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THE ROLE OF CEMS IN DOE THERMAL TREATMENT

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ABSTRACT

The Department of Energy (DOE) currently operates four thermal treatment facilities that are permitted under regulations for hazardous waste combustors. As regulations become more stringent and public stakeholders become more influential, permitting these facilities is increasingly difficult. As they become more available, continuous emission monitors (CEMs) may offer the potential to assure regulators and the public of the safe operation of treatment facilities. The Mixed Waste Focus Area (MWFA) has participated in the development and testing of a variety of CEMs that could have application to DOE facilities.

I. INTRODUCTION

DOE operates several thermal waste treatment for the treatment of mixed hazardous and radioactive waste. These facilities are permitted as hazardous waste incinerators and will subject to the new rule for Maximum Achievable Control Technology (MACT) for Hazardous Waste Combustors.

In theory, CEMs offer a better way to control pollutants and monitor compliance with emission regulations. The MACT Rule provides incentives to use CEMs to reduce waste feed characterization and to reduce dependence on operating parameters for compliance verification. If a sufficient suite of CEMs were available, Environmental Protection Agency (EPA) has publicly stated a willingness to eliminate comprehensive testing and reduce scope of trial burns and waste feed characterization. As part of the MACT Rule, EPA has published draft performance specifications that precede availability of CEMs. EPA appears open to creative, perhaps staged relaxation of these performance specifications to encourage implementation of CEMs as long as the risk to public health is not increased. However, CEMs techniques for some analytes are more complex than most commercially available CEMs. Technical risks present serious barriers to successful deployment. Of these barriers, performance verification is one of the most important.

There are three principal drivers for development of CEMs:

1. CEMs offer the potential for simplified compliance in the face of increasingly stringent emission regulations.

2. CEMs can provide opportunities for process performance improvement.

3. CEMs can provide assurance for the public that DOE waste treatment processes are operating within permitted emission limits.

The mission of MWFA CEM program is to define and help execute a technology development and demonstration strategy that will result in deployment of CEMs to monitor waste treatment processes for DOE. There are two overall objectives of this program:

1. Accelerate development of technologies that meet, or nearly meet clearly defined performance specifications.

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2. Minimize redundancy and coordinate CEM technology development with other government sponsors such as Department of Defense (DoD), EPA, and other DOE offices.

To accomplish these objectives, the MWFA has initiated CEM development programs, particularly for multiple metals, dioxins, and mercury. These programs have involved both technology development and demonstrations.

II. MULTI-METALS

Current multi-metal monitoring methods involve periodic manual sample collection followed by off-line sample analysis. This is a very time consuming and costly process. Also, as currently practiced, these analyses are only conducted during trial burns and other comprehensive tests, every 18 to 24 months. Several development programs have been undertaken to overcome this limitation.

Developers have produced multi-metal CEMs for real-time monitoring of hazardous trace metal emissions. Several of these CEMs have been tested in three comparative demonstration tests, beginning in April 1996 and ending in September 1997. Three CEMs were tested in each of the first two tests. In the final test, seven CEMs were tested in a pilot-scale rotary kiln at the EPA Office of Research and Development facility in Research Triangle Park, NC. The intent of these tests was to determine if any of the monitors was ready to undergo long-term validation tests in a joint DOE/EPA effort. Table 1 gives a listing of the seven CEMs that participated in the September 1997 tests.

These tests were designed to measure the performance of multi-metal CEMs for regulatory compliance applications. As such, the tests focused on six metals currently slated for regulation in the draft EPA MACT Rules: arsenic, beryllium, cadmium, chromium, lead, and mercury (note that antimony was dropped from the draft MACT Rule during 1997). Results for those seven CEMs were compared with results from simultaneous flue gas sampling using conventional EPA Reference Method (RM 0060) sampling trains and analytical procedures.

The most important performance issue is whether a CEM can quantitatively measure all six metals. To address this issue, two parameters were measured: 1) detectability (at the concentrations tested, compared with required method detection limits (MDLs)), and 2) relative accuracy, which is the average CEM measurement compared with the EPA reference method measurement during the same time period.

Of the monitors tested, only the Navy/ Thermo Jarrell Ash Inductively Coupled Plasma (ICP) system was able to detect all six metals. The others were able to detect two to five metals. Only ICP and X-Ray Fluorescence were able to detect mercury and arsenic, which have proven to be very problematic for other monitors. Table 2 shows the relative accuracies of the seven CEMs for each of the six metals at both the high and low target concentrations.

Based on the results of these tests, it was determined that no multi-metal CEM is currently ready for long term testing. All require additional developmental work, particularly in the area of field calibration.

III. DIOXINS AND FURANS

EPA has established very stringent emission limits for dioxins and furans. A major problem for waste treatment facilities is understanding where in these systems dioxins and furans are formed. To better understand the formation mechanisms requires an ability to measure dioxins as a function of various operating parameters.

Currently, dioxin analysis can only be performed by manual methods, which require three to five weeks for the analysis results to become available. A near real-time diagnostic monitor would greatly aid in the development of dioxin control strategies. To address that need a program has been initiated to develop a coordinated program of monitor development and mechanistic studies leading to control strategies.

Compounding the problem of monitoring for dioxins is that there are 210 individual congeners of which only 17 are governed by regulations. The resulting requirements for sensitivity and selectivity severely challenge the abilities of most monitoring techniques.

In a scoping effort funded by EPA and MWFA a resonance enhanced multi-photon ionization/mass spectroscopy (REMPI/MS) system was tested to see what its potential might be for dioxins. This very preliminary test showed that the system can detect tetra-chlorinated dioxins at concentrations as low as 10 ppt. Although this detection limit is not sufficient, the test at least showed that there is potential for the technique.

