



Project Summary

Technical Resource Document Treatment Technologies for Solvent Containing Wastes

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The full *Technical Resource Document for Treatment Technologies for Solvent Containing Wastes* compiles available information on those technologies. It is intended to provide support for the land disposal prohibition, currently being considered by the EPA, and to provide technical information for those individuals and organizations concerned with the subject waste streams.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Background

Solvents are low molecular weight organic compounds that are widely used by all segments of American society. As a result of their widespread usage and their mobility within the environment, their presence is frequently detected in all media, including ground water. To combat the potential negative effects of solvent contamination, the 1984 amendments to the Resource Conservation and Recovery Act (RCRA) directed EPA to ban certain solvent wastes from land disposal to the extent required to protect human health and the environment. The ban is effective 8 November 1986, two years after the enactment of the amendments.

EPA has taken steps to meet this deadline by evaluating the availability and technological capability of land disposal alternatives. As a result of this evaluation, a 2-year national variance was proposed for wastewaters, solvent contaminated soils, and inorganic sludges and solids contain-

ing less than 10,000 ppm of organic constituents. The variance was based on a determination by EPA that the available capacity of alternative treatment technologies capable of achieving high destruction or removal efficiencies (i.e., low ppm range) for these wastes will be insufficient to accommodate the quantities managed in land disposal units.

The categories of wastes subject to the 8 November 1986 land disposal restrictions are identified in the 14 January 1986 Federal Register¹. They include organic wastes characterized as RCRA waste codes F001 through F005 and commercial chemical products, manufacturing intermediates and spill residues containing solvents identified in these codes (i.e., priority solvents of concern). Land disposal restrictions for other RCRA wastes will be developed and implemented at later dates.

Scope

This summary of the Solvents Technical Resource Document provides information that can be used by environmental regulatory agencies and others as a source of technical information describing waste management options for solvents and other wastes containing low molecular weight organic compounds. These options include waste minimization (i.e., source reduction, reuse, recycling), treatment and disposal of waste streams. Although emphasis is placed on the collection and interpretation of performance data for proven technologies, the full range of waste minimization processes and treatment/recovery technologies that can be used to manage solvent wastes is discussed (see Table 1).

Table 1. Waste Management Alternatives to Land Disposal

| Waste management objective | Applicable waste type(s) | Potential waste management alternative | | | |
|----------------------------|--------------------------|--|--|--------------------------------------|--------------------------------|
| Waste Minimization | | | | | |
| Source Reduction | All | Raw material substitution Product reformulation | Process redesign Waste segregation | | |
| Recycling | All | Reclamation | Reuse (e.g., as a fuel or process solvent) | | |
| Pretreatment | | | | | |
| | Liquid with solids | Screening Floatation | Sedimentation Settling | Filtration Centrifugation | Distillation |
| | Liquid - Two Phase | Decanting Distillation | Floatation | Centrifugation | Extraction |
| | Sludge | Vacuum filtration | Filter press | Centrifugation | Other dewatering |
| | Bulky Solids | Shredders | Hammermills | Crushers | |
| | Low Btu/High Viscosity | Blending | | | |
| Treatment | | | | | |
| Physical | Liquid | Distillation Steam stripping | Evaporation Air stripping | Fractionation Carbon adsorption | Extraction Resin adsorption |
| Chemical | Liquid | Wet air oxidation Other chemical oxidations | Supercritical water oxidation | Chlorinolysis | Ozonation Dechlorination |
| Biological | Liquid | Activated sludge | Aerated lagoon | Trickling filter | |
| Incineration | All | Liquid injection | Rotary kiln | Fluidized-bed | Starved air |
| Other Thermal | All | Pyrolysis processes Plasma systems | Molten glass Electric reactor | Circulating fluid bed Molten salt | |
| Post Treatment | | | | | |
| | Organic Liquid | Decanting | Dehydrating | Fractionation | Thermal destruction |
| | Solid/Sludge | Solidification | Encapsulation | Thermal destruction | |
| | Aqueous Liquid | Carbon adsorption Ozonation | Resin adsorption Other oxidations | Air stripping | Biological Treatment |

In general, treatment process selection will be limited to wastes possessing specific chemical, physical and flow characteristics. Applicable technologies for wastes with varying ranges in initial solvent concentration are provided in Figure 1. A summary of overall performance, applicable waste streams, residuals generation and status of development for the primary solvent waste treatment processes is provided in Table 2.

