REVIEW OF ALTERNATIVE TREATMENT PROCESSES FOR HALOGENATED ORGANIC WASTE STREAMS

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ABSTRACT

Many of the solvent and nonsolvent halogenated organic wastes exhibit high toxicity, mobility, persistence and bioaccumulation. The EPA's Office of Research and Development is conducting a research program to develop information on the applicability, effectiveness, capacity, cost and environmental impact of existing alternative (to land disposal) halogenated waste treatment technologies. Processes evaluated at commercial offsite treatment facilities include evaporation, distillation, steam stripping and fuel blending.

INTRODUCTION

Large quantities of organic solvent and nonsolvent halogenated wastes are generated and land-disposed annually in the United States. The United States Environmental Protection Agency has estimated that 60 million gallons of organic solvent wastes and 1.44 million gallons of nonhalogenated organic wastes were landfilled in 1981. Much larger quantities of these wastes were land-disposed (400 million gallons solvent wastes and 3.1 million gallons of halogenated nonsolvent wastes). The data base used to estimate the volumes of these wastes is the "National Survey of Hazardous Waste Generators and Treatment, Storage, and Disposal Facilities Regulated under RCRA" (1981).

As many of these wastes exhibit high toxicity, mobility, persistence and bioaccumulation, the current land disposal practices may not sufficiently protect human health and the environment. The EPA previously promulgated regulations under the RCRA which restrict the land disposal of ignitable, reactive, incompatible, and liquid wastes, including ignitable solvents, explosive wastes, and reactive cyanides. The EPA is now reviewing existing controls to determine if further restrictions on land disposal of hazardous wastes are warranted and whether alternative waste management methods exist which are technically, environmentally, and economically practical.

WASTE CHARACTERIZATION

An analysis was made of the hazardous wastes listed in the following four RCRA Sections (1):

- ° 261.24 - Characteristics of EPA Toxicity (DOXX)
- ° 261.31 - Non-Specific Process Wastes (FOXX)
- ° 261.32 - Specific Process Wastes (KXXX)
- ° 261.33 - Discarded Commercial Chemical Products, Off-Specification Products, etc. (UXXX and PXXX)

This analysis identifies a total of 142 hazardous halogenated wastes (Table 1). There are 109 halogenated organic compounds represented by the 142 waste codes. Two of the more frequently generated halogenated wastes are F001 and F002:

F001 - Spent halogenated solvents used in degreasing: tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane,

TABLE 1. RCRA-LISTED WASTES CONTAINING HALOGENATED ORGANIC COMPOUNDS (HOCs) (2)

Waste Category	Total Number Listed in Part 261	Total Number Containing HOCs (%)	Listing of Specific Hazardous Waste Codes Containing One or More HOCs
DOXX	17	6 (35)	D012, D013, D014, D015, D016, D017
FOXX	13	2 (15)	F001, F002
KXXX	76	27 (36)	K001, K009, K010, K015, K016, K017, K018, K019, K020 K021, K028, K029, K030, K032, K033, K034, K041, K042 K043, K073, K085, K095, K096, K097, K098, K099, K105
PXXX	107	21 (20)	P004, P016, P017, P023, P024, P026, P027, P028, P033 P036, P037, P043, P050, P051, P057, P058, P059, P060 P095, P118, P123
UXXX	233	86 (37)	U006, U017, U020, U023, U024, U025, U026, U027, U029 U030, U033, U034, U035, U036, U037, U038, U039, U041 U042, U043, U044, U045, U046, U047, U048, U049, U060 U061, U062, U066, U067, U068, U070, U071, U072, U073 U074, U075, U076, U077, U078, U079, U080, U081, U082 U083, U084, U097, U121, U127, U128, U129, U130, U131 U132, U138, U142, U150, U156, U158, U183, U184, U185 U192, U207, U208, U209, U210, U211, U212, U222, U225 U226, U227, U228, U230, U231, U232, U233, U235, U237 U240, U242, U243, U246, U247
Totals	446	142 (32)	

carbon tetrachloride, and chlorinated fluorocarbons; and sludges from the recovery of these solvents in degreasing operations.

F002 - Spent halogenated solvents: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro- 1,1,2-trifluoroethane, ortho-dichlorobenzene, and trichlorofluoromethane; and 1,1,2-trichloroethane; the still bottoms from the recovery of these solvents, and certain spent mixtures /blends.

An example of a halogenated, nonsolvent waste is K001, a wastewater treatment sludge from wood preserving operations using creosote and/or pentachlorophenol. Large quantities of K001 wastes presently are stored in impoundments. Cleaning up these contaminated impoundments is required. Recovery of the creosote and oily components of the K001 sludges could partially offset closure costs. Quantities of other halogenated process wastes which were reported in the Part A data base are given in Table 2. The Part A data base was EPA's initial effort at registering facilities that generated and/or managed hazardous wastes.

