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A NEW INTEGRATED SAMPLING AND ANALYSIS METHODOLOGY FOR ONLINE DETERMINATION OF MERCURY SPECIES FROM FOSSIL FUEL COMBUSTION

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Abstract

A new sampling and measurement methodology to determine Hg^0 and Hg^{2+} has been developed by integrating source dilution sampling and a sensitive ambient mercury speciation monitoring system. Dilution and cooling of stack emissions promote simulation of near ambient conditions while creating sufficiently low emission concentrations for detection of mercury species by a sensitive analyzer. A double-dilution system was equipped with online, automatic control functions to provide 500-2400 fold dilution. Appropriate chemical traps installed at the inlet of the analyzer remove interfering species such as SO_2 and HCl. This integrated concept was initially examined on a natural-gas-fired pilot-scale rotary kiln furnace that was modified for systematic injection of Hg^0, Hg^{2+}, HCl and SO_2 species to simulate coal-fired boiler emissions. Initial results showed that the new method was able to provide a good recovery of Hg^0 and Hg^{2+} injected at the levels normally found in coal-fired boiler emissions. The results from controlled parallel combustion experiments revealed that the Hg species concentrations form the new method were comparable to those obtained using the Ontario Hydro Method, during controlled of the two methods. The average deviation between the two methods was -14.6% to 8.6% at the Hg injection levels of 0.06 to 3.0 $\mu g/m^3$ of total Hg, measured as Hg^0. However Hg^{2+} concentrations obtained from the source dilution method were much lower than those from the Ontario Hydro Method. The results also indicated that much lower detection limit for Hg species at 0.1 ng/m^3 were possible using the dilution sampling method.

Introduction

Mercury, which is a toxic, persistent and accumulative substance, has been identified as the most toxic material in the emissions from coal combustion. Canada plans to publish mercury emission guidelines by 2005 under a national regulatory agenda known as the Canada Wide Standards. The standard is currently being prepared jointly by the federal and provincial governments in order to reduce mercury emissions form the coal-fired electrical power generation sector in the range of 60-90% by 2010. The Canadian plan will also attempt to align with the mercury rule of the United States that will be published in December 2004. Of three dominant mercury species present in coal combustion stack gas, high solubility and reactivity of reactive gaseous mercury (RGM) allow partial removal of Hg^{2+} species by wet scrubbing or sorbent adsorption, where as volatile Hg^0 escapes the control devices easily. Particulate mercury, Hg^p, is known to exist in smallest quantities normally less than 5%. Due to the high volatility of Hg^0 and extreme reactivity of Hg^{2+}, mercury species data from field measurements have been reported to be widely variable. Conventional way of measuring and reporting the emissions as total mercury in the form of Hg^0 is no longer considered to be sufficient. It has been established that Hg deposition rate and type of control strategies depend on the type of Hg species emitted by the combustor. Therefore, characterization of Hg speciation and understanding of their transformations in combustion systems are critical in developing effective control technologies as well as in understanding their subsequent impact on the fate and transportation after entering the atmosphere.

The mercury monitors currently available for source testing utilize pre-cleaning or pre-concentrating chemical solutions to remove interfering components of the stack gas before detection of the two gaseous Hg species (1,2). These continuous monitors usually measure and report Hg concentrations in stack emissions that are detected at one particular sampling time or snap shot information and are non-representative of changing field boiler operating conditions. In addition, they are sampled under high stack temperature regimes and are not comparable to the actual emissions detected in the atmosphere. Since little is known about transformation and fate of the mercury after leaving the stack, measuring the species under simulated atmospheric conditions, such as in source dilution sampling could provide simulated plume species concentrations that would account for the atmospheric transformation effects (3-5). Recently, source dilution sampling methods have gained increased attention due to their ability to provide realistic ambient-compatible data for source apportionment modeling. A new integrated concept of flue gas dilution and removal of acid gases as pre-treatment, to be followed by on-line Hg species detection using an ambient analyzer for source emissions sampling was evaluated. This approach would also allow for integrated sampling of emissions over longer periods to capture more realistic plant releases, compared with a very short, grab-sampling approach. This proof-of-concept was examined on a natural-gas-fired combustion system, which was modified to allow for simulation of coal-fired boiler emissions. It was recognized that the tests would not fully address the effects of other parameters that may be encountered during coal-fired combustion. However, we believe that the new concept could be most effectively tested by using a simpler and cleaner combustion system with Hg injection before moving to a more complicated and costly coal-fired combustion system. The paper describes the results from the initial phase of this research.

