



## Project Summary



# Field Evaluation of Resource Recovery of Hazardous Wastes

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The overall objective of this study was to evaluate the effectiveness of two process kilns in destroying hazardous wastes and quantify stack gas emissions. During two 1-week field testing programs, samples of the hazardous wastes fired in the kilns were collected and analyzed for principal organic hazardous constituents (POHCs), selected trace metals, and chlorides. Air emissions were sampled and analyzed for particulate matter (including trace metals); volatile and semivolatile POHCs found in the wastes and other products of incomplete combustion (PICs); and criteria pollutants including sulfur oxides, nitrogen oxides, carbon monoxide, and hydrochloric acid. Test results indicated that destruction and removal efficiencies (DREs) of POHCs at one site failed to meet the 99.99 percent level. POHC DREs at the second site were generally above this level. This disparity of results was attributed to a difference in kiln operating temperature. Benzene, chlorobenzene, and carbon tetrachloride showed lowest DREs at both sites. Total PIC mass emissions accounted for 25 to 80 percent of the total measured POHC breakthrough. Trace element emissions, which were generally below 10 percent of the measured input rate, were dependent on the collection efficiency of the particulate control devices and waste firing rates.

*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 docu-*

*mented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The full report describes emission results obtained from field testing of two rotary process kilns burning liquid hazardous chemical wastes. The primary objective of the tests was to evaluate the destruction and removal efficiency (DRE) of principal organic hazardous constituents (POHCs) in these waste fuels and identify products of incomplete combustion (PICs) emitted from the two kilns. This work was supervised by the Hazardous Waste Engineering Research Laboratory of the Environmental Protection Agency (EPA-Cincinnati) under contract no. 68-02-3176, task 4B.

### Kiln Descriptions

Figure 1 is a schematic of the site I kiln facility tested in this program and summarizes the key design and operating features. Site I is a rotary kiln dryer tested at a capacity of about 10 kg/s (40 tons/hr) when fired with a heat input capacity of approximately 11 MW (37.5 million Btu/hr). The kiln dries earth-type clays, reducing the moisture content typically from 50 percent to 8 percent. The 8 percent clay product is marketed as cat litter and as an impermeable liner for ponds. This product can be further processed to reduce the moisture to 0.5 percent, resulting in a product that is

