings to assess final cleanup is less expensive than use of soil borings alone. Usually a complete materials balance on a given site is impossible because most sites have an unknown amount of VOC in the soil and in the ground water.

(7) Soil vapor extraction systems are usually only part of a site remediation system.

(8) Although a number of variables intuitively affect the rate of chemical extraction, no extensive study to correlate variables to extraction rates has been identified.

(9) Well spacing is usually based on some estimate of the radius of influence of an individual extraction well. Well spacing has ranged from 15 to 100 feet. Well spacing should be decreased as soil bulk density increases or the porosity of the soil decreases. One of the major differences noted between systems was the soil boring diameter. Larger borings are preferred to minimize extracting liquid water from the soil.

(10) Wells should be constructed with approximately 20 feet of blank casings between the top of the screen and the soil surface to prevent the short circuiting of air and to aid in the extraction of deep contamination.

(11) Initial VOC recovery rates are relatively high, then decrease asymptotically to zero with time. Several studies have indicated that intermittent venting from individual wells is probably more efficient in terms of mass of VOC extracted per unit of energy expended. This is especially true when extracting from soils where mass transfer is limited by diffusion out of immobile water.

(12) Optimal operation of a soil vapor extraction system may involve taking individual wells in and out of service to allow time for liquid diffusion and to change air flow patterns in the region being vented.

(13) Air injection has the advantage of controlling air movement, but injection systems need to be carefully designed.