CONTINUOUS EMISSION MONITORS IN THE DOE COMPLEX

Stephen Priebe
Idaho National Engineering and Environmental Laboratory

ABSTRACT

DOE operates thermal treatment systems for a variety of mixed, low, and high-level wastes. Each of these facilities is part of one or more compliance agreements between DOE sites and their respective states. Treatment facilities operate under regulatory permits, which are becoming increasingly stringent, threatening future operation of many of these facilities. Complicating the issue further are public stakeholders who are becoming increasingly active in their desire to know that DOE's treatment facilities are not emitting hazardous and radioactive pollutants. Current compliance efforts tend to focus on limiting the amount of hazardous material in the waste feed to the treatment system and by monitoring certain operating parameters within the process. These waste feed limits and operating parameter limits are based on a test burn in which the facility is operated at specific conditions to establish the acceptable operating envelope. However, this methodology does not ensure that emission from the facility remain below acceptable limits. The only way to ensure that the facility is operating properly is to implement continuous emission monitors (CEMs). If acceptable CEMs are used, then not only are the regulators and stakeholders more confident of actual emissions, but the extent of waste feed characterization can be reduced. DOE has undertaken a program of developing and testing CEMs for a range of pollutants, including mercury, multiple metals, dioxins and furans, and particulate matter. This paper will present the results from these tests and describe how the installation of CEMS for these pollutants might impact waste treatment facilities.

INTRODUCTION

Over the course of 50 years of weapons productions and other activities, the Department of Energy (DOE) has produced a significant quantity of a wide variety of wastes. These wastes include low-level radioactive waste, high-level waste, mixed waste (both hazardous and radioactive), and transuranic (TRU) waste. For many years, this waste was stored awaiting final disposition through treatment and/or direct disposal. In recent years, DOE has begun operating treatment systems for several of the wastes. Traditionally, the majority of those systems have involved thermal treatment, such as glass melters, incinerators, and plasma systems. In the future a variety of other processes is expected to be implemented, including steam reforming, thermal desorption, and chemical oxidation. Each of these facilities is or will be part of a compliance agreement between a DOE site and its respective state. They will operate under regulatory permits, which are becoming increasingly stringent, threatening future operation of many of these facilities.

In September 1999, the EPA promulgated a new rule for Maximum Achievable Control Technology for Hazardous Waste Combustors (MACT Rule). The MACT Rule governs most of the regulatory requirements for the operation of incinerators, cement kilns, and lightweight aggregate kilns. Other thermal treatment processes, such as melters, steam reformers, and plasma arc units are not directly covered by the MACT Rule, but permit writers are expected to draw many permit provisions from the MACT Rule. This is particularly true for those regarding emissions. Complicating the issue further are public stakeholders who are becoming increasingly active in their desire to know that DOE's treatment facilities are not emitting hazardous pollutants.

Currently, to ensure that facilities can operate within emission limits, comprehensive test burns are conducted to measure emissions as a function of specific operating parameter limits (OPLs). OPLs establish an acceptable operating envelope, including such factors as waste feed rate, contaminant concentration, and operating temperatures and pressures. With few exceptions, actual emissions are not measured directly or continuously during normal operation. The test burn methodology cannot assure either the regulators or the public that emissions from the facility remain below acceptable limits.

Continuous emission monitors (CEMs) offer the potential to provide a continuous, near real-time record of emissions for a variety of potential pollutants. The purpose of this paper is to present the state of readiness of CEMs for particulate matter, mercury, multiple metals, and dioxins and furans. This will be followed by a discussion of why and how CEMs might be deployed on DOE waste treatment systems.

PARTICULATE MATTER (PM)

PM CEMs have been used on incinerators in Europe for several years, but have seen limited use in the U.S. EPA has been interested in adopting a rule that included a requirement for PM CEMs. So, in 1996, DOE and EPA jointly funded a test of existing, commercially-available PM CEMs at an operating hazardous waste incinerator. The results of that test indicated that PM CEMs could meet EPA's performance specifications, so the MACT Rule included a requirement for them. However, the EPA delayed implementation while they develop a protocol for site-specific calibration and use of the monitors.

There are two primary concerns when considering the application of PM CEMs in DOE treatment facilities. The first is calibration of the instrument. EPA has proposed that the calibration yield a correlation coefficient of at least 0.95. To achieve this requires that the CEM be challenged over its entire response range. To challenge the high range of the instrument requires a PM concentration greater than the emission limit under the MACT Rule, but EPA has indicated that this would be allowed during the relatively short time of calibration. Unfortunately, this is not an option for DOE facilities, because of the presence of radionuclides.

