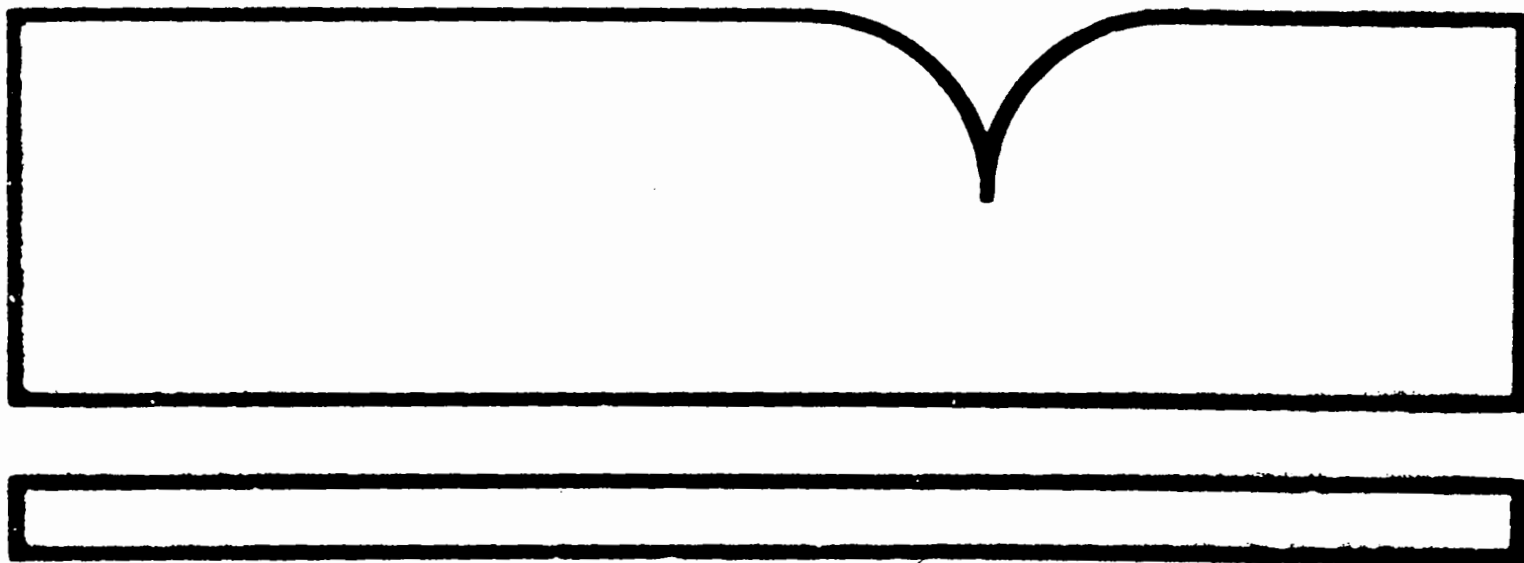Boilers Cofiring Hazardous Waste
Effects of Hysteresis on
Performance Measurements

(U.S.) Environmental Protection Agency
Cincinnati, OH

Apr 88

BOILERS COFIRING HAZARDOUS WASTE: EFFECTS OF

HYSTERESIS ON PERFORMANCE MEASUREMENTS

By

Ivars J. Licis
Thermal Destruction Branch
Alternative Technologies Division
Hazardous Waste Engineering Reesearch Laboratory

and

Howard B. Mason
Acurex Corporation
555 Clyde Avenue
Mountain View, California

EPA Project Officer
Ivars J. Licis

1. REPORT NO. EPA/600/D-88/038	2.	3. RECIPIENT'S ACCESSION NO. PB88-198698/AS

4. TITLE AND SUBTITLE Boilers Cofiring Hazardous Waste: Effects of Hysteresis on Performance Measurements	5. REPORT DATE April 1988
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) Licis, Ivars J. and Mason, Howard B.	8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS IDB, ATD, HWERL Cincinnati, Ohio and Acurex Corporation Mountain View, California	10. PROGRAM ELEMENT NO. D129
	11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS Office of Research and Development Hazardous Waste Engineering Research Laboratory U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

The Hazardous Waste Engineering Research Laboratory (HWERL) has conducted full scale and pilot scale boiler testing to determine hazardous waste destruction and removal efficiencies (DRE's) and other associated boiler performance parameters during the last five years. This effort investigated several anomalous boiler performance areas dealing with non-steady and off-design boiler operation and included measurements of volatile and semi-volatile organics in the flue gas as well as the fate of some heavy metals introduced into the system. The tests were performed at pilot scale and investigated hysteresis effects, phenomena detected during earlier full-scale testing. These hysteresis effects are defined as the propensity for a boiler to retain certain organic components of the feed material (beyond the duration to a typical sampling protocol), to be released over a longer time frame in an unspecific manner. Additionally, a long time effect has been observed that manifests itself as a gradual buildup of background concentration during successive testing of initially clean hardware. This effort attempted to identify the presence of these effects beyond random variation, background concentrations and sampling problems such as sample contamination. These tests were partially successful at characterizing hysteresis phenomena as well as establishing a qualitative significance of these effects on the accuracy of DRE and other performance measurements.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 17
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE A03 12.95

EPA Form 2220-1 (Rev. 4-77)   PREVIOUS EDITION IS OBSOLETE

i

NOTICE

This document has been reviewed in accordance with
U.S. Environmental Protection Agency policy and
approved for publication. Mention of trade names
or commercial products does not constitute endorse-
ment or recommendation for use.