Another potential technique for monitoring dioxins is fast gas chromatography/mass spectroscopy (GC/MS). This technology was developed to detect explosives and narcotics in airport security systems. Recently declassified, the technique has been shown to be able to detect dioxins, though selectivity and sensitivity have not been established.

To address the problem of dioxin emissions from incinerators, a project has been initiated to develop a strategy for controlling the emission of dioxins. The project has two parts: monitor development and mechanistic studies.

The monitoring effort will examine the potential of the two techniques discussed above: REPMI/MS and GC/MS. Initial development will focus on the monitors' use as diagnostic tools to be able to provide data relating operating parameters with dioxin emissions.

In parallel with this monitor development will be the development of dioxin formation models and correlations, which service two purposes. First, correlations will be developed relating the 17 toxic congeners with other indicator species that are present in larger concentrations. A CEM for these indicator species would indicate dioxin emissions, but would be a simpler and less expensive instrument. Second, models and correlations can be used to relate emissions with system operating parameters to provide a better understanding of the dioxin formation mechanisms. This understanding can lead to changes in operation thereby minimizing dioxin emissions.

IV. MERCURY

A significant portion of DOE's mixed waste contains mercury. When processed in a thermal treatment system, mercury is volatilized and ends up in the offgas system. Although most offgas systems will remove some mercury, efficiencies are generally less than 20% and often less. As a result, emissions of mercury are generally controlled by limiting the amount of mercury in the waste feed, which restricts the ability of the facility to process some waste streams. It may be possible to install additional mercury removal equipment, but this would likely require monitoring of the effluent to ensure that the control device is functioning properly.

In a joint program between DOE and EPA, three commercially available mercury monitors were tested during an extended period on an operating cement kiln burning hazardous waste. These monitors are used routinely on incinerators in Europe. Unfortunately, results for the CEMs on the cement kiln showed that the characteristics of the offgas were too severe for the monitors. In general the monitors gave acceptable results while they were operational, but the monitors required extensive maintenance to keep them running.

DOE waste treatment facilities employ scrubbers and extensive particulate matter removal so the offgas is much less severe than was the case in the cement kiln. It may therefore be that a mercury monitor would operate satisfactorily at DOE facilities. Therefore, the MWFA will test a mercury CEM at a DOE incinerator to assess its ability to reliably monitor mercury emissions. If the results of this test are positive, then the monitor will be tested on other DOE facilities.

V. CONCLUSIONS

Continuous emission monitors offer thermal treatment facilities the opportunity to assure regulators and the public that they are operating safely and within permitted emissions limits. CEMs can also provide an operator valuable information concerning the operation of a facility, which can reduce emissions and potentially increase the range of waste fed to that facility.

Table 1. Summary of multi-metal CEM technologies, organizations, and sponsors

CEM TECHNOLOGY	DEVELOPING ORGANIZATION	SPONSORING ORGANIZATION
Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)	U. S. Department of Defense (DoD) Naval Air Warfare Center	U. S. Army Demilitarization Technology Office Commercially available through Thermo Jarrell Ash
Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES)	Diagnostic Instrumentation and Analytical Laboratory (DIAL) at Mississippi State University	U. S. Department of Energy Characterization, Monitoring, and Sensor Technology Crosscutting Program (DOE CMST-CP)
X-Ray Fluorescence	Private. Cooper Environmental Services, Inc.	Private. Cooper Environmental Services, Inc. Commercially available through CES, Inc.
Laser Induced Breakdown Spectrometry - Atomic Emission Spectroscopy (LIBS)	Diagnostic Instrumentation and Analytical Laboratory (DIAL) at Mississippi State University	U. S. Department of Energy Characterization, Monitoring, and Sensor Technology Crosscutting Program (DOE CMST-CP)
Laser Induced Breakdown Spectrometry - Atomic Emission Spectroscopy (LIBS)	Sandia National Laboratories, Livermore, CA	DOE CMST-CP and the U.S. Army Demilitarization Technology Office
Spark-Induced Breakdown Spectroscopy	Physical Sciences Inc.	U.S. Department of Energy, FETC
Microwave Induced Breakdown Spectroscopy	Massachusetts Institute of Technology	U. S. Department of Energy Mixed Waste Focus Area
Calibration Technique for LIBS	Laser Diagnostics	U. S. Department of Energy Characterization, Monitoring, and Sensor Technology Crosscutting Program (DOE CMST-CP)

Table 2. Relative Accuracy of each multi-metal CEM at high and low concentrations.

Concentration	Navy / TJA ICP	CES XRF	DIAL ICP Mono	DIAL ICP HiRIS	DIAL LIBS	Sandia LIBS	PSI SIBS	MIT MIPS	Laser Diag.
High Target (75 μg/dscm)									
As	57%	31%							
Be	36%		38%	92%	49%	176%			128%
Cr	56%	43%	64%		42%	253%	151%	39%	101%
Cd	49%	22%	40%	84%	67%	341%			
Pb	64%	47%	19%		66%		89%	28%	
Hg	96%	53%	43%						
Low Target (15 μg/dscm)									
As	81%	39%							
Be	51%		46%	55%	37%	367%		37%	91%
Cr	76%	46%	76%		19%	196%	163%	98%	65%
Cd	(86%)	(55%)	(84%)		(78%)	(290%)			(112%)
Pb	(103%)	(48%)	(45%)		(37%)		(82%)	(50%)	
Hg	94%	66%	96%						