TREATMENT ALTERNATIVES TO LAND DISPOSAL

Alternatives such as waste reduction, recycling, treatment, and incineration are usually preferable to land disposal. In a recent survey, waste management practices for eight halogenated "K" wastes (Table 3) were obtained from manfacturers of chlorinated aromatics. A total of sixty-five facilities reported their management techniques. Incineration is indicated to be the most prevalent form of treatment with the exception of K099 - untreated wastewater. Storage in tanks, containers and piles, recycle/reuse, and wastewater treatment were the other major management options reported. Alternative treatment technologies applicable to waste solvents and other halogenated organic wastes are discussed in the following sections.

ALTERNATIVE SOLVENT WASTE TREATMENT TECHNOLOGIES

The principal alternative treatment techniques with potential application to

TABLE 2 - WASTE QUANTITY DATA FOR HALOGENATED WASTES

Waste Code	EPA's Part A Data Base (MT)	Waste Code	EPA's Part A Data Base (MT)
F001	1,419,310	K035	119,385
F002	392,282	K041	68,649
K001	34,473	K042	74,518
K009	122,933	K043	79,125
K010	1,028,806	K073	25,349
K015	144,429	K085	27,383
K016	1,061,518	K095	23,597
K017	99,625	K096	9,082
K018	169,741	K097	917
K019	226,043	K098	14,525
K020	162,546	K099	14,979
K021	43,468	K105	918
K028	57,704	D012	120,988
K029	102,920	D013	72,906
K030	259,815	D014	77,898
K032	55,920	D015	69,546
K033	81,611	D016	61,219
K034	36,083	D017	79,617

both halogenated and nonhalogenated wastes, depending upon the physical form, are:

Air Stripping
Steam Stripping
Wet Air Oxidation
Incineration
Distillation
Solvent Extraction
Evaporation
Filtration
Drying
Carbon Adsorption
Resin Adsorption
Biological

Several of these technologies are used to separate and concentrate dilute solvent mixtures before further processing. The preferred treatment alternatives for waste solvents include reduction or elimination of the wastes generated at the point of use, recycle/reuse, and thermal oxidation.

Solvent reclamation techniques e.g. distillation, frequently require preliminary treatment of incoming waste materials. Technologies for solvent waste "pretreatment" include simple settling and flotation, screening, and filtration to remove solids. In some treatment facilities, thin-film evaporation is employed to separate solids from the recoverable organics. The separated residues may then be blended into a chlorine substitute suspension for use in manufacturing low alkali cement, a fuel for use at kilns and furnaces permitted to burn hazardous wastes, or stabilized for disposal at a secure landfill site. In addition to distillation, other general types of solvent reclamation technologies which are considered to have application to halogenated solvent waste streams are evaporation, fractionation, and steam stripping. A brief discussion of these technologies follows.

DISTILLATION (NON-FRACTIONATING)

Steam distillation is likely the most commonly used technique for recovery of halogenated solvents. Steam distillation is a process in which separation of materials is achieved by using their differences in boiling points. The two general types of simple steam distillation processes differ in the method of steam use, through coils or direct injection. Stills with steam coils (Figure 1) are widely used onsite by operators which do not have high solvent demands. Direct injection steam stills (Figure 2) are most effectively used on low boiling solvents that are not miscible in water. In tests conducted for the HWERL, a commercial solvent reclaimer distilled two batches of halogenated and two batches of nonhalogenated solvents. Over 90 percent of the initial solvents were recovered for reuse in less critical application (Table 4).

TABLE 4. FATE OF WASTE SOLVENT

	Volume (Percent)
Initial	1540 gallons
Recovered as Solvents	1400 gallons (91)
Recovered as Fuel	60 gallons (4)
Still Bottoms	60 gallons (4)
Wastewater	20 gallons (1)

About 60 gallons of still bottoms required solidification due to high chloride content. This facility usually disposes of low chloride distillation residues in fuel blends.

EVAPORATION

The two types of evaporators or separators usually employed to recover spent solvents are the scraped surface evaporator and thin-film evaporator. A scraped surface evaporator (Figure 3) is designed to facilitate density separation of spent solvent materials. This type of separator is suited for solvent streams with a high concentration of suspended solids and sludges. The thin-film separator (Figure 4) operates on the same principle as the scraped surface separator except that a film of liquid material is spread against the vessel wall where it is exposed to heat. The thin-film evaporator may be best suited for reclaiming low boiling point solvents. The five largest recycling facilities in California use thin-film evaporation to reclaim solvents directly or as preliminary treatment (3).

