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# HAZARDOUS WASTE MANAGEMENT

## TREATMENT TECHNOLOGIES FOR HAZARDOUS WASTES: PART II

# Alternative Techniques for Managing Solvent Wastes

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*There are economic and regulatory incentives for considering alternatives to the direct land disposal of solvent-bearing hazardous waste streams (EPA Hazardous Waste Codes: F001, F002, F003, F004, and F005). These alternatives include recycle/reuse (including use as a fuel substitute), destruction of a stream's solvent component, and treatment prior to land disposal. This paper reviews these three waste management alternatives and discusses their applicability to solvent waste streams having various physical characteristics. Seven waste treatment techniques which may be used to handle solvent wastes are described: incineration, agitated thin-film evaporation, fractional distillation, steam stripping, wet oxidation, carbon adsorption, and activated sludge biological treatment.*

In November 1984, Congress amended the Resource Conservation and Recovery Act (RCRA) to restrict the land disposal of a number of hazardous wastes. Various types of waste will be banned from land disposal* unless the EPA determines that: 1) there are land disposal options which do not threaten human health and the environment, or 2) there are waste treatment options which will alter the waste and thereby minimize the risk of its land disposal.[1] The first two wastes are scheduled to be banned in November 1986. They are dioxin and solvent wastes.

This article characterizes the solvent wastes which Congress listed for banning and describes techniques for treating these wastes, either to make them amenable to land disposal, or as alternatives to land disposal. An earlier article in this journal[2] described those treatment techniques which are applicable to dioxin wastes.

## Solvent Wastes

### Sources

The 1984 RCRA Amendments specify five categories of solvent wastes which are to be banned from land disposal. They have EPA Waste Codes F001, F002, F003, F004 and F005. These wastes are comprised of certain spent halogenated and nonhalogenated solvents as listed in Table I, along with sludges or still bottoms from the recovery of these solvents.

The five solvent waste categories include two containing halogenated solvents (F001 and F002) and three containing nonhalogenated solvents (F003, F004 and F005). All except category F003 were listed by the EPA because their solvent component is toxic. The compounds in category F003, are hazardous because they are ignitable. This category has already been banned from land disposal, but will be discussed here since many solvent-derived waste streams contain these chemicals.

### Characteristics

Large volumes of solvent wastes are generated annually in the United States. It is estimated that in 1981, 3.1 billion gallons of these wastes were generated. Of these, approximately 1.2 billion gallons would be covered by proposed land disposal restrictions.[3] Solvent wastes are usually organic liquids or sludges (e.g., still bottoms are included) at the point of generation. However, in some instances they become mixed with water between the point of generation and disposal, and the resultant of aqueous waste streams are included in the solvent waste category. The treatment of these aqueous, organic liquid, and sludge waste streams will be the focus of this article.

### Degree of Required Treatment

As noted above, all but the F003 wastes are listed because of the toxicity of their constituents. Land disposal of these wastes may not eliminate the health effects and the flammability of F003 solvents for which they were originally listed. The low molecular weight organic constituents of solvent wastes may react with synthetic liners used in landfills and surface impoundments, thereby reducing liner integrity. Their low molecular weight also makes the organic constituents mobile and some have been shown to readily pass through liners. In addition, these compounds are all volatile to some degree and will be emitted to the air at the disposal site. The EPA is considering all these factors in determining to what degree wastes must be treated in order to minimize the risks of land disposal. At present, it appears that if pretreatment regulations are set on the basis of maximum concentrations that will be allowed in the land disposal of solvent wastes, levels of a few parts per million or less will be required.

## Waste Treatment Alternatives

There are four principal options to

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* The amendments excluded deep well injection from the ban until after November 1988.

Table I. Regulated waste solvents.[a]

| EPA Waste Code | Solvents[b] |
|---|---|
| F001 | Spent halogenated solvents used in degreasing: tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons |
| F002 | Spent halogenated solvents: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloro- 1,2,2-trifluorethane, ortho-dichlorobenzene, and trifluoromethane. |
| F003 | Spent nonhalogenated solvents: xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, *n*-butyl alcohol, cyclohexane and methanol. |
| F004 | Spent nonhalogenated solvents: cresols and cresylic acid, and nitrobenzene. |
| F005 | Spent nonhalogenated solvents: toluene, methyl ethyl ketone, carbon disulfide, isobutanol, and pyridine. |

[a] Source: 40 CFR 261.31.

[b] Besides spent solvents containing these compounds, still bottoms from the recovery of these spent solvents are also included under each of the five waste codes.

direct land disposal of solvent wastes. They are:

1. Destructive treatment, including thermal oxidation;
2. Removal of toxic or flammable constituents prior to land disposal;
3. Recycle/reuse, including use as a fuel substitute; and
4. Reduction or elimination of waste generated.

The fourth option is one which is being pursued by many generators, since it is often preferable to the increasing costs of waste management. This article will address the first three options.

The choice of treatment technique will be dependent upon several factors, including: waste composition, waste volume and treatment cost. This article addresses the influence of waste composition on choice of treatment technique. First, we discuss general procedures for deciding how to treat three broad categories of solvent-bearing wastes: 1) aqueous and mixed aqueous/organic liquids, 2) organic liquids and 3) sludges. Then we describe a number of specific treatment techniques which are applicable to solvent wastes.

For the purposes of this paper, we distinguish between streams of very low solids content and those with greater than 1 or 2 percent solids content, which we define as sludges. Streams of low solids content are defined as, aqueous, mixed aqueous/organic or organic streams. Aqueous streams have water content of 95 percent or higher, while organic streams are defined as containing 50 percent or more organic liquids. Mixed aqueous/organic streams fall in between.

There will always be some ambiguity regarding the choice of one of these three categories for a given waste, and the exact composition of the waste stream and economic considerations will dictate what treatment steps are most important. However, categorization of solvent wastes into these three groups helps to structure the following discussions of available the treatment options.

Table II. Treatment processes potentially applicable to aqueous and mixed aqueous/organic solvent waste treatment.

- Phase separation
  - Decanting/sedimentation
  - Filtration
  - Flotation
  - Centrifugation
- Preliminary treatment
  - pH adjustment
  - Dissolved solids precipitation
- Organic component separation
  - Air or steam stripping
  - Fractional distillation
  - Solvent extraction
  - Carbon or resin adsorption
- Organic component transformation
  - Biological degradation
  - Chemical oxidation
  - Incineration
  - Wet oxidation

## Aqueous and Mixed Aqueous/Organic Wastes

Generally, any liquid waste composed of more than 50 percent water and small amounts of solids can be classified as an aqueous or a mixed aqueous/organic waste. A simplified decision tree for treating these wastes is shown in Figure 1 and potentially applicable treatment techniques are listed in Table II. In some cases, it may be appropriate to treat these wastes directly by incineration (see Incineration, below). In most instances it will be more economical to use other treatment techniques (although future regulations could shift this balance or make incineration the only allowable option). If the waste consists of two liquid phases, simple phase separation can be used first to remove the undissolved organic phase which can then be reused or treated following the steps in Figure 2. Gross solids may also be separated out at this point by such techniques as sedimentation or filtration. Further preliminary treatment of the aqueous stream may be required to remove suspended or dissolved solids, to obtain a proper pH or to prepare the stream in other ways for the principal treatment step. There are two general options available for treating the "pretreated" aqueous stream: 1) removal of the organic constituents (component separation) or 2) in-situ destruction of those constituents (component transformation).

Table III. Treatment processes potentially applicable to organic solvent waste treatment.

