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Project Summary

Distribution of Trace Element Emissions from the Liquid Injection Incinerator Combustion Research Facility

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The EPA is currently developing regulations on trace element emissions from hazardous waste incineration. However, the data base on trace element emissions from incinerators which can be used to support regulations is very sparse. Data on the effects of waste composition and incinerator operation on trace element emissions are particularly lacking. In response to these data needs, a series of tests were conducted at EPA's Combustion Research Facility (CRF) to investigate the fate of volatile trace elements in liquid injection hazardous waste incineration. In these tests, arsenic in the form of arsenic trioxide (As_2O_3) and antimony in the form of antimony trichloride ($SbCl_3$) were added to a methanol base containing varying amounts of chlorobenzene and carbon tetrachloride, and fired in the liquid injection incinerator at the CRF. Test variables included incinerator temperature and excess air level, and feed chlorine content. Test results show a relatively even distribution of both elements between scrubber exit flue gas and scrubber blowdown. Both elements are found in the vapor phase at high temperatures, although most condenses to particulate at scrubber exit temperatures. Designated POHC destruction and removal efficiency (DRE) ranged from 99.99 to 99.999 percent at the afterburner exit to 99.999 to 99.9999 percent in the scrubber exit flue gas. Typical levels of common products of incomplete combustion were measured.

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

In support of the EPA Office of Solid Waste (OSW) hazardous waste incinerator regulation development, a series of incineration tests to determine the fate of two Appendix VIII metals, antimony and arsenic, were conducted at the EPA Combustion Research Facility (CRF) in Jefferson, Arkansas. These metal emission tests are important, because risk assessments show that metal emissions from otherwise properly operated incinerators can be the largest component of risk to human health and the environment.

These tests incinerated mixtures of methanol, chlorobenzene, and carbon tetrachloride, spiked with $SbCl_3$ and As_2O_3. The objectives of the test program were:

- To track emissions of arsenic and antimony through the incinerator system
- To study the distribution of metals between flue gas and scrubber blowdown water
- To explore the relationship between metal emissions and incinerator operating conditions and feed chlorine content
- To evaluate whether the metals

affect waste component destruction
- To extend the data base on volatile products of incomplete combustion (PIC) emissions from the incineration of chlorinated hydrocarbons

Approach

The tests were conducted in the liquid injection incineration system (LIS) at the CRF. The LIS can incinerate pumpable and atomizable liquid wastes.

Figure 1 shows a simplified schematic of the incinerator system which consists of two refractory-lined combustion chambers. The system cleans the combustion product gases with a packed-column scrubber, and an ionizing wet scrubber, followed by an activated carbon bed adsorber and a high efficiency particulate (HEPA) filter. An induced draft fan downstream of the HEPA filter draws a slight vacuum (draft) throughout the incinerator/scrubber system and vents the combustion products via a stack.

The research program studied the effects of three operating parameters: feed chlorine content, incinerator temperature, and combustion excess air. A Box-Wilson factorial experimental design specified 18 test conditions which included 5 levels of variation for each parameter.

Blends of methanol, carbon tetrachloride, and chlorobenzene in the feed produced the various inlet chlorine concentrations (0 to 33.8 percent). Arsenic and antimony were added to these blends in proportions designed to give constant feed concentrations of 12 and 40 ppm respectively for all tests. These concentrations in the feed material ensure that the worst-case concentrations in the stack gas will never exceed the threshold limit values (TLV), of 0.2 mg As/m^3 and 0.5 mg Sb/m^3. Furthermore, if all the trace metals leave the incinerator via the scrubber blowdown water, their concentrations will not exceed the EP toxicity limits (5 mg As/L, no limit established for Sb).

The liquid feed entered the main combustion chamber via a steam-atomized nozzle at about 45 kg/hr (100 lb/hr). Auxiliary propane maintained the incinerator at the specified temperature which ranged from 1,137° to 1,450°C (2,079° to 2,642°F). Combustion air entered via swirl registers in the burner to produce from 5.9 to 11.7 percent excess oxygen at the incinerator exit.

