

A STUDY OF DIOXIN AND FURAN FORMATION USING HOT FILTRATION FOR OFFGAS TREATMENT

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ABSTRACT

This paper addresses dioxin/furan formation issues in relation to the U.S. Department of Energy's (DOE) thermal waste treatment system's needs.

The test objectives for the initial dioxin/furan tests were to measure the effect of particulate removal at various elevated operating temperatures on dioxin/furan formation, and to document the performance of the ceramic and high-efficiency particulate air (HEPA)-grade, sintered-metal filters. The first step in testing was to establish that dioxins/furans could indeed be produced under a given operating condition. The process conditions were then adjusted to meet the primary test objective.

An appropriate test bed configuration was developed specifically for this test. A test process gas slipstream of nominally 2 pounds per minute (lb/min) was taken from a main process gas stream of nominally 8 lb/min. Test bed components included a ceramic hot filter in series with a sintered-metal, HEPA-grade filter downstream of a primary thermal waste treatment chamber and a natural gas afterburner. A plasma arc torch was used for the first test, which was run on two separate days, and a natural gas alternate thermal driver was used for the last four tests. The surrogate feed recipe was formulated for its ability to produce dioxins/furans, and to approximate DOE incinerator conditions when burned. The feedrate was adjusted to produce short periods (puffs) of reducing conditions to enhance dioxin/furan generation. Dioxin/furan sampling was accomplished by using the

U.S. Environmental Protection Agency's (EPA) Method 23, "Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans Emissions from Stationary Sources."

The test program was based on the hypothesis that dioxin/furan compounds form at 400 to 950 °F in the presence of catalytically active solids, such as offgas particulate. It was expected that by filtering dioxin/furan formation-enhancing particulate at a temperature above the expected dioxin formation temperature, dioxin/furan formation could be retarded, if not eliminated, according to the specified process conditions.

The work was performed by MSE Technology Applications, Inc. (MSE), in Butte, Montana, under the direction of the DOE's Mixed Waste Focus Area (MWFA) and the DOE's Western Environmental Technology Office (WETO).

INTRODUCTION

The proposed EPA's Maximum Achievable Control Technology (MACT) standard for dioxin/furan is 0.2 nanograms per dry standard cubic meter (ng/dscm), expressed as the toxicity equivalence quotient (TEQ) relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD).

There are 210 possible chlorinated dioxin/furan compounds, all of which may be generated simultaneously in a combustion process. These are frequently referred collectively as the 210 dioxin/furan congeners. Of the 210 possible compounds, only 17 (those with chlorines substituted at the 2-, 3-, 7-, and 8-ring positions) are considered to be toxic and are regulated. Accordingly, Method 23 calls for the analysis only of tetrachlorinated and higher compounds and requires specific identification and quantitation for the 17 toxic compounds.

The 17 toxic dioxins/furans have varying toxicities depending on the number and location of the substituted chlorines. To assess the overall toxicity of a dioxin/furan mixture, the EPA requires that toxicity of the sample be expressed as the equivalent of the most toxic isomer, 2,3,7,8-TCDD. This is accomplished by multiplying the concentration of each of the 17 toxic isomers by a toxicity equivalence factor ranging from 1 (for 2,3,7,8-TCDD) to 0.001 (for octachlorinated dioxins/furans), and then summing the result to a single number. The final result is referred to as the TEQ and is normally expressed in units of nanograms toxicity equivalence quotient per dry standard cubic meter.(1)

Possible dioxin/furan emission problems were identified at the DOE's Waste Experimental Reduction Facility (WERF) and Consolidated Incineration Facility (CIF) thermal waste treatment units. These problems may affect the ability of these units to meet the proposed EPA MACT standard. MSE, through the DOE's MWFA, was tasked with setting up a test bed and running tests that attempted to simulate characteristics of the WERF and the CIF offgas to better understand the dioxin/furan formation mechanisms and ultimately offer the DOE potential solutions to the problem.

The WERF and the CIF incinerators process wastes contain soil, metals, oils, halogenated solvents, and finely-divided inorganic material, among other constituents. The incinerators are operated under general oxidizing conditions; however, the potential exists for momentary oxygen (O₂)-deficient conditions resulting from nonuniform feedrates. Momentary O₂-deficient conditions may be a factor in the offgas dioxin/furan concentrations observed at the WERF and the CIF. An attempt was made to mimic some of the suspected key dioxin formation process conditions at the WERF and the CIF in the testing at MSE.