FRACTIONAL DISTILLATION

Two types of fractionation processes are commonly employed by industry to reclaim spent solvents: bubble tray or packed column. The bubble tray column (Figure 5) is used when a high purity product is desired. Pretreatment is usually required since solid materials carried over tend to build up on the trays and reduce the contact areas between the vapor and liquid phases, decreasing the overall efficiency. Settling in a tank followed by thin-film separation can remove solids to improve the purity of the liquid feed to the fractionation column. The packed

TABLE 3. CURRENT MANAGEMENT PRACTICES FOR SPECIFIC HALOGENATED PROCESS WASTES ACCORDING TO EPA's INDUSTRY STUDIES PROGRAM[a]

Waste Code	Waste Stream Description	Management Technique[b]							
		STR	IW	LF	IN	RR	SI	BB	Total
K016	Heavy ends or distillation residues from the production of carbon tetrachloride	2	-	1	3	1	-	-	7
K017	Heavy ends (still bottoms) from the purification column in the production of epichlorohydrin	1	-	-	2	1	1	-	5
K018	Heavy ends from the fractionation column in ethyl chloride production	1	-	-	2	1	1	-	5
K019	Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production	8	-	-	9	5	-	-	22
K020	Heavy ends from the distillation of vinyl chlorine in vinyl chloride monomer production	3	-	-	5	1	-	-	9
K028	Spent catalyst from the hydrochlorinator reactor in the production of 1,1,1-trichloroethane	-	-	1	1	2	1	-	5
K085	Distillation of fractionation column bottoms from the production of chlorobenzene	-	2	-	2	-	1	-	5
K099	Untreated wastewater from the production of 2,4-D	1	-	-	-	-	6	-	7
	TOTALS	16	2	2	24	11	10	0	65

[a] Source: EPA's Industry Studies Data Base

[b] STR: Storage in tank, container, or pile
LF: Landfill
RR: Recycle/reuse
BB: Burned in boiler
IW: Injection well
IN: Incinerator
SI: Wastewater treatment in surface impoundment

NOTE: Numbers in column refer to the number of facilities surveyed which reported the given management technique.

column fractionation system (Figure 6) differs from the bubble-tray system in that the column is packed with rings to increase the surface contact area and flow residence time. This modification can result in a higher quality reclaimed solvent. Separation or removal efficiencies of 99 percent and greater are possible for individual volatile components via fractional distillation.

STEAM STRIPPING

Steam stripping by direct injection of live steam can be used to treat aqueous wastes (less than 10 percent organics in water) and wastes containing over 10 percent organics. This process is used by some waste recyclers for recovery of volatile organics. However, a disadvantage is that additional treatment steps may be required to further reduce volatiles in the subsequently increased aqueous waste stream (4).

ALTERNATIVE NONSOLVENT HALOGENATED ORGANIC WASTE TREATMENT

As with the solvents, other halogenated organic wastes usually require preliminary treatment, depending on the physical matrix. Examples of some processes which could pretreat aqueous or non-aqueous wastes (5):

Sedimentation/skimming
Filtration
Neutralization
Dissolved air flotation
Heavy metal removal
Fluid extraction
Vacuum filtration
Grinding
Blending

In general, settling, flotation or filtration will accomplish solids removal from liquid wastes. Liquids and solids destined for incineration may require grinding and blending to produce a homogeneous injectable mixture with specific moisture, halide and heat contents. At one treatment facility tested by a HWERL Contractor, organic materials including paint, paint sludges, varnish and spent solvents were ground to reduce the solids particle size to a few microns. The final blend was suitable for burning in an incinerator or cement kiln (total organic halide less than 1 percent, heat value over 10,000 Btu/lb).

Other treatment methods for non-aqueous halogenated wastes include chemical dechlorination and chlorinolysis.

INCINERATION

For many halogenated organic wastes, incineration is the desirable disposal method because essentially complete destruction is possible. Incineration can be accomplished using a variety of methods depending on the physical characteristics of the waste. For example, the type of incineration selected may depend upon the viscosity of the liquid and the amount and size of solids. A rotary kiln or fluidized bed may be chosen for a viscous, high solids waste. Liquid injection would probably be chosen for a waste with low viscosity and low solids because of the lower cost of this process (5).

AQUEOUS WASTE TREATMENT

Generic treatment options for aqueous halogenated organic wastes include biological, chemical, and physical processes. Generally, only dilute aqueous wastes with an organic content of less than 1 percent are amenable to biological treatment and/or carbon adsorption (physical process). Wet air oxidation (chemical process) is usually applicable to wastes which are too dilute to incinerate economically and yet too toxic to treat biologically. Supercritical water oxidation is a newer chemical process where liquid phase oxidation destroys aqueous wastes containing high organic concentrations (1-20 percent). UV/ozone is another chemical process in which an aqueous waste is subjected to ultraviolet radiation and ozone. This method is also usually restricted to a 1 percent or lower concentration of organics.