Figure 2 illustrates the sampling protocol. In addition to the continuous monitors, which measured O_2, CO, and CO_2, volatile organic sampling trains (VOST) collected samples at the afterburner and the scrubber exits. Thermal desorption purge and trap GC/FID analyzed for 22 volatile organic compounds.

EPA reference Method 5 was used to collect samples for particulate load and arsenic and antimony analyses. The Method 5 train was modified to ensure collection of any antimony and arsenic which passed through the particulate filter. It consisted of a probe and a glass cyclone, followed by a filter and five impingers. The first impinger contained 0.1 N NaOH. The second, third and fourth impingers contained 0.2 M $(NH_4)_2S_2O_8$ + 0.02 M $AgNO_3$. The last impinger contained silica gel. Following collection and digestion, furnace atomic adsorption (AA) methods were used to analyze for arsenic and antimony.

Results

Of the 18 planned tests, 12 were completed. The remaining 6 tests were generally unattainable due to flame stability problems at low flame temperatures and low excess air conditions.

Trace Metal Discharges

Good mass balance closure for antimony and arsenic could not be established during these tests. Table 1 lists the fractions of inlet antimony found at the afterburner exit, the scrubber exit and the scrubber blowdown water. As shown in the table, for the three tests where the feed contained nominally 26 percent chlorine, no more than about 1 percent of the inlet antimony, was measured in the afterburner exit flue gas. For one test with the nominally 19 percent chlorine feed, less than 0.1 percent of the inlet antimony was detected in the afterburner exit flue gas. For the remaining tests with nominally 19 percent chlorine feed and the tests with nominally 8 percent and 0 percent chlorine feed, between 25 and

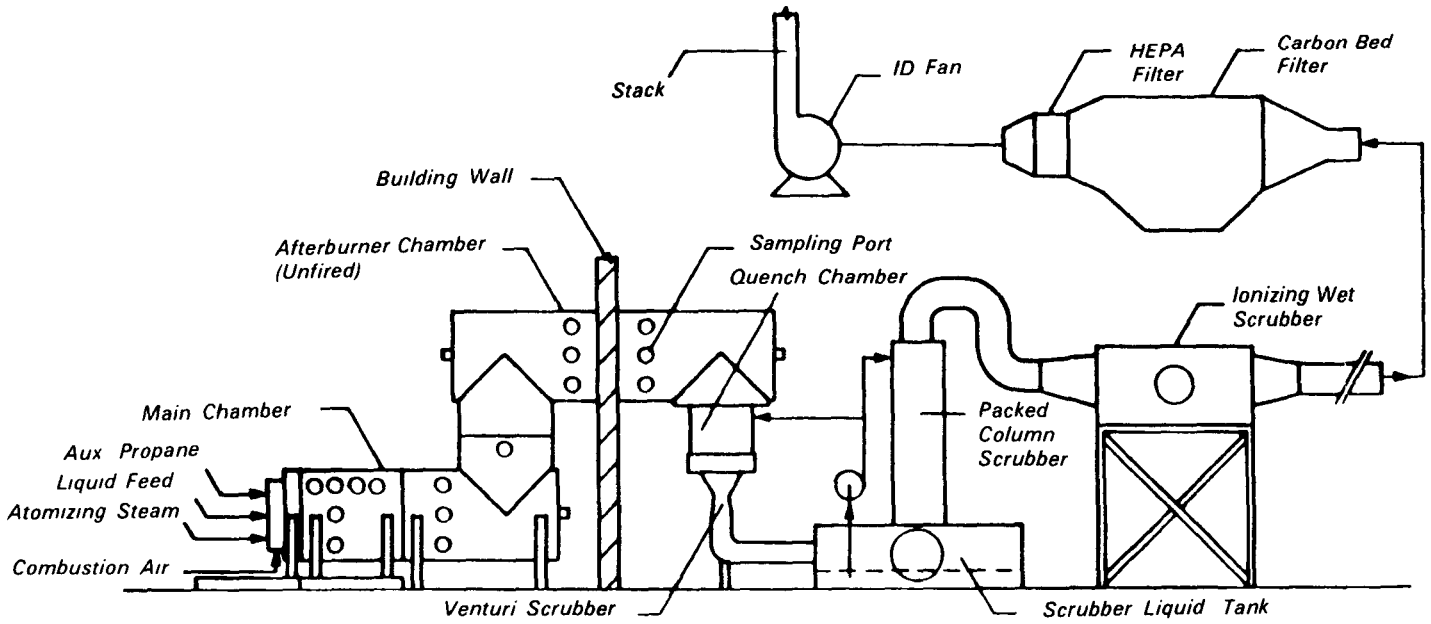
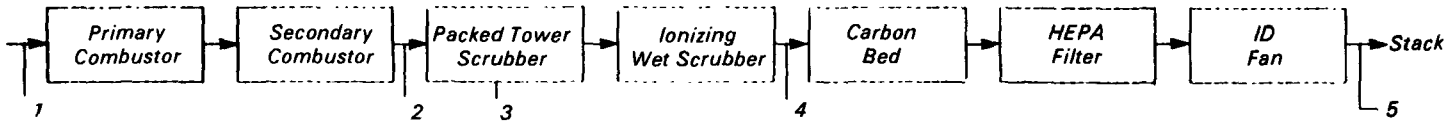