SLIPSTREAM TEST BED SYSTEM DESCRIPTION

The tests were conducted in the experimental offgas test bed shown in Figure 1.

The slipstream test bed (SSTB) provides a flow slipstream of the 6-foot plasma arc centrifugal treatment (PACT-6) system primary chamber gas to various small-scale offgas system components that may be used in an eventual

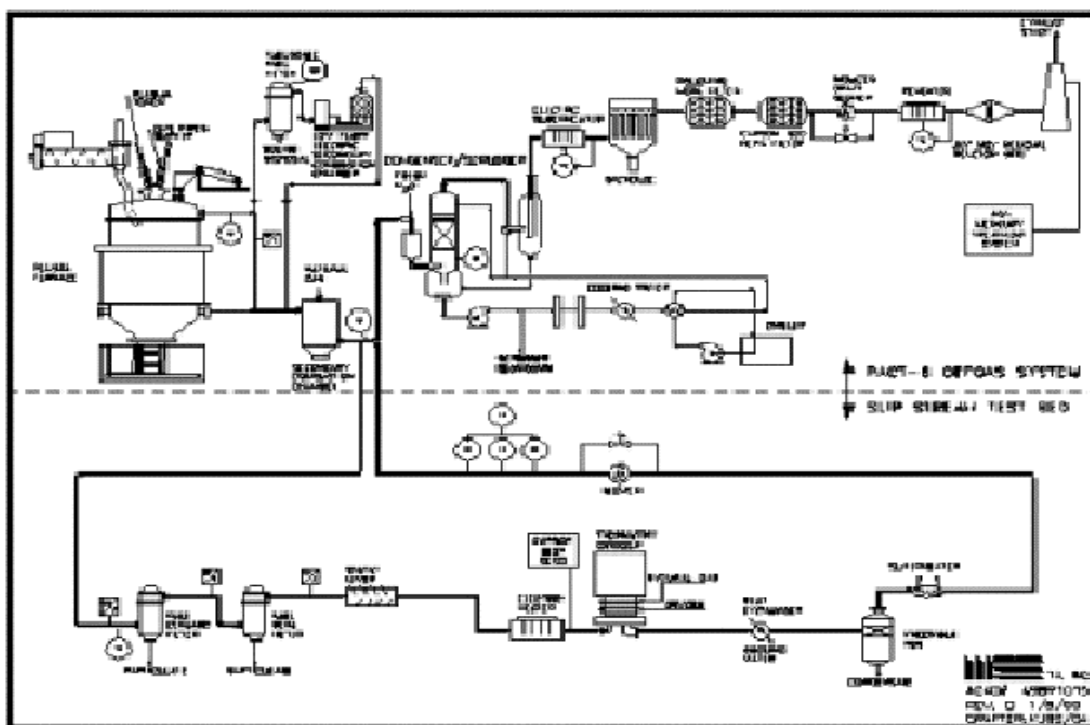
full-scale air pollution control (APC) system. The slipstream is used to allow long-term, steady-state testing of the small-scale components with actual offgas generated under full-scale PACT-6 system processing conditions. The PACT-6 system uses either a 500-kilowatt (kW) plasma torch or a natural gas O₂-enriched combustor as the primary thermal driver, followed by a 400,000-British thermal units per hour secondary combustion chamber (SCC).

The process equipment used in the SSTB is:

- a 1/4-scale, high-temperature ceramic filter;
- a high-temperature, sintered-metal, HEPA-grade filter;
- an in-line heater;
- a flameless electric oxidizer;
- a gas cooler;
- a knockout pot/demister with a condensate receiver and pump;
- a reheater; and
- a positive displacement blower.

During use of the SSTB, gas is drawn from the exit piping of the SCC. Nominally 2 lb/min (one-quarter flow from the primary chamber) is drawn into the test bed. This gas is drawn from the SCC through a refractory-lined pipe to the ceramic filter. Insulated piping was then connected to the 1/4-scale HEPA filter, which supplies offgas at 650 F to the hot HEPA filter.

The gas then passes through an electric reheater to maintain the gas above dewpoint, thus preventing acid from condensing in the system. The flameless electric oxidizer was operated at 400 F to prevent condensation of nitric acid from the offgas oxides of nitrogen (NO_x) inside the unit. The offgas then enters a gas cooler, a moisture removing knockout pot, and a superheater to again heat the offgas above dewpoint. The dry offgas then enters the slipstream blower and returns to the main offgas system wet scrubber, filtering sections, induced draft blower, electric reheater, catalytic NO_x removal section, and finally the stack.



