

# THE ENTROPY QUARTERLY

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## Testing for Multiple Metals

The 1990 Clean Air Act Amendments include many compounds in the Title III list of hazardous air pollutants (HAPs), which were not previously regulated. In addition, metals are also included in the BIF (Boilers and Industrial Furnaces) regulations. Therefore, many more facilities will be testing for heavy metals.

In 1989, Entropy conducted a study for EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) for the measurement of multiple metals in emissions from combustion sources. Entropy submitted a draft emission test protocol to AREAL and the draft method was included in the Methods Manual for Compliance with BIF Regulations in 1990. This test method has been included in SW-846 (RCRA Test Methods) as Method 0012 and at this writing is available in draft form as EPA Draft Method 29.

SW-846 Method 0012/EPA Draft Method 29 can be used for the determination of 16 trace metals: antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), phosphorus (P), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn). The method can be modified to collect particulate matter.

The sampling train for this method is based on the EPA Method 5 sampling train. The nozzle and probe are made of glass. A quartz or glass fiber filter in a Teflon™ filter

(see *Multiple Methods* on page 5)

## Entropy Supplies National Stone Association and EPA with Emissions Factor Data

Entropy's Control Equipment Testing and Optimization (CETO) division has been conducting a series of emissions tests on process units within three stone crushing plants in North Carolina and Virginia. These tests are sponsored by the National Stone Association and by the US Environmental Protection Agency.

The purpose of the tests is to develop more accurate PM10 emission factor data for process equipment within stone crushing plants. PM10 emissions are those emissions less than 10 microns. This test data was needed because little previous emission test data exists for stone crushing plants. Previously available data was applicable only to total particulate, not particulate characterized as less than 10 microns. Annual permit fees based on this pre-existing data would have been substantial.

Testing at the stonecrushing facilities was difficult because the process units of interest were not enclosed. The challenge to Entropy was to develop unique testing procedures in order to accurately measure the PM10 emissions without affecting the emission rates from these open sources. In developing these emission test procedures, Entropy adhered to the following five criteria:

- The test procedure should not affect the rate of PM10 particulate emission;
- The test procedure should isolate the unit being tested from the adjacent sources of PM10;
- The test equipment should not obstruct routine access to the

process equipment by plant personnel;

- Overall test procedures must be economical, practical, and readily adaptable to other plants so that these tests can be repeated by organizations wishing to confirm or challenge the emission factor data developed in this project; and,
- The testing equipment should not create safety hazards for the emission test crew or for plant personnel; nor should it create risks to the plant process equipment.

One of the main PM10 sources at stonecrushing facilities are open top, triple deck, vibrating screens. For this source, Entropy developed a traversing hood sampling system. This unique arrangement allowed the capture of the emissions without influencing the rate at which crosswinds entrained PM10. This ensured that the measured emissions were accurate.

Gas flow rate into the traversing hood assembly was adjusted using a variable-speed, SCR-driven axial flow fan. Testing was done upstream of the fan using EPA Reference Method 201A. The results indicated that the

(see *Stone Association* on page 2)

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- Three Dimensional Flow Profile Studies

## Multiple Metals *continued*

holder is attached to the probe. After the filter, there are seven chilled impingers. The first impinger is empty, the second and third impingers each contain 100 mL of 5% nitric acid ( $\text{HNO}_3$ ) to 10% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), the fourth impinger is empty, the fifth and sixth impingers each contain 100 mL of 4% potassium permanganate ( $\text{KMnO}_4$ ) to 10% sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and the seventh impinger contains pre-weighed silica gel. The sample components are recovered separately, digested, and analyzed by inductively coupled argon plasma spectroscopy (ICAP) and/or atomic absorption spectroscopy (AAS). Mercury can only be quantified by cold vapor atomic absorption spectroscopy (CVAAS).

If particulate matter is to be collected using the multiple metals train, it is recommended that a separate EPA Method 101A sampling train be used for determining mercury to prevent front-half mercury bias. If EPA Method 101A is used to determine mercury, the fifth and sixth impingers may be eliminated from the multiple metals sampling train.

To quantify emissions reliably, the sampling method must be precise and the analytical method must be sensitive. Based on quad-train testing performed during method development, the precision expressed as the relative standard deviation of the sampling method ranges from 5% to 15%. Analytical sensitivity is measured by the analytical detection limits. The ICAP analytical detection limits (based on SW-846 Method 6010) range from 0.3 ng/mL for beryllium to 75 ng/mL for phosphorus and selenium. Several interferences may affect the sensitivity of ICAP analysis. Iron is an interferent in the analysis of arsenic, chromium, and cadmium; aluminum is an interferent in the analysis of arsenic and lead. The AAS analytical detection limits (based on SW-846 Method 7000) range from 5 ng/mL for beryllium, cadmium, and zinc to 200 ng/mL for antimony. The use of

*(see Multiple Methods on page 6)*

## Three-Dimensional (3-D) Flow Profile Studies

The Acid Rain monitoring regulations of 40 CFR Part 75 require the installation, certification, operation, and maintenance of a continuous flow rate monitor in conjunction with a gas continuous emissions monitoring system (CEMS). Installation and certification of this equipment is required by November 15, 1993 for 110 Phase I affected sources and by January 1, 1995 for 2000 Phase II affected sources. Many sources, particularly those not previously regulated under 40 CFR Part 60, may have difficulties in selecting suitable sites for monitoring flow rates. A poor measurement location may adversely affect the accuracy of data from both continuous flow rate monitors and from manual flow rate determinations during relative accuracy tests.