- Solids removal
  - Sedimentation
  - Filtration
  - Centrifugation
  - Flotation
  - Evaporation
- Organic component separation
  - Fractional distillation
  - Solvent extraction
  - Resin adsorption
  - Steam stripping
  - Air stripping
- Organic component destruction
  - Incineration

Dissolved solvents may be removed by such techniques as steam or air stripping. If such organic component separation processes are used, a new liquid organic stream will be created and some off-gases may be generated. Any byproduct liquid stream can be handled as shown in Figure 2. If the discharge rate of organic vapors is high, this residual stream will have to be captured and disposed of properly. Depending upon the effectiveness of any of these principal treatment techniques, the resultant aqueous stream may have a sufficiently low concentration of hazardous constituents to allow for direct land disposal, such as in a solar evaporation pond. Or, it may be acceptable for discharge to a municipal wastewater treatment system. If it does not meet environmental standards for one of these types of disposal, further, "polishing" treatment steps (e.g., carbon adsorption) will be required.

Alternatively, chemical oxidation, biological degradation, or incineration can be used to transform solvent constituents into $CO_2$ and water, or to some other compounds which have little impact of the environment. Since such treatment techniques operate most efficiently at low organic concentrations, they may reduce solvent concentrations sufficiently by themselves. In cases of highly toxic constituents, where very low (i.e. parts per billion) concentrations must be obtained, further treatment of the aqueous stream may be required.

### Organic Waste Streams

There are two principal alternatives to land disposal for managing wastes containing over 50 percent liquid organics and low solids content. These are:

1) Reuse (including use as fuel substitutes), and
2) Incineration.

Their use in managing organic liquid solvents streams is outlined in Figure 2. Table III presents processes that are potentially applicable to organic liquid waste in the treatment steps shown in Figure 2. Frequently, the waste stream must undergo some kind of pretreatment before incineration or reuse. As with aqueous streams, solids removal is usually the first consideration and similar removal techniques will be applicable. Once the major solid components have been removed from a waste which have a potential for reuse, separation of the organics in the waste is often desirable. For example, organic impurities are generally unacceptable if the predominant compound is intended as a manufacturing feed stock, but may be acceptable for some degreasing operations. Similarly, if several compounds are present at high concentrations, it may be most profitable to separate them for different uses. Both are situations in which organic separation processes are required as a final step in solvent reclamation.

Sludges from solids removal steps will contain some fraction of liquid solvent and will need to be treated as described below. The bottoms from some organic separation steps may be sludges, high boiling organic liquids, or aqueous phases. These may require further treatment prior to disposal, or can be directly reused (e.g., as a fuel).

### Sludges

As defined for the purpose of this article, sludges are wastes containing at least a few percent solids. There are four basic options to sludge treatment:

1. Solids removal, followed by treatment as a liquid waste;
2. Direct destruction of the waste (including reuse as a fuel substitute);
3. Removal of the solvent component, followed by sludge destruction; and
4. Removal of the solvent component, followed by stabilization/solidification.

Potentially applicable treatment techniques are listed in Table IV.

Solids removal techniques were addressed above when discussing Figures 1 and 2. Those techniques are generally only applicable to wastes with less than 20–30 percent solids content.