TEST OBJECTIVES

The hot dioxin filtration test objectives were:

- to simulate, as closely as feasible, offgas compositions and system configurations for the DOE WERF and CIF incinerators;
- to determine the feasibility of operating the ceramic and sintered-metal HEPA filters at the upper end of their operating temperature range with the simulated offgas of the DOE incinerators;
- to evaluate the ability to maintain steady-state operation greater than 1,300 °F at the inlet of the ceramic filter;
- to evaluate the ability to produce dioxins/furans upstream of the ceramic filter by measuring dioxin/furan concentrations at the outlet of the primary chamber and at the inlet of the Pall ceramic filter;
- to measure the net removal (or formation) of dioxin/furan by the ceramic filter and sintered-metal HEPA filter by measuring dioxin/furan concentrations at the outlet of the ceramic filter and at the outlet of the HEPA filter; and
- to measure particulate removal efficiency for the ceramic filter and the high-temperature HEPA filter.

TEST RESULTS

Eight tests, designated HITPR-1 and HF-DEMO-2 through -8 were performed to date that are relevant to this paper. During HITPR-1, only an 900 F temperature was achieved at the inlet of the ceramic filter. Test HITPR-1 was run in parcels on two separate days. The offgas piping was reconfigured, more insulation was applied, and temperatures of up to 1,450 F were achieved for the tests that followed, with the exception of HF-DEMO-3.

HF-DEMO-3 did not reach target temperatures because of ambient air leaking into faulty process pipe flanges. The main focus of this paper will be on HF-DEMO-2 through -8 since the target inlet to the ceramic filter temperature was achieved.

The results of HITPR-1 are discussed briefly for completeness. More detail on HITPR-1 can be found in the *Controlled Emissions Demonstration Project Fiscal Year 1998 Final Report*.⁽²⁾

Offgas samples were taken for dioxin/furan analysis using the procedures described in the EPA's Method 23, Determination of Polychlorinated Dibenzo-p-dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF) from Stationary Sources.⁽¹⁾ The terms dioxin and furan shall be used interchangeably with PCDD and PCDF, respectively for the remainder of this paper. The sampling points are shown in Figure 1.

Test HITPR-1

The plasma arc torch, operated at a power level of 400 kW, was used as the thermal source for this test. The primary feed material for HITPR-1 was a sand, polyvinyl chloride (PVC), and carbon steel-based mixture fed through a screw feeder with a smaller quantity of 1,1,1-trichlorethane (1,1,1-TCA)/Microcel mixture fed simultaneously using a conveyor feeder. Material in the screw feeder was fed at 250 pounds per hour (lb/hr), with a total of 1,000 pounds. Material on the conveyor feeder was fed at a rate of 3.3 lb/hr.⁽³⁾

One Method 12 particulate sample was successfully taken at the inlet of the ceramic filter. That sample showed significant particulate loading, 1.5 grains per dry standard cubic foot (gr/dscf), which is a typical particulate emission while running the plasma torch.

This test was run on two days. On both days, PCDDs/PCDFs were detected in the offgas; however, different trends were observed. On the first day, total PCDD/PCDF concentrations (tetra- through octa-congeners) were 61 ng/dscm at the ceramic filter inlet, 137 ng/dscm at the ceramic filter outlet, and 221 ng/dscm at the sintered-metal HEPA outlet, indicating an increase in the PCDD/PCDF concentrations at each subsequent downstream sampling location. Corresponding TEQs were 1.8 nanograms toxicity equivalence quotient per dry standard cubic meter

(ng TEQ/dscm), 3.6 ng TEQ/dscm, and 3.6 ng TEQ/dscm, respectively. This trend suggested that PCDDs/PCDFs were being formed in offgas treatment components, possibly on particulate retained on the ceramic and hot HEPA filters. It is important to note the temperature gradient across the filter was up to 600 F during this test.

In contrast, during the subsequent test day, PCDD/PCDF concentrations were much higher overall, but declined at each subsequent downstream sampling location. Total PCDD/PCDF concentrations were 10,600 ng/dscm at the primary chamber outlet, 1,200 ng/dscm at the ceramic filter inlet, 590 ng/dscm at the ceramic filter outlet, and 160 ng/dscm at the HEPA outlet. Corresponding TEQs were 248 ng TEQ/dscm, 28 ng TEQ/dscm, 14 ng TEQ/dscm, and 3 ng TEQ/dscm, respectively. This trend indicated that the ceramic and HEPA filters were removing PCDDs/PCDFs, suggesting that the PCDDs/PCDFs were possibly bound to particulates.