The accuracy of a flow rate monitor depends on the flow vectors at the monitoring location and on the operating principles of the specific monitoring device being considered, (i.e., how the instrument responds to non-axial flow vectors). In the ideal situation, all flow will be axial, that is, the flow will be parallel to the longitudinal axis of the duct. A flow profile study can determine actual flow conditions at a proposed measurement location. Such studies are required as supporting information for justifying alternative flow monitoring locations or for justifying alternative flow monitoring methods.

The principal device for determining the severity of non-axial flow is the three-dimensional (3-D) pitot probe. This probe, when operated properly, provides the resultant angle of the actual flow vectors at individual points within the flow stream. In addition, it provides the velocity head corresponding to the axial flow vector. Hence, volumetric flow rates can be calculated even when non-axial flow conditions exist.

EPA Method 1 (40 CFR Part 60, Appendix A) contains procedures and guidelines on the use of 3-D pitot tubes. According to EPA Method 1, an acceptable measurement location is one with an average resultant angle of  $\leq 20^\circ$  and a standard deviation  $\leq 10^\circ$ . These criteria were established to insure acceptable measurements of isokinetic sampling rates and accept-

able particulate matter concentrations using the combination of EPA Method 5/Method 2 (particulate probe with attached Type S pitot tube). Obviously, the Method 1 criteria were not designed for the Acid Rain regulation where high accuracy is essential because of its market-based emissions allowance system (i.e., a system where allowances are transferred or traded). Therefore, knowing when and how to use 3-D pitot tubes and Type S pitot tubes is essential to obtaining accurate information.

Entropy conducted studies that were instrumental in the early revisions of EPA Method 1 to include the procedures for justifying alternative locations. In addition, Entropy has conducted 3-D studies, both in the lab and in the field, for the Environmental Protection Agency and numerous industrial clients. This experience has provided Entropy with an unmatched background and understanding of the 3-D's principle of operation. It is critical that a testing firm understand the adequacy of the calibration procedures in EPA Method 1, Section 2.5, for acid rain applications. When conducting 3-D testing the significance of errors in pitch and yaw angle measurements and the significance of errors in pitch and yaw angle measurements on resultant and axial velocity vectors are important. The adequacy of test section velocities for calibration and physical characteristics of 3-D pitot tubes affect accuracy. The transferability of a calibration curve to other 3-D pitot tubes, and interpretation of the flow profile studies are areas of Entropy expertise.

Entropy has been providing CEM services required in 40 CFR Part 75 since 1976. Entropy is capable of helping affected sources, during the planning process, in conducting flow profile studies, selecting installation sites, selecting monitoring equipment, and conducting performance certification tests. For more information on our CEM services, call Tony Mastrianni at 1-800-486-3550. For technical information on 3-D pitot tubes, call Wayne E. Reynolds or Roger T. Shigehara at the same number. □

*Roger Shigehara  
Director, Research Division*

## EPA Methods and Procedures

**Method 18** ..... *Revised*  
Measurement of Gaseous Organic Compound Emissions by  
Gas Chromatography

**Method 26** ..... *Revised*  
Determination of Hydrogen Halide and Halogen Emissions  
from Stationary Sources – Midget Impinger Method

**Method 26A** ..... *Proposed*  
Determination of Hydrogen Halide and Halogen Emissions  
from Stationary Sources – Isokinetic Method

**Method 30-30F** ..... *Draft*

30: Criteria for and Verification of a Permanent or  
Temporary Total Enclosure

30A: Volatile Organic Compounds Content in Liquid Stream

30B: Volatile Organic Compounds Emissions in Captured  
Stream

30C: Volatile Organic Compounds Emissions in Captured  
Stream (Dilution Technique)

30D: Volatile Organic Compounds Emissions in Fugitive  
Stream from Temporary Total Enclosure

30E: Volatile Organic Compounds Emissions in Fugitive  
Stream from Building Enclosure

30F: Volatile Organic Compounds Content in Liquid Input  
Stream (Distillation Approach)

**Method 301** ..... *Final Rule*  
Field Validation of Pollutant Measurement Methods from  
Various Waste Media

**Method 304** ..... *Proposed*  
Method for the Determination of Biodegradation Rates of  
Organic Compounds

**Method 305** ..... *Proposed*  
Method for the Measurement of Individual Volatile Organics  
in Wastewater

**Part 75 Continuous Emission Monitoring** ..... *Final Rule*

*Appendix A:* Specifications and Test Procedures

*Appendix B:* QA/ QC Procedures

*Appendix G:* Determination of CO<sub>2</sub> Emissions

*Appendix H:* Revised Traceability Protocol No. 1

# U.S. Generating Company

## Fax Message

DATE: March 9, 1993

TO: Mr. Hamilton S. Oven

FACSIMILE NO.: (504) 523-5431

COMPANY: c/o Land Market French Quarter

NO. OF PAGES: 11  
(including this one)

CITY/STATE: New Orleans, LA

FROM: Kent Fickett

PHONE NO.: 301/718-6860

SPECIAL INSTRUCTIONS: Please deliver to Mr. Oven upon arrival

If transmittal is incomplete or illegible, please call Cindy Burgess at 301-718-6898.