Experimental

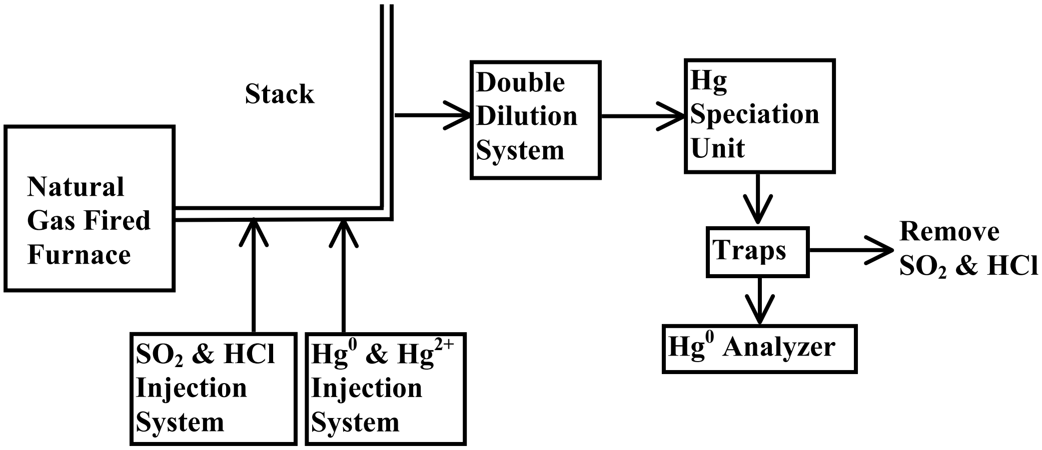

Fig. 1. Schematic of the integrated on-line Hg measurement system.

Fig. 1 shows a schematic diagram of the experimental combustion equipment and the integrated on-line measurement system. It consisted of a natural-gas-fired combustion unit, injection systems for SO_2, HCl and Hg species, a double dilution system and the on-line ambient mercury speciation and detection instrumentation.

Combustion Facility

A pilot-scale natural-gas-fired rotary kiln furnace was used to generate simulated coal-fired boiler emissions. The kiln furnace, shown in Fig. 2, is 4.27 m long with ID of 0.41 m. The 450 MJ/h combustor is equipped with emission control units including afterburner, cyclone, baghouse and two-stage wet scrubber. However, the baghouse was bypassed to avoid possible

Hg losses on its surface when injecting elemental mercury and mercury II chloride into the system. A 7.6 cm wide port on the 20.3 cm diameter duct downstream of the cyclone was installed for systematic injection of different levels of Hg^0, Hg^{2+}, SO_2 and HCl. Two 10.2 cm sampling ports were installed downstream of the injection port for simultaneous sampling with the Ontario Hydro Method and the CETC system. Gaseous stack emissions of O_2, CO, CO_2, SO_2 and NO_x were monitored using standard continuous emission analyzers while HCl levels were monitored using a Thermo Environmental Instruments Model 15C HCl analyzer. It should be noted that the furnace was used in a previous Hg emission control research study, which involved Hg injection into the combustion system. As a result, there may be residual Hg emissions within the unit that could be released during kiln firing. Necessary background check of the system was therefore incorporated in the test procedures.