The total TEQ in all of the HITPR-1 samples was caused more by 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-PeCDF) than by any other of the 17 toxic PCDD/PCDF congeners. Congener profiles dominated by furans are generally indicative of soot-related PCDD/PCDF information.

The data from HITPR-1 was valuable in another manner. Running with cooler process conditions was crucial to the logic of the tests as we attempted to show that dioxins/furans were actually being produced in a cooler configuration to establish a baseline.

Tests HF-DEMO-2 through -8

Tables I through III show the feedstock recipe used for tests HF-DEMO-2 through -8. The feedstock components were chosen for their ability to act as effective catalysts or precursors in the formation of dioxins/furans under the process test conditions and also for their ability to approximately simulate the WERF and the CIF feed conditions. The particulate, sized less than 325 mesh to provide a large surface area, was fed into the vertical section of the offgas piping at the outlet of the primary combustion chamber (PCC) at a rate of 10.2 grams per minute. The organic liquid feed, intended as dioxin precursors, was fed at a rate of 10 milliliters per minute. The plastic was fed in batches on a conveyor bucket feeder belt in an effort to create the desired momentary reducing conditions. Each 342-gram (g) batch contained equal parts of acrylonitrile-butadiene-styrene (ABS) and PVC. This plastic was fed at a rate of 1 batch dump every 2 minutes. Notice that there was a significant amount of chlorine (Cl) in the plastic feedstock, mostly from the PVC.(4)

Table I. Particulate feed.

Compound	Weight Percent	Percent Cl
Aluminum Oxide	5	0
Calcium Oxide	2	0
Copper Oxide	10	0
Iron Oxide	50	0
Magnesium Oxide	1	0
Potassium Carbonate	1	0
Sodium Carbonate	1	0
Silicon Dioxide	30	0
Total Weight Percent	100	0

Table II. Liquid feed.

Compound	Mixture Ratio	Percent Cl
3,4-Dichlorophenol	40.8 g	43.5
1,1,1-TCA	1,000 milliliters	79.7

Table III. Plastic feed.

Compound	Weight Percent	Percent Cl
PVC	50	56.7
ABS	50	0
Total PVC/ABS Weight Per Conveyor Cell	342 g	28.4

Table IV shows the operating conditions for the tests. Temperatures ranged from 850 to 1,400 F at the inlet to the ceramic filter and 360 to 390 F at the outlet of the hot HEPA filter. This temperature profile met the objectives of this test series, as the estimated temperature windows for dioxin/furan formation and reformation were present.

EPA Method 23 offgas samples were taken and analyzed for dioxins/furans during four tests, HF-DEMO-2

through -5. For each test, dioxin/furan offgas samples were taken at four locations: 1) the outlet of the PCC (SP 1); 2) 5 feet upstream of the ceramic filter inlet (SP 2); 3) at the inlet of the high-temperature HEPA filter (SP 3); and 4) at the outlet of the HEPA filter (SP 4) (refer to Figure 1). The samples were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry at a commercial laboratory certified to perform Method 23 dioxin/furan analyses.

An EPA Method 23 sampling train consists of several components, including a probe, a filter, organic resin trap, and an impinger solution train. The filter is intended to trap particulates that may contain adsorbed dioxins/furans. The organic resin is intended to trap any gas-phase dioxins/furans that do not condense on upstream components of the sampling train. The method calls for two solvent rinses, toluene and a combined acetone/methylene chloride rinse.

Ordinarily, rinses of each section of the sampling train, the filter, and the organic resin are sent to the laboratory in separate containers where they are combined during extraction and analysis. The laboratory then reports results in units of nanograms of each analyzed compound per sample. The desired final reporting units are nanograms per dry standard cubic meter in the gas drawn through the sampling train. Therefore, the laboratory results (in nanograms) are divided by the volume of gas (corrected to a moisture-free basis and to standard temperature and pressure) drawn through the sampling train.

In an effort to distinguish between particulate and vapor-phase dioxins/furans, two of the HF-DEMO-3 test samples were treated differently than described above in an effort to determine where in the sampling train the dioxins/furans were being trapped.

The laboratory was asked to analyze fractions of two of the samples, as follows:

- for the sample taken at the outlet of the PCC, split the sample into three fractions; the combined rinses upstream of the filter, the filter, and the organic resin and rinses downstream of the filter; and
- for the sample taken at the outlet of the HEPA filter, split the sample into two fractions; the filter and rinses upstream of the filter and the organic resin and rinses downstream of the filter.