ii

BOILERS COFIRING HAZARDOUS WASTE: EFFECTS OF HYSTERESIS ON
PERFORMANCE MEASUREMENTS

Ivars J. Licis*, HWERL, USEPA; Howard B. Mason, Acurex Corporation

ABSTRACT

The Hazardous Waste Engineering Research Laboratory [HWERL] has
conducted full scale and pilot scale boiler testing to determine hazardous
waste destruction and removal efficiencies [DRE's] and other associated
boiler performance parameters during the last five years. This effort inves-
tigated several anomalous boiler performance areas dealing with non-steady
and off-design boiler operation and included measurements of volatile and
semi-volatile organics in the flue gas as well as the fate of some heavy
metals introduced into the system. The tests were performed at pilot scale
and investigated hysteresis effects, phenomena detected during earlier full-
scale testing. These hysteresis effects are defined as the propensity for a
boiler to retain certain organic components of the feed material [beyond the
duration of a typical sampling protocol], to be released over a longer
time frame in an uspecified manner. Additionally, a long time effect has
been observed that manifests itself as a gradual buildup of background con-
centration during successive testing of initially clean hardware. This effort
attempted to identify the presence of these effects beyond random variation,
background concentrations and sampling problems such as sample contamin-
ation. These test were partially successfull at characterizing hysteresis
phenomena as well as establishing a qualitative significance of these effects
on the accuracy of DRE and other performance measurements.

Introduction

The USEPA has been investigating the performance of boilers and other
industrial furnaces and their ability to destroy hazardous waste cofired with
a convential fuel such as natural gas, oil, or coal. The investigations
included the testing of over 14 full-scale boilers, and a number of labora-
tory and pilot scale tests. The tests typically determined DRE, the main
organic constituents in the flue gas, characterized effluents and residues
and recorded the associated boiler operating parameters and continuous
emissions monitoring parameters such as O_2, CO, CO_2, SO_x and NO_x and total
unburned hydrocarbons (TUHC).

The results of these investigations showed that high levels of DREs
could be expected (a mass weighted average for the 14 full-scale tests of
99.998 was calculated)[1] over a broad range of boiler designs, waste
characteristics and operating conditions.[2]

The DRE values during sub-stoichiometric air settings, malfunctioning
burner atomizer tests, and waste flow transients were found to be uniformly
high and very similar to those during normal operation.

Three full-scale boiler tests were conducted at non-steady off-design
conditions to map the DRE window and identify operating conditions which
could cause DRE values to fall below the acceptable four nines limit. No DRE
limits were found within the constraints of allowable plant operation during
the three tests.

A number of phenomena identified during the full-scale boiler testing
were left unexplained however, and certain questions pertinent to boiler per-
formance in destruction of hazardous waste were left unanswered.

During several of the full-scale tests, chlorinated organics were ob-
served in the baseline data at the same order of magnitude, a day after

cofiring of these substances had ceased. Between the earlier tests and the baseline sample the following day the boiler had been operated on natural gas only. Instrument error and contamination were ruled out.

Soot blowing 's a routine method by which the heat transfer surfaces are preened to maintain heat transfer efficiency. Limited data were obtained during soot blowing cycles indicating that higher organic concentrations were detectable in the gas phase. However only the gas phase was analyzed. Organics adsorbed or otherwise present on the part: late were not assessed.

- The hazardous organics present in the flue g. . . 2 typically separated into two groups. The principal organic hazardous constituents (POHCs) are used for determining DRE. The remaining hazardous organics are sometimes referred to as Products of Incomplete Combustion or PICs. The PIC's, as defined for the full scale boiler testing, were the semivolatile and volatile organic (other than POHC's) detected via the modified method 5 (MM5) and the volatile organics sampling train (VOST) respectively. For the full-scale boiler tests, it was found that, while the average DREs were uniformly high, the concentration of PICs relative to POHCs were at ratios ranging from less than one (1) to 700. This phenomenon was considered significant in that available data showed PIC to POHC ratios were generally one (1) for hazardous waste incinerators. A ten-fold increase in PICs could have the same effect on stack emissions as a reduction of the DRE by one nine (i.e. a starting 99.99 would become 99.9).

Limited data (one test) were obtained at full-scale to determine the fate of heavy metals co-fired in boilers as part of hazardous waste. Because the metals are not destroyed by the thermal process, data regarding the fate, form and particulate size distribution are important for evalating boiler performance.

The above topics were incorporated into a pilot-scale test program to complete the data base initiated by the full-scale test program. This paper focuses on the pilot-scale effort and, more specifically, on the hysteresis effects investigated and their significance to the measurement of boiler performance.

Defining The Problem

The protocols for assessing boiler performance include the determination of their DRE. The calculation of DRE requires the sampling and analysis of the boiler flue gas for hazardous organics identified as POHCs. In addition, it has been of interest to determine the remaining organic constituents because the full-scale boiler tests have indicted that, in relation to incinerators, boilers can produce larger amounts of PIC concentrations.

The methods for sampling organics have evolved over the duration of hazardous waste incineration testing and at present are basically a volatile organics sampling train (VOST) and a Modified Method 5 train (MM5) for semi-volatiles (3). Both trains are usually necessary to characterize the organic destruction efficiency of a boiler. For many of the boiler tests a simplified VOST train called a mini-VOST has been used in addition to the VOST. The three organics sampling trains concentrate the organics in the flue gas by adsorbing them onto polymeric resins over a period of time. The time required for each sampling train is a function of expected concentrations in the flue gas and detection limits of the organic species to be analyzed. Typical sampling times encountered during boiler testing are:

VOST - 20 min.
mini-VOST - 10-15 min.
MM5 - 3-4 hrs.