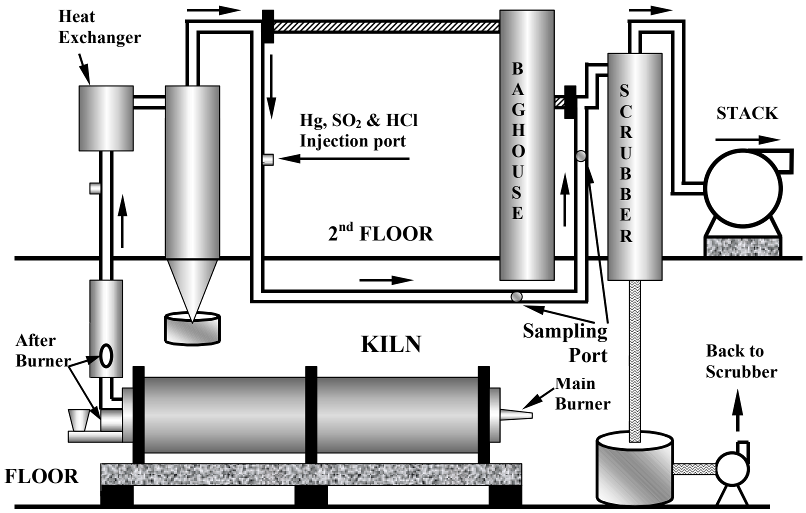

Fig. 2. CETC rotary kiln facility.

Hg^0, Hg^{2+}, SO_2 and HCl Injection Systems

Since mercury concentration in natural-gas-fired combustion flue gas is non-representative of normal Hg levels found in coal-fired combustion systems, selected levels of elemental mercury and mercury II chloride were injected into the stack exhaust to increase flue gas Hg concentrations. A commercially available Hg° and Hg^{2+} generator, VICI Metronics Model 500, was employed. With the Hg generator and the kiln furnace operating at its normal conditions, Hg^0 and Hg^{2+} concentrations in the flue gas could be theoretically brought up to 4.3 $\mu g/m^3$ and 4.6 $\mu g/m^3$ respectively. These would fall in the levels normally found in coal-fired power plant emissions, ranging from 2 $\mu g/m^3$ to 20 $\mu g/m^3$ with Hg^0 to Hg^{2+} ratios between 10 and 90%. Similarly the SO_2 and HCl levels in the natural-gas-fired flue gas were artificially increased to levels normally found in coal-fired boiler emissions using a SO_2 and HCl injection system. This also allowed investigations of the effects of HCl and SO_2 on mercury speciation system. Cylinder gases of 100% SO_2, 10% HCl and Argon with special regulators were used.

Double Dilution System

Hg concentrations in the coal-fired combustion systems are about four orders higher than the ambient Hg levels and are apparently beyond the operating range of ambient Hg monitors. The flue gas samples from the furnace were therefore diluted sufficiently to ensure that the sample concentrations are in the working range of the ambient Hg detection unit. A double dilution system was designed that would allow for dilution of stack gas in the range of 400-2400 fold. The dilution scheme used was a 30 fold in dilution chamber 1 followed by an additional 4 to 80 fold in dilution chamber 2, giving a total dilution ratio up to 2400 fold. It was expected that with such a high dilution ratio the temperature regimes of stack plumes, where atmospheric condensation and accumulation of constituents take place, could be closely simulated.