Messages:

ASSESSMENT OF CARBON INJECTION MERCURY EMISSION CONTROL  
FOR CEDAR BAY

1.0 GENERAL

A carbon injection test for reduction of mercury emissions from the Cedar Bay project has been proposed. The proposed test is believed to be the result of two factors: (1) increasing concern about the adverse health and environmental impacts of mercury and mercury compounds in the area of the project and (2) interest in carbon injection control on the Lee County waste-to-energy (WTE) facility and the potential use on coal fired boilers with flue gas desulfurization. The Cedar Bay project uses coal fired circulating fluidized bed boiler (CFB) technology in which the mercury emissions are an order of magnitude lower than in municipal waste combustion. The technology was reviewed and vendors contacted to develop a test plan concept. Findings generally discourage testing of carbon injection at the Cedar Bay plant. The combustion conditions, sulfur removal process, and operational features of CFB, unlike those in municipal solid waste (MSW) combustion facilities and coal fired systems with flue gas desulfurization (FGD), do not appear favorable for effective carbon injection control. The results of the review and inquiry work performed to date is summarized below with our assessment of the proposed test.

1.1 Fuel Characteristics

Type of fuel, its chemical composition including mercury content and chemical form in which it occurs determines, along with other factors, the uncontrolled and controllable rate of emission of mercury from combustion devices. Municipal solid waste (MSW) contains elemental mercury in discarded items such as batteries, thermometers, and mercury switches, and chemical compounds of mercury in items such as paints, pigments, plastics, laboratory wastes. Since a substantial fraction of the total mercury in MSW exists as elemental mercury, it vaporizes easily during MSW combustion (@2000° - 2500°F) and forms elemental mercury vapor. Mercury in the gaseous state is difficult to remove unless it is changed to a particulate form. It is to be noted that coal contains mercury in chemically combined form (as mercury compounds) and not as elemental mercury. Because of the high proportion of elemental mercury in MSW and its gaseous state in the combustion/flue gases (EPA, 1990), the uncontrolled emission rate of mercury from MSW combustion is much higher than from coal combustion. Concentration of mercury in MSW flue gases is reported to be in the range of 200 - 1400  $\mu\text{g}/\text{Nm}^3$  or more (EPA 1989a), whereas in bituminous coal flue gases the mercury concentration is an order of magnitude lower 20 -135  $\mu\text{g}/\text{Nm}^3$  (EPA 1989b).

Due to the lower heating value of MSW, almost 4 - 5 times more MSW has to be combusted per million Btu compared to coal which results in higher uncontrolled mercury emissions per million Btu compared to coal. Other important differences exist between MSW and coal such as higher chlorine in MSW which promotes the formation of  $\text{HgCl}_2$ .

1.2 Combustion Conditions

Besides fuel mercury content and its chemical form, the combustor design and operating conditions determine the emission rate of mercury. MSW combustors have mass-burn (large particle size) grates with average combustion zone temperature of 2000 -2500°F and local hot spots which volatilize mercury as well as its compounds. The CFBs have relatively low temperature (1550 - 1650°F) circulating fluidized beds. Also, CFBs have limestone in the combustion zone where heat is released and throughout the steam generation gas path. This limestone is calcined ( $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ ) in the CFB to generate highly porous quick lime, CaO. Sulfur dioxide in the flue gas diffuses into and attaches to the surfaces of the lime particles. Mercury vapor and some of its compounds will also diffuse into the lime pores and be adsorbed or condensed as temperature reduces along the flue gas path.

Because of the circulating bed of lime and ash, the dense particulate loading in the CFB flue gas provides a large surface area for adsorption/condensation of mercury compared to MSW combustors which are designed to limit elutriation of solids during combustion.

Distribution of ash between fly ash (exiting boiler with flue gas) and bottom or bed ash is also different for the MSW and CFB combustors. Mercury retention and removal with bottom ash may be greater in the CFB than MSW combustor.

### 1.3 Effect of Existing Air Pollution Control Devices

A combustor is followed by one or more pollution control systems such as selective noncatalytic reduction (SNCR) for  $\text{NO}_x$  control, spray dryer FGD for acid gas control, and an electrostatic precipitator (ESP) or fabric filter (FF) for particulate control. Ammonia injection for SNCR can generate small amounts of hygroscopic (sticky) ammonia-sulfur compounds which could affect condensation of mercury vapors or agglomeration of fine solid mercury compounds. There are uncertainties regarding the effect of excess ammonia on chlorine compounds which react with mercury to form solid  $\text{HgCl}_2$ .