2

The resulting concentrations of organics calculated from these measurements are average values over the span of time sampled. The duration of a typical test point is therefore defined by the MM5 sampling interval. One or more VOST or mini-VOST samples may be taken during this interval.

In order to demonstrate a DRE of 99.99, the sampling and analysis methods must be able to provide resolution to the third decimal place (i.e. 99.999) or detect the target substances at a concentration 1/100,000 of the feed value. Many test series (for both boilers and incinerators) have relied on a method that enhances resolution of the target substances by injecting surrogate organics species with the waste (or instead of the waste). The surrogates are injected at feed concentrations to provide flue gas concentrations above detection limits at the required levels of destruction.

The use of surrogates and sampling trains in the manner discussed presumes that conditions within the boiler are generally at equilibrium during the sampling period. Specifically:

1. The combustion products within the boiler system come to an equilibrium within a short period of time (for liquid injection units this would be on the order of the gas phase retention time).

2. The combustion products within the boiler system generated by the injected surrogates closely follow the injection schedule (i.e. they start and stop at approximately the same times).

3. For the purposes of sampling organics the boiler firing history is insignificant.

During full-scale boiler testing, data were obtained that appear to conflict with the above presumptions.

Case Study: A boiler burning non-chlorinated waste was being tested for POHC and PIC destruction by injection of chlorinated organics with natural gas used as the primary fuel. At the conclusion of testing, the boiler was left running overnight burning pure natural gas. On the following morning, a baseline run was conducted using oil as primary fuel. Although no chlorinated components were present in the feed the flue gas was found to contain chlorinated species on the order of magnitude of those recorded during conclusion of the previous day's testing. A repeat test confirmed the first readings.

On the strength of this example and other similar data a pilot-scale effort was launched to investigate the existence and impact of hysteresis effects on boiler performance measurements.

Toward Solving the Problem

In order to provide a test platform for investigating hysteresis effects, a pilot-scale facility was configured and operated in a manner simulating the time and temperature profile of an industrial boiler. Figure 1 illustrates the operating envelope of the simulator and also the time/temperature profiles of a typical industrial boiler and, for comparison, a coal-fired utility boiler. The test facility is discussed in more detail later.

A pilot-scale test facility was selected to enable exploration of the boiler operating envelope at non-steady and off-design conditions beyond those possible at a full-scale field installation. Additionally, closely controlled test conditions would have been difficult to maintain at an operational full-scale facility.
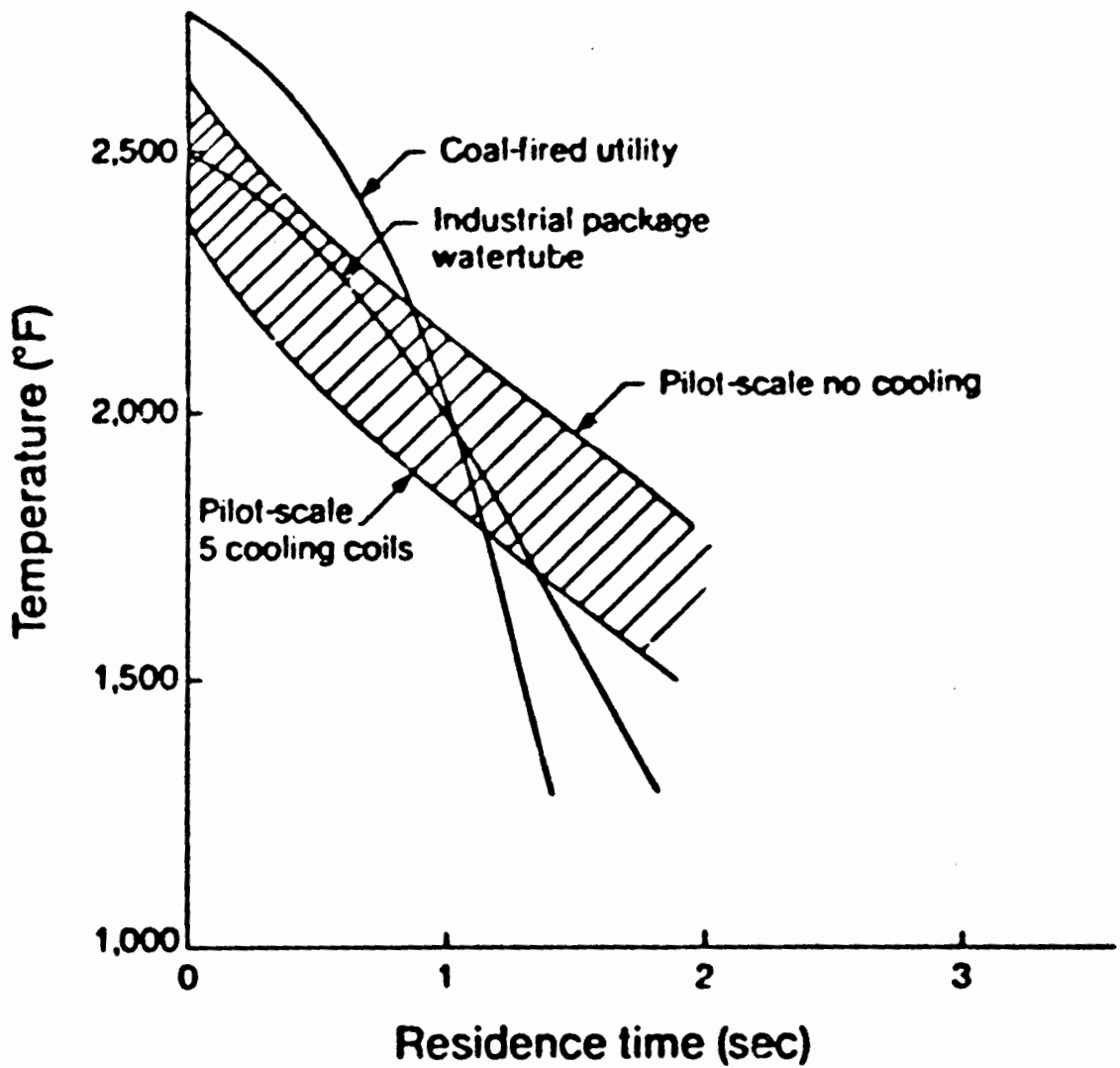
3