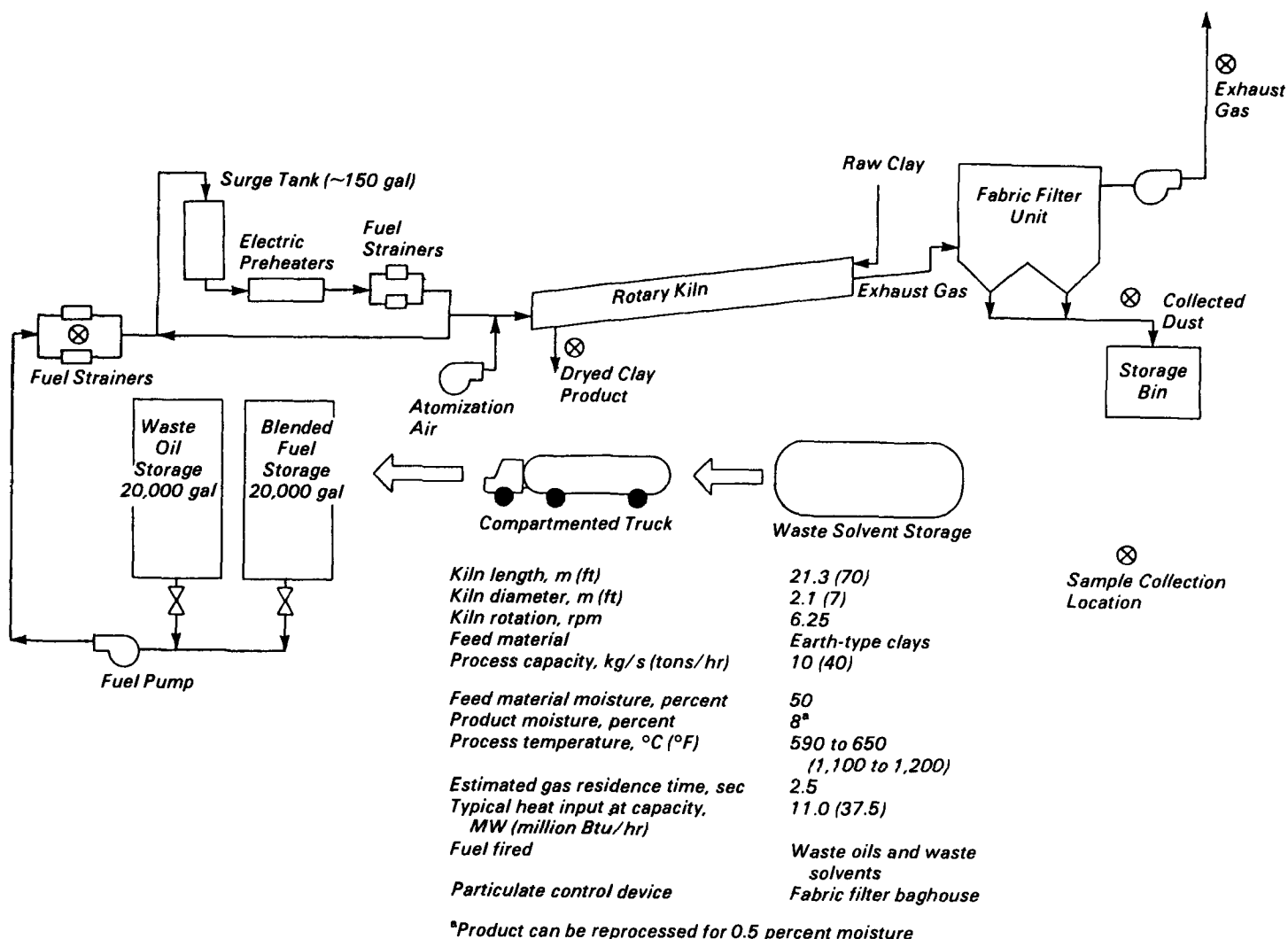


Figure 1. Process flow schematic and sample collection locations—site I.

marketed as an oil and grease absorbant. However, the principal product at site I is the 8 percent clay.

The plant receives and stores burnable liquid wastes. These wastes are blended with reclaimed or virgin oil before being fired in the kiln. The single burner is fired with a typical 20/80 mixture of waste fuel and reclaimed oil, resulting in an early combustible fuel. The kiln process temperature ranges between 590° and 650°C (1,100 and 1,200°F) with an estimated gas residence time of 2.5 sec. This is a relatively low-temperature environment for efficient hazardous waste destruction. Flue gas particulate emissions are controlled with a fabric filter baghouse.

Figure 2 is a schematic of the site II kiln facility tested in this program and summarizes the key design and operat-

ing features. Site II is a rotary aggregate kiln that processes shales into a lightweight aggregate material by promoting various heat activated chemical reactions and liberating carbon dioxide from the raw material. This causes the aggregate to expand, resulting in a lightweight product. A process temperature greater than 1,040°C (1,900°F) is generally required to achieve this reaction. The kiln capacity of site II is about 2.5 kg/s (12 tons/hr). Its typical production rate is between 2.3 and 2.5 kg/s (9 to 12 tons/hr), requiring a heat input on the order of 7.9 to 8.8 MW (26 to 30 million Btu/hr). The gas residence time is about equal to that of the site I kiln at 2.3 sec. The fuel burned is generally a combination of pulverized coal and hazardous waste solvents injected through two concentric burners.

Liquid waste solvents, transferred from an isolated tank farm, are air atomized and injected into the kiln along with pulverized coal. Additional air is pulled into the kiln through openings near the flame end of the kiln by an induced draft (ID) fan. Fuel flow is adjusted by a controller that measures the temperature of the kiln wall, compares this value with a present level, and adjusts the fuel flow accordingly. The maximum permitted liquid fuel firing rate is 370 ml/s (350 gph). Dust-laden gases from each kiln are treated in separate air cleaning systems consisting of a multiclude followed by a crossflow gravity spray wet scrubber. Spent scrubber water is sent to a settling pond for clarification before being discharged to a local stream. Dust collected by the multiclude is landfilled or sometimes reprocessed in the kiln.