Determination of the overall applicability of these technologies for treating spent solvents requires an understanding of the nature of solvent wastes and current waste management practices. Thus, the range and variability in data requirements include solvent waste physical, chemical, and flow (i.e., rate, periodicity) characteristics which, in turn, necessitates an understanding of solvent waste industrial origins. An analysis of current waste management practices serves to identify available methods which have proven to be both technologically and economically capable of treating solvent wastes. To a significant extent, waste management alternatives which will permit industry to meet EPA disposal requirements have already been implemented. This occurred

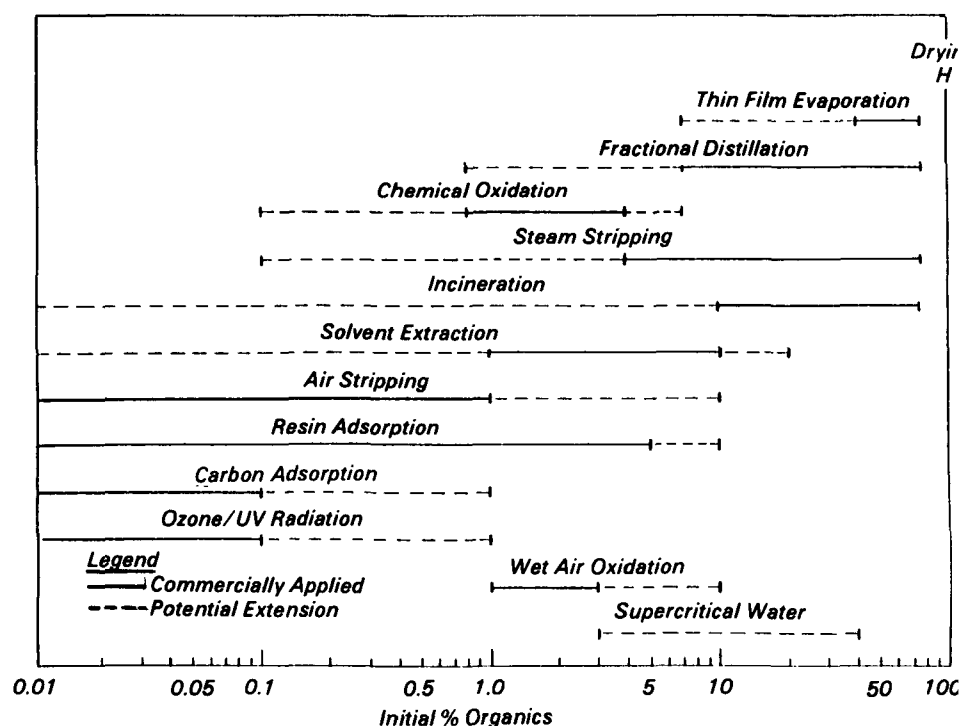


Figure 1. Approximate ranges of applicability of treatment techniques as a function of organic concentration in liquid waste streams.
Source: References 1 and 11.

Table 2. Summary of Solvent Treatment Processes

| <i>Process</i> | <i>Applicable waste streams</i> | <i>Stage of development</i> | <i>Performance</i> | <i>Residuals generated</i> |
|---|--|---|---|---|
| Incineration | | | | |
| <i>Liquid injection incineration</i> | <i>All pumpable liquids provided wastes can be blended to Btu level of 8500 Btu/lb. Some solids removal may be necessary to avoid plugging nozzles.</i> | <i>Estimated that over 219 units are in use. Most widely used incineration technology.</i> | <i>Excellent destruction efficiency (>99.99%). Blending can avoid problems associated with residuals, e.g., HCl.</i> | <i>TSP, possibly some PICs, and HCl if halogenated organics are fired. Only minor ash if solids removed in pretreatment processes.</i> |
| <i>Rotary kiln incineration</i> | <i>All wastes provided Btu level is maintained.</i> | <i>Over 40 units in service; most versatile for waste destruction.</i> | <i>Excellent destruction efficiency (>99.99%).</i> | <i>Requires APCDs. Residuals should be acceptable if charged properly.</i> |
| <i>Fluidized bed incineration</i> | <i>Liquids or nonbulky solids.</i> | <i>Nine units reportedly in operation-circulating bed units under development.</i> | <i>Excellent destruction efficiency (>99.99%).</i> | <i>As above.</i> |
| <i>Fixed/multiple hearths</i> | <i>Can handle a wide variety of wastes.</i> | <i>Approximately 70 units in use. Old technology for municipal waste combustion.</i> | <i>Performance may be marginal for hazardous wastes, particularly halogenated wastes.</i> | <i>As above.</i> |
| Use as a Fuel | | | | |
| <i>Industrial kilns</i> | <i>Generally all wastes, but Btu level, chlorine content, and other impurity content may require blending to control charge characteristics and product quality.</i> | <i>Only a few units now burning hazardous waste.</i> | <i>Usually excellent destruction efficiency (>99.99%) because of long residence times and high temperatures.</i> | <i>Requires APCDs. Residuals should be acceptable.</i> |
| <i>High temperature industrial boilers</i> | <i>All pumpable fluids, but should blend halogenated organics. Solids removal particularly important to ensure stable burner operation.</i> | <i>Several units in use.</i> | <i>Most units tested have demonstrated high DRE (>99.99%).</i> | <i>Waste must be blended to meet emission standards for TSP and HCl unless boilers equipped with APCDs.</i> |
| Other Thermal Technologies | | | | |
| <i>Circulating bed combustor</i> | <i>Liquids or nonbulky solids.</i> | <i>Only one U.S. manufacturer. No units treating hazardous waste.</i> | <i>Manufacturer reports high efficiencies (>99.99%).</i> | <i>Bed material additives can reduce HCl emissions. Residuals should be acceptable.</i> |
| <i>Molten glass incineration</i> | <i>Almost all wastes, provided moisture and metal impurity levels are within limitations.</i> | <i>Technology developed for glass manufacturing. Not available yet as a hazardous waste unit.</i> | <i>No performance data available, but DREs should be high (>99.99%).</i> | <i>Will need APC device for HCl and possibly PICs; solids retained (encapsulated) in molten glass.</i> |
| <i>Molten salt destruction</i> | <i>Not suitable for high (>20%) ash content wastes.</i> | <i>Technology under development since 1969, but further development on hold.</i> | <i>Very high destruction efficiencies for organics (six nines for PCBs)</i> | <i>Needs some APC devices to collect material not retained in salt. Ash disposal may be a problem.</i> |
| <i>Furnace pyrolysis units</i> | <i>Most designs suitable for all wastes.</i> | <i>One pyrolysis unit RCRA permitted. Certain designs available commercially.</i> | <i>Very high destruction efficiencies possible (>99.99%). Possibility of PIC formation.</i> | <i>TSP emissions lower than those from conventional will need APC devices for HCl. Certain wastes may produce an unacceptable tarry residual.</i> |
| <i>Plasma arc pyrolysis</i> | <i>Present design suitable only for liquids.</i> | <i>Commercial design appears imminent, with future modifications planned for treatment of sludges and solids.</i> | <i>Efficiencies exceeded six nines in tests with solvents.</i> | <i>Requires APC devices for HCP and TSP; needs flare for H₂ and CO destruction.</i> |
| <i>Fluid wall advanced electric reactor</i> | <i>Suitable for all wastes if solids pretreated to ensure free flow.</i> | <i>Ready for commercial development. Test unit permitted under RCRA.</i> | <i>Efficiencies have exceeded six nines.</i> | <i>Requires APC devices for TSP and HCl; Chlorine removal may be required.</i> |

