



## Project Summary

# Case Studies of Hazardous Waste Treatment to Remove Volatile Organics

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Three treatment processes were investigated for the removal of volatile organic (VO) compounds from hazardous waste: thin-film evaporation, steam stripping, and steam stripping with carbon adsorption. The data collected included the VO removal effectiveness, air emissions from the process, cost, and process limitations.

Pilot-scale tests of a thin-film evaporator treating refinery sludges showed that greater than 99 percent removal of purgeable organics and over 10 to 75 percent of extractable organics (depending on operating conditions) could be obtained. Two full-scale steam strippers treating aqueous wastewaters containing about 6,000 ppm purgeable organics were tested. Total VO removal efficiencies of 99.8 and 99.999 percent were obtained. At a full-scale steam stripper/carbon adsorption unit, 92 percent reduction in extractable organics was obtained by the stripper alone, while an overall removal efficiency of greater than 99.6 percent was obtained by the stripper followed by carbon adsorption.

*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

The U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS) is developing regulations under the 1976 Resource Conservation and Recovery Act

(RCRA) and its 1984 amendments to control air emissions from hazardous waste treatment, storage, and disposal facilities (TSDF). The purpose of the air emissions regulations is to protect human health and the environment from emissions of volatile compounds and particulate matter.

Sources of volatile organic (VO) emissions include storage tanks, treatment processes, surface lagoons, landfills, land treatment, and drum storage and handling facilities. Approximately 5,000 TSDF locations exist in the United States where one or more of these activities is in progress. Most of these sites are part of industrial facilities, and the rest are commercial facilities that accept wastes from offsite.

Research has concentrated on the characterization of uncontrolled emissions from these sources by using field measurements and by determining the reliability of emission models. Recent investigations have identified a number of options for controlling VO emissions from TSDF. These include restricting the VO concentrations of wastes going to sources where emission rates would be high, i.e., the "pretreatment" of waste to remove volatiles, and the use of in-situ (i.e., add-on) control techniques at the TSDF.

The purpose of the field tests reported here was to collect data for the support of regulations that consider waste pretreatment as an alternative for the control of volatile air emissions from TSDF. To the extent possible, these data were collected from processes that were treating hazardous wastes or that were treating wastes with physical characteristics similar to hazardous wastes in

order to permit a comparison of pretreatment to other emission controls. For the purposes of these tests, the term "volatile organic (VO)" includes those compounds which can be identified in wastes using separation *via* purging, or acid or base/neutral extraction (e.g., EPA Methods 624 and 625).

Field data collected on several waste treatment techniques helped determine (1) how efficiently they remove volatiles from hazardous waste streams, (2) what the removal costs are, (3) how the byproducts from the pretreatment technologies are collected and disposed of, and (4) what limitations (in terms of waste types, volatile concentrations, etc.) are placed on the use of such treatment techniques.

### **Approach**

The processes selected for evaluation included a pilot-scale thin-film evaporator used to treat refinery sludge, two steam strippers used to remove purgeable organic compounds from industrial wastewater, and one steam stripper used in combination with liquid-phase carbon adsorption to remove semivolatile (i.e., extractable) organic compounds from wastewater. Preliminary site visits were conducted to observe and discuss the process operation and to collect information on process limitations, costs, operating conditions, and potential sampling points.

Detailed sampling and analysis plans, which also included the quality assurance plan, were written for each site. These plans provided details on the proposed sampling and analytical approaches, sampling points and number of samples, and the quality assurance/quality control (QA/QC) procedures and goals. Liquid samples were collected at the influent and effluent to each treatment unit. Samples of process residuals, such as sludge, recovered organics, and air emissions, were also taken. Steam stripper tests lasted for two days at each site. The pilot-scale TFE test lasted for four days.

The thin-film evaporator (TFE) study was a pilot-scale evaluation of the TFE for removal of VO from petroleum refinery sludges. These sludges were non-hazardous refinery wastes that were chosen because they had physical properties (e.g., boiling point curves) similar to API separator and DAF unit sludges (which are listed hazardous wastes). The study was performed at three tempera-

tures and three flow rates, and under both vacuum and atmospheric pressure.

Two full-scale steam strippers used to treat industrial wastewater containing about 6,000 ppm of purgeable organics were tested. The tray column stripper at Plant H processes about 850 L/min of water that contained primarily ethylene dichloride and chloroform. The packed column steam stripper at Plant I processed about 42 L/min of water that contained primarily methylene chloride and chloroform. At Plant I, an upstream decanter was used to remove solids and organic phases from the waste stream. This decanter was also sampled.