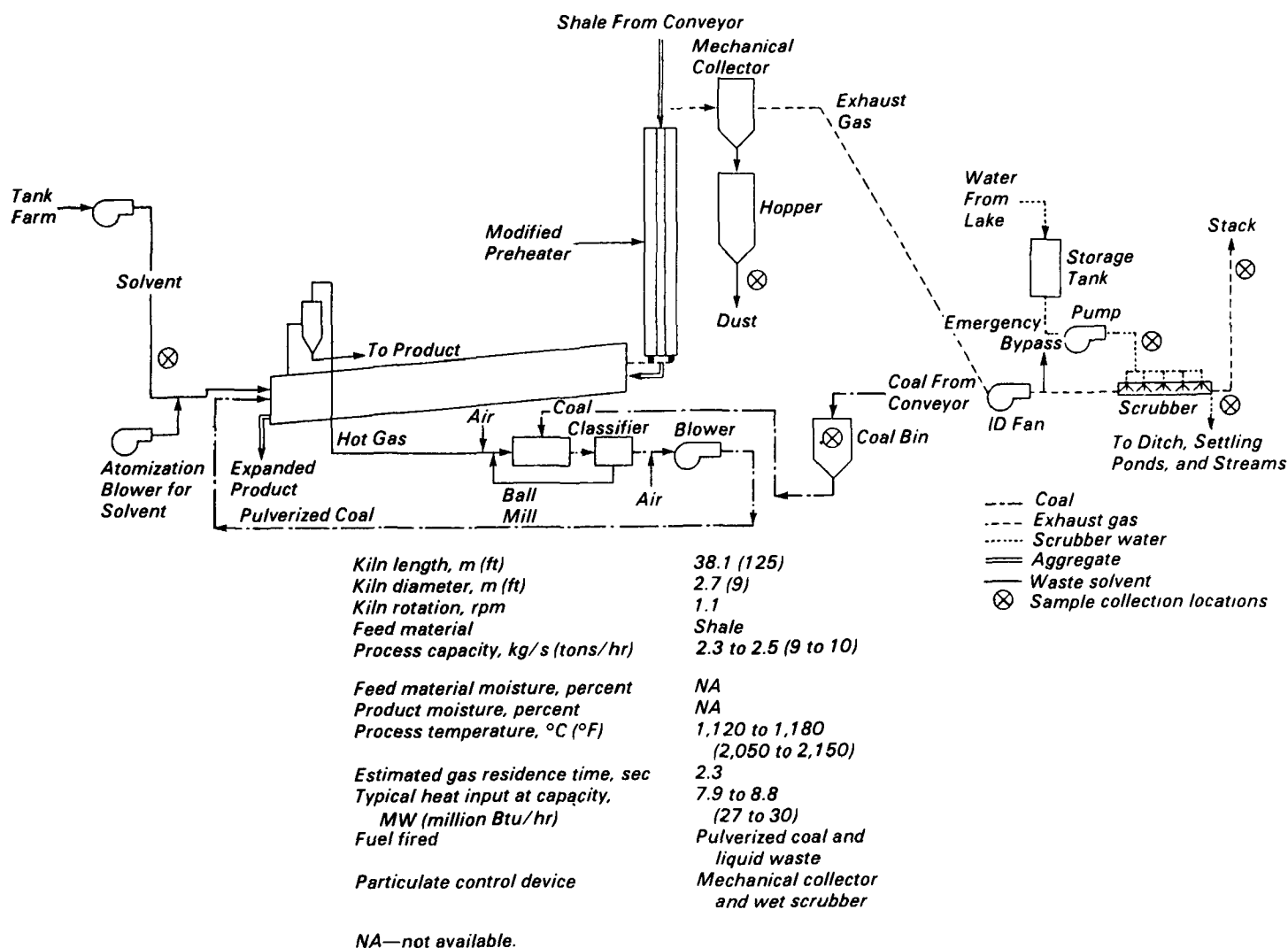


Figure 2. Process flow schematic and sample collection locations—site II.

## Test Program

The test program at site I consisted of three tests with the kiln firing a blend of liquid waste and waste oil. Four tests were performed at site II. During the first two tests the kiln fired a combination of pulverized coal and liquid waste. This mode of operation is typical for this site. During the remaining two tests, the kiln was fired with liquid waste only. Table 1 summarizes the operation of both kilns during these tests. Significant burner combustion stability problems were experienced during the first test at site I. These problems, which caused interruptions in the test program, were believed to result from excessive preheating of the waste fuel mixture. This

excessive preheating was corrected during the second and third tests. Kiln operation at site II was uninterrupted by any recorded upsets due to combustion conditions.