Figure 1. Simplified schematic of the EPA liquid injection incinerator system



Sampling Point	Parameter											
	Waste Feedrate	Waste Feed	Auxiliary Fuel Feedrate	Air Feedrate	Scrubber Blowdown	CM's (O_2, CO, CO_2, NO_x)	Volume Flow	M5 (Particulate, Metals)	VOST (Volatile Organics)	Temperature	Pressure	Relative Humidity
1	X	X	X	X								
2						X	X	X	X	X	X	X
3					X		X					
4							X	X	X	X	X	X
5						X	X	X[a]		X	X	X

[a] Particulate only.

Figure 2. Sampling protocol

101 percent of the input antimony was measured in the afterburner exit flue gas.

Between 15 and 84 percent of the inlet antimony was measured in the scrubber discharge streams (flue gas plus blowdown). Scrubber blowdown water accounted for 5 to 75 percent of the inlet antimony. Scrubber exit flue gas accounted for between 3 and 21 percent of the inlet antimony. Comparable fractions of antimony were generally measured in these two streams for a given test.

Mass balance closure in the afterburner exit flue gas was quite poor for four tests. However, for 4 of 5 tests at the nominally 19 percent chlorine feed, two at nominally 8 percent chlorine feed, the one with no, and the one with about 34 percent chlorine feed, mass balance closure was within a factor of 3. This is in the range of acceptable mass balance closure based on past experience. Closure results are generally better at the scrubber discharge. Still, closure within a factor of 3 was obtained for only 7 tests.

The inability to attain better mass balance closure in the tests was likely affected by the fact that accumulation of element concentrations in recirculating scrubber liquor was not taken into account.