Figure 1. Boiler time/temperature profiles.

Test Objectives

The pilot-scale test program included a larger effort for characterizing off-design and unsteady state boiler operations as well as a smaller test series cofiring heavy metals. Under the hysteresis portion of the program two objectives were identified:

1. Determine if hysteresis effects are present at levels significant to DRE and PIC measurements.

2. Characterize the hysteresis effects in terms of maximum values and time variations.

Test Description

The pilot-scale facility is a field-erected watertube boiler simulator with 4, wall fired burners (see Figure 2) (2). The overall height of the furnace is 3.7m (12 ft). The firebox is a 1 meter (38 in.) wide by 1.1 meter (44 in.) deep, refractory lined chamber. The unit represents a 1 to 14 scale, front wall fired, field erected boiler that is intended to represent industrial hazardous waste cofiring practice in the larger size boilers.

The heat input rating is 0.44 MW (2.5 million BTU/hr) with a maximum heat release rate of $484kJ/m^3hr$ (13,000 BTU/ft^3hr). The boiler temperature for the furnace (measured at the beginning of the convective section is in the range of 980°C to 1200°C (1800°-2200°F). A schematic of the boiler system is presented in Figure 3. The burners used for the test are single register, concentric jets with variable swirl intensity in the annular air supply, based on a design developed by the International Flame Research Foundation (IFRF). The heat transfer system consists of closed loop heat exchange tube bundles that can be positioned in various locations along the convective pathway (see Figure 4). Various sampling locations were used during the test. The bulk of the sampling was done at Port 10 (see Figure 4). This position simulated stack emission conditions and was also used for continuous emissions monitoring (CEM), VOST, MM5 and HCl measurements. Samples were taken at several points to determine POHC profiles across the hot end of the convective section (Ports 8 and 9) and to determine concentrations near the burner (Port 4). Additional cooling coils were used to increase the size of the operating envelope. The coils were placed within the firebox to vary temperature and residence time at temperature. The coils were placed along the walls of the firebox both above and at the levels of the burners. The bottom curve of the operating envelope (see Figure 1) represents a test condition with all cooling coils in place in the firebox.

Three test fuels (natural gas, #6 oil and pulverized coal) were cofired with simulated hazardous waste. The hazardous waste consisted of 5% weight) each chlorobenzene, trichlorobenzene, trichloroethylene and carbon tetrachloride mixed with 80% distillate (#2) oil. Typical elemental waste composition was:

	Percent
C	76.59
H	11.07
N	0.54
S	0.17
O	1.97
Cl	9.66

Heating value of the waste was 39 MJ/Kg (17,130 BTU/lb) Data acquisition for the continuous emissions monitoring (O_2, CO, CO_2, NO_x, SO_x, THC and opacity) was performed via microcomputer and automatic data logger and
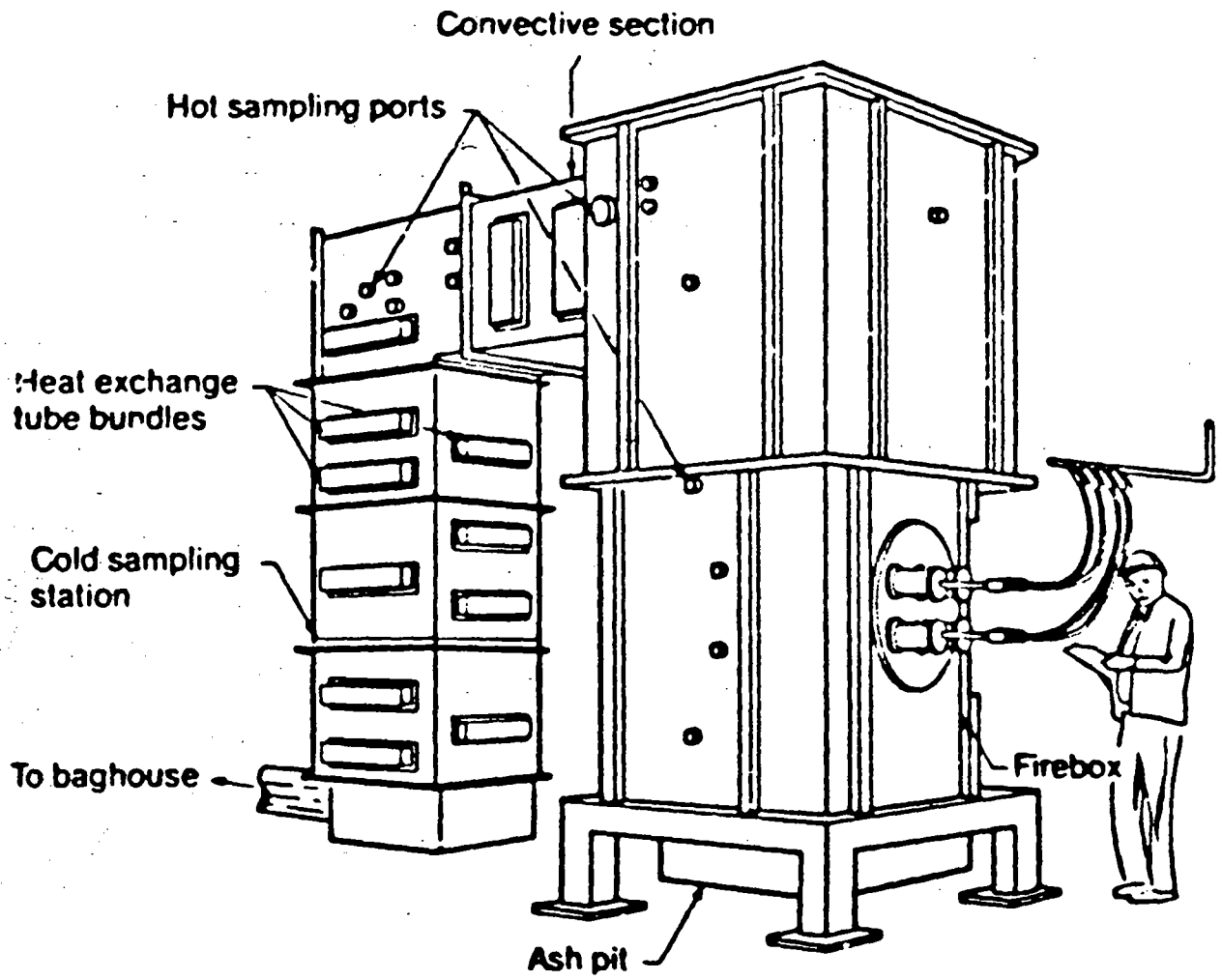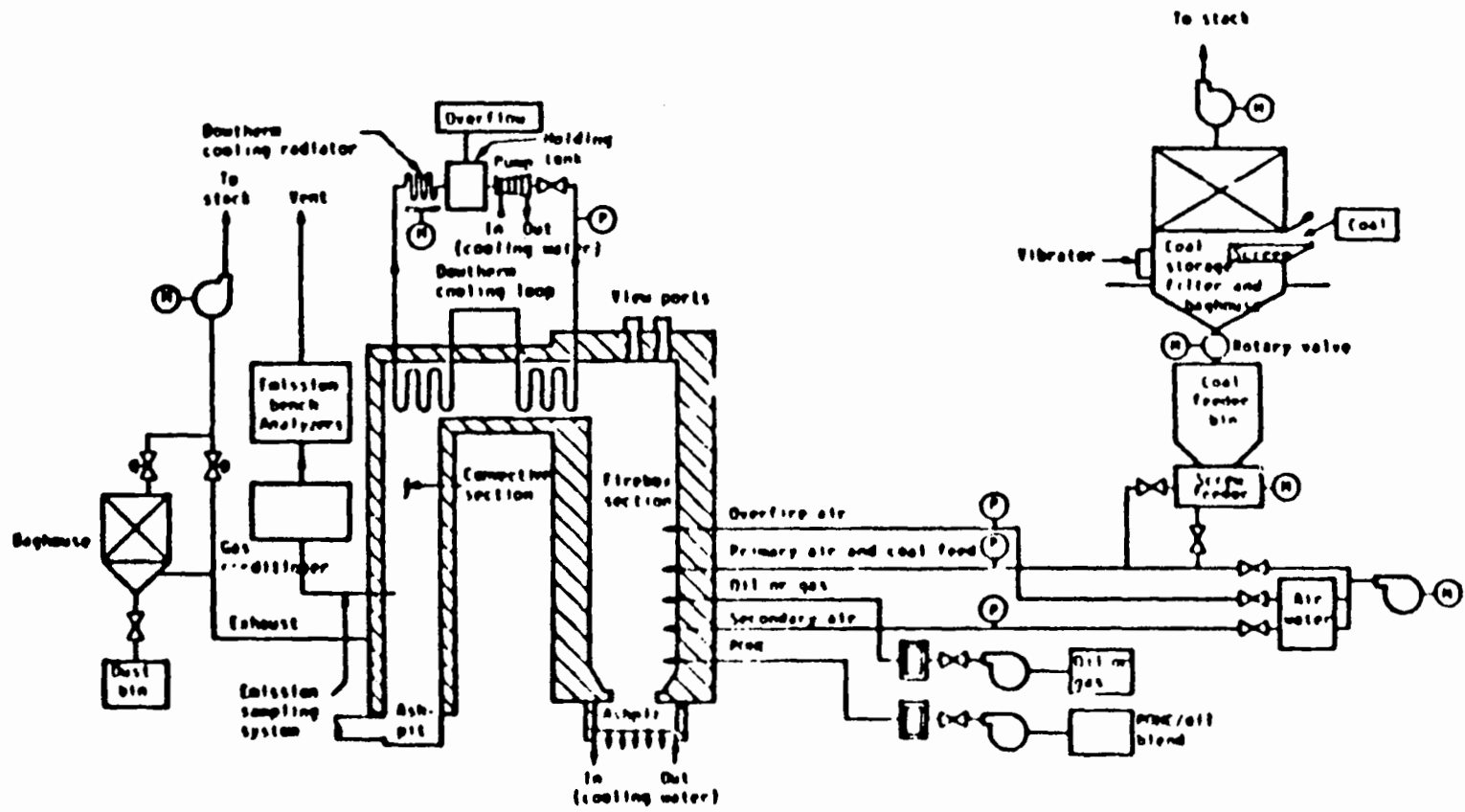
5

Figure 2. Pilot-scale boiler simulator.