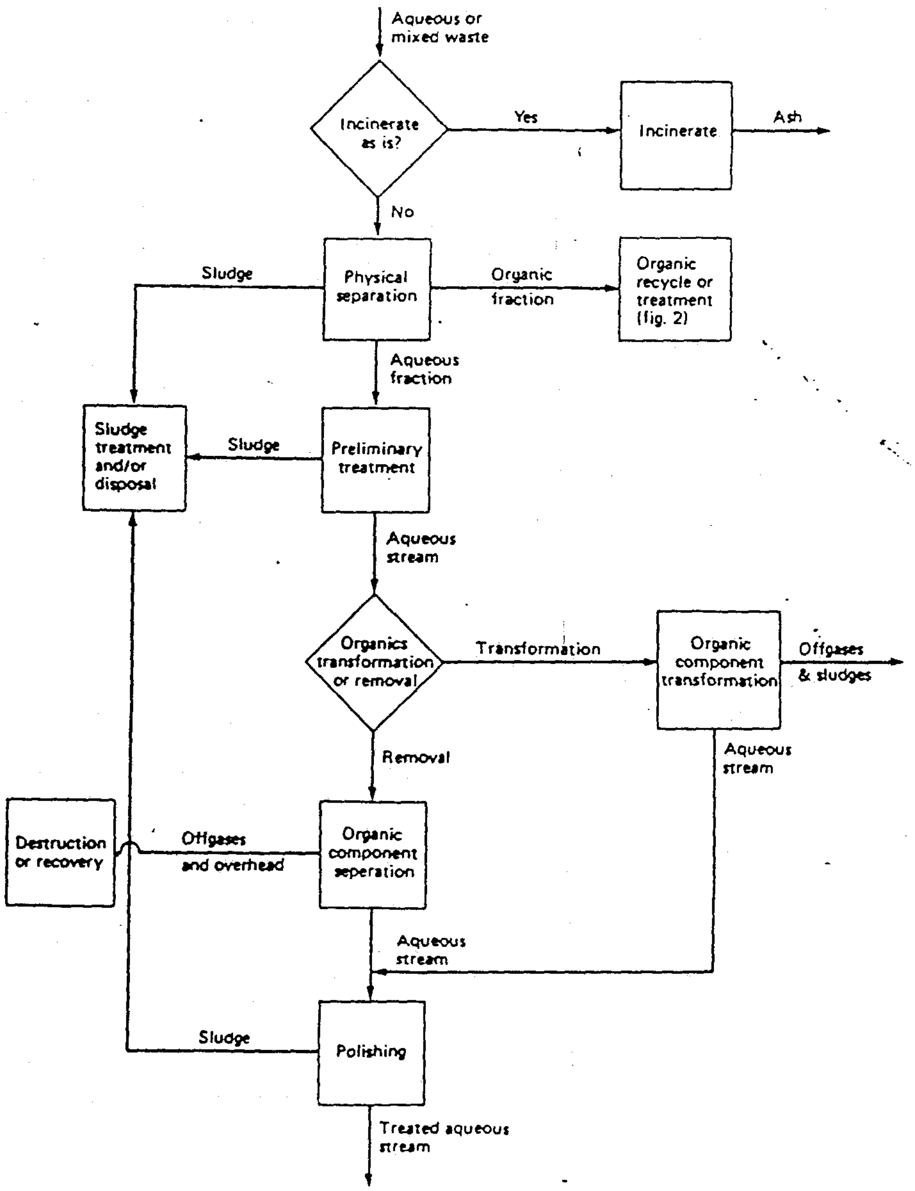

**Figure 1.** Simplified decision chart for aqueous and mixed aqueous/organic solvent waste stream treatment.

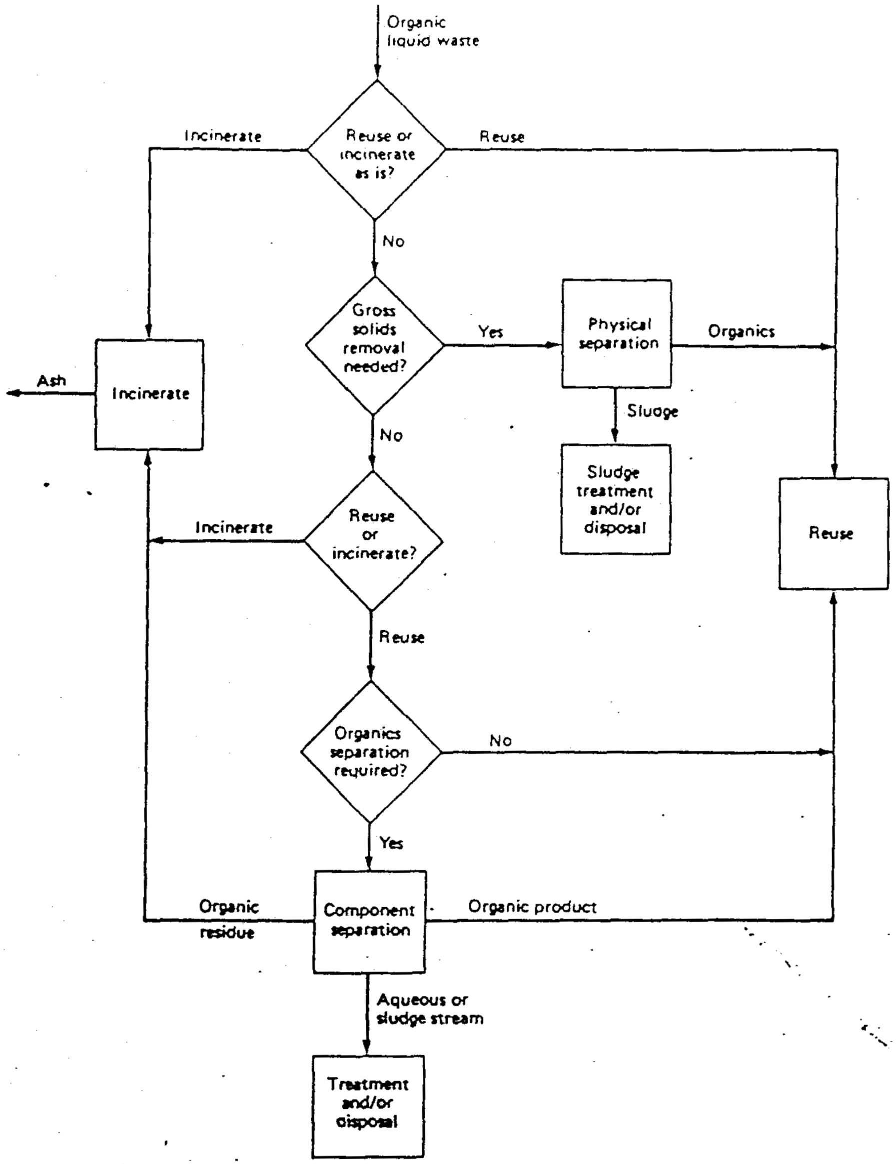

**Figure 2.** Simplified decision chart for organic liquid solvent waste stream treatment.

For solvent sludges of higher solids content, ultimate disposal will generally be direct thermal destruction, treatment plus thermal destruction or, possibly, stabilization/solidification. The choice between these three options will be dictated to a large extent by 1) amenability of the waste to thermal destruction; 2) monetary benefits from solvent recovery from the waste and 3) technical and regulatory requirements for stabilization/solidification.

Direct destruction can be accomplished through thermal incineration or wet oxidation. These two processes are discussed in more detail below. Sludges can also be used as fuel substitutes in a number of industrial processes, including cement kilns, blast furnaces and aggregate drying kilns. Use in these processes requires that the wastes be atomizable, have low chlorine content and have a Btu content of over 8,500 Btu/lb.

There are several techniques which can be used for solvent removal, including drying processes, screw evaporators, or air or steam stripping. Our observation is that only a small percentage of recycling firms are using such techniques for solvent removal from sludges produced by other treatment processes (e.g., thin-film evaporation). Instead, they are incinerating or landfilling such sludges. It therefore appears that in the current, pre-land disposal ban regulatory climate, there is little economic incentive for solvent removal from wastes of high solids content.

Stabilization and solidification of wastes can be accomplished by processes which utilize cements, fly ashe lime, pozzolans and similar materials. Thermoplastics and other polymeric materials are also sometimes used to microencapsulate hazardous compounds. However, there still is uncertainty about the general applicability of stabilization/solidification to solvent wastes, since organic compounds often interfere with the reactions involved in such processes. EPA is conducting research on the effectiveness of various solidification techniques and is developing criteria which stabilized-/solidified wastes must meet in order to make them acceptable for land disposal.[4]

**Table IV.** Treatment processes potentially applicable to solvent sludges.

- Organic component separation
  - Air or steam stripping
  - Evaporation
  - Drying
- Organic chemical destruction
  - Incineration
  - Wet oxidation
- Stabilization/solidification
  - Cement-based fixation
  - Pozzolanic fixation
  - Urea-formaldehyde polymerization
  - Thermoplastic encapsulation

## Solvent Treatment Techniques

As is evident from Tables II–IV, there are numerous waste treatment techniques applicable to solvent wastes in order to recycle them or to dispose of them in an environmentally safe manner. The rest of this paper will discuss a select number of those techniques: 1) incineration, 2) techniques which are frequently used for recycling (i.e. treating wastes with high organic content of 50 percent or higher), and 3) techniques which may be used to remove or transform organic constituents in aqueous or mixed waste streams with low to medium organic concentrations. (For a general discussion of waste treatment options, including initial phase separation and water polishing processes, see References 5–8)

In the following discussion, the waste treatment techniques are broken out by the concentration of organics in the waste which they are typically used to treat. Although there is not a clean-cut categorization of treatment techniques based on influent waste stream organic concentration, three general categories of concentration are used: high (10–100 percent), low-medium (0.1–10 percent), and low (below 1000 ppm).

The discussion of each of these techniques will include a brief description of its operation principles and its current uses for solvent waste treatment. A description of the limitations associated with using these techniques to treat solvent wastes, if any, will be provided, with particular emphasis on treating 1) solvents containing halogenated versus nonhalogenated compounds and 2) liquid versus sludge streams.

### Streams of High Solvent Concentration

*Incineration.* Incineration is the thermal oxidation of wastes at high temperatures for the purpose of destroying the material. There are approximately 200 hazardous waste incinerators operating in the United States under permits which require them to destroy waste stream principal organic hazardous constituents (POHCs) with an efficiency of at least 99.99 percent.

There are two principle types of hazardous waste incinerators in use in this country: liquid injection and rotary kiln. A liquid injection system consists of one or more refractory lined combustion chambers into which waste and any required fuel are injected through atomizing nozzles. The nozzles are arranged to promote a turbulent flow of the waste through the chambers to ensure exposure of all waste to high temperatures and to combustion air. Typical chamber residence times and temperatures are 0.5–2 seconds and 700–1650°C, respectively. The combustion gases are cooled and pass through a series of pollution control devices prior to release to the atmosphere. Liquid injection incinerators can only handle atomizable wastes and are not generally designed for wastes which will leave large amounts of ash residue.[9,10]

A rotary kiln incinerator is a refractory-lined cylinder mounted at a slight incline and followed by an afterburner (Figure 3). The kiln mixes waste and combustion gases through its rotary motion, converting waste to gases and an ash residue through partial burning and volatilization. The gases then pass to the high temperature afterburner where the combustion reactions are completed. Rotary kilns are capable of handling solids, sludges, liquids or gaseous wastes.[9,10]

Essentially all solvent wastes of high organic content should be amenable to incineration in either liquid injection or rotary kilns. In fact, it is estimated that 60 percent of the wastes being incinerated in 1981 were solvent-derived wastes.[11] While the majority of these incinerated solvents were nonhalogenated liquids, halogenated liquid and solvent sludges were also disposed of through incineration.

