DETERMINATION OF STATE-OF-THE-ART REAL-TIME CONTINUOUS OFF-GAS MONITORING DEVICES FOR LOW-LEVEL RADIOACTIVE AND MIXED WASTE INCINERATION

Marc G. Schneckenberger, P.E.
Ecology and Environment, Inc.
Lancaster, New York

Madeleine Nawar
USEPA
Office of Air & Radiation Protection
Washington, DC 20460

ABSTRACT

The topic covered by this paper is an ongoing preliminary worldwide survey to determine which continuous emission monitoring (CEM) systems, if any, are being employed on low-level radioactive waste (LLW) and mixed waste (MW) incinerators. Specifically, the survey has targeted CEM systems that quantify/measure heavy metals and radionuclide emissions on a real-time basis. The survey is sponsored by the United States Environmental Protection Agency (EPA) Office of Radiation and Indoor Air in cooperation with the United States Department of Energy Office of Environmental Management. Preliminary and limited survey data have shown that heavy metals CEM systems are not commercially available, but are in the development/demonstration stages at this time. In addition, only a very few LLW and MW incinerators employ radionuclide CEM devices at this time.

INTRODUCTION

A preliminary worldwide survey sponsored by the United States Environmental Protection Agency (EPA) Office of Radiation and Indoor Air in cooperation with the United States Department of Energy Office of Environmental Management is currently being conducted to determine which continuous emission monitoring (CEM) systems, if any, are being employed on low-level radioactive waste (LLW) and mixed waste (MW, a combination of radioactive waste and RCRA hazardous waste) incinerators. Specifically, the survey has targeted CEM systems that quantify/measure heavy metals and radionuclide emissions on a real-time basis. These CEM systems contain isokinetic flow instrumentation, detector(s)/analyzer(s), equipment controllers, recording equipment, and in some cases excitation devices. This paper discusses the preliminary findings of the survey. Those monitoring systems that provide continuous sampling and batch analysis are not considered real-time CEM systems and have been excluded from consideration in the survey and this paper. CEM systems capable of providing real-time data (e.g., continuous sampling and analysis with only short periods, minutes, between sampling and data availability) are herein referred to as CEM systems.

The survey was conducted in a two-step process. The first step was to identify incinerators with appropriate CEM systems and CEM system manufacturers through data bases, literature, and industry contacts. The first step also included telephone calls and telefaxes to further determine the appropriateness of these incinerators, CEM systems, and CEM system manufacturers. The second step consisted of sending out one survey form to the incinerator owner/operator and another survey form to the CEM system manufacturers identified in step one. At this time ten surveys have been sent to incinerator owner/operators, including four in the United States and one each in Belgium, Germany, Sweden, Switzerland, France, and the United Kingdom. A total of 12 survey forms has been sent to CEM system manufacturers, including 11 in the United States and one in Denmark. Currently, three survey forms for incinerators and seven survey forms for CEM system manufacturers have been returned. Additional information contained in this paper has been obtained through telephone calls, telefaxes, and other literature.

The thermal destruction units briefly discussed in this paper incinerate LLW and MW. The LLW or MW incinerators employ numerous thermal destruction technologies, but these technologies are not a consideration of this paper or the related survey. Also, for purposes of this paper, all European incinerators that burn radioactive wastes are identified as MW incinerators. The waste type classification priority in Europe is the radioactivity level of the waste, and hazardous waste components are not addressed in the classification process. Mixed waste, as regulated by the EPA Resource Conservation Recovery Act (RCRA) and the Nuclear Regulatory Commission (NRC), is not applicable to the classification/identification or regulatory methods employed in Europe. Therefore, any incinerated radioactive waste could potentially be MW.

Heavy metals CEM systems have not yet become commercially available and therefore are not used to monitor LLW or MW incinerator emissions, nor are there regulations at this time governing their use. However, a number of technologies currently in the development/demonstration stages have the potential to continuously monitor heavy metals emissions from LLW or MW incinerators.