The HEPA outlet sample was expected to contain much lower levels of dioxins/furans because any dioxins/furans adsorbed on particulates should have been removed by the ceramic and HEPA filters. In addition, any dioxins/furans at the HEPA outlet were expected to be present predominantly as a vapor rather than adsorbed on particulates, and therefore, should have been trapped mainly on the organic resin.

These two fractional samples were analyzed as planned, except that for the PCC outlet sample, the acetone/methylene chloride probe rinse was lost in shipping. Since acetone/methylene chloride is the first rinse used in Method 23 sampling and because visible condensate/particulate was noted on the probe, a substantial fraction of the dioxins/furans present in that sample may have been lost with the rinse. That would result in the reported value being incorrectly low. The acetone/methylene chloride probe rinse for the HF-DEMO-4 PCC outlet sample was also lost in shipping and those results would be expected to be incorrectly low as well.

The analysis results indicated that a substantial fraction of the dioxins/furans was captured on the organic resin, rather than on the filter, for both the PCC outlet sample and the HEPA outlet sample. It seems clear from these results that any alternative dioxin/furan sampling method must be capable of capturing both particulate and vapor-phase dioxins/furans. An alternative method to EPA methods is desirable because of the lengthy time it takes to get final laboratory results. Faster turnaround is desired to more quickly characterize existing hazardous waste incinerators (HWI).

General results of dioxin/furan distribution across the test bed filter section, expressed as nanograms per dry standard cubic meter, are shown in Table V. Several trends are evident.

The test conditions produced high, but widely varying concentrations of dioxins/furans at the PCC outlet, with total concentrations ranging from 44,000 to 167,000 ng/dscm.

In general, dioxins/furans were present in lower concentrations at each successive downstream sampling location. An exception to this was that concentrations appeared to substantially increase across the ceramic filter during the HF-DEMO-3 test, from 14,600 to 34,500 ng/dscm.

Table IV. Summary of Operating Conditions

	HF-DEMO-2	HF-DEMO-3	HF-DEMO-4	HF-DEMO-5	HF-DEMO-6	HF-DEMO-7	HF-DEMO-8
Pall Inlet Temperature	1,300 to 1,400 F increasing	850 to 1,100 F	1,356 to 1,386 F increasing	1,340 to 1,360 F increasing	1,440 to 1,385 F	1,340 to 1,350 F	1,350 to 1,320 F increasing
Pall Outlet Temperature	750 to 800 F	600 to 550 F decreasing	800 F	700 to 800 F	800 to 750 F decreasing	750 to 800 F	700 F
HEPA Inlet Temperature	550 to 580 F	450 to 400 F decreasing	600 F	550 to 600 F increasing	580 to 550 F decreasing	550 to 580 F	550 to 580 F
HEPA Outlet Temperature	360 to 380 F	350 to 300 F decreasing	390 F	350 to 390 F increasing	380 to 360 F decreasing	360 to 380 F	350 to 370 F
PreO _x Carbon Dioxide (CO ₂)	6 to 10% (off scale high)	2 to 10% (off scale high)	10% (off scale high) spike to 0%	5 to 10% (off scale high)	4 to 10% (off scale high)	4 to 10% (off scale high)	5 to 10% (off scale high)
PreO _x Carbon Monoxide (CO)	0 to 1,600 parts per million (ppm) narrow spikes	5 to 2,000 ppm narrow spikes	0 to 1,400 ppm narrow spikes	10 to 2,500 ppm narrow spikes	10 to 1,600 ppm narrow spikes	0 to 2,000 ppm narrow spikes	0 to 2,000 ppm narrow spikes
PreO _x O ₂	6 to 21% narrow spikes	11 to 21% narrow spikes	8 to 18% narrow spikes	7 to 19% narrow spikes	7 to 20% narrow spikes	8 to 21% narrow spikes	8 to 19% narrow spikes
PCC Gas Temperature	1,980 to 2,020 F	1,980 to 2,020 F	1,960 to 1,980 F	1,960 to 1,980 F	1,960 to 2,000 F	1,950 to 1,980 F	1,950 to 1,980 F
SCC Offgas Temperature	1,925 to 2,000 F	1,950 to 2,000 F	2,000 F	1,980 F	1,980 F	1,990 F	1,980 F
Stack O ₂	8 to 16% narrow spikes	6 to 14% narrow spikes	9 to 16% narrow spikes	11 to 17% narrow spikes	10 to 17% narrow spikes	11 to 17% narrow spikes	11 to 17% narrow spikes
Stack CO	6 to 1,000 ppm (off scale high) narrow spikes	0 to 1,000 ppm (off scale high) narrow spikes	0 to 1,000 ppm (off scale high) narrow spikes	0 to 1,000 ppm (off scale high) narrow spikes	0 to 1,000 ppm (off scale high) narrow spikes	0 to 1,000 ppm (off scale high) narrow spikes	0 to 1,000 ppm (off scale high) narrow spikes
Stack CO ₂	11 to 19% narrow spikes	11 to 19% narrow spikes	12 to 18% narrow spikes	12 to 18% narrow spikes	12 to 18% narrow spikes	11 to 17% narrow spikes	11 to 17% narrow spikes
Stack Total Hydrocarbons	1 to >25 ppm narrow spikes	1 to >25 ppm narrow spikes	1 to >25 ppm narrow spikes	1 to 77 ppm narrow spikes	1 to 65 ppm narrow spikes	1 to 110 ppm narrow spikes	1 to 32 ppm narrow spikes
Date Sampling Start/Stop Time	11/6/98 12:35 to 14:56	11/12/98 13:49 to 16:14	11/17/98 11:40 to 13:46	11/19/98 13:07 to 15:17	12/2/98 11:08 to 12:29	12/4/98 11:40 to 12:56	12/8/98 11:00 to 12:19