## Sampling and Analytical Protocols

The primary objective of the test program was to evaluate the DRE of hazardous organic compounds in the liquid waste fuel and to determine the type and quantities of PIC emissions. Therefore, the sampling and analytical protocols focused on measuring the hazardous organic constituents in the liquid waste fuels and flue gas streams and quantifying the mass flow rate of

each stream. Tables 2 and 3 summarize the protocols used at each test site. Figures 1 and 2 indicate sample collection locations.

Composite samples of the waste fuels were collected and analyzed for POHC concentrations of volatile and non-volatile organics. Trace metals, total chlorides and proximate/ultimate analyses were also performed on each fuel burned during the tests. All flue gas emissions were measured at the stack downstream of particulate collection devices. Measurement equipment used at both sites included continuous gas monitors, volatile organic sampling train (VOST) and a modified version of the EPA Method 6 sampling train for HCl

**Table 1.** Summary of Kilns Operation

Site	Test number	Kiln production kg/s (tons/hr)	Waste fuel flowrate, ml/s (gph)		Waste fuel heat input	
			Range	Test average	MW (million Btu/hr) <sup>a</sup>	Percent of total
I	1	~6.8 (27) <sup>b</sup>	205-216 (195-205)	210 (200)	7.45 (25.4)	100
	2	~7.6 (30) <sup>b</sup>	226-263 (215-250)	238 (226)	8.41 (28.7)	100
	3	~7.6 (30) <sup>b</sup>	220-252 (209-240)	237 (225)	8.39 (28.6)	100
II	1 <sup>c</sup>	2.17 (8.62)	220-284 (209-270)	242 (230)	6.07 (20.7)	59
	2 <sup>c</sup>	2.25 (8.94)	142-255 (135-243)	197 (187)	5.01 (17.1)	47
	3	2.19 (8.69)	270-348 (257-331)	315 (300)	8.50 (29.0)	100
	4	NA	270-354 (257-337)	318 (302)	8.71 (29.7)	100

<sup>a</sup>Calculated from the fuel higher heating values.<sup>b</sup>Not a measured value.<sup>c</sup>Tests 1 and 2 correspond to the kiln firing a combination of waste fuel and pulverized coal. During Tests 3 and 4, the waste fuel accounted for 100 percent of the fuel fired in the kiln.

NA—Not available.

measurements. Particulate emissions were also sampled using the EPA Method 5 equipment and protocol. This sampling train was modified for site I to allow sampling of semivolatile and non-

volatile organics using an organic sorbent cartridge. Solid and liquid waste discharge streams from particle collection devices were also sampled. Analyses of these streams were limited to wet

scrubber effluents for volatile organics, trace metals and chlorides. No volatile organics were detected in the wet scrubber effluent collected during these tests. Kiln products were not part of the sampling and analysis protocol.

Waste fuels at both sites were artificially spiked with a known quantity of 1,1,2-trichloro-2,2,1-trifluoroethane (Freon 113) to permit a direct comparison of DRE results between these two kilns and to investigate the feasibility of using this compound as a surrogate for DRE measurements of other major POHCs present in the waste fuels.

### Criteria Emissions

Table 4 summarizes the results of criteria gaseous and particulate emissions at both test sites. The site I kiln was operated at high excess air levels averaging about 280 percent. This high excess air level cooled the combustion products, resulting in relatively low NO<sub>x</sub> formation. SO<sub>2</sub> emissions corresponded to about 30 to 100 percent of the sulfur input from the waste fuel. Low sulfur recovery may be attributed to partial SO<sub>2</sub> retention in the clay product collected by the baghouse. Hy-

**Table 2.** Sampling and Analysis Protocol for Site I Rotary Kiln Clay Dryer

Sample/collection location	Type of sample/ monitoring equipment <sup>a</sup>	Number of samples <sup>b</sup>	Analysis <sup>c</sup>
Atmospheric flue gas emissions/ stack downstream of fabric filter	• Continuous monitors	Continuous (8 to 10 hr/test)	• O <sub>2</sub> , CO <sub>2</sub> , CO, NO/NO <sub>x</sub> , SO <sub>2</sub>
	• Modified EPA Method 5	3 (1 run/test)	• Semivolatile and nonvolatile organics by GC/MS
	• VOST	9 (3 runs/test)	• Particulate matter by gravimetry
	• Modified EPA Method 6	6 (2 runs/test)	• Trace metals by atomic absorption
Fuel (waste oil and liquid burnable waste blend)/ fuel strainers	• Composite sample	3 (1 per test)	• Volatile organics by GC/MS
			• HCl by titration with silver nitrate
			• C, H, N, O, S, and HHV by ASTM methods
			• Total chloride, ASTM P808
Fabric filter collected dust/ fabric filter hopper			• Volatile organics by GC/MS
			• Semivolatile and nonvolatile organics by GC/MS
			• Trace metals by atomic absorption
	• Composite sample	3 (1 per test)	No analysis performed

<sup>a</sup>Appendix A (Volume I) presents a detailed description of sampling equipment and protocols used.<sup>b</sup>Does not include blanks, spikes, or other quality control samples.<sup>c</sup>Appendix B (Volume I) presents a detailed description of analytical equipment and protocols used.