The steam stripping/carbon adsorption unit at Plant G was used to remove semivolatiles from water, which contained nitrobenzene, 2-nitrotoluene, and 4-nitrotoluene. The industrial wastewater flow rate for this packed column stripper was 500 L/min. The carbon adsorption columns contained about 20,000 kg of carbon.

The data were analyzed to determine the process removal efficiency for the specific organic compounds found in the waste. Removal efficiencies were calculated for each constituent and for total VO. Measurements of vent flow rates and vapor concentrations were used to calculate or estimate air emissions from the process. Process residuals were characterized in terms of quantity and VO content. In addition, cost data were collected and evaluated to provide an assessment of the total cost of the process and the cost-effectiveness for VO removal.

## **Summary of Findings**

### **General Conclusions**

Each of the processes investigated successfully removed VO from the wastes. The TFE removed over 99 percent of the VO from petroleum refinery sludge, the two chemical industry steam strippers removed 99.8 to 99.999 percent of the VO (purgeable organic compounds) from the wastewater, and the steam stripper/carbon adsorber removed 99.6 percent of the VO (primarily semivolatiles) from aqueous wastes. The results are summarized in Tables 1, 2, and 3.

Table 1 shows that steam strippers can reduce purgeable organics from 6,000 ppm to less than 9.8 ppm at Plant H or to less than 37 ppb at Plant I. Semivolatiles may be reduced by steam stripping

from over 600 ppm to about 48 ppm as shown in Table 2. Carbon adsorption of these semivolatiles reduced concentrations to below detection limits (<0.8 ppm). The TFE generally reduced volatile compounds by over 99 percent. Semivolatiles such as naphthalene and methylnaphthalene were removed efficiently (85-97 percent) at the higher temperature runs (Table 3).

The applicability of each of these processes depends in part on the solids content of the wastes. The TFE can handle sludges that contain high-boiling oils (17 to 25 percent oil) and solids (2 to 3 percent solids). The steam stripper tests showed that solids may need to be removed prior to steam stripping to 0.01 g/L (as done at Plant I) or the operator may experience fouling and frequent cleaning (as seen at Plant H with 1.4 g/L). Solids removal prior to steam stripping generates a sludge containing VO that may be a troublesome disposal problem.

The various processes that generate air emissions are preliminary treatment tanks (e.g., solids decanters), feed and storage tanks, condensate collection and storage tanks, and process vents (e.g., condenser vents). Condenser efficiencies for volatile organics ranged from 91 percent (cooling tower water at 21°C) to 99 percent for a condenser cooled with refrigerated glycol (2°C).

### **Thin-Film Evaporator (TFE) Conclusions**

TFEs are able to process nonhomogeneous feed streams such as oily refinery sludges. The major process limitations are that the feed and bottoms product must be pumpable and the feed should not foam excessively during processing.

The TFE was found to have very high removal efficiencies of VO compounds from the waste sludges that were tested. In each of the three methods used to assess the reduction of volatiles, the removal efficiencies for VO compounds were greater than 99 percent. The removal efficiency for VO was greatest when the TFE was operated at the highest temperature (320°C). VO removal at this temperature generally exceeded 99 percent, with no clear trends relative to changes in feed rate. The percent of semivolatiles removed from the feed ranged from 10 to 75 depending on the TFE operating conditions.

There were difficulties when the system was operated at high tempera-

**Table 1. Summary of Steam Stripper Performance for Purgeable Volatile Organics**

Compound	In (ppm)	Out (ppm)	Percent Reduction
<i>Plant H</i>			
1,2-Dichloroethane	5,630	0.097	99.998
Chloroform	271	9.6	96.5
1,1-Dichloroethane	11	<0.01	>99.9
1,2-Dichloroethene	8.9	<0.01	>99.9
Vinyl Chloride	8.4	<0.01	>99.9
1,1,2-Trichloroethane	7.5	<0.01	>99.9
Other Volatiles	14	<0.01	>99.9
<b>Total</b>	<b>5,950</b>	<b>&lt;9.8</b>	<b>&gt;99.8</b>
<i>Plant I</i>			
Methylene chloride	4,490	0.011	99.999
Chloroform	1,270	0.006	99.999
Carbon Tetrachloride	55	<0.005	>99.99
Chloromethane	33	<0.005	>99.98
Other volatiles	11	<0.005	>99.95
<b>Total</b>	<b>5,860</b>	<b>&lt;0.037</b>	<b>&gt;99.999</b>