Table 2. (Continued)

| Process | Applicable waste streams | Stage of development | Performance | Residuals generated |
|-------------------------------------|--|--|--|---|
| <i>In situ</i> vitrification | Technique for treating contaminated soils, could possibly be extended to slurries. Also use as solidification process. | Not commercial, further work planned. | No date available, but DREs of over six nines reported. | Off gas system needed to control emissions to air. Ash contained in vitrified soil. |
| Physical Treatment Methods | | | | |
| Distillation | This is a process used to recover and separate solvents. Fractional distillation will require solids removal to avoid plugging columns. | Technology well developed and equipment available from many suppliers; widely practiced technology. | Separation depends upon reflux (99+ percent achievable). This is a recovery process. | Bottoms will usually contain levels of solvent in excess of 1,000 ppm; condensate may require further treatment. |
| Evaporation | Agitated thin film units can tolerate higher levels of solids and higher viscosities than other types of stills. | Technology is well developed and equipment is available from several suppliers; widely practiced technology. | This is a solvent recovery process. Typical recovery of 60 to 70 percent. | Bottoms will contain appreciable solvent. Generally suitable for incineration. |
| Steam Stripping | A simple distillation process to remove volatile organics from aqueous solutions. Preferred for low concentrations and solvents with low solubilities. | Technology well developed and available. | Not generally considered a final treatment, but can achieve low residual solvent levels. | Aqueous treated stream will probably require polishing. Further concentration of overhead steam generally required. |
| Air Stripping | Generally used to treat low concentration aqueous streams. | Technology well developed and available. | Not generally considered a final treatment, but may be effective for highly volatile wastes. | Air emissions may require treatment. |
| Liquid-Liquid Extraction | Generally suitable only for liquids of low solid content. | Technology well developed for industrial processing. | Can achieve high efficiency separations for certain solvent/waste combinations. | Solvent solubility in aqueous phase should be monitored. |
| Carbon Adsorption | Suitable for low solid, low concentration aqueous waste streams. | Technology well developed; used as polishing treatment. | Can achieve low levels of residual solvent in effluent. | Adsorbate must be processed during regeneration. Spent carbon and wastewater may also need treatment. |
| Resin Adsorption | Suitable for low solid waste streams. Consider for recovery of valuable solvent. | Technology well developed in industry for special resin/solvent combinations. Applicability to waste streams not demonstrated. | Can achieve low levels of residual solvent in effluent. | Adsorbate must be processed during regeneration. |
| Chemical Treatment Processes | | | | |
| Wet air oxidation | Suitable for aqueous liquids, also possible for slurries. Solvent concentrations up to 15%. | High temperature/pressure technology, widely used as pretreatment for municipal sludges, only one manufacturer. | Pretreatment for biological treatment. Some compounds resist oxidation. | Some residues likely which need further treatment. |
| Supercritical water oxidation | For liquids and slurries containing optimal concentrations of about 10% solvent. | Supercritical conditions may impose demands on system reliability. Commercially available in 1987. | Supercritical conditions achieve high destruction efficiencies (>99.99%) for all constituents. | Residuals not likely to be a problem. Halogens can be neutralized in process. |
| Ozonation | Oxidation with ozone (possibly assisted by [UV]) suitable for low solid, dilute aqueous solutions. | Now used as a polishing step for wastewaters. | Not likely to achieve residual solvent levels in the low ppm range for most wastes. | Residual contamination likely; will require additional processing of off gases. |
| Other chemical oxidation processes | Oxidizing agents may be highly reactive for specific constituents in aqueous solution. | Oxidation technology well developed for cyanides and other species (phenols), not yet established for general utility. | Not likely to achieve residual solvent levels in the low ppm range for most wastes. | Residual contamination likely; will require additional processing. |