**Table 3. Sampling and Analysis Protocol for Site II Rotary Aggregate Kiln**

Sample/collection location	Type of sample/ monitoring equipment <sup>a</sup>	Number of samples <sup>b</sup>	Analysis <sup>c</sup>
Atmospheric flue gas emissions/ stack downstream of wet scrubber	• Continuous monitors	Continuous (8 to 10 hr/test)	• O <sub>2</sub> , CO <sub>2</sub> , CO, NO/NO <sub>x</sub> , SO <sub>2</sub>
	• EPA Method 5	12 (3 runs/test)	• Particulate matter by gravimetry
			• Trace metals by atomic absorption
	• VOST	12 (3 runs/test)	• Volatile organics by GC/MS
	• Modified EPA Method 6	8 (2 runs/test)	• HCl by titration with silver nitrate
Liquid waste fuel/burner or fuel storage tank	• Composite sample	4 (1 per test)	• C, H, N, O, S, and HHV by ASTM methods
			• Total chloride, ASTM P808
			• Volatile organics by GC/MS
			• Trace metals by atomic absorption
Coal/pulverized coal hopper	• Composite sample	2 (1 per test)	• Trace metals by atomic absorption
			• C, H, N, O, S and HHV by ASTM methods
Mechanical collector dust/ multicyclone hopper	• Composite sample	4 (1 per test)	No analysis performed
Wet scrubber influent and effluent/inlet and outlet of wet scrubber	• Composite sample	8 (1 per test for each stream)	• Volatile organics by GC/MS
			• Trace metals by atomic absorption
			• Total chlorides, ASTM P808

<sup>a</sup>Appendix A presents a detailed description of sampling equipment and protocols used.

<sup>b</sup>Does not include blanks, spikes, or other quality control samples.

<sup>c</sup>Appendix B presents a detailed description of analytical equipment and protocols used.

**Table 4. Summary of Criteria Emission Results**

Site	Test condition	O <sub>2</sub> (percent)	CO <sub>2</sub> (percent)	CO (ppm) <sup>a</sup>	SO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	HCl (mg/s)	Total solid particulate (mg/s)
Rotary kiln dryer— site I	Waste fuel firing	14.9-16.4 (15.9) <sup>b</sup>	3.6-4.0 (3.1)	15-110 (54)	3-53 (27)	49-74 (60)	110-490 (230)	8.8-20.2 (15.5)
Aggregate kiln— site II	Cofiring (coal and waste fuel)	5.0-11.0 (8.9)	6.0-13.1 (8.8)	NA	720-1,840 (1,200)	195-460 (296)	760-1,090 (960)	535-2,330 (1,130)
	Waste fuel firing	5.0-10.0 (7.6)	6.7-11.9 (9.4)	NA	872-1,583 (1,330)	210-280 (245)	410-840 (600)	583-776 (720)

<sup>a</sup>Parts per million by volume as measured on a dry basis.

<sup>b</sup>Number in parentheses represents the arithmetic average of three test measurements for site I and two test measurements for each of the two test conditions at site II.

NA—No CO measurement was available for site II because of instrument failure.

drochloric acid emissions represent 25 to 30 percent of the total chlorine fired with the waste fuel.

The kiln at site II was operated at significantly lower excess air levels, averaging about 80 percent for the cofired tests and 50 percent for the waste-fuel-only tests. Lower combustion air volumes resulted in higher kiln process temperatures and lead to higher NO<sub>x</sub> emissions compared with site I. Sulfur dioxide emissions were significant for both cofiring and waste-fuel-only tests. Total sulfur input (coal and waste fuel) could not account for all the SO<sub>2</sub> measured. Sulfur-out divided by sulfur-in ranged from 3.3 to 12. It is likely that the aggregate contributed SO<sub>2</sub> to the flue gas. Sulfur removal efficiencies of the wet scrubber could not be calculated because of lack of sulfur measurements in the flue gas entering the scrubber or the waste discharge stream from the scrubber.