Halogenated solvent constituents have lower heat content than nonhalogenated solvent constituents and result in hydrochloric acid in exhaust gases. These two drawbacks can be overcome by blending with nonhalogenated wastes and by use of HCl emissions control devices. Solvents sludges, some of which are currently being sold to cement kilns as supplementary fuel, can be handled in rotary kilns. Particulate control equipment must be adequate to meet existing emissions regulations.

While the heating value of wastes decreases with increased content of water and other inorganics, these wastes still can be incinerated. Supplementary fuel can be used to produce the required combustion chamber temperature or the waste stream can be blended with other wastes to provide an adequate heating value of the incinerator feed. In some cases, operators mix wastes of high water content with other highly flammable wastes in order to limit the combustion chamber temperatures to within design specifications, while maintaining high feed rates. Alternatively, water can serve as a source of hydrogen to promote more complete combustion of high molecular weight hydrocarbons.[11]

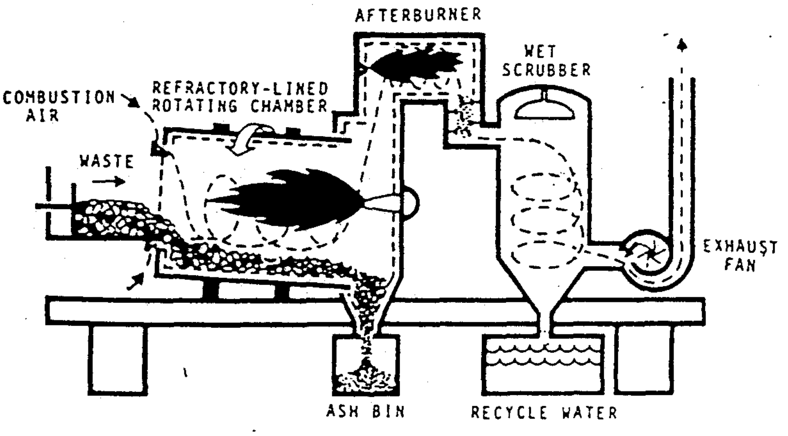

**Figure 3.** Rotary kiln incineration. Source: adapted from brochure of Combustion Engineering, Inc., Chicago, Illinois.

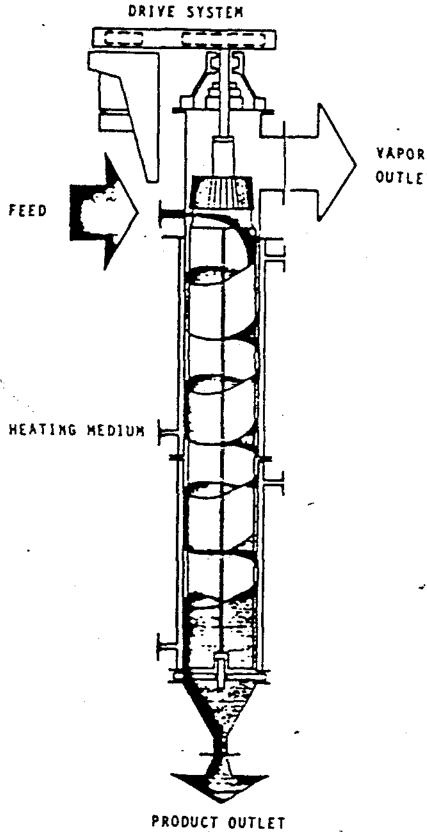

**Figure 4.** Flow path of agitated thin-film evaporator. Source: adapted from Reference 13.

The ashes from waste incineration must be analyzed to determine whether or not they are hazardous. Nonhazardous ashes can be disposed of in landfills following standard procedures for such wastes, while hazardous ashes will have to be stabilized prior to disposal at a RCRA-permitted site.

*Agitated Thin-Film Evaporation.* Evaporation is the removal of a solvent (including water) as a vapor from a solution or a slurry (a pumpable solid-liquid mixture).[12] Agitated thin-film evaporation relies on the exposure of a large surface area of heated waste to atmospheric or vacuum conditions to enhance the separation of more volatile constituents from the waste by evaporation. Waste is spread on the walls of a cylindrical or tapered tube by an assembly of wiper blades. A heated outer shell elevates the temperature of the waste.[13] Figure 4 shows one design of a thin-film evaporator. Typical operating characteristics of such units are shown in Table V.

Table V. Typical operating characteristics of thin-film evaporators.[a]

Size: 1 to 430 ft$^2$ of heat transfer surface
Capacity: Steam heated:
Water evaporation, 160 kW/m$^2$ (50,000 Btu/h ft$^2$)
Organics distillation, 63 kW/m$^2$ (20,000 Btu/h ft$^2$)
Hot oil heated: organics distillation, 25kW/m$^2$ (8,000 Btu/h ft$^2$)
Operating pressure: Standard (full vacuum to atmospheric pressure)
Special (any positive pressure)
Heating steam in jackets: Up to 1.4 MPa (200 psig)
Maximum hot-oil temperature: Up to 350°C (650°F)
Liquid throughput: Up to 900–1100 kg/m$^2$ (200–250 lb/h ft$^2$)
Pressure drop (vapor flow): 0.5 mm Hg
Overhead to bottoms splits: Up to 100 to 1
Residence time: Uncontrolled, 3–10; Controlled, 3–100 s
Product viscosities: Up to 10,000 cp. at operating conditions
Blade tip speed: Nonscraping blades, 9–12 m/s (30–40 ft/s)
Scraping blades, 1.5–3 m/s (5–10 ft/s)
Recommended maintenance: Twice a year, more often when processing extreme products

[a] Source: Reference 13.

There are two major advantages from waste agitation by the wiper blades. First, it creates turbulence in the liquid, increasing the transfer of heat to the waste and of volatiles to the waste surface, where they evaporate. Second, the wiper blades maintain a more uniform film and even flow of the liquid through the unit, which is particularly important when the waste is viscous and/or contains solids.

Agitated thin-film evaporators are the "work horse" of many solvent waste recycling firms. They provide the first step in the processing of those solvent wastes which are suitable for recycling, i.e., those with sufficiently high percentage of recoverable organics (typically over 60–70 percent). Wastes are treated by agitated thin-film evaporation to separate the solvents from solids and high boiling organics. The overhead fraction is often processed further by distillation, water extraction, etc., prior to reuse. Currently, some solvent-bearing bottoms are sold as a supplemental fuel. Alternatively, bottoms are being disposed of in secured landfills, a process which is likely to become unacceptable. These bottoms should be amenable to incineration.

Thin-film evaporators can be used to treat liquid wastes and sludges of low solids content. Waste viscosities generally cannot exceed 100 poise and the size of solids in a sludge is limited by the clearance of the agitator blades (typically less than 2.5 mm). Reactive wastes, such as those which will polymerize, cannot generally be treated using thin-film evaporators because of the elevated temperatures. However, some agitated thin-film evaporators are designed to minimize the waste residence time in order to reduce this problem.[13]

There is little distinction in the ability of agitated thin-film evaporators to process halogenated or nonhalogenated wastes, except that the bottoms from halogenated waste treatment are not generally acceptable as a supplementary fuel unless the concentration of halogenated compounds is less than a few percent.