Particulate control devices such as ESP or FF remove mercury adsorbed on the ash particulates or mercury present as fine solids compounds ( $\text{HgCl}_2$ ,  $\text{HgO}$  or  $\text{HgSO}_4$ ). Since fabric filters are generally known to be more efficient in filtering out fine (as well as coarse) particulates compared to ESP, emissions of mercury after FF are expected to be lower than from ESP. Note that flue gas temperature (cooling) and mercury concentration levels determine how much mercury will condense as particulate so it can be filtered out.

Lime slurry spray-dryer (dry FGD) systems and wet FGD systems cool the flue gases and enhance mercury condensation on particulate. For coal firing the spray dry systems are designed to optimize sulfur dioxide removal. The scrubber residence times and gas temperatures are favorable for the removal of trace metals including mercury. In circulating fluid bed coal combustion the sulfur capture occurs during combustion at the temperature for optional formation of calcium sulfate. Residence time in the CFB is selected to maximize carbon burn out and sulfur capture.

To summarize, there are numerous factors affecting mercury emission and subsequent control within the combustor and the associated air pollution control system. With very limited data on the interaction and relative significance of these factors, the process design and test results for carbon injection control of mercury emissions on MSW can not be extrapolated to coal fired CFB. With low mercury concentration in the flue gas and without the benefit of residence time at lower temperature as in spray dryers, the effect of carbon injection on the CFB process is expected to be minimal. Quantitative effects of specific design parameters needed to design a test are not available since neither benchscale nor pilot testing has been performed on CFB. Adding to this uncertainty and unavailability of data is the lack of a suitable generally agreed mercury sampling and measurement technique. This problem has been recognized by the U.S. Congress which while enacting the Clean Air Act Amendments of 1990, asked EPA to conduct a 4-year study on mercury and other air toxics and report to Congress by December 1994.

## 2.0 REGULATORY ASPECTS

There are currently no mercury emission limits for coal fired CFB. Under the federal PSD regulations (40 CFR 52.21), best available control technology analysis and limits apply if mercury emission exceeds 0.1 ton/year.

For MSW combustors, EPA plans to propose a mercury emission limit in the range of 100 to 200 µg/dscm, or 60 to 90 percent removal, by weight (EPA, 1993).

The state of Florida DER has recently (2-25-93) proposed more stringent draft standards limiting mercury emission limiting standards for MSW combustors. These are not applicable to the Cedar Bay Cogeneration Project which utilizes coal fired CFBs. However, since comparisons and assessments of new Hg control technologies are often made with this more advanced application category, it is interesting to compare the two (CFB Vs MSW) combustors.

The proposed Florida mercury emission limits are set at 70 µg/dscm corrected to 7%O<sub>2</sub>. The importance of flue gas temperature is recognized by proposing a not-to-exceed limit of 300°F at the inlet to the fabric filter.

It is to be noted that the Cedar Bay emissions will be lower than both of these limits for short as well as long averaging periods without the need to install an add-on mercury removal system. The controlled emissions (with CFB/FF system) are estimated as approximately 64.1 µg/dscm short term average, 39.3 µg/dscm annual average and 9.2 µg/dscm as long term average. Also, these emission levels from the Cedar Bay project have been shown to meet (Cedar Bay Cogeneration Project Air Quality Analysis, Feb. 1993) all ambient air quality and health criteria.

Recent literature review and vendor contacts (Joy Env. Tech, 1993, Flakt, Inc, 1993) indicate that coal fired combustors do not have mercury emission limits imposed nor requirements for add-on controls anywhere in the world.

### 3.0 MERCURY REMOVAL/CONTROL TECHNOLOGIES

As stated earlier, the extent of mercury removal is dependent on numerous factors including fuel mercury content and form in which it occurs, combustion conditions, and air pollution control system design. From a process design standpoint, these factors determine concentration, temperature, residence time and gas to solids interaction. The currently available mercury control methods and the emerging technologies with potential application to coal fired combustors are reviewed in consideration of the process differences.

#### 3.1 Current Mercury Removal Methods

One obvious method of limiting emissions is to select a fuel with low mercury content and high heating value. However, fuels are selected based on numerous reasons other than trace metal content. Hence, fuel selection is generally not a sufficient approach to Hg emission reduction. Note, however, that selecting a higher heating value fuel (e.g., 12,500 Btu/lb coal versus about 4,000 Btu/lb MSW) reduces the mercury emissions by a factor of three for the same mercury content (1 ppm). In addition, since coal contains at least 3 to 4 times lower mercury per unit mass than MSW, its uncontrolled emission rate is about an order of magnitude lower than for MSW.

Selection of the combustion system can also limit mercury emissions. The lower temperature in a CFB boiler limits the release of volatile trace metals. The presence of large amounts of limestone and porous lime in the CFB help to trap a portion of the mercury and its compounds. To the extent mercury is retained with the CFB solids, the air emission is correspondingly reduced.

