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Project Summary

Technical Resource Document: Treatment Technologies for Halogenated Organic Containing Wastes, Volume I

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This halogenated organics technical resource document (TRD) is one of a series of five TRDs that are being prepared by the Hazardous Waste Engineering Research Laboratory. It provides information that can be used by environmental regulatory agencies and others as a source of technical information describing alternatives to the land disposal of nonsolvent halogenated wastes. These alternatives include waste minimization/recovery, treatment, and disposal of waste streams. Although emphasis is placed on the presentation of performance data for proven technologies, information dealing with the applicability of other emerging technologies is presented as well.

The treatment technologies discussed in this TRD include biological treatment as well as the following physical, chemical, and thermal treatment technologies:

Physical Treatment

Distillation
Evaporation
Steam-Stripping
Solvent Extraction
Carbon Adsorption

Chemical Treatment

Wet Air Oxidation
Supercritical Water
UV/Ozone Oxidation
Chemical Dechlorination
In Situ Vitrification

Thermal Treatment

Incineration Molten Glass Molten Salt Pyrolysis

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).

Introduction

EPA, as directed by the 1984 amendments to the Resource Conservation and Recovery Act (RCRA), is in the process of evaluating the availability and technical feasibility of land disposal alternatives for waste containing nonsolvent, halogenated organics. Prohibition of the land disposal of these wastes is scheduled for July 8, 1987. The wastes of concern, shown in Table 1, include halogenated organic pesticides listed as D type RCRA wastes on the basis of EP toxicity; halogens identified as present in many specific K type process waste streams; and nonsolvent halogens, listed in Part 261.33, identified as P and U type RCRA wastes.1

Scope

This halogenated organics technical resource document (TRD) is one of a series of TRDs that are being prepared by the Hazardous Waste Engineering Research Laboratory. It provides infor-

Table 1. RCRA-Listed Wastes Containing Halogenated Organic Compaounds (HOCs)

Waste Category	Total Number Listed in Part 261	Total Number Containing HOCs (%)				•	zardous Was e or More HO			
DOXX	17	6 (35)	D012	D013	D014	D015	D016	D017		
KXXX	76	27 (36)	K001 K020ª K041 K098	K009° K021° K042° K099	K010° K028° K043 K105°	K015ª K029ª K073ª	K016° K030° K085°	K017ª K032ª K095ª	K018ª K032 K096ª	K019ª K033 K097
PXXX	107	23 (21)	P004 P033 P058	P017 P035 P059	P023 P036 P060	P024 P037 P090	P025 P043 P095	P026 P050 P118	P027 P051 P123	P028 P057
UXXX	233	64 (26)	U006 U029 U041* U049 U073 U132 U185 U233	U017 U030 U042 U060 U081 U138 U192 U235	U020 U033 U043 U061 U082 U142 U207 U237	U023 U034 U044ª U062 U097 U150 U212 U240	U024 U035 U045° U066 U127 U156° U224 U242	U025 U036 U046ª U067 U128 U158 U230 U243	U026 U038 U047 U068 U129 U183 U231 U246	U027 U039 U048 U072 U130 U184 U232 U247
Totals	433	120 (28)								

^aContains or represents a specific halogenated organic compound addressed in the solvent TRD. ¹ Source Reference 1.

mation that can be used by environmental regulatory agencies and others as a source of technical information describing alternatives to the land disposal of nonsolvent halogenated wastes. These alternatives include waste minimization/recovery, treatment, and disposal of waste streams. Although emphasis is placed on the presentation of performance data for proven technologies, information dealing with the applicability of other emerging technologies is presented as well. Many of the technologies discussed here as applicable to halogenated organcis are also applicable to dioxins and halogenated solvent. Thus, frequent reference is made to the previously prepared solvent TRD2 and dioxin TRD3 since these represent extensive sources of information and data that can be directly related to the treatment of halogenated organic wastes.

