MANAGEMENT OF HAZARDOUS WASTES CONTAINING HALOGENATED ORGANICS

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ABSTRACT

The 1984 RCRA amendments direct EPA to study available treatment technologies for waste streams containing halogenated organic compounds. If it is determined that existing technology and capacity is sufficient for management of these wastes, then effective July 8, 1987, wastes containing halogenated organic compounds will be prohibited from land disposal. This paper presents estimates for volumes of halogenated wastes generated and managed in the U.S. and a brief overview of treatment technologies that have been demonstrated to be effective in handling these streams. Also presented are descriptions of and preliminary sampling results from two treatment facilities evaluated by GCA during our continuing performance evaluation program for EPA's Hazardous Waste Engineering Research Laboratory (HWERL).

INTRODUCTION

In the 1984 RCRA amendments, halogenated wastes are defined as any hazardous waste containing halogenated organic compounds (HOCs) in total concentration greater than or equal to 1,000 mg/kg.[1] Unless ongoing studies show that there is insufficient technology and/or capacity for managing these wastes, they will be prohibited from land disposal on July 8, 1987. Similar land disposal restrictions are already in effect in California and New York State.[2] In California, hazardous wastes containing HOCs in total concentration greater than or equal to 1,000 mg/kg were restricted from land disposal effective January 22, 1983. In New York State, hazardous waste containing more than 5 percent by weight (50,000 mg/kg) of halogenated chemicals were prohibited from land disposal after March 31, 1985.

WASTE GENERATION

National estimates of quantities of halogenated organic wastes generated and land disposed are given in Table 1. As shown, relatively small quantities of solvents and nonsolvents are land disposed, compared to total generation. Most of the land disposed quantity for solvents is handled by deepwell injection, while for nonsolvents, about half is landfilled and half is deepwell injected.

WASTE TREATMENT ALTERNATIVES

EPA has proposed regulations for implementation of the land disposal prohibitions, including treatment standards and effective dates for waste solvents (FR, Vol 51 ,No. 9, January 14, 1986, pp 1602-1766). The Agency concluded that biological degradation, steam stripping, air stripping, carbon

TABLE 1. ESTIMATES OF VOLUMES (10^6 gal/yr) GENERATED AND LAND DISPOSED FOR HALOGENATED WASTES

Category	Solvents	Nonsolvents
Total Quantity Generated	4,200	24.2
Total Quantity Land Disposed	400	3.1

Source: References 3 and 4.

adsorption, distillation, incineration, and use as a fuel substitute are demonstrated technologies for treatment of (halogenated) solvent wastes and that resin adsorption, chemical oxidation, wet air oxidation, chemical reduction, encapsulation, and chemical fixation/solidification have potential applicability but are not yet fully demonstrated. EPA has defined best demonstrated achievable technology (BDAT) as steam stripping, carbon adsorption, biological treatment, or some combination for waste (halogenated) solvents amenable to separation/removal techniques and either incineration or use as a fuel substitute for wastes not amenable to separation/removal methods. Final treatment processes with potential application to halogenated organic wastes are similar to those available for solvents and include nonaqueous and aqueous technologies:

1. Nonaqueous waste treatment--
   - Liquid injection incineration
   - Rotary kiln incineration
   - Fluidized-bed incineration
   - Molten salt incineration
   - Plasma arc incineration (pyrolysis)
   - High temperature fluid wall reactor
   - Lime/cement kiln coincineration
   - Chemical dechlorination
   - Chlorinolysis
2. Aqueous waste treatment and wastewater treatment--
   - Wet air oxidation
   - Activated carbon adsorption
   - Steam stripping
   - Biological treatment
   - UV/ozonation
   - Supercritical water oxidation

Table 2 presents an overview of each of these technologies as applied to various physical matrices. Detailed discussions of each process are available in the literature.[4]

FIELD STUDIES

GCA has conducted preliminary investigations of commercial hazardous waste treatment, storage, and disposal facilities (TSDFs) as part of a continuing program for HWERL. The purpose of this work is to gather background and performance data on various treatment processes for use by HWERL (and ultimately EPA's Office of Solid Waste) in the development of regulations pertaining to waste-specific land disposal restrictions.