Selection and design of the air pollution control system also limits mercury emissions. Gaseous mercury or its compounds can be collected in particulate control devices by change of phase to solid form by absorption or condensation. The lower the flue gas temperature the better the removal (or, collection) of mercury/compounds by adsorption or condensation on particulate. Figure 1 illustrates this condition. Lowering flue gas temperature from 350 to 250°F reduces mercury saturation concentration from 39,700 mg/m<sup>3</sup> to 7,860 mg/m<sup>3</sup>. The Hg vapor in the flue gas above its saturation level at the lower (cooler) temperatures is then condensed and deposited on solid surfaces close to the flue gas. Besides equipment surface, a large condensation/adsorption surface area is offered by fine particulates (and, if porous, its internal void surfaces). Once adsorbed or condensed on particulates, a more efficient removal of particulates results in lower mercury emissions.

MSW combustors have higher mercury concentrations, a greater proportion of which is elemental mercury, and higher combustion temperature so almost all mercury/compounds vaporize and stay in the gaseous form. Also in MSW combustion there is less surface available for condensation/adsorption of mercury/compounds when the flue gases cool as they move through the system. The higher gaseous mercury concentration and lower particulate concentration in MSW combustors favor injection of additives and spray dryer cooling to reduce mercury emission rates.

#### 3.2 Emerging Add-on Control Technologies

Municipal waste combustors release more mercury/compounds as well as other organics than coal fired CFBs. Because of the greater number of MSW combustors in Europe and proximity of population centers, research and development efforts were initiated to limit these mercury and organics emissions. After several years experimentation, activated carbon injection has emerged as an add-on technique to reduce mercury and organic emissions. Since there are several undesirable technical and cost impacts of this technology, R & D continues to focus on other methods such as sodium sulfide (Na<sub>2</sub>S) injection, other absorbents such as lignite coke, sodium hypochlorite (NaOCl) and wet scrubbers. A brief overview of the status and features of these emerging processes is provided below.



### 3.2.1 Activated Carbon Injection

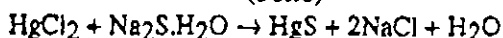
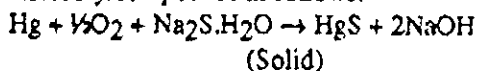
When flue gases containing mercury vapor or its compounds in vapor form are contacted by the high porosity/high surface area activated carbon particles injected into the flue gas they are adsorbed (residual surface forces attract and retain the vaporized mercury and mercury compounds onto these extensive surfaces. The amount of carbon injected depends, among other factors, on the amount of mercury to be removed and its vapor phase concentration (Freundlich's Isotherm:  $x/m = k C^{1/n}$  where  $x$  is the amount of mercury adsorbed on mass  $m$  of carbon when in contact with concentration  $C$  of mercury).

Carbon injection is a relatively new technique. There are no known applications of this technology on coal fired combustors either in USA or other countries in the world. There are no currently operating pilot test facility using this technique in USA or abroad. (An EPA sponsored test was conducted on a municipal waste combustor in Stanislaus County, California in July-August 1991.)

However, a few MSW-fired facilities (Zurich, Switzerland; Amager, Denmark; Kassel and Gieselbullach, Germany; and Burnaby, B.C., Canada) are using or plan to use this technique. Several of these facilities use carbon injection in conjunction with a lime spray-dryer absorber. Tests on large scale MSW combustors yielded mercury removal efficiencies in the range of 48-97%. However, with no carbon injection, these systems showed 15 to 92% mercury removal. Thus the mercury removal attributable to carbon injection alone is very unclear.

### 3.2.2 Sodium Sulfide (Na<sub>2</sub>S) Injection

This concept involves injection of a dilute aqueous solution of Na<sub>2</sub>S in the combustion gases to react with its mercury/compounds as follows:



Both reactions produce mercuric sulfide as a stable solid so it can be removed in a fabric filter or precipitator. A few MSW combustion plants in Europe are using this process in conjunction with dry sorbent injection process. One Canadian MSW combustion plant (Burnaby, B.C.) used this process for two years but switched to activated carbon process recently. There are no commercial U.S. applications of this Na<sub>2</sub>S process. There are several problems and uncertainties associated with this process such as corrosion, hazardous nature of Na<sub>2</sub>S, potential for inactivation by lime or other chemicals in the flue gas, inadequate mixing, unwanted side reactions, potential hazard from Na<sub>2</sub>S generating toxic H<sub>2</sub>S gas, etc. This technique, therefore, requires further investigation at the pilot plant level under U.S. conditions before the potential for application to coal firing can be considered.

### 3.2.3 Wet Scrubbers

It is generally believed that wet scrubbers (e.g. flue gas desulfurization spray tower absorbers), where flue gases are cooled and saturated with water vapor from aqueous slurry of lime/limestone or other alkali, may be more advantageous for mercury condensation and removal than dry scrubber systems. Experimentation at pilot and commercial facilities (including a recent one at Fort Dix MSW combustor plant in N.J.) yielded mercury removal efficiencies between 17 and 75% (average of 43%). Wet scrubbers produce difficult to disperse wet stack plumes, corrosion and scaling problems, and wet sludges that are difficult to dispose of in landfills.