The Europeans and Scandinavians have used radionuclide continuous sampling systems and batch analysis for decades. However, the data received at this time are inconclusive regarding the use of CEM systems for MW incinerators in Europe. At this time, MW (radioactive) waste incinerators are not uniformly required to employ radionuclide CEM systems throughout Europe. U.S.-based incinerator operations have only recently used radionuclide CEM systems on LLW or MW incinerators, and the use of these systems is currently not required.

Table I presents a representative group of those LLW or MW incinerator (thermal destruction equipment) owner/operators that have acknowledged use of radionuclide CEM systems. To date, no known LLW or MW incinerators (as indicated by the preliminary survey results) incorporate heavy metals CEM devices because they are only in the development/demonstration phases and are not commercially available.

Preliminary survey results indicate that the LLW and MW incinerators routinely incorporate high efficiency particulate air (HEPA) filters as part of the air pollution control (APC) system. The HEPA filters are designed to remove a very high percentage of particulate emissions from the off gases. Thus, the off gases that emerge from the HEPA filter and enter the stack contain very small amounts of particulates that are typically very fine. Radionuclide CEM system monitoring typically takes place after the off gases pass through the HEPA filters (i.e., downstream of the HEPA filters).

Heavy metals CEM systems, radionuclide CEM systems, and a brief summary of findings are discussed below.

HEAVY METALS CEM SYSTEMS

Most CEM technologies use either *in situ* methods (in which the emissions are determined within the gas stream as it moves through the process train) or extractive methods (in which the gas stream is extracted from the process train and the emissions are then analyzed). These same methods are applicable to heavy metal CEM devices. At this time, the author is aware of only one *in situ* method, which is currently being developed by Sandia National Laboratories in Livermore, California, and is termed Laser Spark Spectroscopy (LASS). This *in situ* method incorporates laser-induced spark-emission spectroscopy to continuously monitor metal aerosol emissions. The laser energy from a high-power, pulsed Nd: YAG laser vaporizes metal-containing particles creating a small plasma cloud or "spark." Measurements of light emission by excited-state ions and atoms contained in this plasma serve to identify and quantify the elemental species of the original particle. Field demonstrations of this device are expected to take place during the summer of 1994.

Currently a number of extractive CEM technologies are being developed, including inductively coupled plasma-atomic emission spectrometry (1,2) and hazardous element sampling train (HEST) (3). Both of these extractive CEM systems are integrated technologies that incorporate isokinetic sampling equipment, sample interface, and metals analyzer(s). Another technology being developed to monitor emissions, although it is not a CEM system, is a Modified EPA Method 29 sampling train using EPA-approved analytical procedures. This latter technology may be used as an interim device until the CEM devices can be made available, but as it is not considered a CEM device at this time, it will not be considered for this paper. Similarly, another proposed technology would provide continuous sampling, but without continuous analysis of the sample. In this proposed technology, which would incorporate isokinetic sampling, the off gas will pass through a proprietary liquid scrubber. The sample then contained in the liquid would be nebulized (as would the liquid), which would generate an aerosol. The aerosol would then be used as a sample input into an ICP unit for metals analysis. Because this technology is currently only conceptual and has not been developed as a CEM system, it will not be considered for this paper.

The ICP-AES technology is currently being developed within the United States and abroad for use as a continuous heavy metals emissions monitoring device. ICPs have been in use for over a decade for process control applications and much longer in laboratory metal concentration analysis. ICP CEM systems must first extract the sample by incorporating an isokinetic sampling system and then condition the off gas for acceptance by the ICP analyzer (using a sampling interface). Typically the sampling interface will remove most of the off-gas moisture and then control/reduce the air flow to the ICP analyzer. The isokinetic sampling system may pull off gas at a rate of about 15 liters per minute, while the ICP analyzer requires approximately a 1-liter-per-minute flow rate. The CEM systems employing ICPs must be able to extract the gas stream (without allowing particulate fall out or adhesion) and must develop an interface(s) with sufficient flexibility to ensure and demonstrate accuracy, reproducibility, and efficiency. It is the sample interface that is critical to this method and the device that is currently under development by a number of institutions/corporations. The ICPs currently being used incorporate a number of plasma types such as argon gas, mixed gas, and air-sustained plasma, each with its own advantages and disadvantages.