A second concern emerges when considering how to use PM CEMs in a facility that has high efficiency particulate air (HEPA) filters. The level of PM at the exit of a properly

functioning HEPA filter can be orders of magnitude lower than the new emission limit of 34 mg/dscm established by the MACT Rule. This level is below the level of detection for the current generation of PM CEMs. Indeed, it may be below the level of detection for the EPA reference method (Method 5i), which was established during the 1996 test, to account for the low PM levels under the MACT Rule. The reference method is the standard against which the performance of a PM CEM must be judged.

To address these issues, DOE has undertaken a study at the Diagnostic Instrumentation and Analysis Laboratory (DIAL), which will examine how a PM CEM can be used for compliance in a treatment facility with HEPA filters. DIAL has a flexible combustion test stand with a full air pollution control system that allows testing under a wide range of conditions. The study is expected to be completed by mid 2002 and is being performed in cooperation with EPA and will consist of two related efforts. First, a protocol will be developed for calibrating the instrument, which may also require modifying Method 5i for very low PM levels. The second is to establish how the CEM will be used for compliance. It is likely that a CEM will measure zero, *i.e.* below minimum detection limit, during normal HEPA filter operation. However, if the HEPA filter were to fail, then the instrument must be able to detect that failure. The study at DIAL will determine what type and degree of HEPA filter failures can be detected by a PM CEM.

MERCURY

Mercury is present in much of DOE's waste, but exact quantities and forms are not often known. Because most treatment facilities do not have control technology for mercury, facility designs and permits assume that all mercury present in the feed is emitted to the atmosphere. This has not generally been a problem, but under the MACT Rule, the allowable emission of mercury (130 µg/dscm) will be two to three times lower than is the case currently. At the MACT offgas concentration, and assuming no removal in the APCS, the maximum mercury concentration in the waste feed would be less than about 10 ppm. Sampling and analyzing waste feed for mercury to that level is very costly and greatly increases the potential for exposure to radionuclides. If reliable CEMs are available, DOE could easily offset their cost with savings in waste characterization. However, it may still be necessary to characterize waste that is known to contain significant levels of mercury. Such waste could then be blended with non-mercury bearing waste.

Like the PM CEMs, mercury CEMs have been used for several years in Europe, but have not been used in the U.S. Also in 1996, , EPA/DOE jointly conducted a test of commercially-available mercury CEMs at a cement kiln that burns hazardous waste to determine their readiness for implementation. That test indicated that none of the current CEMs could meet EPA's proposed performance specification for relative accuracy, sensitivity, and calibration.. A principal reason for their failure was the very harsh conditions in the cement kiln offgas. High particulate matter, moisture and sulfur dioxide all caused severe maintenance problems.

Examining the test data, it appeared that the monitors did perform reasonably well when they were actually working. As a result, it was felt that in the much milder conditions present in a hazardous waste treatment process for DOE, the current mercury CEMs would function well. Therefore, the MWFA conducted a test of a single CEM at the Toxic Substances Control Act incinerator (TSCAI) in Oak Ridge, TN during normal operation of the incineration. The CEM was installed on the stack of the incinerator and operated very smoothly with very few problems. Performance of the CEM was compared against EPA Reference Method 101 during two relative accuracy test audits (RATAs). Relative accuracy is a measure of the error between the observed CEM measurement and the reference method during the same period of time. Two levels of mercury were observed, 60 µg/dscm and 5 to 10 µg/dscm. At the higher concentration, the CEM met the goal of a 20% relative accuracy, but at the lower concentration, the relative accuracy was about 300%.

There are a couple of possible reasons for the discrepancy in the second RATA. First, there may be a system bias in the CEM that could be accounted for with a site-specific correction. In other words, there could be something within the incinerator offgas that causes the CEM to always give a higher concentration than is correct. By performing a site-specific correction would remove that bias. The second relates to the reference method itself, which had a standard deviation 10 times higher than for the CEM. The reference method mercury concentration ranged from 2 to 10 µg/dscm with a standard deviation of , while the CEM measured concentration ranged only from 20 to 24 µg/dscm with a standard deviation of . It must be noted that the reference method was developed for higher concentrations (50 µg/dscm) of mercury and is generally accepted, even by EPA, to be less accurate at low concentrations (<10 µg/dscm).