Table 2. (Continued)

| <i>Process</i> | <i>Applicable waste streams</i> | <i>Stage of development</i> | <i>Performance</i> | <i>Residuals generated</i> |
|-------------------------------------|--|---|---|---|
| <i>Chlorinolysis</i> | <i>Suitable for any liquid chlorinated wastes.</i> | <i>Process produces a product (e.g., carbon tetrachloride). Not likely to be available.</i> | <i>Not available.</i> | <i>Air and wastewater emissions were estimated as not significant.</i> |
| <i>Dechlorination</i> | <i>Dry soils and solids.</i> | <i>Not fully developed.</i> | <i>Destruction efficiency of over 99% reported for dioxin.</i> | <i>Residual contamination seems likely.</i> |
| <i>Biological Treatment Methods</i> | | | | |
| | <i>Aerobic technology suitable for dilute wastes although some constituents will be resistant.</i> | <i>Conventional treatments have been used for years.</i> | <i>May be used as final treatment for specific wastes, may be pretreatment for resistant species.</i> | <i>Residual contamination likely; will usually require additional processing.</i> |

in response to increased regulatory requirements and the improved economic viability of solvent waste minimization and treatment options. The latter resulted from increased disposal costs, liability, and technological developments.

Solvent waste generation, characteristics and management practices are briefly summarized below. This is followed by a discussion of potential waste management methods, including source reduction and recycling, which are applicable to solvent wastes (see Table 1). Emphasis is placed on identifying treatment process design and operating factors and waste characteristics which affect treatment/recovery of solvent wastes. This discussion concludes with a summary of technical and economic factors which should be considered in the selection of an optimal waste management system.

Solvent Waste Generation, Characteristics and Management Practices

Of the more than 8 billion gallons of organic solvent compounds consumed annually, approximately 60 percent consists of priority solvents which may ultimately be affected by the upcoming land disposal restrictions. Of this, 64 percent are non-halogenated solvents. These are widely used in the paint and allied products industry as ingredients and wash solvents and in general industry applications as cold cleaners. The remainder are halogenated compounds which are primarily used as vapor degreasers, cold cleaners, and dry cleaning solvents.

Hazardous solvent wastes are generated at a rate of 4 to 8 billion gallons annually, the majority of which are dilute, solvent contaminated aqueous wastes. However, the bulk of waste solvent constituents are

found in non-aqueous streams; i.e., greater than 1 percent total organics. Of these, roughly 1.5 billion gallons are managed in RCRA treatment, storage, and disposal facilities with 60 percent being recycled.

Although there are some exceptions, nonaqueous solvent waste generation and recycling tend to parallel solvent consumption. This occurs because solvents are used in nonconsumptive applications and are recycled (onsite or offsite) to approximately the same extent. On average, low cost solvents typically result in larger volume waste streams (e.g., wash solvents) which provides comparable economic incentives (e.g., high disposal cost, economies of scale) to recover relative to more expensive solvents; e.g., chlorinated degreasing solvents. In addition, nonhalogenated waste solvents and treatment residuals find widespread use as fuel supplements relative to halogenated compounds.

Organic liquids comprise the vast majority of currently recycled waste solvents with aqueous, solid, and sludge wastes contributing little to total recycled quantity. Landfills are used as the primary management method for a disproportionately high fraction of solids, sludges, halogenated, and low volume solvent wastes. Conversely, large volume, liquid, and nonhalogenated solvents have a higher tendency to be treated via other methods; e.g., tanks and wastewater technologies.

Although over one-third of currently landfilled solvents wastes contain over 10 percent solvent, these wastes tend to be low volume streams which generators could not justify reusing or recycling. However, higher disposal costs, recent technological developments (e.g., low cost, high recovery package distillation systems), technology transfer, and increased availability of offsite manage-

ment alternatives (e.g., solvent reclaimers, waste exchanges) have resulted in a corresponding increase in solvent recycling.