Table V. Dioxin/Furan Testing

HF-DEMO-2				
Sampling Location	Temperature	Total PCDD/PCDF (ng/dscm)	Total TEQ (ng/dscm)	TEQ Change (%)
PCC Outlet	777 C (1,430 F)	67,400	1,350	-
Pall Inlet	798 C (1,469 F)	3,720	74.9	-94.5 (across afterburner)
HEPA Inlet	331 C (628 F)	3480	97.6	+30.3 (across Pall)
HEPA Outlet	132 C (270 F)	353	12.5	-87.1 (across HEPA)
HF-DEMO-3				
PCC Outlet	786 C (1,446 F)	167,000	2,180	-
Pall Inlet	517 C (963 F)	14,600	230	-89.4 (across afterburner)
HEPA Inlet	236 C (456 F)	34,500	667	+190 (across Pall)
HEPA Outlet	97.8 C (208 F)	8,260	329	-50.7 (across HEPA)
HF-DEMO-4				
PCC Outlet	806 C (1,483 F)	43,900	551	-
Pall Inlet	797 C (1,466 F)	10,800	158	-71.3 (across afterburner)
HEPA Inlet	342 C (648 F)	3,150	70.6	-55.3 (across Pall)
HEPA Outlet	128 C (263 F)	3,420	43.9	-37.8 (across HEPA)
HF-DEMO-5				
PCC Outlet	819 C (1,506 F)	120,000	2,730	-
Pall Inlet	805 C (1,482 F)	44,700	589	-78.4 (across afterburner)
HEPA Inlet	329 C (625 F)	14,300	406	-31.1 (across Pall)
HEPA Outlet	117 C (242 F)	3,410	126	-68.9 (across HEPA)

At the PCC outlet and generally at other sampling locations as well, furans were present in greater concentrations than dioxins.

From more detailed data that are not shown in Table V, higher chlorinated species were favored over lower chlorinated species. At the PCC outlet, the octachlorinated furan was present at the highest or second highest concentration relative to the other compounds for each test except HF-DEMO-5.

The HF-DEMO-5 test differed from the other tests, with a relatively lower degree of chlorination of furans (penta-, hexa-, and hepta-chlorinated furans were present in greater concentration than the octachlorinated furan).

As mentioned above, dioxin/furan concentrations appeared to increase across the ceramic filter during the HF-DEMO-3 test, suggesting that dioxins/furans may have been generated within the ceramic filter during that test. The dioxin/furan congener concentration profile during the HF-DEMO-3 test did not appear to differ from the other tests, suggesting that whatever process led to increased dioxins/furans across the Pall filter, it did not result from a dramatically altered chemistry in the overall system. This detailed dioxin/furan congener information can be found in the *Hot Filter Dioxin Test Report*.⁽⁵⁾

The dioxin/furan TEQs for the HF-DEMO-2, -3, -4, and -5 tests are also shown in Table V. The TEQs at all sampling locations were well above the MACT standard of 0.2 ng TEQ/dscm.