This test was successful enough that we have planned a six to nine month test of several mercury CEMs beginning in the latter half of 2001. This test will also be carried out at the TSCAI. In addition, we have provided input to a test of five commercial mercury CEMs by the EPA Environmental Technology Verification Program conducted in January 2001.

MULTIPLE METALS

From the standpoint of air emissions governed by the MACT Rule, multiple metals (MM) include cadmium, lead, arsenic, beryllium, and chromium. In general, DOE facilities do not have a great problem meeting the emission limits for these metals, because they are present mostly in particulate phase, and DOE facilities have extensive PM control for radionuclides. Therefore, the levels permitted in the waste feed are high enough that controlling emissions by limiting waste feed is not as problematic as it is for mercury. Therefore, the benefit to be gained through the use of MM CEMs is not as great as for mercury CEMs.

This does not mean there is no incentive to deploy MM CEMs. As mentioned earlier, the public has become increasingly interested in that emissions, including hazardous metal emissions are monitored and communicated on a continuous basis. However, the state of

development for MM CEMs is not as advanced as for mercury and particulate matter CEMs

In 1997, DOE and EPA sponsored a one-week test of seven MM CEMs that are under various stages of development. The test was intended to determine if any monitor was ready to undergo long-term verification testing. The test, conducted in an EPA pilot-scale incinerator included the full spectrum of multiple metals, including mercury. EPA Reference Method 29 was used to determine relative accuracy. The test showed that none of the CEMs could meet the requirements for relative accuracy and minimum detection limit established by EPA. Only one instrument, an inductively coupled plasma system could detect all six metals, Hg, Cd, Pb, As, Be, Cr. Hg and As proved to difficult for most of the instruments. The minimum detection limits for the metals of interest were as low as about 5 µg/dscm. At the other end of the scale, some instruments were unable to detect even the highest level available, which was about 70 µg/dscm.

There is considerable development going on for MM CEMs capable of detecting the full range of metals. Improvements have been made since the 1997 test, but as yet no system is generally available commercially. However, as the state of the technology improves, there may be calls from the public to implement MM CEMs even if they do not meet all of the EPA draft performance specifications. This could be problematic from the viewpoint of a facility, if the performance of a CEM is tied to a waste feed cutoff.

DIOXINS AND FURANS

Dioxins and furans (D/F) present a somewhat different problem compared with the other contaminants above. Unlike hazardous metals, D/F emissions are not directly related to the waste feed, because their principal source is through formation in the combustion system or the air pollution control system. The mechanisms for this formation are not totally understood despite considerable research.

Complicating the problem further, the regulatory levels of D/F are extremely low and only 17 of 210 congeners are regulated. The emission limit of the total of those seventeen is 0.2 ng TEQ/dscm. TEQ is the toxic equivalent, which is the product of the concentration of each congener and its associated toxicity factor. Therefore, individual congeners must be measured down to about 0.005 ng/dscm, or about 5 parts per quadrillion. No "real-time" monitor can do this. The current method for measuring D/F involves a two to six hour sample followed by offsite analysis, which takes four to six weeks. Therefore, to understand how the D/F emissions respond to changing process conditions is an extremely laborious and costly procedure.

To address this problem, we have initiated a program consisting of three parts, which are closely related and interdependent. The first part of the program, is the development of a monitor that offers the potential of being able to detect individual D/F congeners at very low concentrations. The technique is pulsed-jet resonance enhanced multi-photon ionization (jet REMPI) spectroscopy. Simply put, this technique uses laser excitation of molecules, for selectivity of individual congeners, followed by a mass spectrometer, to

achieve very low detection limits. The current detection limit is about 100 ppt, but is expected to be reduced to sub-parts per trillion. The second part of the program is the study of the formation and destruction mechanisms for D/F to better understand where they might be a problem in DOE's treatment systems. The final part of the program is the identification of a monitoring technique that could detect particular species that are precursors or indicators of the D/F congeners that make up the TEQ.

A laboratory-based instrument has been developed by SRI International to fully validate the capabilities of the jet-REMPI technique. This instrument is being developed for use as a research or diagnostic tool, not for use as a compliance CEM. At a cost of more than $400,000, it is unreasonable to assume that individual facilities would be required to deploy such a CEM. Its use as a diagnostic tool would allow a facility to better understand the relationship between operating conditions and D/F emissions. Based on the results of this laboratory instrument, a fieldable monitor will be fabricated and tested in FY2002/2003.