Particulate emissions were significantly higher for site II by as much as two orders of magnitude than for site I. This result is attributed primarily to a lower collection efficiency of the wet scrubber compared to the fabric filter of site I. Furthermore, higher particulate emissions for the cofired tests at site II were the result of flyash contribution from pulverized coal and scrubber water entrainment detected during test 1.

## Volatiles Organic Emissions and DRE

Figure 3 illustrates the volatile POHC DRE results obtained at both sites. Each bar is indicative of the range in DRE obtained for the major volatile POHCs. Bars with upper dashed lines correspond to DRE results greater than the indicated level.

DREs for site I POHCs failed to meet the 99.99 percent level, the current regulatory level for hazardous waste incinerators. Several of the components failed to meet the 99.9 percent level as well. The low DREs are attributable primarily to the relatively low process temperatures in the kiln. However, test results also point out the likelihood that low concentration POHCs would fail to achieve high DREs, possibly because of the sensitivity of state-of-the-art sampling and analytical techniques in measuring low concentration organics as well as the susceptibility of background contamination of these results. More importantly, the contribution of

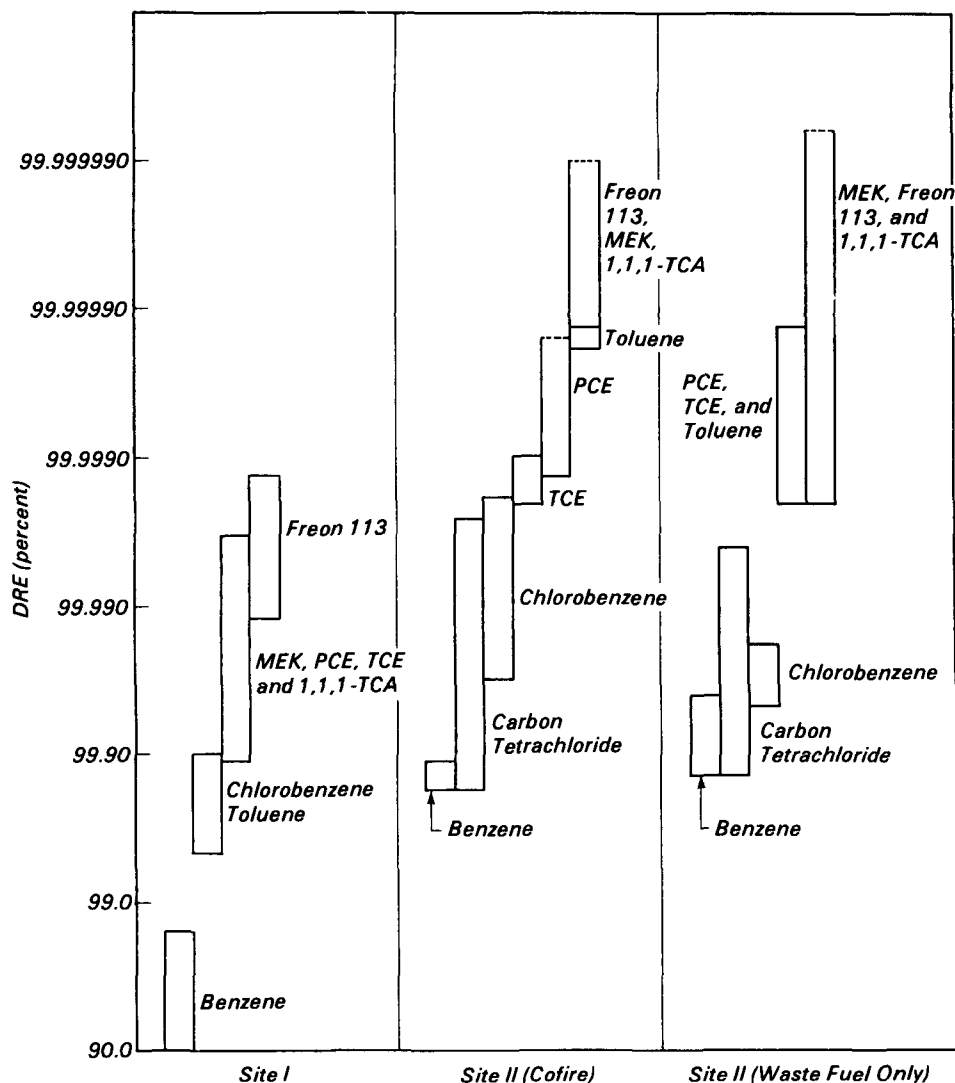


Figure 3. Summary of site I and site II DRE results.