This trend in recycling should be accelerated upon implementation of the land disposal restrictions since recycling and other forms of waste minimization will become the next lowest cost alternative for managing many solvent wastes. In the short term, use of evaporation technologies which yield high solvent recoveries will reduce overall solvent quantity requiring land disposal but probably result in the generation of more solvent solids and sludges (less than 10,000 ppm solvent). These wastes and aqueous streams will be subject to a two year extension of the land disposal ban as noted previously. In that period, implementation of waste minimization efforts should decrease net volume of solvent waste requiring disposal and create a shift in the distribution of these waste from aqueous to sludge/solid physical form.

EPA feels that alternative treatment capacity for solvent wastes will be available under the proposed disposal ban schedule. This determination was based on estimates of current waste quantities disposed, small quantity generator disposal requirements, projected residuals generated as a result of increased use of recovery technologies and available treatment capacity. Capacity shortfalls should not occur as a result of the conservative assumptions used in EPA's analysis regarding available treatment capacity. EPA assumed that only available offsite incineration and wastewater treatment would be available as land disposal alternatives due to lack of data on other options. Specifically, data gaps include available onsite capacity, impact of waste minimization, availability of emerging treatment process-

es capable of yielding high removal efficiencies, and uncertainties surrounding the future regulation of hazardous waste use as a fuel. EPA was not able to consider these in its analysis despite the fact that they will result in both lower demand and increased available treatment capacity.

Waste Minimization

Waste minimization alternatives consist of two basic approaches, source reduction and recycling. Individual case studies of waste minimization programs have been extensively documented, which show net cost savings and rapid payback periods on equipment purchases for both large and small waste generators. For example, over a period of 3 years, IBM reported a waste reduction of 234 million pounds of solvent wastes at five plants which resulted in a net cost savings of 120 million dollars. Due to the site specific nature of these applications, it is difficult to estimate the national impact of future activities on overall waste generation. Waste minimization programs are likely to significantly decrease solvents currently land disposed. To date, these programs have been more commonly applied to solvent wastes relative to other hazardous wastes primarily as a result of favorable economics.

Source reduction represents a preventive approach to hazardous waste management which can be accomplished through raw material substitution, product reformulation, process modifications, or waste segregation. Recycling can either take the form of direct reuse in a process which tolerates lower solvent quality specifications or involves some form of reclamation prior to reuse. Considerations for both source reduction and recycling include impacts on product quality, process performance, and net cost savings relative to the use of virgin products and other waste management options.

Primary recycling methods currently in use include some form of distillation or evaporation, decanting filtration, and less commonly, fractionation and steam stripping. Extraction and adsorption processes are less frequently used to recover RCRA solvent wastes. The majority of priority solvents are recycled as a reclaimant while ignitable wastes are primarily used as fuel supplements. Other recycling methods include direct reuse as a feedstock. Halogenated solvents are finding increased use as cement kiln and iron blast furnace fuel supplements with small amounts being used as an extender in the manufacture of concrete blocks and asphalt.

Pretreatment

The purpose of pretreatment is to remove restrictive waste characteristics to simplify or reduce costs of subsequent treatment. Most pretreatment methods involve physical separation of different phases or chemical species or modification of the waste physical form. Commonly applied pretreatment methods have been summarized in Table 1 for various waste types.

Physical Treatment Processes

Physical treatment processes are the most commonly applied methods used to treat solvent wastes. Highly concentrated organics (i.e., greater than 10 percent solvent) are generally treated through some form of distillation/evaporation. Steam stripping is used for insoluble organic species and fractionation used for separating mixtures or recovering high purity products. Steam stripping can also be used, along with solvent extraction and resin adsorption, for aqueous wastes with organic solvent levels below 10 percent. Air stripping and carbon adsorption are only economically applied to wastes with solvent concentration at 1 percent or less.

Pretreatment requirements include varying degrees of solids, oil, grease, metals, and nonhazardous organic contaminant removal to prevent fouling of heat or mass transfer surfaces. Waste constituents which are generally most difficult to separate via physical mechanisms include those which are highly soluble (e.g., alcohols) and those which have low volatility relative to the bulk of the waste stream; e.g., nitrobenzene or cresol contaminated wastewater. Under favorable conditions, adsorption and stripping processes are capable of yielding residual products which can be discharged without requiring additional treatment.

Distillation/evaporation processes are the most widely applied technologies for recovering concentrated organic wastes. Separation efficiencies of well over 90 percent have been reported. However, removal is limited due to constraints imposed by vapor liquid equilibrium (e.g., azeotrope formation, low differential vapor pressure), restrictive waste characteristics (e.g., presence of contaminants that foul heat transfer or packing surfaces, low thermal decomposition and autoignition temperatures, high viscosity), and economics; e.g., high residence time, capital cost and operating temperature and low pressure requirements. With conventional equipment, bottoms must be kept in a

pumpable state which often represents the most limiting factor in solvent recovery.