Another CEM metals technology currently under development/demonstration is the HEST. The HEST system is currently being used in the field to collect stack samples, which are analyzed in a laboratory. This technology is being designed into a multimetals CEM system with the collection of an isokinetic sample and its analysis. In this system, stack gas is isokinetically extracted and drawn through a filter that captures both particulate and gas phase species. After a filtration period of about 10 minutes, the filter, which may be in the form of a filter tape, will be drawn into a position where it will be excited by X-rays from an X-ray tube. The characteristic X-rays from the stack gas metals will be quantified with an energy dispersive X-ray spectrometer. The entire system will be computer controlled and the results transmitted to a plant control room. At this time the HEST CEM system is in the design stage.

RADIONUCLIDE CEM SYSTEMS

Radionuclide CEM systems have been used on LLW and MW incinerators in the United States for only a short time. At this time the preliminary survey returns are inconclusive for Europe; no MW incinerator has been identified that incorporates a radionuclide CEM system. The author knows of no *in situ* CEM system used for the detection of radionuclides for an LLW or MW waste incinerator and knows of no research and development effort for this purpose. The rest of this section will be devoted to a discussion of extractive CEM systems currently employed for use in LLW or MW incinerators.

LLW and MW incinerators may potentially create releases of radioactive particulates, iodine (normally in a vapor state), and/or noble gases. Therefore, a typical real-time CEM equipment train would include a number of radiation detectors, counters, and recorders.

Extractive radionuclide CEM systems consist of integrated technologies that incorporate isokinetic sampling equipment and radiation detectors.

The first device in the CEM equipment train is an in-stack/duct nozzle to extract off gas. Preferably the nozzle(s) extracts the off gas using a method that is isokinetic and quantitatively verifiable. In order to accomplish the isokinetic sampling, the nozzle(s) must meet ANSI N13.1 or equivalent standards.

The next CEM device in the equipment train is a particulate radiation detector. The particulate radiation detector typically includes a fixed or moving tape filter system to filter out particulate matter greater than approximately 0.3 micron. The main advantage of a moving tape filter system is its ability to require fewer filter changes over a given time period. As previously stated, HEPA filters are normally incorporated on LLW and MW incinerators and, as a result, the off-gas stream contains relatively small amounts of small-sized particles. Consequently, even a fixed filter need only be changed out daily at most. Filter change-outs avoid particle build up, which would interfere with the isokinetic flow of the off gas through the CEM system. The filter is located in close proximity to the radiation detector in order to provide real-time data. The detector should be able to measure specific radionuclide(s) that could potentially be released. This determination is typically based on specific radionuclide activities in the initial waste stream (e.g., using proper waste stream analysis and identification procedures). Through the proper identification of specific radionuclides in the waste stream, potential radionuclide emissions can be identified for the proper selection of detectors.

The next CEM device in the equipment train would be a detector that measures iodine, which is normally in the vapor state when entering the detector device. The iodine detector typically employs a fixed charcoal or silver zeolite filter system. The main advantage of a silver zeolite filter is that it absorbs noble gases at a lower rate than a charcoal filter. Thus, if noble gases are to be detected downstream of this CEM device and iodine filter interference is to be minimized, a silver zeolite iodine filter system may be considered preferable. The iodine detector is normally a gamma detector.

The last radiation detection device in the CEM equipment train would typically be a noble gas detector. The noble gas detector measures an off-gas volume in a chamber in which a radiation detector is present. The noble gas detector usually is equipped with a beta detector and possibly a gamma detector, depending on the composition of the initial waste stream. Interference from cesium or cobalt can occur if prefilters are not placed in line prior to the noble gas detector. However, in the CEM equipment train described above, the radiation particulate detector filter and the iodine detector filter provide the necessary prefilters for accurate noble gas detector results.