#### 4.0 Assessment

Activated carbon injection in conjunction with a spray-dry absorber (SDA)/scrubber has been utilized in a few MSW-fired combustors in Europe and Canada. This relatively new technology has demonstrated Hg removal efficiencies in the 48-97% range with 6 to 70 mg/m<sup>3</sup> carbon injection and 15-92% removal without additive injection. There are no commercial MSW combustors in U.S. utilizing this technology. Only one MSW-fired energy recovery facility in U.S. has planned to use this technology by late 1994. Carbon will be injected as a slurry in the spray-dryer. Fabric filter will be used for particulate collection. About 70% mercury removal is expected for the total system (activated carbon/SDA/FF). There is as yet, no commercial design nor operating experience with activated carbon injection system in the USA either on MSW or CFB combustion systems to draw upon for application to CFB.

Finely powered activated carbon presents fire, explosion, and health hazards. Storage, handling and process activities in closed vessels and ducts in the presence of air presents opportunities for fire and explosion. Design of systems to minimize these risks is necessary, even for short term testing.

Activated carbon is an expensive material at about \$1/lb (or \$2,000/ton). One of the vendors has estimated about \$3 million per year as direct carbon cost for the Cedar Bay facility (Joy Env. Tech., Inc. 1993). Other direct and indirect costs include power consumption, equipment depreciation, and disposal costs. Budgetary estimates of capital costs of the carbon injection system are approximately \$1 million and \$21 million without and with spray dryer absorber respectively.

Presence of activated carbon in the CFB ash and limestone-SO<sub>2</sub> reaction products could adversely affect the agglomeration and eventual recycle/reuse of the CFB waste solids.

With no directly applicable design or operating data, design of a full scale system test would be difficult. To predict Hg removal with any degree of certainty will be impossible. As stated above there are large differences between MSW and CFB fuels, combustion conditions, and air pollution controls. Even well established experienced equipment vendors of activated carbon systems could not predict (Joy Env. Tech. Inc., 1993) with any certainty the percentage Hg removal with carbon injection in a coal fired CFB with no spray dryer absorber. In fact, the vendors do not expect much mercury removal with carbon injection without a spray-dryer. All of their R & D work has been in association with spray dryers.

While the carbon injection process may have potential to reduce mercury emissions under the right conditions, the best facilities for testing the concept are engineering research centers where process variables can be controlled to evaluate the potential of this process. Commercial plants such as Cedar Bay do not provide the right conditions and facilities to conduct a test for which no benchscale nor pilot scale work has been performed.

As outlined earlier, there are significant process differences between MSW combustors and CFBs which affect the application of activated carbon injection for mercury control. The influence of these factors is summarized below:

1. CFBs have limestone/lime in the combustion zone where mercury is released. Temperatures and residence time profiles are different in the two processes so the extent of flue gas cooling and mercury condensation/adsorption on the particulates in the flue gas is different. With lower CFB combustion temperatures and larger amounts of solids (including unburned carbon) mercury removal due to carbon injection is expected to be very low.

2. All of the MSW combustors utilizing carbon injection also have some type of spray-dry scrubber. The scrubbers cool the flue gases so that mercury can condense/adsorb onto the carbon and other particles present. Spray-dry scrubbers provide residence time and promote gas solids contacting. Without a spray dry scrubber, carbon injection for mercury control in CFB is not expected to be effective.
  
3. Since the MSW combustors have a high initial Hg concentration level, there is adequate driving force for adsorption and condensation on the injected activated carbon particles when temperature conditions are favorable. With CFBs operating generally at an order of magnitude lower Hg concentration, it is unlikely that significant removal can take place. Most of the carbon injection tests have been with high initial Hg concentration of typical MSW combustors.

5.0 CONCLUSIONS

Based on an extensive review of all available data and discussions with carbon injection system vendors and independent engineering consultants, the following conclusions can be drawn:

- a. The activated carbon injection process is being utilized on a few European MSW-combustors and planned for one Canadian MSW combustor. These plants use the carbon injection in conjunction with the spray-dryer absorber and a particulate control device. Total mercury removal efficiency of 48 to 97% has been reported with carbon injection and 15 to 92% without carbon injection. There are many uncertainties associated with mercury removal sampling and measurement techniques. The percentage removal attributable to carbon injection is thus unclear.
- b. The effectiveness of the carbon injection without a spray-dryer absorbers is not known because no such data exists for coal-fired boilers, CFBs or even MSW combustors. In fact, carbon injection system vendors expressed serious doubts about significant mercury removal without spray-dryers.
- c. Coal mercury content is much lower than in MSW. Chemical forms (combined versus elemental) of mercury are also different in the two fuels. Combustion conditions are also different in MSW versus CFB combustors. Combustion zone temperature, unburned carbon levels, chlorine levels are all different for the two fuel combustors. With all these differences, much uncertainty exists relating to suitability and effectiveness of carbon injection technology on Cedar Bay CFBs.
- d. The low temperature CFB boilers, low mercury content coal, high particulates (porous lime, fine ash and acid gas removal byproducts) loading and resulting surface area for mercury capture by adsorption and/or condensation in a high efficiency baghouse, all combine to enhance mercury removal so that the emission rate is estimated as 9 ug/dscm as a long-term average. This emission rate is significantly lower than the Federal or Florida limit (70 ug/dscm) proposed for MSW combustors. Further reduction of this already low mercury level, with an uncertain technique (carbon injection in coal-fired CFB with no spray-dryer absorber) is not expected to be effective.
- e. For the Cedar Bay plant, approximate costs of carbon injection system operation are estimated as \$3 million per year for just the carbon consumption. This equates to more than fifteen million dollars per ton removed if the system reduced the mercury emissions by fifty percent. In addition the capital costs for a mercury injection system with and without spray-dryer absorber are about \$21 million and \$1 million respectively.
- f. Injection of carbon in the CFB flue gas may adversely affect the bag filters because of its fine particle size. Other unidentified operational problems may result.
- g. Activated carbon presents a fire and explosion hazard in storage and handling at the plant.
- h. CFB solid wastes may be processed for recycle/reuse in various applications. An increase in carbon content is likely to adversely affect processing and the potential for recycle/reuse.
- i. Effectiveness of carbon injection can be best tested at pilot plant facilities with trained staff and appropriate support facilities. A commercial plant such as Cedar Bay is not a desirable facility for obtaining reliable test results.

6.0 REFERENCES

EPA, 1989a: EPA air Docket A-90-45, item 11-M-37, September 1991.

EPA, 1989b: "Estimating Air Toxics Emission From Coal and Oil Combustion Sources", EPA Report No. EPA 450/2-89-001, April 1989. (Calculated values from mercury content of coal).

EPA, 1990: "The Impacts of Particulate Emissions Control On the Control of Other MWC Air Emissions", Brna and J. Kilgroe, U.S. EPA. Journal AWMA, pp. 1324-1330, 1990.

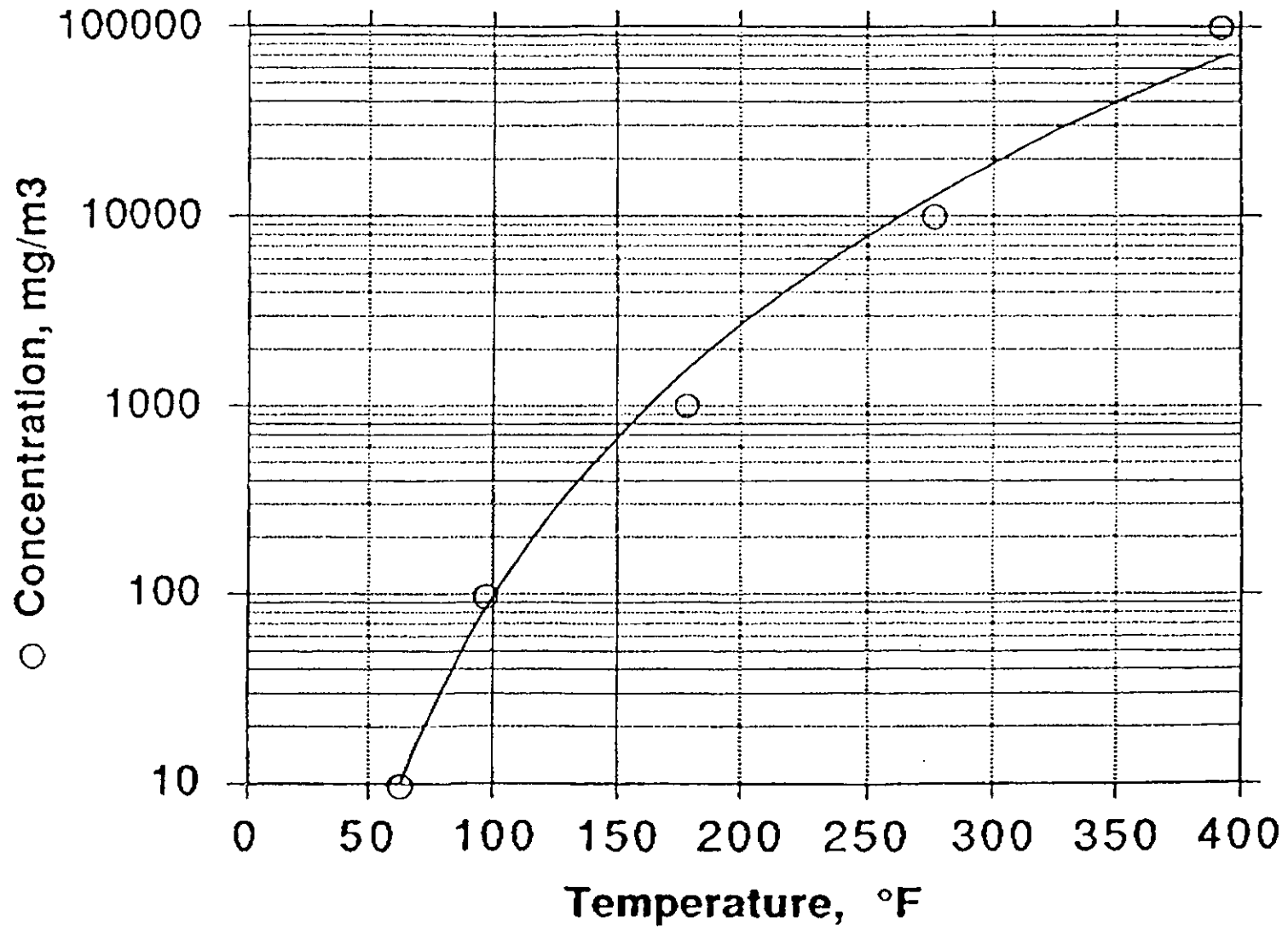
Flakt, Inc. 1993: Budgetary Quotation for activated Carbon System, January 1993.