**Table 2. Summary of Steam Stripper and Carbon Adsorber Performance for Semivolatiles (Plant G)**

	Nitrobenzene	2-Nitrotoluene	4-Nitrotoluene	Total
<i>Concentrations (ppm)</i>				
To stripper	505	78	51	634
From stripper	41	2.4	4.4	48
From adsorber	<0.8	<0.8	<0.8	<2.4
<i>Percent reduction</i>				
Stripper	92	97	91	92
Adsorber	>98	>67	>82	>95
Overall	>99.8	>98.9	>98.4	>99.6

**Table 3. Summary of Thin-Film Evaporator Results for Two Temperatures**

Compound	In	Out <sup>a</sup>	Percent Reduction	Out <sup>b</sup>	Percent Reduction
Toluene	2,800	5.8-6.1	99.8	2.7-4.6	99.8-99.9
2-Methylnaphthalene	790	320-660	16-59	99-120	85-87
Naphthalene	765	160-520	32-79	24-46	94-97
m-Xylene	280	1.3-3.8	99-99.5	0.7-0.9	99.7-99.8
o,p-Xylene	280	1.4-4.4	98-99.5	0.7-0.9	99.7-99.8
Benzene	230	<0.01-1.0	99.6->99.9	<0.01-0.6	99.7->99.9
Ethylbenzene	180	0.7-2.1	99-99.6	0.4-0.6	99.7-99.8
Styrene	160	0.8-2.5	98-99.5	1.2-1.6	99-99.3

<sup>a</sup> From Runs 5 and 7 at 150°C.<sup>b</sup> From Runs 8 and 10 at 320°C.

ture (320°C) under vacuum, as some carryover of feed into the condensate was observed. The condensate from the vacuum runs was a milky-white emulsion that would require additional treatment to separate the oils.

The gas flow rates and total VO emissions from the TFE condenser were highly dependent on the waste being processed. The first waste, an emulsion tank sludge, showed only minimal (less than 250 mL/min) flows from the condenser, and the second waste, oily tank bottoms, showed much higher (0.75 to 10 L/min) vent gas flow rates. All of the condenser vent gas concentrations were greater than 10,000 ppm (reported as hexane). The high VO concentrations in the vent gas were due to the vapor pressure of light hydrocarbons at the cooling water temperatures. A glycol-cooled condenser, a two-stage condenser (first stage cooling water, second stage chilled glycol), an incinerator, or some other appropriate control device could be used to reduce these emissions. The condenser and vent gas control system should be designed specifically for the waste to be treated because different wastes may contain different quantities of noncondensable or difficult-to-condense compounds.

The approximate capital and operating costs of TFEs when used to process petroleum waste sludges using various operational modes range from comparable to less than the cost of conventional land treatment. The cost of TFE sludge treatment was either \$27.60, \$40.60, \$97.40 or \$128/Mg depending on the mode of operation as compared to a cost of \$110/Mg for land treatment. The process does not eliminate land treatment and the cost analysis assumes that the sludge from the TFE is disposed of by land treatment.

### Plant I Stream Stripping Conclusions

The steam stripper reduced the total VO concentration by over five orders of magnitude from a feed concentration of roughly 6,000 ppm (0.6 percent) to less than 0.037 ppm. The removal of total VO was approximately 99.999 percent.

The primary condenser removed about 91 percent of the total VO in the vapors. Efficiencies for individual constituents ranged from 89 percent for chloromethane to 94 percent for chloroform. The secondary vent condenser (with cooling tower water) did not appear to provide

measurable control or condensation of VO. Theoretical calculations indicate that using refrigerated glycol cooling on the secondary condenser may improve its control efficiency for total VO to 68 percent.

The major air emission sources for the process are the solids decanters, storage tank, and noncondensibles from the steam stripper. Emissions were estimated as 2.7 grams (g) per L of water treated. For an average treatment rate of 41.6 liters per minute (L/min) or 11 gallons per minute (gal/min) for 75 percent of the year, annual emissions are estimated as 44 megagrams per year (Mg/yr) or 1.4 grams per second (g/s). These annual emission estimates assume a constant feed concentration of 6,000 ppm.