Values ranged from a low of

12.5 ng TEQ/dscm at the HF-DEMO-2 HEPA outlet to a high of 2,730 ng TEQ/dscm at the HF-DEMO-5 PCC outlet. Significant removal of dioxin/furan was taking place, however.

Even though detailed analysis indicated that the more highly chlorinated compounds dominated the concentration profiles, most trends appeared to be the same whether the results were expressed as concentrations or TEQs. That is, furans were more significant than dioxins, and generally, both concentrations and TEQs were lower at each successive downstream sampling location, with the exception of the samples taken across the ceramic filter during the HF-DEMO-3 test. It is interesting to note that in that case, two compounds, 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-hexachlorodibenzofuran almost entirely accounted for the increase in TEQ.

During the HF-DEMO-2 through -5 test series, dioxin/furan concentrations at corresponding sampling locations differed widely by a factor of four at the PCC outlet and by more than an order of magnitude at the other sampling locations. However, the highest measured PCC outlet concentration was for the HF-DEMO-3 test. Since the acetone/methylene chloride probe rinse for that sample was lost in shipment and the reported result is, therefore, known to be incorrectly low, in all likelihood, the true PCC outlet dioxin/furan concentrations ranged over an order of magnitude as well.

Three of the four tests were conducted under nearly identical conditions of feed, temperature, and O₂ stoichiometry. The exception was the HF-DEMO-3 test, which was conducted with a lower temperature at the ceramic filter inlet (950 F versus 1,450 F for the other tests), and particulate was not injected due to particulate feeder plugging problems. Temperatures were similarly lower at the HEPA inlet and outlet sampling points for HF-DEMO-3; however, the PCC temperature was comparable to the other tests.

As can be seen from Table V, the HF-DEMO-3 test yielded the highest dioxin/furan concentrations at the PCC outlet, the HEPA inlet, and the HEPA outlet, and the second highest concentration at the ceramic filter inlet. The fact that the ceramic filter and the hot HEPA filter were operated at relatively cooler temperatures might explain the elevated dioxin/furan concentrations downstream of those units, but does not explain the elevated concentration at the PCC outlet. Also puzzling is that particulate injection was expected to enhance dioxin/furan formation; however, the particulate feeder was plugged at the end of this test, and it appeared that no particulate had been injected. At present, a satisfactory explanation for the elevated PCC outlet concentration for the HF-DEMO-3 test is not available even though it is clear that this test stands out as having the highest overall dioxin/furan concentrations.

The EPA's Method 12 was used to measure particulate and total metals across the test bed filter section during tests HF-DEMO-6 through -8 to assess the effects of particulate loading on dioxin/furan generation. These tests were conducted with the same target test conditions used for the dioxin/furan sampling tests. Similarly to the dioxin/furan tests, particulate samples were taken at a sampling port 5 feet upstream of the ceramic,

high-temperature filter and at the inlet and outlet of the sintered-metal, high-temperature, HEPA-grade filter. In contrast to the dioxin/furan tests, no sample was taken at the outlet of the PCC.

Particulate loading measurements are shown in Table VI. Total particulate at the inlet to the ceramic filter ranged from 500 to 800 mg/dscm, less than 2 mg/dscm to 94 mg/dscm at the inlet to the hot HEPA filter, and less than 2 mg/dscm to 4.5 mg/dscm at the hot HEPA outlet. The sampling particulate detection limit was estimated to be 2 mg/dscm. The filter section of the test bed reduced particulate to less than 5 mg/dscm on all three tests, which was well below the anticipated MACT standard requirement of 0.015 grains per dry standard cubic meter or 34 mg/dscm. Information on the removal efficiencies of specific metals can be found in the *Hot Filter Dioxin Test Report* .(5)

SUMMARY AND CONCLUSIONS

This test series demonstrated that dioxin/furan can, by control, be emitted from the SCC of a HWI simulated process. Five to twenty-five percent of the dioxin measured at the outlet of the PCC was present at the inlet to the hot filter section. This same effect could be present at the WERF and the CIF since their processes are similar.

Dioxin/furan congener profiles vary with the type of human origin production source. A congener profile exhibits the various dioxin/furan concentrations present in the source's offgas and may serve as a source signature. The profiles observed for this test series appear to correspond closely to typical profiles for HWIs.(6)

Table VI.
Particulate testing.