Joy Env. Tech, 1993: Budgetary Quotation for activated Carbon System, January 1993.

EPA, 1993: Telecon with EPA Triangle Research Park Office March 3, 1993.

FIGURE 1: SATURATION VAPOR CONCENTRATION  
OF MERCURY VS TEMPERATURE

○  $y = 2.2619e-08 * x^{(4.8129)}$  R= 0.99648





State of Florida  
DEPARTMENT OF ENVIRONMENTAL REGULATION

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To: _____	Location: _____
To: _____	Location: _____
From: _____	Date: _____

# Interoffice Memorandum

TO: Buck Oven  
FROM: Bruce Mitchell  
THRU: Clair Fancy  
Date: March 8, 1993  
SUBJ: Proposed Amendment to the CBCP Proposed Certification Specific Condition No. II.A.9. Introduction

Buck:

We have looked at the proposed amendment to the No. II.A.9. introduction. Based on 40 CFR 60.46a(g), CEMs are used for demonstrating compliance once the initial performance test is completed in accordance with 40 CFR 60.8. Therefore, the suggested language is inappropriate and should not be added to the existing language. Also, Clair was involved with the discussion on this and concurs.

If there are any questions, please give me a call or E-mail me a response. Thanks.

Bruce Mitchell

- (15) Method 101A or EPA Method 29 for mercury.
- (16) Method 104 for beryllium.
- (17) Method 201 or 201A for PM10 emissions.
- (18) Ammonia (NH<sub>3</sub>) Method to be determined by the Department.

9. Continuous Emission Monitoring for each CFB

CBCP shall install, certify, calibrate, operate, and maintain continuous emission monitoring systems (CEMS) for opacity, SO<sub>2</sub>, NO<sub>x</sub>, CO, and O<sub>2</sub> or CO<sub>2</sub>, pursuant to all applicable requirements of Rule 17-296.800, F.A.C., Chapter 17-297, F.A.C., 40 CFR 60 Subpart A, 40 CFR 60 Subpart Da, 40 CFR 60 Appendix B, and 40 CFR 60 Appendix F. The permittee may elect to install, certify, calibrate, operate, and maintain multiple span continuous emission monitoring systems for sulfur dioxide and nitrogen oxides providing certification tests and calibrations are performed for each span. Each of the continuous emission monitoring systems for sulfur dioxide and nitrogen oxides shall continuously record data on a span that satisfies the requirements of 40 CFR 60.47a. Any exception to the above must be specifically authorized by DER in writing and in accordance with state and federal regulations. Where appropriate, DER may authorize use of CEMS for the purpose of determining compliance with emission limitations.

40 CFR 60.46a (3) Compliance Provisions

a. CEMS data shall be recorded and reported in accordance with Chapter 17-297, F.A.C., and 40 CFR 60.49a and 60.7. A record shall be kept for periods of startup, shutdown and malfunction.

b. A malfunction means any sudden and unavoidable failure of air pollution control equipment or process equipment or of a process to operate in a normal or usual manner. Failures that are caused entirely or in part by poor maintenance, careless operation or any other preventable upset condition or preventable equipment breakdown shall not be considered malfunctions.

c. The procedures under 40 CFR 60.13 shall be followed for installation, evaluation and operation of all CEMS.

d. Opacity monitoring system data shall be reduced to 6-minute averages, based on 36 or more data points, and gaseous CEMS data shall be reduced to 1-hour averages, based on 4 or more data points, in accordance with 40 CFR 60.13(h).

e. For purposes of reports required under this certification, excess emissions are defined as any calculated average emission concentration, as determined pursuant to Condition No. 10 11 herein, which exceeds the applicable emission limit in Condition No. 3.



I N T E R O F F I C E   M E M O R A N D U M

**Date:** 07-Apr-1993 04:45pm EST  
**From:** Sue Sullivan TAL  
SULLIVAN S  
**Dept:** Office of Secretary  
**Tel No:** 904/487-0472  
**SUNCOM:**

**TO:** Bruce Mitchell TAL

( MITCHELL\_B )

**Subject:** CEMS condition

Please review the proposed change and indicate concurrence.

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