*Fractional Distillation.* In the most general sense, the term "distillation" describes the separation of two or more components of a liquid mixture by the vaporization and recovery of the vapor.[12] Distillation involves application of heat to a liquid mixture, vaporization of part of the mixture, and removal of heat from the vaporized portion to condense it. The resultant distillate is richer in the more volatile components, and the residual bottoms are richer in the less volatile materials.[13]

In simple distillation, or "equilibrium vaporization," there is one equilibrium present between the liquid and gas phases in the process. Simple distillation, like evaporation, yields a crude separation of the feed stream components. The condensate will be richer in the more volatile constituent, but often simple distillation is inappropriate for

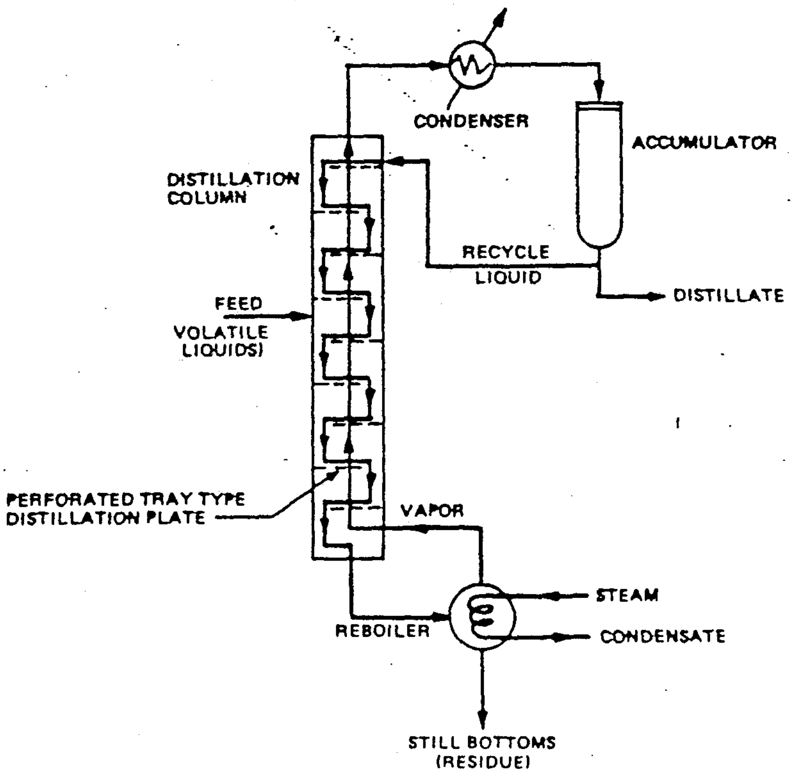

Figure 5. Continuous fractional distillation system. Source: Reference 5.

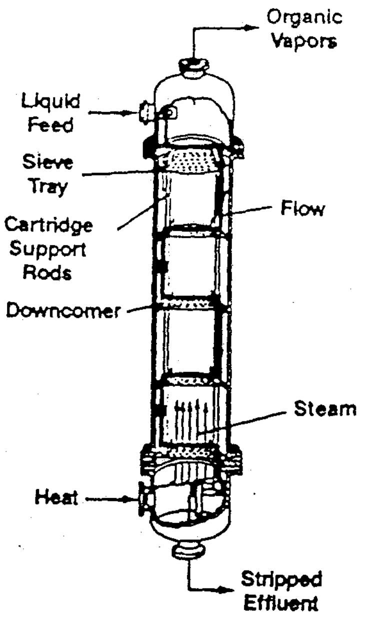

**Figure 6.** Continuous steam stripping column—perforated tray type. Source: Pfaudler, Rochester, New York.

solvent reuse because of impurities of less volatile components which are carried over from the feed stream.

Multi-stage, or "fractional," distillation produces an overhead product which is more enriched in low boiling components than is possible with a single evaporation and condensation operation. Fractional distillation utilizes a series of liquid-vapor equilibria inside a vertical tower to provide a vapor which has progressively higher concentrations of the most volatile component.

Figure 5 shows a continuous fractional distillation column. Waste is fed into the middle of the column. The concentrations of more volatile components of the waste are increased in the upper, or "enrichment," section of the column, while in the lower, or "stripping," section of the column volatile components have progressively lower concentrations. The distribution of less volatile components in the column is just the opposite. When desired, reflux from the condenser is fed back into the top of the column to yield even higher concentrations of high volatiles in the overhead vapor.

In a batch fractional distillation unit there is no stripping section to the column. Waste is charged to the reboiler and the column just serves to enrich the concentration of volatile components in the distillate. Part of the condensate is generally returned to the top of the column to provide a countercurrent liquid stream to contact with the rising vapor. This "partial reflux" may be used to lengthen the distillation time while minimizing the amounts of less volatile compounds which are distilled, thus removing more of the volatile components from bottoms. Partial refluxing was required, for example, when using distillation to reduce the organic composition of aqueous wastes in the examples described below.

Since the volatile components in the overhead of a fractional distillation column will be more concentrated than in a single stage evaporater, their concentrations in the process bottoms will be even lower. Fractional distillation is, for example, used by some recycling firms to reduce the concentration of organics in their wastewater discharge to levels acceptable to municipal treatment facilities. Organic concentrations below 1000 ppm have been obtained in such instances. For example, recent field tests by the EPA at one recycling firm studied the batch fractional distillation of two mixed aqueous/organic streams. One contained approximately 95 percent water; 3 percent methylethyl ketone; and 2 percent alcohol, chlorinated hydrocarbons and other organics. The second stream contained 77 percent water, 21 percent acetone, and 2 percent other organics. Fractional distillation of these two streams resulted in 99 percent removal of the organics in the aqueous bottoms.[13]

As with thin film evaporation, distillation can be used to remove both chlorinated and nonchlorinated solvents from a waste stream. The solids content of a distillation stream is limited, however, since solids may clog the column or the coils in the reboiler. For this reason, many waste recycling firms use thin film evaporators to separate out solids prior to fractional distillation.