Fractionation is used for separating mixtures of volatile organics from waste streams containing minimal solids content. It is frequently applied as a post treatment purification step. The other extreme in high volume processing equipment is agitated thin film evaporators. These units can handle wastes with viscosities up to one million centipoises and have been economical in processing wastes with as little as 6 to 8 percent recoverable solvent. These units are widely applied by commercial solvent reclaimers due to their high potential recoveries and minimal pretreatment requirements. Removal efficiencies are maximized in these units as a result of their capability of processing high viscosity wastes in turbulent conditions. This minimizes the adverse effect of mass transfer resistance on volatilization rate and enables residual solvent levels to be reduced below 100 ppm under favorable conditions.

Recent technological innovations in distillation/evaporation equipment include development of semi-batch, low volume, package systems which permit processing to solid or sludge bottoms products. Use of these and other solids handling equipment (e.g., drum dryer, jacketed heating vessel with mechanical driver to maintain waste flow) result in maximum solvent recovery and minimum volume of waste requiring subsequent disposal. Alternatively, mixing distilling liquids with nonvolatile carrier fluids (e.g., waste oil allows for higher recovery efficiency while maintaining pumpable bottoms. These techniques and equipment are currently applied primarily to halogenated solvent wastes to minimize disposal/blending costs but will find widespread use for all solvents when land disposal is no longer a viable management option.

Steam stripping is most effectively applied in aqueous solutions (less than 10 percent solvent) for the removal of volatile components (boiling point less than 150°C, Henry's law constant greater than 10^{-4} atm-m³/mole) that are only slightly soluble in water (less than 1000 ppm). It can also be used for stripping organic solutions when water forms low boiling azeotropes with the compounds to be removed and does not adversely affect overhead or bottoms quality. Steam stripping is widely applied to separate halogenated and certain aromatics from water, but is less effective for stripping miscible organics such as ketones or alcohols. Since there are no

heat transfer surfaces and bottoms remain fluid, steam stripping can tolerate higher contaminant quantities relative to conventional distillation. Under ideal conditions, bottoms products may not require additional treatment.

In general, steam stripping is more cost effective than air stripping for waste with appreciable solvent content; i.e., greater than 1 percent. Air stripping has only found significant commercial application in treating solvent contaminated water supplies with concentrations of a few parts per million or less. The technology has demonstrated high removal efficiencies for volatile organics and, thus, may find increased use as a polishing treatment step; e.g., for compounds resistant to biodegradation or exhibiting low adsorption characteristics.

Liquid-liquid extraction is not a commonly used treatment method but it has potential for treating aqueous wastes which are not readily treated through more conventional methods. Extraction can be attractive in cases where the solutes are present at high enough concentrations to prohibit use of adsorption, are toxic to biological organisms, and when steam stripping is less effective as a result of low solute volatility or formation of azeotropes. Extraction is most cost effective when solutes are in the 1 to 10 percent concentration range. Costs can be high as a result of solvent regeneration requirements and post treatment costs associated with removal of residual solvent from the treated aqueous stream.

Carbon and resin adsorption can be used for treating dilute aqueous wastes to levels which permit discharge as a nonhazardous waste. Carbon adsorption is a widely applied technology for effluent polishing. It can be used to treat wastes with up to 5000 ppm organics and 1000 ppm inorganics. However, it is more typically used for wastes with less than 1000 ppm organics due to high regeneration costs (thermal regeneration is typically required). Activated carbon is most effective in removing nonpolar, low solubility (less than 0.1mg/ml), high molecular weight (greater than 100) compounds. Pretreatment to remove oil and grease (less than 10mg/l), suspended solids (10 to 70 mg/l depending on carbon treatment flow configuration) and nonhazardous organics (biological pretreatment) which compete for adsorption sites or clog macropores minimizes required regeneration frequency. Powdered activated carbon is frequently used in conjunction with biological treatment. The carbon acts as a buffer to mini-

mize the adverse effects of high or variable concentrations of toxic compounds.

Resins are significantly more expensive than natural carbon base materials; however, they offer improved processing capabilities. Resins can be manufactured to have higher polarity and more controlled pore size distributions and are consequently capable of achieving higher removal efficiencies for certain compounds. They are more easily regenerated through extraction processes which extends their capability for treating wastes with higher initial solvent concentration (up to 5 percent). This is especially desirable if recovery of solvent is economically feasible.

Finally, adsorption and extraction processes are also used as a polishing step for dehydrating solvent streams such as decanted overhead products from distillation or steam stripping. Drying methods which are currently in use include caustic extraction and molecular sieve, calcium chloride and ionic resin adsorption.

Chemical Treatment Processes

Chemical treatment methods for solvent wastes include oxidation, chlorinolysis, and dechlorination processes. The most important of these processes is oxidation. Of particular interest is the supercritical water oxidation (SWO) process developed by MODAR, Inc. The first commercial SWO unit is now being designed to treat up to 30,000 gallons of aqueous waste per day with installation scheduled for late 1987. Although the characteristics of the aqueous waste have not been made public at this time, a solvent concentration of about 10 percent is reported to be thermally optimal for the process. On the basis of reported test data, the destruction and removal efficiency (DRE) is anticipated to be at the six nines level for all halogenated and nonhalogenated solvent constituents.