CONCLUSION

There are alternative management methods available for treating many waste streams containing halogenated organic materials subject to the land disposal ban legislation. Commercial hazardous waste treatment facilities employ practical and economically viable processes for waste halogenated solvents and other organic wastes. Because of the Congressional mandate to protect human health and environment, some of these processes now employed in commercial and onsite treatment of wastes may need improved equipment design and instrumentation together with effective operating and maintenance procedures in order to comply with this provision of the RCRA.

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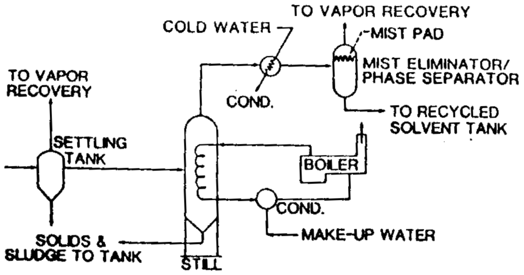

FIGURE 1. TYPICAL STEAM-COIL STILL SYSTEM

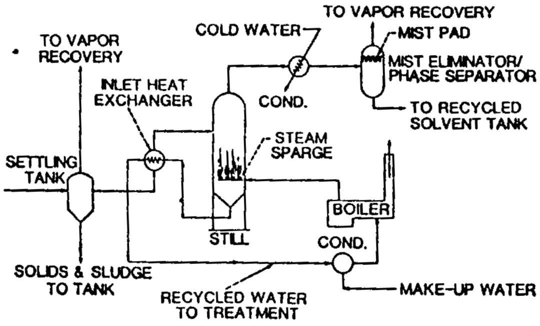

FIGURE 2. TYPICAL STEAM-STRIPPER STILL SYSTEM

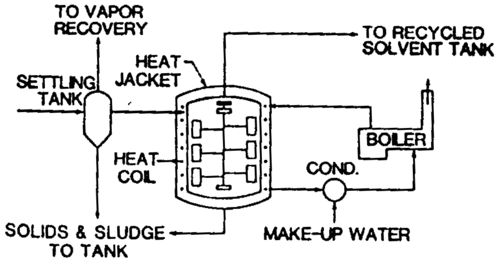

FIGURE 3. TYPICAL SCRAPED-SURFACE SEPARATOR SYSTEM

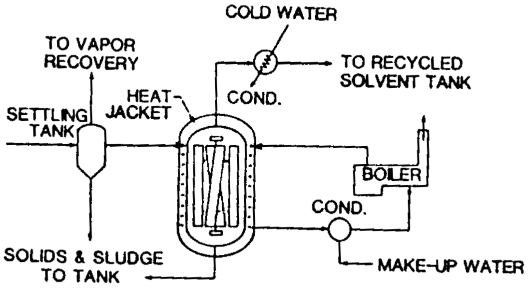

FIGURE 4. TYPICAL THIN-FILM SEPARATOR SYSTEM

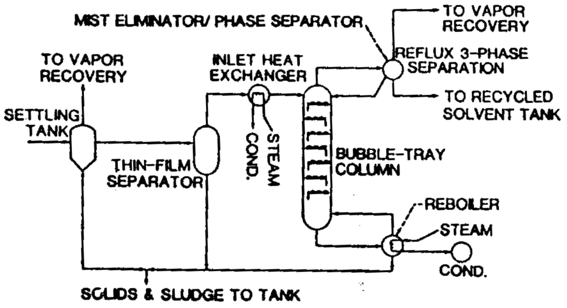

FIGURE 5. TYPICAL BUBBLE-TRAY COLUMN FRACTIONATION SYSTEM

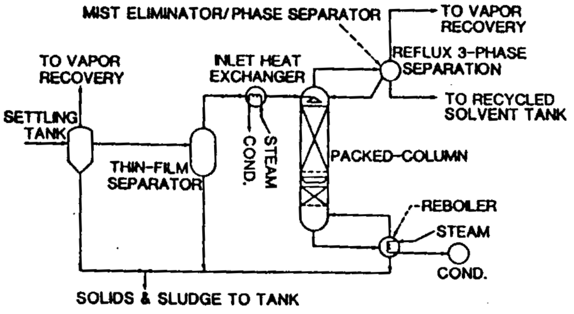

FIGURE 6. TYPICAL PACKED-COLUMN FRACTIONATION SYSTEM

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