Fractional distillation is frequently

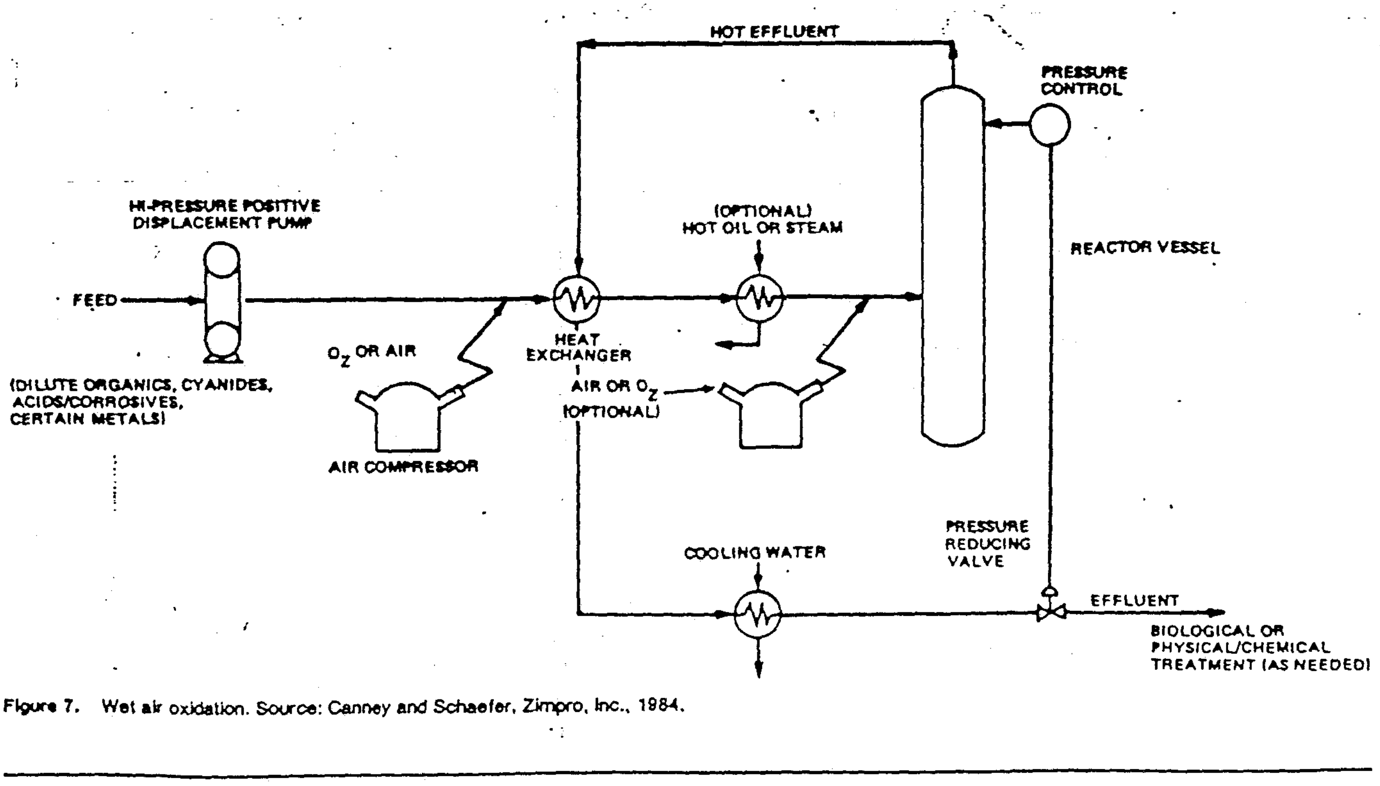

**Figure 7.** Wet air oxidation. Source: Canney and Schaefer, Zimpro, Inc., 1984.

found at solvent recycling firms. Such units provide adequate separation of solvent components from liquid waste streams to allow many of the solvents to be recycled, even to processes requiring high solvent purity, such as electronic component manufacturing.

### Streams of Low to Medium Solvent Concentration

*Steam Stripping.* Steam stripping is a form of simple distillation in which steam is injected into a waste in order to separate the more volatile components out of the waste. Steam stripping is not generally used for streams of high organic content, since the processor usually wants to avoid further water contamination.

Steam stripping can be performed in the batch or continuous mode. In the batch process, waste is charged to a boiler and steam is injected directly into the waste. The injection of live steam both heats the waste to volatilize low boiling components and creates turbulence in the waste, thus increasing the rate of volatilization. The gases which are condensed from a steam stripper will contain water along with the more volatile organic components of the waste in the form of a two phase mixture. This mixture is decanted and the organic component is drawn off for reuse or disposal. The aqueous layer is fed back to the stripper for further treatment.[14]

In continuous steam stripping, waste flows down a column while steam flows up (see Figure 6). The column is designed to promote heat transfer from the steam to the waste, to cause turbulence in the waste and to create a large waste surface area. All of these properties promote transfer of volatile components from the waste to the gas phase. Different liquid-vapor equilibria exist in the column, with the highest relative concentration of the most volatile components found at the top.

Both steam strippers and batch distillation units can be used to remove volatile organics from aqueous or mixed organic waste streams. Batch distillation can be used to separate the various organics from each other as part of the stripping process. Such a separation will not occur with steam stripping, but if separation of the organics in the overhead is unimportant, steam stripping is the preferred mode of operation since it has lower capital costs and is generally cheaper and easier to operate. In addition, steam strippers are not as easily fouled as batch distillation reboilers because there are no coils involved and the steam maintains the waste in a turbulent state.

One major drawback to steam stripping is the wastewater residual that is produced after decanting. If the volatiles to be removed from the waste do not readily dissolve in water, then the organic concentration of the aqueous decantent is low enough that further treatment of this water is either not needed, or can be accomplished by simply mixing the material with the feed. However, if the volatilized organic is somewhat water soluble (e.g., methyl ethyl ketone) further treatment of the aqueous effluent will be necessary before discharge.

*Wet Oxidation.* Wet oxidation is an industrial wastewater treatment technique which has been used to treat waste streams which are too toxic to be biodegraded but too dilute to be economically incinerated.[15-17] The process is potentially applicable to solvent sludges, if adequate steps are taken to destroy those portions of the solvents which volatilize during treatment. Wet oxidation involves the oxidation of organic compounds by oxygen or air at high temperatures and pressures. If the reaction is sufficiently exothermic, it can be thermally self-sustaining.

A simplified schematic diagram of a continuous wet oxidation process is shown in Figure 7. In this "wet air oxidation" unit, waste is mixed with air under pressure, heated and then fed to a reaction vessel. The effluent is passed through an influent heat exchanger and discharged to a separator, where noncondensible gases are separated from the liquid and directed into a two-stage water scrubber/carbon bed adsorber, vapor treatment system. This particular reactor was designed to operate at 280°C, 136 atmospheres and 2.3 $m^3/h$ (10 gpm).

Because of its high capital cost, wet oxidation has received limited use in treating conventional wastewater; it was originally considered cost-effective only where energy recovery was possible.[18] The technique has been shown to be economical for hazardous wastes due to the high cost of other disposal alternatives.[16]

Due to its limited application, it is difficult to draw generalities about the applicability of wet oxidation to solvent waste streams. Randell[19] has shown that it may have potential. In batch laboratory tests, he found that greater than 99 percent destruction of aliphatics, halogenated aliphatics, and aromatics can be obtained. However, halogenated aromatic compounds are resistant to destruction under conventional operating conditions. Other problems were identified when processing solvent-bearing wastes in the field. Field units are typically operated in a continuous mode and a portion of the solvents (all of which are volatile to some degree) are released with the process off-gas from such units and must be captured and destroyed.[18]

The volatilization of significant amounts of solvents from aqueous streams during wet oxidation suggests that this technique may have no more usefulness than steam or air stripping unless there is other material present in the waste which needs to be destroyed or might foul an air or steam stripper. For this reason, wet oxidation is likely to be most applicable to solvent-bearing sludges, such as still bottoms. For such wastes, continuous-mode wet air oxidation would destroy the heavy organics and some fraction of the solvents. Volatilized solvents could be handled by incineration, or by condensation and solvent reuse. Alternatively, batch wet oxidation could be used and the volatilized organics recycled until they were destroyed.[20]

### Streams of Low Solvent Concentration

*Carbon Adsorption.*[14] Liquid-phase carbon adsorption removes organics from dilute aqueous streams by adsorbing them onto an activated carbon matrix of high surface area. This matrix can then be regenerated using thermal oxidation, which destroys the organics, or using a nondestructive process (e.g. steam stripping), which allows for reclamation of the organics. Regeneration has found increased use as disposal of spent carbon becomes more expensive.

Carbon adsorption has been used extensively to remove organic pollutants from drinking water and wastewater streams. It is has been applied to aqueous streams with organic solute concentrations up to 1 percent, but is generally used for streams of less than 1000 ppm organics. The carbon loading (weight fraction of solute adsorbable on carbon) increases as the influent solute concentration increases, thereby resulting in more efficient solute removal and carbon utilization. The flow rate of the waste stream does not affect the technical capabilities of the removal process, but does impact treatment economics since carbon treatment benefits significantly from economies of scale, especially where thermal reactivation is used.

Some pretreatment of the waste stream may be required prior to processing through carbon. Suspended solids in the waste influent generally are reduced to less than 50 ppm by settling and filtering, although levels of up to 2000 ppm have been handled in specially designed units.

Oil and grease in the waste stream should be less than 10 ppm to avoid carbon fouling. High levels of dissolved inorganics may cause scaling or loss of carbon activity during thermal carbon reactivation, but in many cases such problems can be minimized through pH control and softening of the waste influent or by acid washing of the carbon before reactivation.