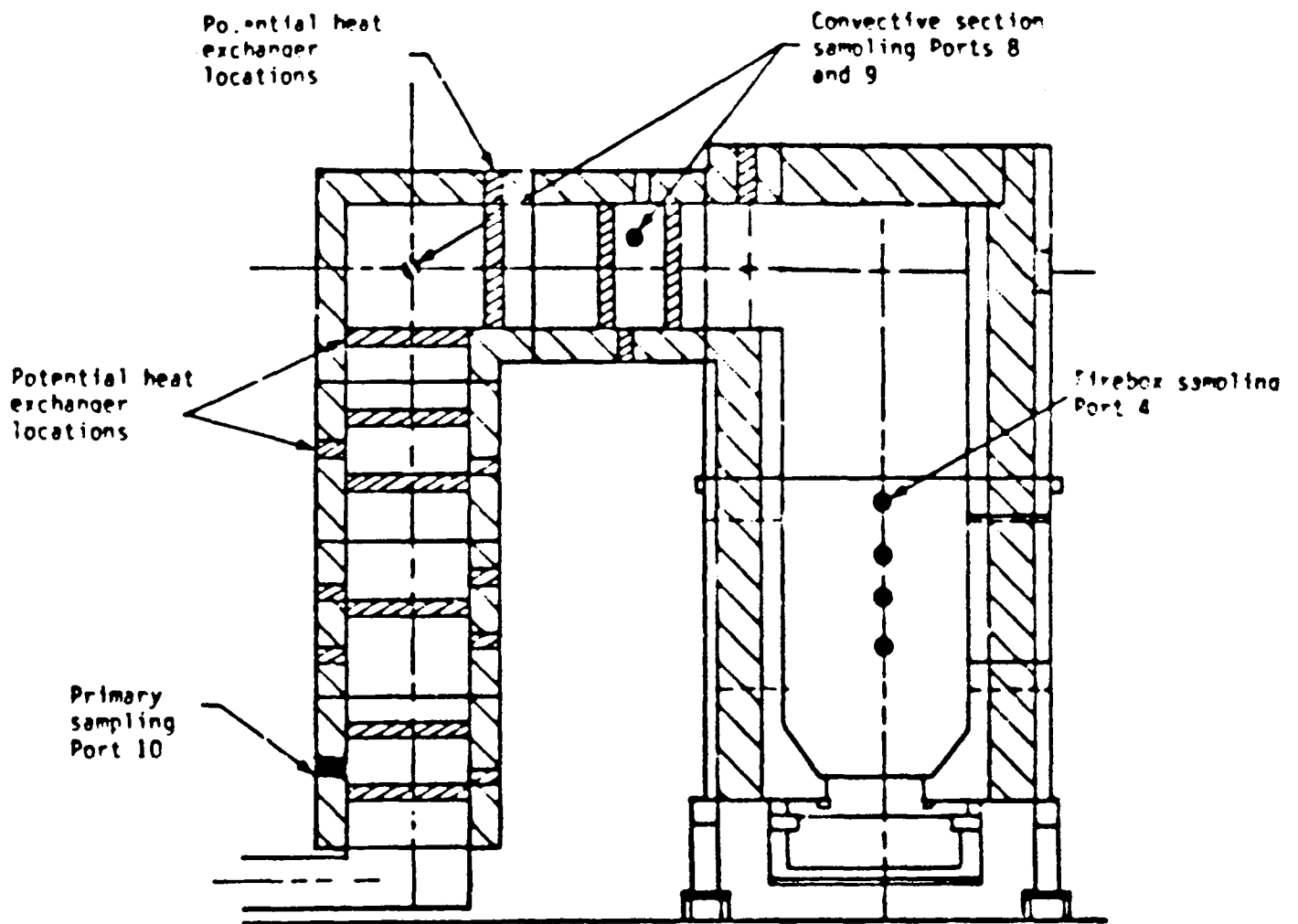Figure 3. Pilot-scale boiler schematic.

Po.ential heat
exchanoer
locations

Convective section
samoling Ports 8
and 9

Potential heat
exchanger
locations

Firebox samolino
Port 4

Primary
sampling
Port 10

Figure 4.   Sampling locations and potential convective heat exchanger
locations in the pilot-scale test facility.

8

recorded every 5 minutes. The boiler operating parameters such as temperature pressures and flow rates were also recorded.

The investigation of hysteresis effects involved three test series. The organics data was acquired by VOST, mini-VOST, and MM5 sampling trains.

Because the overall test program was one of screening for the impact of various phenomena on DRE and PIC concentrations, only a few data points were taken in each category and emphasis was placed on the volatile organics and the mini-VOST technique. The rationale was that beside this being a much more economical screening method (over the MM5), the volatile organics were considered highly significant in this area and the short sampling time (10-15 minutes), on-site data analysis capability (ideally 30 min. cycle) provided a feed-back loop that was very valuable in steering the direction of the testing.