PIC formation to total POHC emissions may play a greater role in determining the DRE results of low-concentration POHCs. DREs for the spiked Freon 113 were the highest of any of the volatile organic compounds detected in the waste fuel at site I, exceeding the 99.990 percent level on the average. The firing rate or concentration in the waste fuel of Freon 113 was the highest of any of the other volatile POHCs.

Site II DRE results indicate destruction efficiencies exceeding 99.99 percent for most volatile POHCs except for benzene, chlorobenzene, and carbon tetrachloride (cofiring tests only). These high DREs were obtained for both the cofiring and waste-fuel-only test conditions and are attributable to the high kiln process temperatures compared to

site I. Low DREs were obtained for volatile POHCs present in the fuel in the lowest concentrations, generally less than 150 ppm corresponding to firing rates lower than 58 mg/s. Again, this result of lower DREs associated with low POHC concentrations may indicate the significance of background organic emission levels in combustion products. DREs for Freon 113 at site II also exceeded DREs for any of the other POHCs.

## Products of Incomplete Combustion

Table 5 summarizes emission results of volatile organics that were not detected in the waste fuels of site I or site II. These compounds are identified as products of incomplete combustion

**Table 5.** Volatile PIC Emissions,  $\mu\text{g/s}$ 

Compound	Site I	Site II	
	Waste fuel only (tests 1, 2, and 3)	Cofiring (tests 1 and 2)	Waste fuel only (tests 3 and 4)
Carbon tetrachloride	4.1 to 494 (173) <sup>a</sup>	NA	NA
Chloromethane	0 to 67 (30)	156 to 547 (350)	600 to 968 (780)
Bromomethane	5.2-11 (8.0)	7.2 to 37 (22)	8.1 to 8.9 (8.4)
Vinylchloride	18 to 44 (28)	12 to 19 (16)	13 to 14 (14)
Dichloromethane	0 to 72 (30)	NA	NA
1,1-dichloroethane	0 to 55 (18)	--	--
Chloroform	0 to 3.9 (2.5)	2.5 to 8.6 (5.5)	5.1 to 6.4 (5.8)
Chloroethane	0 to 4.1 (1.4)	--	--
1,2-dichloropropane	0 to 2.8 (0.9)	NA	NA
1,1,2,2-tetrachloroethane	0 to 2.6 (0.9)	--	--
1,1-dichloroethylene	--	1.9 to 4.0 (3.0)	2.0 to 2.8 (2.4)
Trans-1,2-dichloroethylene	--	0.5 to 1.4 (1.0)	1.0 to 1.1 (1.1)
Total PICs	51 to 670 (290)	190 to 610 (400)	630 to 1,000 (810)
$\Sigma \text{ PICs}/\Sigma \text{ POHCs}^b$	0.14 to 0.30 (0.25)	0.64 to 0.91 (0.83)	0.72 to 0.83 (0.76)

<sup>a</sup>Each entry is the arithmetic average of the measurements for each test. Number in parentheses is the average for number of tests indicated.

<sup>b</sup>Sum of PIC emissions divided by the sum of breakthrough volatile POHC emissions including toluene and benzene.

--Dashes indicate emission level or blank corrected emissions were below detection limits. NA—Not applicable. Compound was a POHC.

(PICs). For site I, highest PIC emissions were contributed by carbon tetrachloride. These high average emissions are attributed to test 1 results, which indicate high carbon tetrachloride emissions of about 500  $\mu\text{g/s}$ . DREs for test 1 were also lower than DREs measured during the remaining two tests. Total volatile PIC emissions accounted for about 14 to 30 percent of the total POHC breakthrough measured.

For site II, chloromethane emissions accounted for nearly all the PICs detected with 570  $\mu\text{g/s}$  on the average for all tests. Higher chloromethane emis-

sions were measured for the waste fuel firing tests 3 and 4. The ratio of total PICs to total POHC breakthrough ranged from 0.76 to 0.83.

### Trace Metal Emissions

Selected trace metals were sought in the analysis of fuels and flue gas emissions to quantitate the emissions of the inorganics from the two process kilns burning hazardous liquid wastes. Analysis of metals was generally limited to the 13 EPA-designated priority pollutant elements. Table 6 summarizes the results of these measurements.