The ability to have data within minutes rather than weeks will allow researchers to generate more data efficiently over a much wider set of experimental conditions. A jet-REMPI CEM could greatly speed up the pace of research into all facets of dioxins and furans. The EPA Office of Research and Development has obtained a jet REMPI instrument from SRI similar to the one above. They are using this instrument in their mechanistic studies of the formation of D/F. Understanding the formation of D/F will allow researchers to identify precursors or indicator species for the D/F TEQ. It is expected that such indicators would be present in higher concentrations and would be easier to detect than the dioxins and furans themselves. Correlations between the indicators and the D/F TEQ will probably be site or facility specific and jet-REMPI can be used to establish those site-specific correlations. Once such a correlation is established, a lower-cost monitoring, such as gas chromatography/mass spectroscopy, could be used as continuous emission monitor.

Why Should DOE Use CEMs?

In the MACT Rule, EPA states that their preferred method of compliance assurance is through the use of verifiable continuous emission monitors (CEMs). For those contaminants, for which EPA considers CEMs available, the MACT Rule requires their use. These include only carbon monoxide, total hydrocarbons, and particulate matter. A CEM for oxygen is also required, but only to correct other emissions to a standard oxygen concentration. CEMs for mercury, semi-volatile and low-volatile metals, and dioxins and furans were determined not to be sufficiently mature to require their use. Why then should DOE facilities be interested in deploying these CEMs? Is there value in investing in CEMs? What advantages can they offer?

There are three general applications of CEMs that may make sense for facilities to consider. These are alternative compliance, public assurance, and improved process control. Often, more than one of these advantages will apply. Any application of a CEM will require that the CEM has a verified accuracy and is very reliable, so that it does not

negatively impact the overall reliability of the facility, particularly if the CEM is tied to a waste feed cutoff. Cost is, of course, an important consideration, but accuracy and reliability will determine the potential applicability of any CEM.

In the MACT Rule, EPA allows facilities to petition for the optional use of CEMs for alternative compliance in lieu of other operating parameter limits, including extensive waste feed characterization. As discussed earlier, extensive sampling and analysis of radioactive waste is very costly and increases personnel exposure to radiation so, reducing the need for waste feed characterization is a strong incentive to use CEMs. This can be particularly true for facilities processing mercury-bearing waste.

A concern many facility owners have regarding CEMs for alternative compliance is the fear that it will lead to excessive waste feed cutoffs. While it is true that the data from a CEM will be tied to waste feed cutoff, it must be pointed out that compliance is not based on instantaneous readings, but rather on a rolling average. For example, instantaneous readings from a CEM would be averaged into one-hour block averages, which are then used to calculate a twelve-hour rolling average. This will greatly smooth out spikes in the emissions data.

Public assurance is becoming a much greater incentive to facility owners. The public has expressed a strong desire for DOE to implement CEMs where the technology maturity warrants such use. This was demonstrated at the TSCAI in Oak Ridge where a special state panel was set up to make recommendations regarding CEMs for the TSCA incinerator. The panel recommended that Oak Ridge implement CEMs for metals as they became available. As an interim measure, the facility has developed a semi-continuous monitor that continuously samples the offgas and can provide an analysis daily or weekly. This is deemed as being better than simple waste feed characterization for knowing actual emissions from the incinerator. It also provides an archival record of emissions for future reference.

Process control is not generally thought of in relation to CEMs. However, there are a couple important applications that may make sense. Because the emission of dioxins and furans is not tied directly to waste feed in a way that is clearly understood, determining how to operate a facility to minimize dioxin formation is difficult. It is also very costly and time consuming to obtain sufficient data to correlate emissions to operating conditions. A CEM, used as a diagnostic tool, could provide such correlations much more readily. In a relatively short time, dioxin emission data could be taken at a wide variety of operating conditions.

A second process control application of CEMs arises from the ability to monitor the rolling average. If the emission of a particular contaminant, such as mercury, begins to rise, it could indicate an unknown anomaly in the waste feed, or a problem elsewhere in the system. In either case, remedial action can be taken to correct the problem.

SUMMARY

If history is any indication, operating permits for waste treatment facilities will become more stringent. Either through regulatory mandates or public pressure, continuous emission monitors will be required for some potential pollutants. In the near-term, particulate matter and mercury are likely targets. Somewhat later will be multiple metals, where the technology is not yet mature. A requirement for a CEM for direct measurement of dioxin/furan TEQ is unlikely, though a CEM to measure surrogates could be available in five to ten years.

CEMs can offer potential cost and operating advantages, including alternative compliance, public assurance and improved process control.