The double dilution system has two 1.82 m long stainless steel cylindrical chambers with 10.2 cm in diameter and is surface coated with Teflon® to minimize emission losses. Each chamber has a mixing section and a Venturi pump attached on the top. The 15 cm mixing section was constructed with 1.27 cm diameter stainless steel tubing and fittings, having Reynolds number up to 18000 to provide turbulent mixing of flue gas and dilution air. There are four sampling ports installed near the bottom of the mixing section that are dedicated for the Hg sampling as well as fine particulate sampling. $PM_{2.5}$ sampling will be incorporated in future work. The two dilution chambers provided 16 to 40 s residence time before sampling, depending on the total flow passing through them. The Venturi pump was connected to the mixing section by a 1.27 cm cross which also provided ports for the dilution air, power supply and sensor connections. The diluted flue gas exiting the Venturi pump was guided to the mixing section by a nozzle, a piece of 0.64 cm tubing, which was heated by a Kapton heater. In addition, a heating mantle was installed wrapping around the Venturi pump and its accessories to provide and maintain required temperatures for the units. By this arrangement, flue gas sample losses, particularly Hg species losses, and flue gas pre-condensation were minimized. A commercially available heatless dry air system with a capacity of 26 SCFM was employed to provide contamination free (particularly Hg free) air as dilution air. In order to avoid Hg species losses and flue gas pre-condensation, the flue gas sampling probe, all sample transportation lines and Venturi pumps were maintained in elevated temperatures. Four mass flow controllers, two pressure transducers and five thermocouples were installed throughout the system and are connected to the dedicated electronic data acquisition modules and computing devices for on-line process control and data monitoring. A reasonably accurate dilution ratio calculation was accomplished using calibrated Venturi pumps and mass flow controllers. A 0.91 m long special stack sampling probe similar to the US Environmental Protection Agency sampling Method 5 (M5) probe was designed and fabricated for this project. A smaller 0.79 cm diameter glass liner, fitted with a 0.64 cm nozzle was used to minimize Hg species losses in the probe.

SO_2 and HCl Removal Traps

Acid gases in the flue gas including HCl, SO_2 and NOx may interfere with the Hg detection system of the analyzer. Therefore, an in-house trap, constructed with a Teflon tube filled with sodium carbonate and Tenax, was prepared and installed upstream of the analyzer to remove SO_2 ,HCl and hydrocarbons without removing elemental mercury.

Mercury Speciation and Detection Units

A Tekran Model 1130 Hg speciation unit and a Tekran Model 2537A Hg analyzer were used to monitor Hg° and Hg^{2+} concentrations in sample gases exiting the second dilution chamber. Necessary optimization of experimental parameters for each Hg injection level was made to achieve appropriate dilution of the stack gas. This was an important step since the Hg species concentration in diluted sample must fall in the optimum working range of the Hg speciation and detection units.

Hg Species Measurements

A typical Hg species measurement protocol normally requires 1.5 h of furnace stabilization, 0.5 h for calibration of emission analyzers and 0.5 h for the preparation of dilution system. The Hg speciation and detection sequence involves 10 minutes of internal cleaning and flushing the system, 20 minutes of Hg^0 sampling during which Hg^{2+} is retained on the KCl denuder, 15 minutes of internal cleaning, followed by a thermal desorption for 15 minutes. The preparation, calibration and operating procedures for the Hg speciation unit and Hg analyzer were carried out following the recommended protocols by the instrument manufacturer. The sampling and analysis operation procedures for the integrated double dilution and on line Hg analysis require a familiarity of the overall laboratory test rig. The procedural details are therefore omitted. The

Ontario Hydro Method was used in parallel as a reference protocol in evaluating the new methodology (6).

Results and Discussion

Background Hg levels of the combustion system were examined prior to and after completion of the Hg sampling experiments. For these background checks, a total dilution ratio of 120 fold, 30 fold in the first dilution chamber followed by 4 fold in the second dilution chamber, was employed. The results showed total mercury concentrations ranging from 0.018 to 0.023 $\mu g/m^3$ with 60.9 to 66.7% Hg° and 33.3 to 39.1% Hg^{2+}. These were similar to the Hg levels found in laboratory indoor air during the preliminary examinations. During these experiments, kiln operating parameters were maintained at stable conditions. Gaseous emissions in flue gas including O_2, SO_2, CO, NOx and CO_2, as well as other kiln operating parameters were monitored and recorded using on-line data acquisition systems. Typical results are reported in Table 1.

Table 1. Typical kiln operating conditions from formal tests.