For site I, copper, lead, and zinc constituted the major metals, having concentrations of 400 to 700 ppm in the waste fuel. Other detected metals were cadmium, chromium, and nickel, all having fuel concentrations of less than 5 ppm. Emissions ranged from nondetected for cadmium to 130  $\mu\text{g/s}$  for zinc. Lead emissions were found to be about 80  $\mu\text{g/s}$  on the average. Emissions of these trace metals generally constituted less than 1 percent of the total input rate. This was found to be especially the case for lead, copper, and zinc. It is likely that most of these metals were absorbed on baghouse-collected flyash or trapped in the clay product of the kiln.

Lead and zinc were the major metals in the waste fuel at site II, with average concentrations of 860 ppm and 210 ppm, respectively. Chromium also exceeded 100 ppm. During cofiring (tests 1 and 2), pulverized coal contributed a minor fraction of these metals. Highest emissions were measured for lead (7.6 mg/s), followed by chromium (1.5 mg/s), and zinc (1.0 mg/s). On the average, the measured emissions of all trace metals accounted for 1.7 to 8.0 percent of the total input rate.

Results of waste firing only, tests 3 and 4 for site II, indicate an increase in lead emissions to 25 mg/s, followed by zinc at 4.4 mg/s, and chromium at 1.3 mg/s. With the exception of mercury, nickel, and antimony, which were not detected, total metal emissions accounted for 3.9 to 17 percent of the total input rate on the average. Therefore, the results obtained during this test program indicate that, although the site II kiln was more efficient in thermal destruction of organics, it had a higher percentage of trace metals emissions. This result is attributed to the higher process temperatures, which may prevent metal adsorption on the flue gas entrained particulate matter combined with the lower efficiency of the wet scrubber in controlling particulate emissions. The increase in lead and other metal emissions during the waste-fuel-only tests may be the result of reduced entrained particulate/metal interaction. Coal flyash generated during the cofired tests may have contributed to metal adsorption.

**Table 6. Trace Element Emissions**

Element <sup>a</sup>	Site I		Site II			
	Waste fuel only		Cofiring		Waste fuel only	
	Flue gas emissions (μg/s)	Mass balance out/in (percent)	Flue gas emissions (μg/s)	Mass balance out/in (percent)	Flue gas emissions (μg/s)	Mass balance out/in (percent)
Antimony	--	--	<5.7	NA	<5.8	<0.25
Cadmium	<5.8	<2.5	100 to 174 (140)	6.4 to 9.5 (8.0)	440 to 450 (450)	16 to 18 (17)
Chromium	10 to 29 (20)	1.2 to 2.9 (2.1)	1,290 to 1,740 (1,500)	5.7 to 5.8 (5.8)	1,170 to 1,400 (1,300)	3.2 to 4.8 (4.0)
Copper	12 to 92 (52)	0.01 to 0.11 (0.05)	260 to 430 (350)	1.4 to 2.0 (1.7)	1,020 to 1,120 (1,070)	3.5 to 4.3 (3.9)
Lead	66 to 96 (81)	0.05 to 0.07 (0.06)	6,300 to 8,850 (7,600)	3.6 to 5.4 (4.5)	25,000	9.4 to 9.9 (9.7)
Mercury	--	--	<0.6	NA	<0.6	<0.5
Nickel	5.0 to 35 (20)	20 to 13 (7.5)	<14 to 190 (<100)	<1.1 to 11 (<5.5)	<14	<1.8
Zinc	59 to 130 (95)	0.05 to 0.11 (0.08)	690 to 1,310 (1,000)	1.5 to 3.2 (2.4)	4,290 to 4,570 (4,400)	5.3 to 5.9 (5.6)

<sup>a</sup>Analysis was limited to priority pollutant elements. Metals listed are those that were detected in the fuels and flue gas emission stream.

<sup>b</sup>Number in parentheses is the arithmetic average of three test measurements for site I and two test measurements for site II. Averages are generally rounded to two significant figures.

--Dashes indicate element not detected in the fuels or flue gas at site I.

NA—Not available. Mass balance cannot be computed because of unknown element contribution from coal.

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The complete report, entitled "Field Evaluation of Resource Recovery of Hazardous Wastes," (Order No. PB 86-211 869/AS; Cost: \$16.95, subject to change) will be available only from:

National Technical Information Service  
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The EPA Project Officer can be contacted at:  
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