While thermal regeneration is the most frequently used alternative to direct disposal of spent carbon, nondestructive regeneration processes are also available. Steam stripping is generally applied to remove highly volatile compounds, including some solvents, from carbon. Alternatively, another solvent can be used to remove the adsorbate from the carbon. Distillation is then used to separate the two organic compounds, allowing reuse of the solvent that was originally removed from the waste stream by carbon adsorption.

The degree to which carbon adsorption can be used to remove small concentrations of solvents from wastewater stream will be dependent on a number of factors, including the compound(s) to be removed, concentrations of other organics in the stream and choice of carbon material. Most of the compounds listed as solvents are priority pollutants and studies of these pollutants show that in distilled water their affinity for water varies over two orders of magnitude.[21] A comparison of a carbon's affinity of 1,2-dichlorobenzene dissolved in distilled water to its affinity in a wastewater containing 200 mg TOC/L showed a decrease in affinity by factors of 3 to 9 for four different carbons.[22] Comparison of affinity of benzene and carbon tetrachloride for different commercial granular carbons showed a variation of up to a factor of 3.[23] The overall conclusion from these several studies is that the ability of carbon adsorption to remove solvent compounds from waste streams is dependent upon stream composition and treatment process design and will require bench-scale tests to ensure treatment optimization.

*Activated Sludge Biological Treatment.* A number of biological degradation processes have been used to destroy organic pollutants in industrial and municipal wastewaters. These include: activated sludge, aerated lagoons, trickling filters, and stabilization ponds.

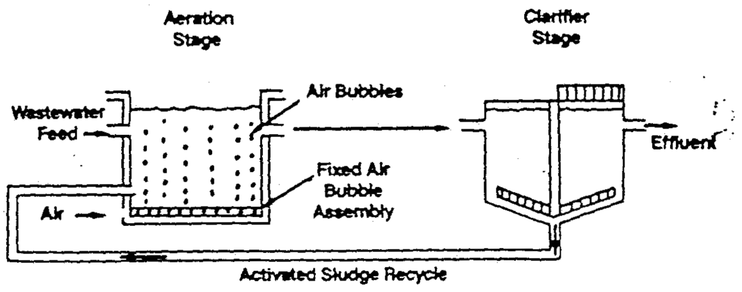

Figure 8. Activated sludge biological treatment.

There are several factors which must be considered when comparing the biological degradation techniques applicable to aqueous waste streams, including: efficiency of degradation, required holding time and susceptability to destruction of the microbial environment. Aerated lagoons, stabilization ponds and trickling filters have been found to be resistant to microorganism destruction due to variation in influent stream composition. However, they each have a drawback when compared to activated sludge. Trickling filters are generally not efficient enough to be used alone for biodegradation; they are usually followed by some other biological treatment process. Trickling filters are often used upstream of activated sludge systems to provide a more uniform influent composition. Aerated lagoons also have lower removal efficiencies than activated sludge systems and are less flexible in maintaining effluent limitations under varied influent loading. Stabilization ponds are more sensitive to inorganics and solids than are the other three processes and require substantial land acreage and suitable climatic conditions.[5]

Activated sludge treatment is extensively used in industry and is probably the most cost-effective method of destroying organics present in aqueous waste streams. It is characterized by a suspension of aerobic and facultative microorganisms maintained in a relatively homogenous state by mixing or by the turbulence induced by aeration. These microorganisms oxidize soluble organics and agglomerate colloidal and particulate solids in the presence of dissolved molecular oxygen. The process can be preceded by sedimentation

**Table VI.** Removal efficiency of activated sludge systems for selected organics in industrial wastewater.[a]

| Compound | Systems studied | Removal efficiency,[b] % Range | Median |
|---|---|---|---|
| Benzene | 9 | 75 to >99 | >99 |
| Carbon tetrachloride | 1 | | 98 |
| Chloroform | 20 | 9 to >99 | >99 |
| Methylene chloride | 8 | 38 to 99 | 69 |
| 1,1,1-Trichloroethane | 8 | 94 to >99 | >99 |
| Toluene | 33 | 17 to >99 | 95 |
| Xylene | 1 | | >99 |

[a] Source: Reference 24.
[b] Removal efficiencies are based on influent and effluent stream concentrations; partitioning of organics between biodegradation, stripping and sorption was not identified.

to remove larger and heavier solid particles if needed. The mixture of microorganisms, agglomerated particles, and wastewater (referred to as mixed liquor) is aerated in an aeration basin. The aeration step is followed by sedimentation to separate biological sludge from treated wastewater. The major portion of the microorganisms and solids removed by sedimentation are recycled to the aeration basins to be recombined with incoming wastewater, while the excess, which constitute the waste sludge, is sent to sludge disposal facilities.[22] A schematic of a typical activated sludge process is shown in Figure 8.

Activated sludge systems have been used extensively by industry for wastewater treatment, including those which produce solvent-bearing wastes: organic chemicals manufacturing, petroleum refining, paint and ink formulation, and gum and wood chemicals. In general, the systems should be able to readily degrade alkanes, alkenes, and aromatics. Halogenated hydrocarbons are degraded more slowly, but can be destroyed in many cases (see below). Potentially significant amounts of highly volatile solvents may be released from the system through volatilization, especially if the system is not properly operated (e.g., well mixed). In such instances, covered aeration basins with air pollution control may be required. If there are metals in the influent stream, these will often be concentrated in the waste sludge, posing problems for proper documentation or land disposal of this byproduct.

The activated sludge system treats aqueous organic streams having less than one percent suspended solids. The approximate upper limit to biological oxygen demand (BOD) of the influent stream which can readily be handled is 10,000 mg/L. The biodegradation process produces $CO_2$, water, organic products of partial biodegradation and microorganism cellular material.[23]

High efficiencies for removal of solvents from industrial wastewater streams have been obtained. Table VI presents data selected from a compilation of activated sludge efficiencies.[24] Removal efficiencies will vary depending upon a number of factors, including the concentration of the solvent relative to other organics in the waste stream, the variability of organics concentration with time and the operation of the activated sludge system. The percentages of removal shown are based on influent and effluent stream concentrations; the partitioning of the organics between biodegradation, stripping and sorption are not identified. System designs which capture stripped organics from offgases and which properly dispose of biosludge are required. Some form of thermal destruction is probably the best means of disposing of those compounds which leave the system through these two routes, instead of being biodegraded.

Activated sludge systems cannot tolerate high fluctuations in influent concentrations, but a number of steps can be taken to reduce this problem. Neutralization and equalization of the waste stream, as well as suspended solids removal, usually precede the activated sludge system. Trickling filters may also be employed upstream to reduce variations in waste stream composition. In addition, two operating characteristics of the process itself promote tolerance to such variations. First, activated sludge systems can be designed to thoroughly mix pollutants in the aeration basin. Secondly, recirculation of the activated sludge at 25–100 percent of the influent flow rate greatly helps to acclimate the biomass in the lagoon to the influent pollutants.[23,24]

## Summary

The toxicity, mobility and/or flammability of solvent wastes make it difficult to land dispose of them without significantly endangering the environment. Increased costs for this approach to disposing of these wastes and regulations which severely restrict such disposal will force waste generators to either reduce solvent generation rates or to utilize waste treatment or recycling as solvent waste management alternatives.

Alternatives to direct land disposal appear to exist for all solvent wastes, although the choice will be dependent upon waste composition, production rate and economics. Some techniques, such as incineration, are from a technical standpoint applicable to most solvent wastes, regardless of their composition. Recycling of solvent wastes which contain sufficiently high amounts of liquid organics to make recovery economical is presently practiced widely in the United States. Similarly, wastes with sufficient Btu value and low chlorine content are being used in a number of locations as fuel substitutes.

