

HIGH VACUUM THERMAL PROCESS FOR DESTRUCTION OF DIOXINS IN INEEL/WERF FLY ASH

J.W. Adams,* P.D. Kalb,* and D.B. Malkmus**

*Brookhaven National Laboratory, Upton NY

**Sepradyne/Raduce, Inc., Denton TX

ABSTRACT

This study investigated the use of an indirectly heated, high temperature (900 °C), high vacuum (28" Hg) rotary kiln, developed and patented by Raduce, Inc. (subsidiary of Sepradyne Corp.), to treat a dioxin contaminated mixed waste incinerator ash from the Idaho National Engineering Lab (INEEL) Waste Experimental Reduction Facility (WERF). The Raduce process differs from conventional thermal processing systems (e.g., direct-fired incinerators and indirect heated thermal desorption units) primarily due to the combination of a high vacuum and rotary mixing action achieved by means of a proprietary rotating vacuum seal. Treatment in the absence of an oxidative environment distinguishes the technology from conventional techniques and eliminates products of incomplete combustion. A 500 cm³ bench-scale rotary vacuum thermal desorption and destruction unit (DDU) was used at Brookhaven National Laboratory (BNL) to demonstrate this thermal treatment process. Dioxins and furans were successfully decomposed at both low (450 °C) and high (700-800°C) temperature regimes. Dioxin homologue concentrations in the untreated ash ranged between 30 and 565 ppb and furan homologue concentrations ranged between 78 and 267 ppb. After thermal treatment, dioxin/furan homologue concentrations were close to non-detectable (the highest dioxin concentration was reported at 0.067 ppb and the highest furan concentration was 0.119 ppb) for samples treated at both 450°C and 750°C. In addition, substantial volume and mass reduction of the ash was achieved. Stabilization of the nonvolatile residues by a post-treatment encapsulation process will be required to reduce the leachability of Resource Conservation and Recovery Act (RCRA) metals to levels below the EPA Toxicity Characteristic Leaching Procedure (TCLP) requirements.

INTRODUCTION

Raduce, Inc (a subsidiary of Sepradyne Corp.) uses a patented indirectly heated high vacuum rotary thermal desorption and destruction process for extraction and thermal decomposition of volatile components from hazardous and mixed waste. To date, this technology (also known as retorting) has been successfully deployed for the removal of toxic metals from soils and mining sludges and is currently being tested for the removal of mercury from mixed waste soils. Through the combination of heat, rotation, and vacuum, the process removes volatile species (e.g., arsenic, cadmium, mercury) and recovers them in an impinger/condensor. Depending on process time and temperature, however, extracted organic components may be totally destroyed. The objective of this work at BNL was to conduct bench-scale treatability testing of the Raduce high temperature, high vacuum process for destruction of dioxin/furans contained in mixed-waste fly ash generated at the Idaho National Engineering Lab (INEEL) Waste Experimental Reduction Facility (WERF) incinerator. This work was supported by the U.S. Department of Energy (DOE) Mixed Waste Focus Area (MWFA).

The Raduce process differs from conventional thermal processing systems (e.g., direct-fired incinerators and indirect heated thermal desorption units) primarily due to the combination of a high vacuum and rotary mixing action achieved by means of a proprietary rotating vacuum seal. Treatment in the absence of an oxidative environment distinguishes the technology from conventional techniques and prevents generation of any products of incomplete combustion. For example, products of incomplete combustion (PICs), dioxins and furans can be formed when organic compounds are broken down in the presence of oxygen, chlorine and other gases. The rotary vacuum system quickly and uniformly distributes heat to the waste and enhances removal of volatilized species, minimizing re-absorption on the waste substrate. Other advantages of the Raduce process include:

- Ability to separate or destroy hazardous constituents from mixed waste
- Reduction in operational costs due to large throughputs and less heat energy required under high vacuum conditions
- Reduction in capital costs due to simpler off-gas treatment requirements and simplified permitting, because the technology is classified as a recycling or resource recovery process, not incineration.
- Improved volume reduction of wastes, lowering costs for transportation and disposal.

- Inherent ability to prevent any system over-pressurization

PROCESS DESCRIPTION

A bench-scale indirectly heated high vacuum rotary thermal desorption and destruction process unit (shown in Figure 1) was assembled and installed at the BNL Environmental and Waste Management Group laboratories for treatability testing of surrogate and actual waste samples. The waste is heated under vacuum in the rotating process vessel where dioxins and furans are decomposed. Since the objective of this effort was contaminant destruction, not removal and capture, the usual impinger/condensor unit was by-passed and off gases were routed directly to a charcoal column prior to venting through a HEPA filtered ventilation hood.