HF-DEMO-6			
Sampling Location	Temperature	Particulate Matter (mg/dscm)	Particulate Matter Change (%)
Pall Inlet	760 C (1,400 F)	763	-
HEPA Inlet	331 C (628 F)	93.9	-87.7 (across Pall)
HEPA Outlet	118 C (244 F)	4.5	-95.2 (across HEPA)
HF-DEMO-7			
Pall Inlet	786 C (1,447 F)	884	-
HEPA Inlet	312 C (594 F)	24.5	-97.2 (across Pall)
HEPA Outlet	110 C (230 F)	0.0	-100 (across HEPA)
HF-DEMO-8			
Pall Inlet	781 C (1,437 F)	534	-
HEPA Inlet	307 C (585 F)	0.0	-100 (across Pall)
HEPA Outlet	104 C (220 F)	2.1	nondetect

Results of the HITPAR-1 test indicated that high levels of dioxin/furan could be produced in the test bed, that expected high levels of particulate were indeed being formed by the plasma process, and that some dioxin/furan removal was taking place as expected in the test bed filter section. Further information on this test can be found in the *Controlled Emissions Demonstration Project Fiscal Year 1998 Final Report*.(2)

For the HF-DEMO-2 through -8 tests, effective removal of dioxin/furan took place in the hot filter section, albeit above the anticipated MACT standard allowable limit of 0.2 ng/dscm TEQ. Further testing of the hot filter section different temperatures may yield better results. Also, a wet scrubber would probably ensure condensation and removal of the remaining dioxin/furan. This concept could also be tested in the future.

The SSTB filter section very efficiently removed particulate well below the anticipated MACT standard level of 0.015 gr/dscf (34 mg/dscm). This indicates that a properly placed high-temperature rated filter section would likely remove PCC transuranic carryover material upstream of a wet scrubber and other downstream APC devices. This is a significant attribute of hot filtration as less of the system would be less radioactively contaminated, and therefore, would be easier to maintain and the final decommissioning and decontamination task would be less intensive. Further verification testing may take place in Fiscal Year 2000 depending on additional test data needs of the DOE's MWFA and the DOE's thermal waste treatment units.

It should be noted that bench-scale dioxin/furan testing is being executed at MSE in conjunction with innovative sampling and gas chromatography/mass spectrometry analysis methods development. The resulting test data may help answer some of the questions on dioxin/furan formation and reformation mechanisms and processes. The test data will be reported in a publication to be presented subsequent to this writing.

REFERENCES

1. "Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Stationary Sources," 40 Code of Federal Regulations, Part 266, Appendix IX, U.S. EPA
2. "Fiscal Year 1998 Controlled Emissions Demonstration Project Final Report," PTP-52, MSE, (1998)
3. "Controlled Emissions Demonstration Project Hot Filter Test Plan," PTP-43, MSE, (1998)
4. "Controlled Emissions Demonstration Project Phase II Hot Filter Test Plan," PTP-47, MSE, (1998)
5. "Hot Filter Dioxin/Furan Final Test Report," PTP-(to be determined), MSE, (1999)
6. DAVID CLEVERLY, ET.AL., "The Congener Profiles of Anthropogenic Sources of Chlorinated Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans in the United States," (1997)

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APPENDIX A

ACRONYMS

1,1,1-TCA	1,1,1-trichlorethane
2,3,4,7,8-PeCDF	2,3,4,7,8-pentachlorodibenzofuran
2,3,7,8-TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
ABS	acrylonitrile butadiene styrene
APC	air pollution control
CIF	Consolidated Incineration Facility
Cl	chlorine
CO	carbon monoxide
CO ₂	carbon dioxide
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
g	gram
gr/dscf	grains per dry standard cubic foot
HEPA	high-efficiency particulate air
HWI	hazardous waste incinerator
kW	kilowatt
lb/hr	pounds per hour
lb/min	pounds per minute
MACT	Maximum Achievable Control Technology
mg/dscm	milligrams per dry standard cubic meter
MSE	MSE Technology Applications, Inc.
MWFA	Mixed Waste Focus Area
ng/dscm	nanograms per dry standard cubic meter
ng TEQ/dscm	nanograms toxicity equivalence quotient per dry standard
cubic meter	
NO _x	oxides of nitrogen
O ₂	oxygen
PACT-6	6-foot plasma arc centrifugal treatment
PCC	primary combustion chamber
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzofurans
ppm	parts per million
PVC	polyvinyl chloride
SCC	secondary combustion chamber
SSTB	slipstream test bed
TEQ	toxicity equivalence quotient
WERF	Waste Experimental Reduction Facility
WETO	Western Environmental Technology Office