To date, fifteen TSDFs have been visited under this program and two facilities handling halogenated organic streams have been evaluated through field measurement activities. A brief discussion of these sampling programs follows.

Plant A

This facility handles both halogenated and nonhalogenated solvent wastes designated as F001-F005. Still bottoms containing volatile halogenated organic compounds are processed in a nonagitated thin film evaporator (TFE) to remove residual solvent. In addition, the company treats other spent halogenated solvents using a combination of direct steam injection (roughing still) and indirect, convection heated (polishing still) distillation.

TABLE 2. TREATABILITY MATRIX FOR HALOGENATED NONSOLVENT WASTES

Treatment alternative	Aqueous streams	Inorganic streams	Organic liquids	Organic solids
Established Technologies				
Rotary kiln incineration		X	X	X
Fluidized-bed incineration			X	X
Liquid injection incineration			X	
Lime/cement kiln coincineration			X	
Carbon adsorption	X			
Steam stripping	X			
Biological treatment	X			
Emerging Technologies				
Molten salt incineration			X	X
Plasma arc incineration (pyrolysis)			X	X
High temp. fluid wall destruction		X	X	X
Supercritical water oxidation	X			
UV/ozone treatment	X			
Wet air oxidation	X			
Chemical dechlorination			X	
Chlorinolysis			X	

Sampling was conducted on the TFE on three different days: one while processing a waste oil containing 1,1,1-trichloroethane (1,1,1-TCE) and trichloroethylene (TCE), and the other two during processing of a perchloroethylene (PCE) - oil mixture at two different feed rates. Operating conditions are noted in Table 3 and preliminary results are provided in Tables 4-7.

The TFE operated at atmospheric pressure, temperatures of 250-300°F, and a feed rate of 1.0-2.2 gpm. Runs 1 and 3 involved processing of a waste stream much higher in solvent than normally run through the unit. Lab analyses performed at Plant A prior to waste treatment showed a PCE content of only 3 percent, whereas the generator had claimed that the PCE content was much greater than 20 percent. Thus, Plant A did not do any preliminary treatment on this stream in one of their batch stills. Subsequent analyses (GC/FID and GC/MS) at the GCA laboratory showed much higher PCE levels of around 35 percent. The reduction in solvent from waste feed to separated oil for Runs 1 and 3 was, therefore, much less than expected (20-30 percent) and this stream required additional treatment. Run 2, which involved a waste stream of only 2 percent total solvent, provides a better indication of the TFE's capabilities as solvent reduction from the feed to the bottom stream ranged from 90 percent for PCE to 98 percent for 1,1,1-TCE. Run 2 also showed a significant increase in heat content (due to both solvent and water removal) from the feed to the oil stream as noted in Table 5. Metal analyses as shown in Tables 6 and 7 indicate significant increases in concentration from the feed to the separated oil stream. The highest levels were recorded for copper, zinc, lead, and chromium. This may warrant further attention to these types of facilities since these bottom streams are typically used offsite as supplemental fuels in boilers, blast furnaces, and cement kilns.

One day of sampling was devoted to the steam distillation unit, during which time a waste solvent consisting primarily of 1,1,1-TCE was processed. The feed rate for this unit was variable, but during the 264 minute test period, 10 drums were treated for an average feed rate of 2.1 gpm. The operating temperature ranged from 112 to 212 °F. Samples collected included the roughing still bottoms, the water separated in a coalescer, and solvent product obtained downstream from a second coalescer after the polishing still.

The waste feed to this process was a two-phase liquid (upper phase about 30 percent of the volume and lower phase about 70 percent) wherein the upper phase was found to contain approximately 5 percent 1,1,1-TCE and the lower phase about 100 percent 1,1,1-TCE. Other solvents found to be present in the waste feed included methylene chloride, methyl ethyl ketone, dimethyl ketone, TCE, and PCE. Following water separation, the product stream from the polishing still was 89 percent 1,1,1-TCE. The roughing still bottoms, which were also two-phase, showed 2.8 percent and 4.4 percent 1,1,1-TCE in the upper and lower phases, respectively.

Air monitoring was also conducted at this site using a Century Systems Organic Vapor Analyzer (OVA). These measurements were taken to provide gross estimates of fugitive solvent emissions at the site. Measured values ranged from about 10 ppm (as methane) at a background location to about 700 ppm (methane) at an induction fan located on the roof above the processing area. Several high readings recorded (500-700 ppm) were attributed to minor spills that occurred during the test period.