The last device(s) in the CEM equipment train regulates the air flow through the detector(s) and may include an air pump/fan, flow indicator controller, mass flowmeter, and potentially a flow transmitter/motorized valve. The most advanced radionuclide CEM systems are isokinetic, incorporate special alpha discrimination circuitry to minimize background interference from radon gas and other alpha particle emitters, and speciate radionuclides through the use of spectrometer(s) in communication with the detector(s).

The extractive radionuclide CEM devices normally extract/pull off gas volumes at a rate of 2 to 4 standard cubic feet per minute (scfm). However, the Scientific Ecology Group, Inc., (SEG) incinerator (see Table I) incorporates an extractive and analysis system capable of handling up to 16 scfm. As a result, it is thought that the SEG radionuclide CEM device has increased sensitivity over those devices that pull lower volumes of off gas. SEG reports that the previous radionuclide CEM device, which pulled a lower volume of off gas (e.g., 2 to 4 scfm), detected only cesium and cobalt in the particulate radiation detector. SEG now measures antimony above the detector's lower limit of detection. Also, SEG has increased the sensitivity of iodine detection by an order of magnitude. Although the new CEM device apparently has an increased sensitivity, no direct data comparison of the previous system to the current system is available. Also, it should be noted that the SEG results indicated that all radionuclide levels are still well below regulated levels at this time, even with the apparent increase in radionuclide CEM system sensitivity.

SUMMARY

Although only limited survey data are available, the following can be ascertained from information that is currently available:

- Heavy metal CEM systems are not commercially available at this time and thus are not incorporated or required to be incorporated (regulated) for use on LLW or MW incinerators.
- Heavy metal CEM systems in the development/demonstration stages are integrated systems requiring technologies for isokinetic flow measurement and control, sample filtration, sample excitation, sample analysis and detection, and equipment controls.
- With appropriate funding, some heavy metal CEM systems may be commercially available by as early as 1996.
- Few LLW or MW incinerators incorporate radionuclide CEM systems.
- Radionuclide CEM systems are integrated systems requiring technologies for isokinetic flow measurement and control, radiation detectors, ratemeters/spectrometers and recorders, and equipment controls.

TABLE I
Thermal Destructor and CEM Device Identification

Affiliation	Location	Waste Type	CEM Device Manufacturer	
Scientific Ecology Group, Inc. (SEG)	Oak Ridge, TN	LLW	Kurz Instruments, Inc. EG&G Nuclear Instruments	Off-gas continuous isokinetic mass flow system Quantitative radionuclide detection and recording system
Department of Energy (DOE)	Idaho Falls, ID	Mixed waste	Air Monitor Corp. Eberline Instrument Corp.	Off-gas continuous isokinetic mass flow system Quantitative radionuclide detection and recording system

- Radionuclide CEM systems are commercially available but typically require more than one company's devices. These CEM system devices are designed and integrated to function as a singular radionuclide CEM system.
- Radionuclide CEM systems are not currently regulated (required) to be incorporated on LLW or MW incinerators in the United States or uniformly through Europe or Scandinavia.

REFERENCES

1. G.A. MEYER, "Continuous Metals Monitoring: Real Opportunities for ICP-AES," Spectroscopy (November/December 1993).

2. M.D. SELTZER and R.B. GREEN, "A Continuous Emissions Monitor for Airborne Metals," Chemistry Division, Research Department, Naval Air Warfare Center Weapons Division, China Lake, California.

3. J. COOPER, M. GRUNEBACH, R. SARVER, R. PELTIER, C. SIMONS, B. RITTER, AND T. BARKOWSKI, "A New, Innovative Hazardous Element Sampling Train: Preliminary Test Results for Mercury," Keystone/NEA, 12242 S.W. Garden Place, Tigard, Oregon 97223 (July 1992).