Fig 1. Bench-scale indirectly heated high vacuum rotary thermal desorption and destruction process unit

The process vessel is 316L stainless steel has a capacity of 500 ml. The vessel is 4.5" in diameter by 7" in length, with a single port on one end. A fritted metal tube placed into the orifice allows evolved gases to exit the vessel. The vessel can be operated at temperatures up to 1100°C and is operated by a drive mechanism that can be run at speeds from 1 to 7 RPM using a 345 watts/120 volt power source. Material is fed batchwise to the retort. The process vessel has been configured for solids and has an input hopper and auger system to transfer the material into and out of the unit. The processed material is removed from the vessel through the same orifice by reversing rotation and diverting the material to the output receiver. Based on results, a material can be reinserted into the

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vessel for additional processing as necessary. Gases are then routed through an activated carbon column where any remaining particulates/organics are removed before the gas exits the system.

Process conditions for this bench-scale system are manually monitored, although for larger units, the entire process is monitored and controlled through embedded sensors to ensure process parameters are within adequate safety and operational bounds. For pilot- and production-scale systems, the internal/external temperatures, system vacuum, and off gas flow parameters are monitored and logged via a computerized virtual instrument (VI) graphical interface. These systems are designed to shutdown if critical parameters vary outside of the prescribed operating windows, e.g., the system vacuum level reading reaches a low-level setpoint of 18" Hg or less. They also enable the site operator or an operator remotely monitoring the system via computer modem, the capability for intervention and automatic response to various system parameter alarms.

The off-gas system is controlled by a vacuum pump that can produce up to 28" Hg vacuum. Gas flow may also be valved off to allow a longer residence time for off gas in the process vessel. After exiting the vessel, off gases are then exhausted through a 150 ml activated carbon column. The column is fabricated from 1" 316L SS tubing with 1/4" ports. A secondary containment was installed around the unit to contain and collect any incidental material spills.

PROCESS RESULTS

Four sample containers containing a total of 675 g of dioxin/furan contaminated WERF fly ash were received from Envirocare of Utah where the material is awaiting treatment and disposal. The samples were labeled with ID #: 990407- 1,2,3,4. This ash is traceable to Burn 92 at WERF. Results of total dioxin and furan analyses of the as-received waste are given in Table I. Concentration of toxic metals extracted per EPA Method SW 846-1311 (Toxicity Characteristic Leaching Procedure, TCLP) given in Table II., indicate that the ash will require further treatment following dioxin destruction to meet RCRA Land Disposal Restrictions. Moisture content of the ash was measured for several batches prior to processing using a Sartorius Model MA 30 Moisture Analyzer and averaged 8 wt%.

Table I PCDD/PCDF Total Homologue Summary of As-received Werf Fly Ash

Homologue	Peaks	Concentration (µg/kg)
<i>DIOXINS</i>		
Total TCDD	12	29.92
Total PeCDD	12	66.285
Total HxCDD	7	297.871
Total HpCDD ¹	2	565.006
<i>FURANS</i>		
Total TCDF	15	77.647
Homologue		
Total PeCDF	15	142.728
Total HxCDF	12	258.659
Total HpCDF ¹	4	286.842

¹HpCDD and HpCDF are not regulated as underlying hazardous constituents.

A series of six process runs to treat the dioxin/furan contaminated fly ash were completed. The first four runs were conducted at process temperatures of 700 to 800°C. For the second run and all runs thereafter, the process vessel

was valved off from the off gas system during processing to allow a long residence time for maximum destruction of dioxins/furans in the vessel. For process temperatures above approximately 650°C, however, this resulted in loss of vacuum as decomposition products began to evolve. (With no waste in the vessel, vacuum was held without measurable loss indicating gas is being evolved under these conditions). Following each run, ash was removed from the process vessel and volume and weight measurements were taken (mass balance was maintained by recording changes in the weight of the vessel). Significant volume reduction (e.g., approximately 40%) and weight loss (e.g., approximately 20%) were observed as a result of the decomposition, possibly from loss of metal chloride salts suspected to be contained in the fly ash. Inorganic salt decomposition is suspected since most organics decompose below 500°C. Based on these results, two runs were conducted at a lower temperature (450°C) to try to destroy dioxins without further decomposing inorganic species. At these temperatures significantly less gas evolution was observed and loss of vacuum was much less severe, indicating that decomposition of inorganic constituents was reduced or eliminated.

Table II TCLP Metals Summary of As-received Werf Fly Ash

Element	Concentration, mg/L
Antimony	3.38
Arsenic	2.26
Barium	0.687
Berillium	Undetected
Cadmium	116
Chromium	0.0128
Lead	5.72
Mercury	0.0043
Nickel	0.856
Selenium	0.0651
Silver	0.137
Thallium	0.0713

With reduction in vacuum and increased gas evolution during the higher temperature runs, the gas residence time was reduced and dioxins may have been released to off gas and trapped by the carbon column. Thus the carbon media was replaced and suspect carbon media was treated as a seventh run. A batch-by-batch process log of the seven treatment runs is given in Table III.