In addition to high DRE, another feature of the SWO process is its applicability to the treatment of halogenated organics. Hydrochloric acid formed as a result of oxidation of chlorinated compounds can be neutralized within the system by prior addition of caustic to the feed stream. The chloride salts formed (and other inorganic salts) are essentially insoluble in water at super critical conditions and are removed from the process stream by a separator which is an integral part of the SWO system design. Ultimately, the applicability of SWO to the treatment of solvent wastes in aqueous streams will depend on the economics of the process. The economics in turn, will depend upon the ability of the process equipment to withstand stringent

supercritical temperature and pressure requirements which are in excess of 374 °C and 218 atmospheres.

The wet air oxidation (WAO) process, which operates at subcritical and therefore less stringent temperature and pressure conditions (e.g., less than 320 °C and 200 atmospheres), may also have some application for the treatment of solvent wastes in aqueous media. However, the DREs will not be as high as those achieved by the SWO process. This is particularly true for chlorinated aromatics such as chlorobenzene which are highly resistant to oxidation under WAO conditions. In addition, low molecular weight residuals which resist further degradation, such as acetic acid and formic acid are commonly reported as byproducts of aqueous solvent wastes treated by the WAO process.

The WAO process is an established technology for the treatment of municipal sludges. It has also found application for the treatment of a limited number of specific waste streams, including acetonitrile and coke oven gas scrubbing wastewaters. While the WAO process may also find utility for the treatment of other specific waste streams, it may prove to be most useful as a pretreatment for solvent waste streams which are too dilute to incinerate and yet too toxic to biotreat. Available data indicate that solvent streams that are resistant to biological treatment can generally be detoxified by the WAO process to allow subsequent effective biological degradation.

Other chemical oxidation processes that have been used for the degradation of solvent wastes operate at ambient or only moderately elevated conditions of temperature and pressure. Primary oxidation agents include ozone, hydrogen peroxide, and potassium permanganate. These oxidants have found application as polishing agents for dilute organic contaminated wastewater or as oxidants for specific organics (e.g., aldehydes and phenols) in industrial waste streams. However, their applicability to solvent waste streams appears to be limited. Process residuals are usually found which will often require additional treatment to produce an environmentally acceptable discharge stream. Further, the indiscriminate nature of the oxidation process limits its application to the treatment of hazardous aqueous water. Cost and, in some cases, the need for stringent process control measures, become prohibitive if organic slurries and slurries are to be treated.

There is some evidence to indicate that the efficiency and completeness of oxida-

tion is enhanced by UV photolysis. However, the evidence is limited and the sensitivity of photolysis to the presence of impurities in the process stream is an issue of concern.

The chlorinolysis and dechlorination processes do not appear to have general application for the treatment of solvent wastes. Chlorinolysis is a pyrolysis process conducted in the presence of chlorine to produce low molecular weight chlorinated compounds (e.g., carbon tetrachloride) using chlorine bearing wastes from sources such as the pesticide industry. The process has not yet been utilized in the United States. It requires high levels of capital expenditure and is economically dependent upon the return available from the sale of the chlorinated hydrocarbon product. It is unlikely that the process will become available in the foreseeable future.

The dechlorination processes examined are experimental processes that are being developed primarily for the treatment of highly toxic dioxin compounds. Although they are capable of achieving high solvent DREs, the alkali metal based reactants used in these processes are expensive and highly reactive. Other technologies appear to be more suitable.

Biological Treatment

Despite the almost universal use of cost effective, biological methods for the treatment of wastes, very little information could be found describing DREs for the constituents in solvent-bearing wastes. Data are available for aerobic systems showing discharge concentrations for many solvents that are below the ppm level. However, these data are based on influent levels that, while sufficient to demonstrate significant DREs, are not high enough to exhibit appreciable inhibitory biological effects. Some degree of pretreatment through technologies such as WAO, carbon adsorption, or solvent extraction will be required for many wastes containing high levels of organic compounds, particularly the more biotoxic halogenated compounds. As noted, addition of powdered activated carbon to activated sludge has proven effective in mitigating the inhibitory activity of solvent constituents to biological activity.

Thermal Destruction Technologies

The thermal destruction of organic solvent wastes has been the subject of EPA research for several years. DREs in excess of the 99.99 percent requirement for incinerators have been well documented for most solvents of concern present in various types of waste. Documentation is par-

ticularly extensive for the halogenated compounds considered most difficult to thermally destroy. Incineration techniques that represent proven technology include liquid injection; fixed hearth, including those using starved-air designs rotary kilns, and fluidized-bed incineration. The incineration of many solvent wastes will require air pollution control devices to achieve the incinerator requirements of:

- At least 99 percent removal of hydrogen chloride from the exhaust gas if hydrogen chloride emissions are greater than 4lb/hour; and
- Particulate emissions not exceeding 0.08 grains/dry standard cubic feet, corrected to 7 percent oxygen in the stack gas.