Hazardous Waste Characteristics, Generation and Management

Halogenated organic constituents of concern include all listed halogenated organics not classified as solvents, dioxins, or polychlorinated biphenyls. As shown in Table 2, they include compounds present at 25°C in all physical states (i.e., gas, liquid, and solid) and with highly variable halogen content. The 78

halogenated organic compounds listed in Table 2 are constituents of 120 listed RCRA wastes identified in Table 1. An estimated 24.2 million gallons of these nonsolvent halogenated wastes were generated in 1981,⁴ appreciably less than the range of 765-2,600 million gallons reported for halogenated solvents in Reference 2. The quantities of waste generated are shown below for major halogenated organic waste subgroups.

Halogenated organic subgroup	Estimated maximum quantity generated (10 ⁶ gal/yr)
Pesticides (D wastes)	7.6
Specific processes (K wastes)	12.5
Single constituents (U and P wastes)	4.1
Total.	24 2

About 3.2 million gallons were land disposed in 1981. Treatment alternatives must be found for those wastes which exceed 1,000 ppm halogenated organics if a land disposal ban is instituted, as planned, in July 1987.

Treatment Technologies

A proposed scheme for the treatment of the 3.2 million gallons land disposed in 1981 was provided in Reference 4 and

is shown in Table 3. Treatment technologies were selected on the basis of waste physical form and rely heavily on incineration as a major means of halogen destruction, despite the low Btu value of most halogenated wastes. The physical state of the waste (both that of the constituents and the matrix) and halogen content are key factors in assessing the applicability of treatment technologies. However, the impact of other pertinent physical and chemical properties of the halogenated organic constituents affecting treatability (e.g., Henry's Law constant, partition coefficient, solubility, heat of combustion, etc.) must be considered, along with cost, in selecting the most effective treatment technology. 5-7

Most of the halogenated organic waste streams will require some sort of pretreatment prior to final treatment. General processes include phase separation (e.g., sedimentation, filtration, centrifugation, decantation), component separation (e.g., distillation, separation of aqueous wastes from organics), and chemical transformation (e.g., neutralization and precipitation of heavy metals) Wastes to be incinerated may require additional pretreatment in the form of particle size reduction or modification of viscosity by blending or heating. Some blending of halogens will likely be needed to reduce halogen content to specified limits and to increase the heating value