Table 1. *Antimony Discharge Distributions*

Test No.	Feed Cl content, percent	Primary combustor temperature, °C (°F)	Afterburner exit O_2, percent	Antimony discharge distribution[a] (percent of feedrate)			
				Afterburner exit flue gas	Scrubber discharge streams		
					Flue gas	Blowdown	Total
14	33.8	1,293 (2,359)	9.2	34 (52)	8 (12)	7 (11)	15 (23)
4	26.4	1,307 (2,384)	10.5	0.18[b]	14[b]	22[b]	36[b]
5	27.1	1,137 (2,079)	10.8	0.3 (0.24)	17 (13)	21 (16)	38 (29)
7	26.4	1,399 (2,551)	6.1	1.1 (1.8)	18 (30)	8 (12)	26 (42)
13	18.8	1,203 (2,198)	11.8	0 (0.11)	3 (6.6)	40 (87)	43 (94)
18	18.8	1,176 (2,148)	10.7	32 (53)	9 (14)	75 (124)	84 (138)
16	18.8	1,450 (2,642)	7.4	83 (146)	21 (36)	5 (8.3)	26 (44)
2	18.8	1,336 (2,437)	9.2	79 (104)	15 (20)	9 (12)	24 (32)
3	18.8	1,228 (2,243)	8.4	89 (99)	10 (11)	13 (15)	23 (26)
6	7.6	1,290 (2,354)	10.1	56 (47)	20 (17)	10 (18)	30 (35)
9	7.9	1,425 (2,597)	5.9	101 (83)	17 (14)	18 (15)	35 (29)
15	0.	1,265 (2,310)	8.1	25 (38)	9.4 (14)	7 (11)	16 (25)

[a] *Numbers in parenthesis are based on a feed composition calculated from feed constituent blending proportions*

[b] *No feed sample analysis, value based on a feed composition calculated from feed constituent blending proportions.*

Table 2 shows the distribution of antimony between the particulate and vapor phases in the flue gas at both the afterburner exit and the scrubber exit. The table shows that, at the afterburner exit where temperatures were above 760°C (1,400°F), the vapor phase (impinger samples) contained an average of 55 percent (range 5 to 90) of the collected antimony. At the scrubber exit where the temperature was generally at 74°C (165°F), the vapor phase accounted for an average of 6 percent (range 0 to 38) of the collected antimony.

Tables 3 and 4 list the arsenic mass balance and phase distribution data. In the afterburner exit flue gas, detectable levels of arsenic were measured for 9 tests. The measured fractions of feed arsenic ranged from 1.4 to 245 percent. Eight tests showed better than 10 percent arsenic recovery. Seven of these corresponded to mass balance closure within a factor of 3.

The combination of the scrubber exit gas with the scrubber discharge blowdown accounted for 3.8 to 299 percent of the input arsenic. Mass balance closure around the scrubber was within a factor of 3 for eight tests. More often than not, a greater proportion of arsenic was found in the flue gas than in the scrubber blowdown.

At the afterburner exit, arsenic is distributed between the vapor and particulate

Table 2. *Antimony Flue Gas Distributions*

Test No.	Feed Cl content, percent	Primary combustor temperature, °C (°F)	Afterburner exit O_2, percent	Antimony distribution between particulate and vapor phase in the flue gas (percent)			
				Afterburner exit		Scrubber discharge	
				Particulate	Vapor	Particulate	Vapor
14	33.8	1,293 (2,359)	9.2	32	68	99	1
4	26.4	1,307 (2,384)	10.5	62	38	99	1
5	27.1	1,137 (2,079)	10.8	49	51	62	38
7	26.4	1,399 (2,551)	6.1	53	47	99	1
13	18.8	1,203 (2,198)	11.8	42	58	99	1
18	18.8	1,176 (2,148)	10.7	21	79	100	0
16	18.8	1,450 (2,642)	7.4	76	24	99.9	0.1
2	18.8	1,336 (2,437)	9.2	10	90	82	18
3	18.8	1,228 (2,243)	8.4	22	78	97	3
6	7.6	1,290 (2,354)	10.1	41	59	100	0
9	7.9	1,425 (2,597)	5.9	34	66	98	2
15	0.	1,265 (2,310)	8.1	95	5	99	1