A baseline test series provided information on background levels of PICs and POHCs when firing fuel only (gas, oil and coal). A second series was conducted cofiring waste with oil and gas (coal was cofired during other test series not involved in measuring hysteresis).
The boiler was tested by
cofiring waste during the day, taking a hysteresis sample shortly after cessation of cofiring (< 2 hours) and left overnight while burning natural gas only. A hysteresis sample was taken the successive morning prior to cofiring. On some occasions the unit was left on natural gas over the weekend and a hysteresis sample was taken Monday morning, prior to start of cofiring tests.

Another test series was comprised of taking numerous mini-VOST samples during steady-state operation to establish the width of the noise band (i.e. the amplitude variations in organics concentrations with the feed rate and other operating parameters held as constant as practical).

Additionally, two soot blowing cycles were simulated. Soot blowing was a manual operation performed with a compressed air lance. The concentrations of organics in the gas phase were measured before, during and after each cycle. The first soot blowing cycle was performed with the boiler cofiring #6 oil with the surrogate waste. The second was performed later in the test series with the boilers burning natural gas only. The timing of the second test came after several test series had been conducted that were expected to produce significant sooting and deposits on the boiler interior.

Results
The main objective of the hysteresis testing for this series was to determine if significant hazardous organics were present in the flue gas after cessation of hazardous waste cofiring. Data were taken at three general intervals. These were < 2 hours, 14 to 24 hours (overnight) and an "extended period" (after a weekend of burning natural gas only).

Table 1 presents ratios of average hysteresis values for all PICs and the individual POHCs measured < 2 hours after cessation of cofiring divided by the average concentration values obtained from the gas and oil baseline runs, taken before any cofiring had taken place. The table illustrates the presence of hysteresis. Lack of residual effects would place these values near unity.

Table 2 presents similar results by comparing the same average values of < 2 hours hysteresis with average values obtained during cofiring of

9

gas and oil. The PIC's measured during the pilot scale program are defined as volatile, chlorinated organics (other than those identified as POHC's) detected via the VOST and the mini-VOST. The hysteresis effect is illustrated here because without it the values in this case should be very small and definitely less than unity.

The values of Tables 1 and 2 were normalized to take into account fuel waste flow and airflow rates.

Table 1. HYSTERESIS EMISSION RATIOS
Average Hysteresis Concentrations < 2 hours After Cofiring
vs. Average Baseline Concentrations

Compound	$\dfrac{\text{Hysteresis}}{\text{Oil Baseline}}$	$\dfrac{\text{Hysteresis}}{\text{Gas Baseline}}$
PIC	0.1	10.38
CCl_4	2.0	12.11
TCE	0.7	17.5
MCB	149.0	NA (No BL)

where: CCl_4=carbon tetrachloride; TCE=trichloroethylene; MCB=monochlorobenzene
PIC's = volatile, chlorinated organics detected via VOST or mini-VOST

Table 2. HYSTERESIS EMISSION RATIOS
Average Hysteresis Concentrations <2 Hours After Cofiring
vs. Average Cofiring Concentration For Oil and Gas

Compound	$\dfrac{\text{Hysteresis Conc.}}{\text{Oil Cofiring Conc.}}$	$\dfrac{\text{Hysteresis Conc.}}{\text{Gas Cofiring Conc.}}$
PIC	0.45	9.78
CCl_4	2.0	1.79
TCE	0.93	7.19
MCB	7.0	44.0

Table 3 represents the levels of organic concentrations found during the natural gas firing portions of this test series for which the most abundant data points were taken. Based on this data, it can be seen that the total

Table 3. AVERAGE CONCENTRATIONS OF CHLORINATED COMPOUNDS
FOR GAS/WASTE COFIRING AND HYSTERESIS EFFECTS (ng/l)

	Total Chlorinated Species	CCl_4	TCE	MCB
Gas/Waste Cofiring	4.25	0.47	0.04	0.24
Hysteresis Concentrations (< 2 hr after cofiring)	3.93	0.57	0.25	0.93
Average Hysteresis Concentrations (all points for gas firing)	3.16	0.28	0.21	0.10

chlorinated species average concentrations during cofiring drops to about 92% of the original value in the < 2 hour timeframe and to about 74% when considering the overall average taken at three time intervals from < 2 hours to several days. It is interesting to note that the average concentration of

CCl4 at < 2 hours after cofiring increased to 121% of the cofiring value while monochlorobenzene appears at 388%.

The longer term effects were analyzed by comparing hysteresis levels early in the test series (the first hysteresis sample taken after the first cofiring waste using gas at "normal" operating conditions) with subsequent hysteresis test levels. The test series was started using clean hardware. The hysteresis concentration data were compiled for the total chlorinated species and the three individual chlorinated volatile POHCs over the duration of the test series (see Figure 5). While hysteresis effects for the individual POHC remain approximately the same, the total chlorinated species (PICs and POHCs) seem to increase with increasing fuel/waste firing.

Data from the two soot blowing cycles were also analyzed. Generally concentrations of POHC and PICs were highest during soot blowing and lowest after the cycle was completed, while values before soot blowing were between the two extremes. These concentrations were for the gas phase only and did not consider concentrations of organics contained on the particulate matter.

An attempt was made to correlate furnace temperatures with hysteresis but no consistent trend could be found in the range of 1000°C (1833°F) to 1150°C (2101°F).

Conclusions

Data presented indicate that target organic compounds were present in significant quantities after the cessation of cofiring. Their presence was detectable shortly after cofiring and at reduced concentrations a number of days later. The overall average hysteresis effect based on 13 runs cofiring gas and three (3) cofiring oil showed that around 50% of the original concentrations measured are still being emitted at a mean value of 43 hours (after cessation of cofiring. Because this phenomenon may significantly effect the accuracy of the DRE and organics measurements quantitative and parametric data need to be obtained in future studies.