In 1981, prior to the promulgation of the 1982 incinerator standards, over half of the operating incinerators were not equipped with air pollution control systems for either particulates or acid gases. Although the present status of control device application at incinerators is now being assessed by EPA, it is possible to comply with the incinerator standards by restricting waste feed streams to those low ash, non-halogenated wastes for which control measures will not be necessary.

Because of the broad applicability of thermal destruction to solvent wastes and the added demands for alternatives to land disposal resulting from the 1984 RCRA amendments, a number of emerging thermal technologies are in various stages of development. Several pyrolysis processes, molten glass and molten salt technologies, circulating bed combustion and the in situ vitrification processes are among the more prominent. Pyrolysis processes are particularly well advanced with two processes, a furnace design manufactured by the Midland-Ross Corporation and the Huber advanced electric reactor now operating under RCRA permit status. A third process, under development by Pyrolysis Systems, Inc. of Welland, Ontario, is now undergoing intensive testing by EPA. All of the pyrolysis units should meet DRE requirements but will have to or already have incorporated control systems for particulates and acid gases.

The molten glass furnace is based on technology long established in the glass industry. Although no units are now operating commercially, two companies are actively pursuing development. DREs of 99.99+ percent can be anticipated, although interest in this process has also focussed on its potential for containing solid and inorganic residues within a stable, nonleachable glass matrix. The de-

struction principle is similar in concept to that of the Molten Salt Destruction Technology. This latter technology, under development by Rockwell since 1969, has achieved greater than 99.9 percent DRE. However, solid residues must be freed from the salt matrix during regeneration and may require further treatment. Although three units (maximum capacity 2000lb/hour) have been built by Rockwell, no commercial units have been sold. At the present time no further development is planned by Rockwell.

The circulating bed combustor is an outgrowth of conventional fluidized bed combustion technology. By using high velocities and a circulating bed, potential problems associated with maintaining the critical flow velocity needed for bed stability are avoided. Turbulence is also increased, which should enhance DRE (already demonstrated to be in excess of 99.99 percent for solvents). Addition of limestone to the bed can effectively reduce hydrochloric acid emissions from halogenated solvent combustion. However, pollution control systems will be required to meet the incinerator standards for particulate emissions.

The in situ vitrification process is designed to treat contaminated soils rather than process waste streams. Now under development by Battelle Northwest, DREs in excess of 99.99 percent have been achieved in the laboratory for solvents. An added feature of this technology is the encapsulation of solid wastes in a vitrified matrix which is leach resistant and durable. Work, some of it supported by the Electric Power Research Institute, is continuing, with focus on PCB rather than solvent, contaminated soils.

Use as a Fuel

Thermal destruction of solvents wastes in industrial boilers and other high temperature industrial processing equipment (e.g., cement, lime, and aggregate kilns) has been actively studied by EPA in recent years. Performance data indicate that most industrial boilers and processing units can meet the incinerator DRE standard of 99.99 percent for solvent constituents. No difficulties were encountered in meeting the 4lb/hour emission standard for hydrogen chloride during the combustion of nonhalogenated solvent wastes. Also, no significant changes in particulate emissions were observed that could be attributed to the burning of waste fuels. The particulate emission standard of 0.08 grains per dry standard cubic feet at 7 percent oxygen can be met by a waste with an ash content of about 0.3 percent. The

exact value will depend upon the Btu value of the fuel, its elemental composition, and other factors. Blending of many low ash content wastes with conventional fuel oils prior to combustion could avoid the need to install costly pollution control devices for many wastes.

Land Disposal of Residuals

Ash residues from thermal destruction processes, including burning of wastes in industrial boilers and process equipment, appear to be acceptable for land disposal. However, they and other treatment residuals may be required to undergo solidification or encapsulation prior to land disposal. Present understanding of the interaction of solvent containing wastes and residuals with various solidification materials is limited and long-term interactions can only be inferred from short-term behavior. Potential problems associated with the disposal of process residuals is a major factor in assessing alternatives to land disposal.

Selection of Optimal Waste Management Alternative

Waste management options have been summarized previously in Table 1. These

include source reduction, recycling, use of a treatment system or some combination of these waste handling practices. Selection of the optimal management alternative will ultimately be a function of regulatory compliance, economics, and availability of onsite and offsite systems and equipment. Economic considerations include processing (including pretreatment and post-treatment) and disposal costs,

value of recovered products, and potential adverse effects on product quality or process equipment resulting from waste minimization or reuse of recovered products. Additional consideration in system selection must be given to factors such as safety, public and employee acceptance, liability, and degree of uncertainty in cost estimates and ability to meet treatment objectives.

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The complete report, entitled "Technical Resource Document: Treatment Technologies for Solvents Containing Wastes," (Order No. PB 87-129 821/AS; Cost: \$54.95, subject to change) will be available only from:

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