The vapor flow rate from the primary condenser when it was vented directly to the atmosphere was measured as 57 L/min. The emissions were measured as 2.4 g/L of water treated or 39 Mg/yr (1.2 g/s) for operation for 75 percent of the year. When the primary condenser was vented to the secondary condenser, the flow rate from the secondary condenser was measured at 11 to 13 L/min with an emission rate of 0.5 g/L of water treated or 8.2 Mg/yr (0.26 g/s) for operation for 75 percent of the year. The difference in measured flow rates (57 versus 11 to 13 L/min) suggests that some flow was not sampled because of leaks in the overhead system, overflow pipes, or tank vents. The estimates of annual emissions are based on the conditions during the test with an average feed concentration of 6,000 ppm.

### ***Plant H Steam Stripping Conclusions***

The steam stripper reduced the total VO concentration by approximately three orders of magnitude from a feed concentration of roughly 6,000 ppm (0.6 percent) to an average of 9.7 ppm. Removal of the major constituent (1,2-dichloroethane) consistently exceeded 99.99 percent.

The removal of all constituents was consistently high except for chloroform. The variations in chloroform removal appear to be related to fouling from the accumulation of solids. Suspended solids concentrations in the stripper influent were on the order of 0.1 percent.

The overhead condenser removed 99+ percent of the total VO in the overhead

vapors. The condenser efficiency was much lower for specific individual compounds present at low parts per million levels in the stripper influent. The flow rate from the condenser vent ranged from 1.9 to 4.2 L/s (4.0 to 8.8 ft<sup>3</sup>/min). The condenser vent on this steam stripper was routed to an incinerator. A similar system vented to the atmosphere could emit 12 to 51 Mg/yr of VO.

The cost-effectiveness of the steam stripping operation was approximately \$220/Mg of VO removed. Steam usage for this steam stripper appeared to be optimized because it was lower than values observed for other steam strippers and was also lower than values given in design manuals.

The major operational problem experienced with this steam stripper is the fouling of the heat exchanger and column trays. Solids removal prior to the steam stripper may provide a more consistent operation. The results indicate that a steam stripper can be operated for wastewater containing 0.1 percent solids if the operator is willing to backflush and clean the system periodically. However, if the solids are removed prior to steam stripping, the resulting sludge may be a troublesome disposal problem and an additional source of VO. Consequently, the company has chosen to incur the additional cost of cleaning the existing system periodically instead of installing equipment for the removal, treatment, and disposal of solids.

### ***Plant G Steam Stripping/ Carbon Adsorption Conclusions***

Semivolatile organic compounds can be removed from wastewater using steam stripping and carbon adsorption. Removal efficiencies of 92 percent were observed for the steam stripper, and the carbon adsorber removed more than 95 percent of the organics fed to it. The removal efficiency of the combined steam stripper-carbon adsorber was greater than 99.6 percent.

Air emissions from the condenser vent were very low, and the gas flow from the vent could not be measured reliably. Concentrations of VO in the vent stream varied widely, with total VO (as ppm hexane) between 10 and 2,000 ppm. The maximum air emissions were estimated to be 4.0 g/h.

Carbon was added to the adsorbers in a pulse feed mode at an average of 1.5

times per day, with a carbon addition of 908 to 1,360 kg/charge. The carbon was regenerated offsite and was the major cost of the process. The organic concentrations of the wastewater fed to the adsorber were relatively low (47.8 ppm), and utilization of the carbon was correspondingly low (0.021 kg organics removed/kg carbon used). The total annualized cost of the steam stripper-carbon adsorption system was \$14.30/kg organics removed.

The high normalized operating costs of the system resulted primarily from the low feed concentrations (634 ppm organics) and the high removal efficiency (>99.6 percent) of the steam stripper carbon adsorber. On a water-processed basis, the total annualized cost was \$0.0089/kg water treated (or 0.89 ¢/L).

Approximately 78 percent of the steam used in the steam stripper was condensed into the water being stripped, and 22 percent was condensed with the stripped organics. This condensation into the stripped liquid produces a varying gas/liquid (G/L) ratio within the column: 55 m<sup>3</sup>/m<sup>3</sup> at the base and 24 m<sup>3</sup>/m<sup>3</sup> at the top. The heat exchanger, used to heat the feed with the bottoms from the stripper column, reduced the steam requirements for the column.

Principal variables influencing the effectiveness of the process were the feed rate and steam rate of the process. Downtime of the process was reported as less than 1 percent of operating time, with heat exchanger fouling as the only maintenance problem.

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*The complete report consists of two volumes, entitled "Case Studies of Hazardous Waste Treatment to Remove Volatile Organics:"*

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