Mixed aqueous/organic liqu wastes are also be recycled if their organic component is sufficiently large to make recycling economical. Solvent constituents can be removed from aqueous streams by similar recycling techniques, but the cost will generally exceed the value of the recovered organics. Under anticipated regulatory incentives, such phase separation techniques may soon be the most economic means of disposing of aqueous and mixed aqueous/organic solvent wastes. Alternatively, these low concentration organics can be destroyed through chemical or biological treatment processes, or by incineration.

Sludges of low solids content can be disposed of in the same way as liquid wastes, but some sort of solids separation may have to precede the primary treatment step. Little data are available on the treatment of solvent sludges of high solid content other than by incineration. Techniques exist, however, which should be applicable to separating some fraction of solvent constituents from these wastes.

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## References

1. D. C. White, "EPA program for treatment alternatives for hazardous wastes," *JAPCA* 35: 369 (1985).
2. H. Freeman, R. A. Olexsey, "Treatment technologies for hazardous wastes: part I. A review of treatment alternatives for dioxin wastes," *JAPCA* 36: 66 (1986).
3. Office of Solid Waste, U.S. EPA, personal communications.
4. C. Wiles, Hazardous Waste Engineering Research Laboratory, U.S. EPA, private communication; and *Critical Characteristics and Properties of Hazardous Waste Solidification/Stabilization*, HWERL, U.S. EPA, Contract No. 68-03-3186 (in publication).
5. *Physical, Chemical and Biological Treatment Techniques for Industrial Wastes*, Office of Solid Waste, U.S. EPA, No. SW-148, 1977.
6. A. A. Metry (editor), *The Handbook of Hazardous Waste Management*, Tech-

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nomic Publishing Company, Inc., Westport, CT, 1980.

7. *Wastewater Engineering Treatment, Disposal, Reuse*, Metcalf and Eddy, Inc., McGraw-Hill Book Company, New York, 1979.
8. *Supplemental Report on the Technical Assessment of Treatment Alternatives for Waste Solvents*, Final Report for the Office of Solid Waste, U.S. EPA, Contract No. 68-03-3149, 1984.
9. W. E. Sweet, R. D. Ross, G. V. Verde, "Hazardous waste incineration: a progress report," *JAPCA* 35: 138 (1985).
10. H. M. Freeman, *et al.*, "Thermal destruction of hazardous waste: a state of the art review, *J. Hazardous Materials* (1986).
11. D. Oberacker, R. Mournighan, Hazardous Waste Engineering Research Laboratory, U.S. EPA, private communications.
12. R. H. Perry, C. H. Chilton, *Chemical Engineers' Handbook*, 5th Edition, McGraw-Hill Book Co., New York, 1973.
13. C. C. Allen, S. Simpson, G. Brant, *Field Evaluation of Hazardous Waste Pretreatment as an Air Pollution Control Technique*, HWERL, U.S. EPA, Contract 68-02-3992 (in publication).
14. J. J. Spivey, *et al.*, *Preliminary Assessment of Hazardous Waste Pretreatment as an Air Pollution Control Technique*, HWERL, U.S. EPA, Contract 68-03-3149 (in publication).
15. C. C. Allen, B. L. Blaney, "Techniques for treating hazardous waste to remove volatile organic constituents," *JAPCA* 35: 841 (1985).
16. C. R. Baillod, *et al.*, "Application of Wet Oxidation to Industrial Waste Treatment," AIChE Summer National Meeting, Philadelphia, PA, August 1984.
17. W. Copa, J. Heimbuch, P. Schaefer, "Demonstration of Wet Air Oxidation of Hazardous Waste," in *Incineration and Treatment of Hazardous Waste: Proceedings of the Tenth Annual Symposium*, U.S. EPA, No. EPA-600/9-84-022, 1984.
18. L. A. Pradt, "Developments in wet air oxidation," *Chem. Eng. Prog.* 68: 72 (1972).
19. R. A. Randell, "Wet Oxidation of Toxic and Hazardous Compounds," Zimpro, Inc., Technical Bulletin No. I-610, 1981.
20. W. Copa, Zimpro Corporation, private communication.
21. R. A. Dobbs, J. M. Cohen, *Carbon Adsorption Isotherms for Toxic Organics*, EPA-600/8-80-023, MERL, U.S. EPA, Cincinnati, OH, 1980.
22. W. J. Weber, Jr., M. Pirbazari, *Effectiveness of Activated Carbon for Removal of Toxic and/or Carcinogenic Compounds from Water Supplies*, Final Report, Project CR 804436030, MERL, U.S. EPA, Cincinnati, OH, 1980.
23. Y. H. Kiang, A. A. Metry, *Hazardous Waste Processing Technology*, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1982.
24. *U.S. Environmental Protection Agency Treatability Manual, Volume III*, IERL, U.S. EPA, Cincinnati, OH, EPA-600/2-82-0016, 1983.

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# HAZARDOUS WASTE NEWS

## *Hazardous Waste Disposal Trust Account Program Expanded by Bank*

A special Trust Department program has been expanded by Bank of America to help hundreds of companies in California and other parts of the country comply with tough state and federal financial regulations covering management of hazardous waste facilities.

"Over the past year, California and the Environmental Protection Agency (EPA) have increased their efforts to force owners and operators of toxic waste facilities to comply with the financial requirements of the Resource Conservation and Recovery Act (RCRA) and state law," said John Masterman, chief, RCRA Management Unit/Hazardous Waste Management Section within the state's Toxic Substance Control Division.

"However, businesses in California, especially the smaller ones, are experiencing a great deal of difficulty in obtaining the necessary liability insurance and closure cost assurances required for hazardous waste facilities," Masterman said. There are many reasons for this, including the fact that those policies have high premiums and only a few companies are willing to write them, he added.

According to the EPA, in California alone there are approximately 1,000 facilities which have been classified as hazardous waste treatment, storage, or disposal facilities. A broad and intensive campaign was recently launched by the bank to reach the owners and operators of such sites so that they can begin setting up the special trust accounts which will put them in financial compliance with EPA and state regulations.

"Both California and federal law require companies which own or operate hazardous waste facilities to develop comprehensive plans for closure and, where required, post-closure care of those sites," Masterman explained. Companies must also provide proof that funds will be available to put those plans into action when the facility is closed, he stated.

In addition to California, the bank said that it has already set up a number of these hazardous waste disposal trust accounts for customers in other parts of the United States and will be contacting hazardous waste companies around the country to provide them with any assistance they may require to deal with this problem.

"Clearly we have reached the point where an urgent need exists to protect our environment through the proper treatment and disposal of hazardous wastes. We believe that our role at the bank is to work closely with regulatory agencies and companies throughout the United States to see that this need is met," said Clyde R. Claus, executive vice president and the head of Trust and Private Banking.

"Because of the complexity of the situation, many companies are really not sure where to turn for answers about the alternatives that are available to them for meeting the test for financial compliance," Claus stated.

"To deal with that problem, we have established a very flexible range of options to ensure that companies of all sizes have a way of handling financial compliance requirements relating to their toxic waste facilities. Those bank mechanisms include fully funded trust accounts; partially funded trusts; or unfunded standby trust accounts that are established in conjunction with standby letters of credit or surety bonds," he explained.

Currently, the bank is handling hazardous waste disposal trusts for small businesses as well as large multinational corporations. Costs for the bank service can vary and will depend on such factors as the amount of work required to set up the account and the complexity of administering it.