Table 3. *Arsenic Discharge Distributions*

Test No.	Feed Cl content, percent	Primary combustor temperature, °C (°F)	Afterburner exit O_2, percent	Arsenic discharge distribution[a] (percent of feedrate)			
				Afterburner exit flue gas	Scrubber discharge streams		Total
					Flue gas	Blowdown	
14	33.8	1,293 (2,359)	9.2	126 (26)	30 (6.1)	2.5 (0.5)	33 (6 6)
4	26.4	1,307 (2,384)	10.5	ND	9.0[b]	3.8[b]	12[b]
5	27.1	1,137 (2,079)	10.8	ND	15 (5.1)	6.9 (2.3)	22 (7.4)
7	26.4	1,399 (2,551)	6.1	1.4 (1.7)	49 (58)	5.4 (6.4)	54 (64)
13	18.8	1,203 (2,198)	11.8	ND	ND	3.8 (2.8)	3.8 (2.8)
18	18.8	1,176 (2,148)	10.7	25 (4.0)	13 (2.2)	19 (3.1)	32 (5.3)
16	18.8	1,450 (2,642)	7.4	245 (77)	30 (9.4)	6.0 (1.9)	36 (11)
2	18.8	1,336 (2,437)	9.2	45 (10 2)	19 (4.3)	2.3 (0.51)	21 (4.8)
3	18.8	1,228 (2,243)	8.4	77 (20)	289 (73)	9.8 (2.5)	299 (76)
6	7.6	1,290 (2,354)	10.1	125(32)	60 (15)	21 (5.3)	81 (20)
9	7.9	1,425 (2,597)	5.9	153 (177)	26 (20)	20 (15)	46 (35)
15	0.	1,265 (2,310)	8.1	103 (21)	5 (1.1)	32 (6.6)	37 (7.7)

ND — Not detected.

[a] *Numbers in parenthesis are based on a feed composition calculated from feed constituent blending proportions.*

[b] *Feed sample not analyzed; value based on feed composition calculated from feed constituent blending proportion.*

phases. More often than not, a greater proportion was found in the particulate. At the scrubber discharge, usually all of the arsenic was measured in the particulate.

Destruction and Removal Efficiencies (DRE)

The tests demonstrated acceptable DREs for both carbon tetrachloride and chlorobenzene. Chlorobenzene DREs were higher than those for carbon tetrachloride. Carbon tetrachloride DREs were greater than 99.99 percent at the afterburner exit. These increased to greater than 99.999 percent at the scrubber exit. Similarly, chlorobenzene DREs ranged from 99.999 percent at the afterburner exit to generally better than 99.999 percent at the scrubber exit. The available data do not suggest any discernible effect of temperature, feed composition, excess air, or the presence of arsenic or antimony on DRE. This is in general agreement with previous CRF data which has consistently shown high in DREs for concentrated feed materials.

Products of Incomplete Combustion

Incineration produces low levels of PICs. The CRF routinely analyzes VOST samples for 22 organic compounds with GC/FID. For these tests at the afterburner exit, of these 22 compounds, carbon tetrachloride (POHC) was present at the highest levels (>100 μg/dscm). Other chlorinated alkanes and alkenes were present in the 10 to 100 μg/dscm range. Chlorobenzene (POHC) concentrations were similar to those of the common chlorinated PICs.

At the scrubber exit, PIC concentrations are about one-tenth of those at the scrubber inlet, i.e., afterburner exit. Carbon tetrachloride (a POHC) levels ranged from 4.4 to 31 μg/dscm. The highest concentrations occurred at low excess air conditions. Except for one test, chlorobenzene (the other POHC), levels ranged from 1.4 to 14 μg/dscm and did not appear to correlate with temperature or excess air. Other PICs include methylene chloride which was present in all tests at relatively high levels (11 to 139 μg/dscm). Other chlorinated alkanes and alkenes, hexane, benzene, and toluene were present at levels generally below 10 μg/dscm.

All the data reported above for methylene chloride, 1,1-dichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, benzene, hexane, and toluene are somewhat compromised due to laboratory solvent contamination. However, since the reported results are quite consistent with past experience, they are reported here.