Table 2	. Waste Categorization Based o	n Physical State		
RCRA Waste Code	Compound Name	Molecular Formula	Molecular Weight	Halogen Content (% by Weight)
Gaseous	Compounds (@25°C)			
U043	Vinyl chloride	C ₂ H ₃ CI	62.5	57 CI
U033	Carbonyl fluoride	CF₂O	66	58 F
P033	Cyanogen chloride	CCIN	61.5	58 CI
U045	Methyl chloride	CH ₃ CI	50.5	70 CI
P095	Carbonyl chloride	CCI ₂ O	98.9	72 CI
U029	Methyl bromide	CH ₃ Br	9.5	84 Br
Liquid C	ompounds (@25°C)			
P043	Diisopropyl fluorophosphate	$C_6H_{14}FO_3P$	184	10 F
U062	Diallate	$C_{10}H_{17}CI_2NOS$	270.2	13 CI
U020	Benzene sulfonyl chloride	C ₆ H ₅ ClO ₂ S	176.6	20 CI
U038	Ethyl-4,4'-dichlorobenzilate	C16H14Cl2O3	325.2	22 CI
U048	2-Chlorophenol	C ₆ H ₅ CIO	128.6	28 CI
P028	Benzyl chloride	C_7H_7CI	126.6	28 CI
<i>U030</i>	1-Bromo-4-phenoxy benzene	$C_{12}H_9B_2O$	249	32 Br
P036	Dichlorophenyl arsive	C8H5AsCl2	222.9	32 CI
U097	Dimethyl carbamoyl chloride	C ₃ H ₆ CINO	107.6	33 CI
U042	2-Chloroethylvinyl ether	C ₄ H ₇ CIO	106.6	33 CI
U041	Epichlorohydrin	C ₃ H ₃ CIO	92.5	38 CI
U156	Methyl chlorocarbonate	$C_2H_3CIO_2$	94.5	38 CI
P027	3-Chloropropionitrile	C ₃ H ₄ CIN	89.5	40 CI
U024	Bis(2-chloroethoxy) methane	$C_5H_{10}CI_2O_2$	173.1	41 CI
U027	Bis(2-chloroisopropyl) ether	$C_6H_{12}CI_2O$	171.1	42 CI
U046	Chloromethoxymethane	C₂H₅CIO	80.5	44 CI
U017	Benzal chloride	$C_7H_6CI_2$	161	44 CI
P023	Chloroacetaldehyde	C_2H_3CIO	78.5	45 CI
U006	Acetyl chloride	C_2H_3CI	98.9	45 CI
U025	Bis(2-chloroethyl) ether	C4H8Cl2O	143	50 CI
U023	Benzotrichloride	C7H5Cl3	195.5	54 CI
P017	Bromoacetone	C₃H₅Be	137	58 Br
U235	Tris(2,3-dibromopropyl) phosphate	$C_9H_{15}Br_6PO_4$	697.7	69 Br
U034	Trichloroacetaldehyde	C ₂ HCI ₃ O	147.4	72 CI
U130	Hexachlorocyclopendadiene	C 5 C / 6	272.8	78 CI
U128	Hexachlorobutadiene	C4C/6	260.8	82 CI
U066	1,2-Dibromo-3-Chloropropane	C ₃ H ₅ Br ₂ Cl	236.4	68 Br/ 15 CI
U067	Ethylene dibromide	$C_2H_4Br_2$	187.9	85 CI
U184	Pentachloroethane	C ₂ HCI ₅	202.3	88 CI
U138	Methyl iodide	CH₃I	142	89 <i>l</i>
U068	Methylene bromide	CH ₂ Br ₂	173.9	92 Br
Solid Col	mpounds (@25°C)			
P025	Indomethacin			10 CI

to ensure satisfactory destruction of waste constituents

A distinction between solvent and nonsolvent halogenated compounds that has some impact on the feasibility of recovery/reuse can be generally drawn on the basis of use. For example, many of the nonsolvent halogenated organic wastes are used as pesticides. Recovery or treatment of these materials will be far less feasible than recovery or treatment of halogenated solvents used in degreasing or in other typical applications where concentration levels are high enough to justify economic recovery.

Thus, examples of recovery/reuse of nonsolvent halogenated organic compounds from waste streams are not extensive, although examples of recovery of halogens from specific K type process streams have been noted. One example involves the further treatment of column bottoms from perchloroethylene production by steam strippoing to remove light ends for reuse in the process. The heavier materials, consisting of hexachlorobutadiene, tars, and other heavy materials, could then be further fractionated to recover the hexachlorobutadiene as a product for resale.

A further distinction between halogenated solvents and the other halogenated compounds considered here can be drawn on the basis of molecular weight. Halogenated compounds are generally higher in molecular weight than the solvents. As shown in Table 2, many are solid compounds that will not be amenable to recovery by physical processes such as evaporation or steam stripping. Solvent extraction or adsorption processes could be considered for the recovery or concentration of these low pressure, halogenated vapor compounds.

Potential problems associated with disposal of residuals should also be considered. Residual disposal may be less of a problem for the nonsolvent halogens than for solvents because of the relatively high 1,000 ppm upper concentration limit acceptable for land disposal. Because many of the halogenated organics are solids, immobilization of residuals by solidification/encapsulation processes also may be more likely for these compounds than would be the case for solvents. However, the area of solidification/encapusulation is one requiring additional study before it can be considered viable technology for land disposal of residuals.