Natural gas firing rate	0.129 m^3/min (4.54 SCFM) 296 MJ/h (281,000 Btu/h)
Sampling port temperature	153° C
Room temperature	21° C
Pitot tube ΔP	7.0 Pa (0.028 in H_2O)
Stack draft	80.4 Pa (0.323 in H_2O)
Stack gas emissions	O_2 5.97% CO_2 7.84% CO 16 ppm SO_2 25 ppm NO_x 60 ppm

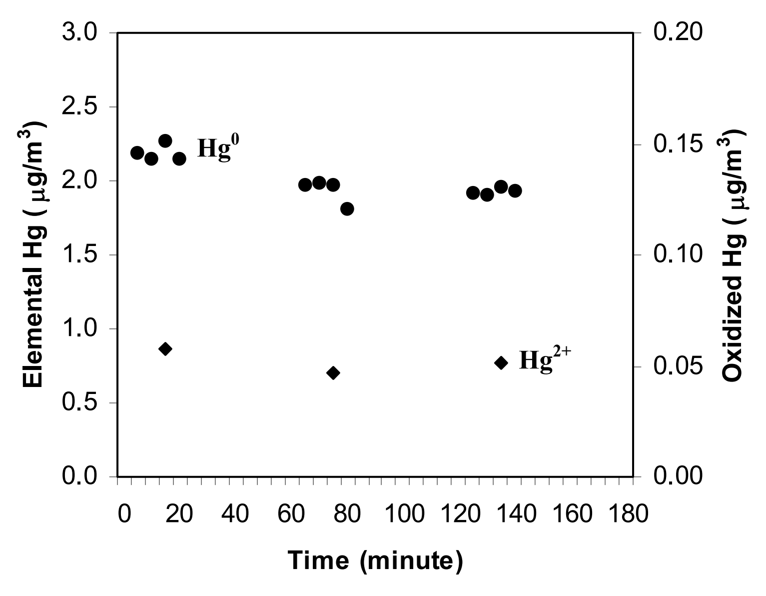

Fig. 3. Hg^0 and Hg^{2+} levels in flue gas from a typical run with Hg injection.

Emission Measurements after Hg Injections

Fig. 3 represents typical data set for a 3 h Hg species measurement experiment using the integrated source dilution technique. A total dilution ratio of 510 fold was accomplished, a 30 fold in the first dilution chamber followed by 17 fold in the second unit. Four Hg^0 readings were obtained in each hour, while only one Hg^{2+} reading was achieved since Hg^{2+} reading came from thermal desorbing the oxidized Hg trapped during the four cycles of 5 min Hg° sampling. Table 2 summarizes the results from three selected runs. Throughout these replicate runs Hg^{2+} concentrations in the stack emissions ranged from 0.014 to 0.035 $\mu g/m^3$, representing 0.6 to 5.5% of total mercury, while Hg° varied from 0.359 to 4.319 $\mu g/m^3$, accounting for 94.5 to 99.4% of total mercury.

The results demonstrated that the CETC methodology was able to monitor a wide range of Hg^0 and Hg^{2+} levels found in coal-fired power plant emissions. Results from three parallel tests for the Ontario Hydro method (OHM) and the dilution method are reported in Table 2 for comparison. The results revealed that the CETC total mercury data matched well with those from the Ontario Hydro Method, with deviations of –0.2 to –12.6%. Negative values indicate that the CETC data are lower in concentrations than the Ontario Hydro method data. However, concentrations of Hg^{2+} from the CETC method were much lower than those from the Ontario Hydro Method, with discrepancies of –73.1 to –89.3%.

Table 2. Comparison of results from CETC method and Ontario Hydro method.