Conclusions

Major conclusions from the test results addressing each of the test objectives noted in the Introduction are:

- Antimony was relatively evenly distributed between the particulate and vapor phases in flue gas samples taken at the afterburner exit. The same was generally true for arsenic, although a greater fraction was found in the particulate phase for the greater number of tests. Most, if not all of the antimony and arsenic was found in the particulate catch of the sampling trains run at the scrubber exit.

- The success in achieving mass balance closure in the flue gas at the afterburner exit, and in the scrubber exit flue gas and scrubber blowdown discharge was in keeping with past experience. Mass balance closure was within a factor of 3 for 6 to 8 of the 12 tests performed for each element/location (afterburner exit or scrubber discharge) combination. Four of the 12 tests had very low (less than 2 percent) both antimony and arsenic recovery in the afterburner exit flue gas. The lowest recovery in scrubber discharges (flue gas plus scrubber blowdown) were better; 15 percent for antimony and 4 percent for arsenic. However, no account was taken for accumulation of the elements in the recirculating scrubber liquor. This may have affected the ability to achieve better mass balance closure.
- Comparable fractions of the input antimony were accounted for in the scrubber exit flue gas and the scrubber blowdown. The same was largely true for arsenic, although a greater fraction of arsenic was found in the scrubber exit flue gas in a greater number of tests.
- No clear dependence of the distribution of arsenic and antimony discharges with the primary test variables was apparent. However, a statistical evaluation of the data obtained is planned in future efforts. This analysis will establish whether statistically significant relationships exist.
- Carbon tetrachloride DRE was greater than 99.99 percent as measured at the afterburner exit; this increased to greater than 99.999 percent as measured at the scrubber exit. Chlorobenzene DRE was greater than 99.999 at the afterburner exit, increasing to generally greater than 99.9999 percent at the scrubber exit No clear dependence of DRE on incinerator operation was apparent. This DRE performance is consistent with past experience at the CRF, so the presence of the elements fed had no apparent effect on POHC DRE.
- Several commonly measured chlorinated C_1 and C_2 hydrocarbons, benzene, and toluene were present in the afterburner exit flue gas at levels in the 10 to serveral hundred μg/dscm range. These same compounds were generally present in the scrubber exit flue gas at levels about a factor of 10 lower.

Table 4. *Arsenic Flue Gas Distributions*

Test No.	Feed Cl content, percent	Primary combustor temperature, °C (°F)	Afterburner exit O_2, percent	Arsenic distribution between particulate and vapor phase in the flue gas (percent)			
				Afterburner exit		Scrubber discharge	
				Particulate	Vapor	Particulate	Vapor
14	33.8	1,293 (2,359)	9.2	70	30	85	15
4	26.4	1,307 (2,384)	10.5	ND	ND	100	0
5	27.1	1,137 (2,079)	10.8	ND	ND	83	17
7	26.4	1,399 (2,551)	6.1	43	57	100	0
13	18.8	1,203 (2,198)	11.8	ND	ND	ND	ND
18	18.8	1,176 (2,148)	10.7	32	68	100	0
16	18.8	1,450 (2,642)	7.4	76	24	100	0
2	18.8	1,336 (2,437)	9.2	83	17	94	6
3	18.8	1,228 (2,243)	8.4	41	59	100	0
6		1,290 (2,354)	10.1	71	29	100	0
9	7.6 7.9	1,425 (2,597)	5.9	69	31	100	0
15	0	1,265 (2,310)	8.1	98	2	100	0

ND — Not detected.

Data quality assurance objectives for measurement precision and accuracy were not fully met for many measurement parameters. However, failure to attain these had little impact on the above-stated conclusions.

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***Robert E. Mournighan** is the EPA Project Officer (see below).*
The complete report, entitled "Distribution of Trace Element Emissions from the Liquid Injection Incinerator Combustion Research Facility," (Order No. PB 87-224 689/AS; Cost: $13.95, subject to change) will be available only from:
National Technical Information Service
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