A summary of the processes that are now being used or have some potential

Table 2.	Continued			
RCRA Waste Code	Compound Name	Molecular Formula	Molecular Weight	Halogen Content (% by Weight)
P058	Fluoracetic acid (Na salt)	$C_2H_2FNaO_2$	137	19 F
P026	o-(1-Chlorophenyl) thiourea	$C_7H_7CIN_2$	187	19 CI
U047	2-Chloronaphthalene	$C_{10}H_7CI$	162.6	22 CI
U150	Melphalan	$C_{13}H_{18}CI_2N_2O_2$	305	23 CI
U035	Chlorambucil	C14H19Cl2NO2	304.2	23 CI
U039	p-Chloro-m-cresol	C_7H_7CIO	142.6	25 CI
P057	Fluoroacetamide	C ₂ H ₄ FNO	77	25 F
U026	Chlornaphazine	$C_{14}H_{15}CI_2N$	268.2	26 CI
U158	4,4'-Methylene-bis-2- chloroaniline	$C_{13}H_{12}CI_2N$	267.2	27 CI
P024	p-Chloroanılıne	C_6H_6CIN	127.6	28 CI
U192	Pronamide	$C_{12}H_{11}CI_2NO$	256.1	28 CI
U237	Uracil mustard	$C_8H_{11}CI_2N_3O_2$	252.1	28 CI
U073	3,3'-Dichlorobenzidine	$C_{12}H_{10}CI_2N_2$	253.1	28 CI
D014, U247	Methoxychlor	$C_{16}H_{15}CI_3O_2$	345.7	31 CI
D016, P035	2,4-D	$C_8H_6CI_2O_3$	221	32 CI
D017, U233	2,4,5-TP	$C_9H_7CI_3O_3$	269.5	40 CI
U232	2,4,5-T	$C_8H_6CI_3O_3$	255.5	42 CI
U060	DDD	$C_{14}H_{10}CI_{4}$	320.1	44 CI
U0 82	2,6-Dichlorophenol	C6H4Cl2O	163	44 CI
U081	2,4-Dichlorophenol	C6H4Cl2O	163	44 CI
U061	DDT	C ₁₄ H ₉ CI ₅	354.5	50 CI
U132	Hexachlorophene	$C_{13}H_6CI_6O_2$	406.9	52 CI
P050	Endosulfan	$C_9H_6CI_6O_3S$	406.9	52 CI
U 231	2,4,6-Trichlorophenol	$C_6H_3CI_3O$	197.5	54 CI
U230	2,4,5-Trichlorophenol	$C_6H_3CI_3O$	197.5	54 CI
P037	Dieldrin	$C_{12}H_8CI_6O$	380.9	56 CI
D012, P051	Endrın	C ₁₂ H ₈ Cl ₆ O	380.9	56 CI
P060	Isodrin	$C_{12}H_8CI_6$	365	58 CI
P004	Aldrın	$C_{12}H_8CI_6$	365	58 CI
U185	Pentachloronitrobenzene	$C_6CI_5NO_2$	295.4	60 CI
U212	2,3,4,5-Tetrachlorophenol	C ₆ H ₂ CI ₄ O	231.9	61 CI
U207	1,2,4,5-Tetrachlorobenzene	$C_6H_2CI_4$	215.9	66 CI
P059	Heptachlor	$C_{10}H_5CI_7$	373 4	67 CI
P090, U 24 2	Pentachlorophenol	C ₆ HCl ₅ O	266.4	67 CI
U036	Chlordane	$C_{10}H_6CI_8$	409.8	69 CI
D015, P123, U224	Toxaphene	C ₁₀ H ₁₀ Cl ₈	413.8	69 CI

for the treatment of halogenated wastes is provided in Table 4. The use of incineration and other thermal destruction processes for nonrecoverable halogenated organics is considered technically feasible. Effective thermal destruction of these compounds has been well documented, provided the wastes are pretreated to upgrade the overall heating value of the waste fed to the process. However, a cost penalty will be incurred as the halogen content of the waste increases, and there will be some incentive to consider other processes. The effectiveness of other treatment processes will depend upon the physical state or the waste matrix, and the concentration and physical/ chemical characteristics of the halogenated organic constituents of the waste. The higher molecular weight halogenated organics will generally be more amenable to adsorption processes and less amenable to chemical and biological treatments than lower molecular weight halogens. Each waste stream/treatment process combination must be considered carefully to establish the adequacy of treatment.