The second objective was to characterize the time/amplitude characteristics of these effects. Although the study was terminated before complete characterization of these effects, some trends were discernable. Starting with clean hardware, it appears that a boiler system accumulates organic compounds with time and that over all, neither burning with natural gas nor soot blowing return the system to the clean state. This effect can be considered as "boiler aging" (4). An eventual "steady-state", if it exists, was not reached within the framework of the 59 days of this series. While the various organic compounds seem to exhibit different behavior patterns within the hysteresis effects, there were not sufficient data for generalizing about these differences.

The effects investigated here were for volatile organics only. Due to lack of developed short sampling time methods, semi-volatile effects are, more difficult to obtain and provide relatively poor resolution (i.e. 3-4 hr average readings). A rough time vs. concentration relationship data-set could be produced as part of a follow-up test.

The organics adsorbed onto sooty particulate need to be investigated. There is a good chance that a significant amount of hysteresis and a significant amount of the mass of organics emitted may be on the solid phase.

Efforts have already been underway to provide more resolution in the area of volatile organic quantities that are present in the flue gas after
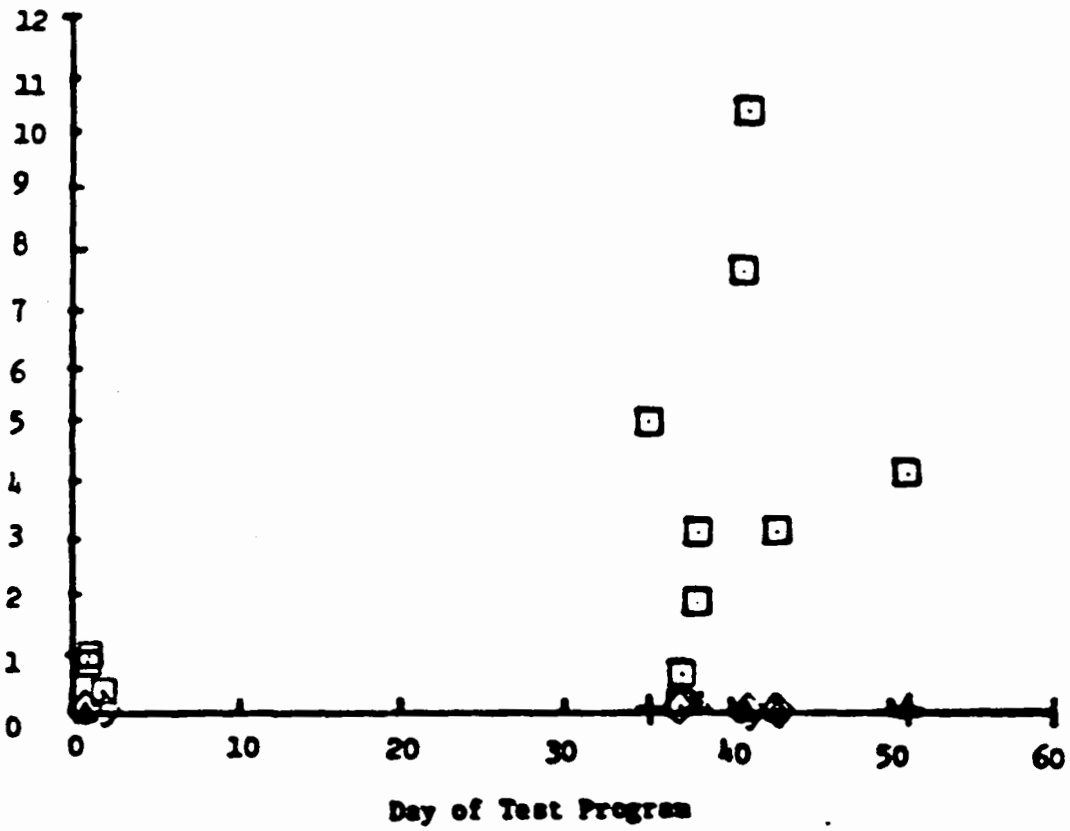
Figure 5. Hysteresis concentration vs. time.
(Data points are ratios to hysteresis concentration on
first day of test)

cofiring ceases. Further studies are planned in determining maximum
hysteresis impact that might be expected in full-scale boilers.

References
1. M. Wool, et.al., December, 1987 "Engineering Assessment Report: Hazard-
   ous Waste Cofiring In Industrial Boiler Under Nonsteady Operating Con-
   ditions" draft report, prepared by Acurex Corporation for U.S. EPA under
   Contract 68-03-3241, Work Assignment 2-9.

2. H.B. Mason, et.al., August 1987 "Pilot-Scale Testing of Nonsteady Boiler
   Waste Cofiring" draft report, prepared by Acurex Corporation for U.S. EPA
   under Contract 68-03-3241, Work Assignment 2-14.

3. U.S. EPA, November 1986 "Test Methods for Evaluating Solid Wastes",
   SW-846, 3rd edition, Office of Solid Waste and Emergency Response,
   Washington, D.C. 20460

4. C.D. Wolbach, March 1988 "Some Technical Aspects of Emission Testing
   During Cofiring of Hazardous Waste In Industrial Boilers" a paper
   presented at the Second Annual National Symposium, Incineration of
   Industrial Wastes, San Diego CA presented by Toxcon.