		CETC		**OHM**		**Diff. of two methods, %**
		$\mu g/m^3$	% of Hg^{Total}	$\mu g/m^3$	% of Hg^{Total}	
Background level before Hg injection runs	Hg^0	0.035	81.4	-	-	-
	Hg^{2+}	0.008	18.6	-	-	-
	Hg^{Total}	0.054	100	-	-	**-**
Low level Hg injection	Hg^0	0.400	96.2	0.300	66.7	33.3
	Hg^{2+}	0.016	3.8	0.150	33.3	-89.3
	Hg^{Total}	0.416	100	0.450	100	**-7.6**
Median level Hg injection	Hg^0	2.008	99.2	2.167	93.6	-7.3
	Hg^{2+}	0.016	0.8	0.149	6.4	-89.3
	Hg^{Total}	2.024	100	2.316	100	**-12.6**
High level Hg injection	Hg^0	2.201	98.4	2.110	94.2	4.3
	Hg^{2+}	0.035	1.6	0.130	5.8	-73.1
	Hg^{Total}	2.236	100	2.240	100	**-0.2**
SO_2, HCl & Hg Injection*	Hg^0	2.207	97.4	1.950	90.3	13.2
	Hg^{2+}	0.058	2.6	0.210	9.7	-72.4
	Hg^{Total}	2.265	100	2.160	100	**4.9**
Background level after Hg injection runs	Hg^0	0.055	87.3	0.025	43.1	120.0
	Hg^{2+}	0.008	12.7	0.033	56.9	-75.8
	Hg^{Total}	0.063	100	0.058	100	**8.6**

* SO_2 = 502 ppm, HCl = 107 ppm

Two possible scenarios could explain the results. First, a mechanism for rapid reduction of Hg^{2+} to Hg^0 due to flue gas double dilution and cooling may be involved. Second, the Ontario Hydro Method may have overestimated Hg^{2+} under the simulated stack gas conditions. There seems to be some evidence of reduction of Hg^{2+} to Hg^0 in power plant plumes from various experimental and field studies. The Energy and Environmental Research Center and Frontier Geosciences Inc., both of USA, reported similar observations from experiments where stack gases from a coal-fired power plant were sampled, diluted and analyzed in a Teflon-lined dispersion chamber (7). These experiments showed a lower Hg^{2+}/Hg^0 ratio in the dilution chamber than in the stack. Another study that involved ambient sampling of Hg species downwind of coal-fired power plants showed that Hg^{2+}/Hg^0 ratio (average 88% Hg^0) at the downwind location was lower than the Hg^{2+}/Hg^0 ratio (average 48% Hg^0) in the stack (8). Secondly, the Ontario Hydro Method might have overestimated Hg^{2+} under simulated flue gas conditions during this study. Researchers from the US Environmental Protection Agency (EPA) found that as little as 1 ppm Cl_2 in a simulated flue gas mixture without appreciable amount of SO_2 led to a bias of approximately 10 to 20% of Hg° misreported as Hg^{2+} when using the Ontario Hydro Method because Cl_2 oxidizes Hg^0 to soluble Hg^{2+} in the front impingers filled with KCl solutions (9). Another study reported the results that are similar to the EPA studies (10). Fortunately, this bias is not likely to be a factor for speciation measurements with the Ontario Hydro Method from actual coal combustion flue gases where presence of SO_2 inhibits this artifact.

The above findings have important implications. The local and regional impacts of power plant emissions or point sources due to Hg wet deposition may have been overestimated in modeling since current models do not account for this change in the Hg^{2+}/Hg^0 ratio in plumes. In addition, concerns of so-called "hot spots" surrounding point sources due to rapid Hg^{2+} wet deposition may not be justified. Additional more tests covering a fairly broad range of conditions should be conducted to provide more definite conclusions.

Emission Measurements after Hg, SO_2 and HCl Injections

A number of experiments were conducted to study the effects of HCl and SO_2 on the Hg speciation and detection systems as these gases are known to interfere with the sensitive Hg analyzers. As described above appropriate chemical traps were designed and installed between the Hg speciation unit and the Hg analyzer to remove SO_2 and HCl without removing any elemental mercury. Sample results from one of the experiments are presented in Table 2. It appears that SO_2 and HCl had little significance in mercury speciation at temperatures and concentrations typically found in this study. Sample dilution has significantly reduced the concentrations of these gases into very low levels that are much easier to remove than undiluted sample stream.