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Table 2.	Continued			
RCRA Waste Code	Compound Name	Molecular Formula	Molecular Weight	Halogen Content (% by Weight)
U183	Pentachlorobenzene	C ₆ HCl ₅	250.3	71 CI
U142	Kepone	$C_{10}CI_{10}O$	490.7	72 CI
D013, U129	Lindane	$C_6H_6CI_6$	290.9	73 CI
U127	Hexachlorobenzene	C 6 C / 6	284.8	75 CI

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Table 3. Summary of Existing Waste Treatment Technologies

Waste Category	Land Disposed Waste Volume (gal/yr)	Existing Treatment Technology	Comment
High chlorine content KXXX wastes	1,673,977 (liquid)	Liquid injection incineration/waste blending/caustic scrubbing	~4,000 Btu/lb
	612,291 (solid)	Rotary kiln incineration	~4,000 Btu/lb
Halogenated aqueous KXXX wastes	O	Filtration/steam stripping/carbon adsorption	
Halogenated aqueous sludge KXXX wastes	23,970	Waste blending/liquid injection incineration	~4,000 Btu/lb
		Rotary kiln incineration	~4,000 Btu/lb
Halogenated high inorganic KXXX liquid wastes	128	Rotary kiln incineration with high efficiency scrubber	~1,000 Btu/lb
		Solidification/land disposal	
Halogenated potential gases	0	Liquid injection incineration/causic scrubbing	Unknown Btu content
Halogenated potential solids	68,216	Rotary kiln incineration with caustic scrubbing	Assumed ~4,000 Btu/lb
Other halogenated organics with inorganic solids	759,274	Rotary kiln incineration with caustic scrubbing	Assumed ~1,000 Btu/lb
Total	3,137,860		

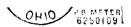
Source: Reference 1.

 Table 4.
 Summary of Halogenated Organic Treatment Processes

Process	Applicable Waste Streams	Stage of Development	Performance	Residuals Generated
Incineration				
Liquid injection incineration	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.	Estimated that over 219 units are in use. Most widely used incineration technology.	Excellent destruction efficienty (>99.99%). Blending can avoid problems associated with residuals, e.g., HCl.	TSP, possibly some PICs, and HCl. Little ash if solids removed in pretreatment processes.