Plant B

GCA also sampled a LUWA agitated TFE at a second TSDF during processing of a halogenated waste stream containing mostly TCE (F001). (Other nonhalogenated streams

TABLE 3. TFE OPERATING CONDITIONS, PLANT A

Run No.	1	2	3
Waste description	PCE/oil mixture from degreasing	1,1,1-TCE and TCE mixture from degreasing	Same as run No. 1
RCRA Waste Code	F001	F001	F001
No. of drums processed	6	6	6
Test duration, min	212*	237	318
Feed rate, gal/min	2.2	1.4	1.0
Avg. temp., °F	300	250	300
Pressure	atmospheric	atmospheric	atmospheric

*The unit was shut down several times during the test period.

TABLE 4. ORGANIC ANALYSES, PLANT A (TFE)

Run No.	1	2	3
Waste Feed			
PCE	37%	1,050 ppm	33%
1,1,1-TCE	3,100 ppm	2,400 ppm	--
TCE	6,500 ppm	1.73%	--
Ethyl benzene	--	210 ppm	--
Separator Oil			
PCE	25%	108 ppm	26%
1,1,1-TCE	--	57 ppm	--
TCE	--	860 ppm	--
Ethyl benzene	--	26 ppm	--
Toluene	--	3 ppm	--
Solvent Product			
PCE	87%	NA	84%
Methylene chloride	6,500 ppm	NA	--

TABLE 5. TOTAL CHLORIDES AND HEAT CONTENT, PLANT A (TFE)

Run no.	Waste feed	Separated oil	Solvent product
	chloride concentration, 10^3 µg/g (heat content, Btu/lb)		
1	239 (13,633)	170 (15,605)	437 --
2	-- (10,287)	-- (18,520)	-- --
3	236 (13,580)	160 (15,230)	548 --

TABLE 6. METAL ANALYSES, PLANT A (TFE RUNS 1 AND 3)

Metal	Metal concentrations, µg/g Run 1 (Run 3)	
	waste feed	separated oil
Cr	1.1 (0.36)	1.0 (0.56)
Cu	5.9 (3.6)	8.2 (4.1)
Pb	4.8 (3.3)	8.6 (1.5)
Zn	9.4 (8.8)	13.0 (12.5)

Note: All solvent products streams < 0.06 µg/g

TABLE 7. METAL ANALYSES, PLANT A (TFE RUN 2)

Metal	Metal concentrations (µg/g)	
	waste feed	separated oil
Ag	7.1	17.7
Cd	9.1	18.3
Cr	15.6	38.7
Cu	570	1,358
Ni	12.2	27.3
Pb	46.3	57.3
Zn	320	734

Note: All solvent product streams < 0.6 µg/g, except: Cu (5.1) and Zn (6.5).

were also sampled at Plant B.) The halogenated stream treated was a combination of degreasing wastes from two paper mills, a transformer manufacturer, and a cannery. Sampling lasted four hours, during which time 342 gallons were processed resulting in an average throughput of 86 gph. This feed rate was roughly one-third of normal (300 gph) due to problems experienced with the still bottoms pump. The percent recovery achieved for this waste stream was 70 percent. The average hot oil (used to heat the TFE) inlet temperature during the run was 311 °F and the average vacuum was 5.6 in Hg. Preliminary analytical results from this facility are not yet available.

CONCLUSIONS

Both theoretical and field investigations conducted to date indicate that there appear to be an adequate variety of demonstrated treatment technologies available for management of halogenated organic waste streams. The relatively small quantities of these wastes that are believed to be land disposed may mean that treatment capacity is also available, although this has not been determined as yet.

Evaluation of two waste treatment facilities handling halogenated organic streams revealed two particularly important observations. First, strict attention was given to the characteristics of still bottom streams so as to avoid subsequent land disposal. Residual solvents are intentionally left in these bottom streams so that they remain pumpable and have sufficient heat content to suit prospective customers. This may be especially important since certain metals were shown to be enriched in the bottom stream (separated oil) at one facility where the ultimate (offsite) use of the bottom stream is as a supplemental fuel in a cement kiln.

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