The results from parallel measurements using the Ontario Hydro method after injection of these species are also included in Table 2. The results were comparable for total mercury, with a deviation of 4.9%. However, the Hg^{2+} reading from the CETC method was significantly lower than those from the Ontario Hydro method, with a discrepancy of –72.4%. A similar assumption on the possible rapid reduction of Hg^{2+} to Hg^0 during dilution may be applicable. However, the hypothesis on Cl_2 oxidization of Hg^0 to soluble Hg^{2+} in the front impingers in the Ontario Hydro Method is not justified here due to the presence of 502 ppm SO_2 in the stack emissions.

Conclusions

A new Hg species measurement method has been developed by integrating the near-plume simulation by sample dilution and a sensitive ambient mercury speciation monitoring system. This concept was examined on a natural-gas-fired pilot-scale rotary kiln furnace that was modified to provide simulated coal-fired boiler emissions. Systematic injection of Hg species, HCl and SO_2 gases enabled simulation of realistic coal combustion emissions. A double dilution system was developed with a capacity of up to 2400-fold sample dilution.

The recovery of Hg^{2+} concentrations ranged from 0.014 to 0.035 $\mu g/m^3$, representing 0.6 to 5.5% of total mercury, while Hg° varied from 0.359 to 4.319 $\mu g/m^3$, accounting for 94.5 to 99.4% of total mercury. The results demonstrated that the new methodology was able to monitor Hg^0 and Hg^{2+} levels normally found in coal-fired power plant stacks.

For total mercury emission measurements, the dilution sampling data compared well with the results from the Ontario Hydro method with deviations of –14.6 to 8.6%. However, Hg^{2+} concentrations from the new method were much lower than those from the Ontario Hydro method with discrepancies of –73.1 to –97.7%. The reasons for the discrepancies could be due to two probabilities. First, a mechanism for rapid reduction of Hg^{2+} to Hg^0 during flue gas double dilution may be involved. Second, the Ontario Hydro Method might have overestimated Hg^{2+} under simulated flue gas conditions in the absence of appreciable amounts of SO_2. Similar results have also been reported in the literature. The findings may have important implications. The local and regional impacts of power plant emissions or point sources due to Hg wet deposition may be overestimated in regional emission modeling since current models do not account for this change in the Hg^{2+}/Hg^0 ratio in plumes. In addition, concerns of so-called "hot spots" surrounding point sources due to rapid Hg^{2+} wet deposition may not be justified.

References

1. Laudal, D.L. and French, N.B., Proceedings of Conference on Air Quality II, McLean, VA, September 2000.
2. Laudal, D.L., In proceedings, A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, IL, August 21-23, 2001.
3. Lee, S. Win, H. Whaley, R. Pomalis and J.K.L. Wong, ASME, EC-Vol. 5, pp.97-105, 1997.
4. Lee, S. Win, R. Pomalis and B. Kan, Fuel Processing Technology, 65-66 (2000): 189-202.
5. Lee, S. Win, J. Air & Waste Manage. Assoc., 51, pp. 1568-1578, 2001.
6. ASTM method D6784-02, Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method).
7. Laudal, D., Final Report for JV Task 24, Cooperative Agreement No. DE-FC26-98FT40321, UND Fund 4727, 2001.
8. Edgerton, E.S., Benjamin, E.H. and Jansen, J.J., Proceedings of Air Quality III: Mercury, Trace Elements and Particulate Matter Conference, Arlington, VA, September 9-12, 2002.
9. Linak, W.P., Tyan, J.V., Ghorishi, B.S. and Wendt, J.O.L., J. Air & Waste Management Association, 51: 688-698, 2001.
10. Laudal, D.L., T.D. Brown and B.R. Nott, Fuel Processing Technology 65-66 (2000): 157-165.