Process	Applicable Waste Streams	Stage of Development	Performance	Residuals Generated
Rotary kıln incıneratıon	All wastes provided Btu level is maintained.	Over 40 units in service; most versatile for waste destruction	Excellent destruction efficiency (>99.99%).	Requires APCDs. Process residuals should be acceptable if charged properly and treated for acid gas removal.
Fluidized bed incineration	Liquids or nonbulky solids.	Nine units reportedly in operation-circulating bed units under development.	Excellent destruction efficiency (>99.99%).	As above.
Fixed/multiple hearths	Can handle a wide variety of wastes.	Approximately 70 units in use. Old technology for municipal waste combustion.	Performance may be marginal for halogenated wastes.	As above.
Industrial kılns	Generally all wastes, but Btu level, chlorine content, and other impurity content may require blending to control charge characteristics and product quality.	Only a few units now burning hazardous waste.	Usually excellent destruction efficiency (>99.99%) because of long residence times and high temperatures.	As above.
Other Thermal Technol	logies			
Circulating bed combustor	Liquids or nonbulky solids.	Only one U.S. manufacturer. No units treating hazardous waste.	Manufacturer reports high efficiencies (>99.99%).	Bed material additives can reduce HCl emissions. Residuals should be acceptable.
Molten glass incineration	Almost all wastes, provided moisture and metal impurity levels are within limitations.	Technology developed for glass manufacturing not available yet as a hazardous waste unit.	No performance data available, but DREs should be high (>99.99%).	Will need APC device for HCI and possibly PICs; solids retained (encapsulated) in molten glass.
Molten salt destruction	Not suitable for high (>20%) ash content wastes.	Technology under development since 1969, but further development on hold.	Very high destruction efficiencies for organics (six nines for PCBs).	Needs some APC devices to collect material not retained in salt.
Furnace pyrolysis units	Most designs suitable for all wastes.	One pyrolysis unit RCRA permitted. Certain designs available commercially.	Very high destruction efficiencies possible (>99.99%). Possibility of PIC formation.	TSP emissions lower than those from conventional combustion; will need APC devices for HCl. Certain wastes may produce an unacceptable tarry residual.
Plasma arc pyrolysis	Present design suitable only for liquids.	Commercial design appears imminent, with future modifications planned for treatment of sludges and solids	Efficiencies exceeded six nines in tests with solvents.	Requires APC devices for HCP and TSP, needs flare for H_2 and CO destruction.
Fluid wall advanced electric reactor	Suitable for all wastes if solids pretreated to ensure free flow	Ready for commercial development. Test unit permitted under RCRA.	Efficiencies have exceeded six nines.	Requires APC devices for TSP and HCI.
In situ vitrification	Technique for treating contaminated soils, could possibly be extended to slurries. Also use as solidification process	Not commercial, further work planned.	No data available, but DREs of over six nines reported.	Off gas system needed to control emissions to air. Ash contained in vitrified soil.

Process	Applicable Waste Streams	Stage of Development	Performance	Residuals Generated
Physical Treatment Me				
Distillation	This is a process used to recover and separate volatile organics. 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 volatiles 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 volatile organic recovery process. Typical recovery of 60 to 70 percent.	Bottoms will contain volatiles. Generally suitable for incineration.
Steam Stripping	A simple distillation process to remove volatile organics from aqueous solutions. Preferred for low concentrations and organics with low solubilities.	Technology well developed and available.	Not generally considered a final treatment, but can achieve low residual organic levels.	Aqueous treated stream will probably require polishing. Further concentration of overhead steam generally required.
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 organic/waste combinations.	Organic compound 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 organics 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 compounds.	Technology well developed in industry for special resin/organic compound combinations. Applicability to waste streams not demonstrated.	Can achieve low levels of organics in effluent.	Adsorbate must be processed during regeneration.
Chemical Treatment P	rocesses			
Wet air oxidation	Suitable for aqueous liquids, also possible for slurries. Organic 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% organics.	Supercritical conditions may impose demands on system reliability. Commercially available in 1986.	Supercritical conditions achieve high destruction efficiencies (>99.99%) for all constituents.	Residuals not likely to be a problem. Halogens can be neutralized in process.
UV/Ozonation	Oxidation with ozone (assisted by UV) suitable for low solid, dilute aqueous solutions.	Now used as a polishing step for wastewaters.	Not likely to achieve residual levels in the low ppm range for most wastes.	Residual contamination likely: will require additional processing of of gases.
Dechlorination	Dry soils and solids.	Not fully developed.	Destruction efficiency of over 99% reported for dioxin	Residual contamination seems likely.
Biological Treatment M	Methods			
	Aerobic technology suitable for dilute wastes although some constituents will be resistant.	Conventional treatments have been used for years.	May be used as final treatment for specific wastes, may be pretreatment for resistant species.	Residual contamination likely; will usually require additional processing.



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The complete report, entitled "Technical Resource Document: Treatment Technologies for Halogenated Organic Containing Wastes, Volume I," (Order No. PB 88-131 271/AS; Cost: \$38.95) will be available only from:

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