Composite samples from the high and low temperature process runs as well as samples of the carbon media before and after thermal treatment (a total of four samples) were sent to Southwest Research Institute (SwRI) for dioxin/furan analyses. Analytical results are given in Table IV.

Table III WERF Fly Ash DDU Process Summary

Date	Batch #	Ash Weight, g		Moisture %	Test Duration Minutes	Final Temp	Volume Reduction/Mass Reduction ¹
		Pre	Post				
5-14-99	WERF 99407-4-2	91.9	50.54	7.3	92	700°C	64% vr ; 45% wr
5-27-99	WERF 99407-4-2	59.26	42.93	8.3	270	750°C	40% vr ; 27.5% wr
5-28-99	WERF 99407-4-1	73.67	53.66		165	800°C	27.2 % wr ²
5-29-99	WERF 99407-4-1	71.7	58.1		180	750°	50% vr; 18.9% wr
6-21-99	WERF 99407-4-4	114.8	83.4	8.35	145	470°C	27.4% wr ²
6-21-99	WERF 99407-4-4	95.75	90.75	8.15	50	450°C	5.5% wr ²
6-22-99	Spent carbon	80	68.2		240	600°C	14.8% wr ²

¹vr: Volume reduction; wr: Weight reduction

²Volume reduction not measured

Table IV PCDD/PCDF Total Homologue Summary of DDU Treated WERF Fly Ash

Homologue	Concentration (µg/kg)			
	WERF 99407-4-1/2 700-800°C Composite	WERF 99407-4-4 450-470°C Composite	Spent carbon Untreated	Spent carbon 600°C Composite
<i>DIOXINS</i>				
Total TCDD	ND	ND	ND	ND
Total PeCDD	ND	ND	ND	ND
Total HxCDD	0.040	ND	ND	0.054
Total HpCDD ¹	0.067	0.018	ND	0.057
<i>FURANS</i>				
Total TCDF	ND	ND	0.030	ND
Total PeCDF	ND	ND	ND	ND
Total HxCDF	0.022	ND	ND	0.012
Total HpCDF ¹	0.051	ND	ND	0.119

ND = Not Detected

¹HpCDD and HpCDF are not regulated as underlying hazardous constituents.

SUMMARY AND CONCLUSIONS

Dioxin and furan removal from WERF fly ash was successfully accomplished using the bench-scale Raduce high temperature, high vacuum process. Dioxin homologue concentrations in the untreated ash ranged between 30 and 565 ppb (regulated dioxins between 30 and 259 ppb) and furan homologue concentrations ranged between 78 and 287 ppb (regulated furans between 78 and 259 ppb). After thermal treatment, dioxin/furan homologue concentrations were close to non-detectable (the highest dioxin concentration was reported at 0.067 ppb and the highest furan concentration was 0.119 ppb) for samples treated at both 450°C and 750°C. These data clearly indicate that dioxin removal in the Raduce process was effective at both high and low temperatures and that dioxins/furans were probably decomposed prior to reaching the off gas carbon filter. To positively establish that dioxins/furans were decomposed by the process rather than removed and deposited internally would require complete analysis of the internal surfaces of the system, which was beyond the scope of this project. However, since exhaust gases exited the vessel at temperatures significantly higher than vaporization/condensation temperatures for dioxins (around 100 °C), were not subjected to cooling other than ambient air, and were not exposed to large surface areas en route to the carbon column, opportunity for deposition via condensation within the system were minimal. This evidence leads to the conclusion that the dioxins/furans were not simply removed from the ash but were destroyed. Based on these data, processing of drum quantities of WERF fly ash at the Envirocare facility using a pilot-scale Raduce system should successfully treat dioxin and furan contamination to meet regulatory criteria.

Elevated TCLP metals concentrations in the as-received fly ash (Table II), however, will require that the waste be treated to reduce leachability of certain toxic characteristic metals, namely antimony (Sb), cadmium (Cd), lead (Pb), and silver (Ag). Recently promulgated Universal Treatment Standard TCLP limits for these metals (Federal Register, 1998) are 1.15, 0.11, 0.75, and 0.14 mg/L, respectively. TCLP testing of the treated ash was beyond the scope of this effort. Post-treatment stabilization/solidification technologies are readily available to reduce leachability of these metals, if required. BNL has developed two technologies which reduce metals leachability by one to two orders of magnitude, i.e., polyethylene microencapsulation and sulfur polymer stabilization/solidification (SPSS).

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REFERENCES

1. Federal Register, Rules and Regulations, Vol. 63, No. 100, May 26, 1998, 28748-28750.