INVESTIGATION OF THE FATE OF MERCURY IN A COAL COMBUSTION PLUME USING A STATIC PLUME DILUTION CHAMBER

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Project Description

Although in-stack mercury speciation measurements are essential to develop and test control technologies and to provide data for input into atmospheric deposition models, the determination of speciation in a cooling coal combustion plume is more relevant for use in estimating mercury fate and effects. However, little is known about the mercury transformations that occur in the plume. The mercury transformations that occur in the plume determine the rate and the form of mercury deposited in lakes and streams.

Therefore, a logical step in mercury research is to apply our knowledge slightly beyond the system to the plume region. Frontier Geosciences developed a static plume dilution chamber (SPDC) that was designed to simulate plume conditions in the atmosphere. The SPDC is a 0.5-m^3 chamber designed to simulate light and rain events and allow extensive mercury sampling as a function of time. A schematic of the SPDC is shown in Figure 1.

Based on previous results, the SPDC showed the potential to simulate plume and atmospheric effects on mercury that may help researchers understand the mercury chemistry in the plume. Although the results at three field tests have demonstrated positive results,[1] the SPDC needed to be tested under controlled conditions with mercury measurement methods that have been shown to correctly speciate mercury.

The EERC, with help from Frontier Geosciences, conducted pilot-scale tests to more fully evaluate the SPDC under more controlled conditions than what occur at a full-scale system. This work was done in partnership with the U.S. Department of Energy (DOE), EPRI, and the U.S. Environmental Protection Agency (EPA) through the EERC's CATM.

Goal

The overall goal of the project was to further develop and then verify SPDC's ability to determine the physical and chemical transformations of mercury in combustion stack plumes. Specific objectives of the

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[1] Prestbo, E.M.; Calhoun, J.A.; Brunette, R.C.; Palidini, M. Hg Speciation in a Simulated Coal Combustion Plume. In *Proceedings of the Air Quality: Mercury, Trace Elements, and Particulate Matter Conference*; McLean, VA, Dec 1–4, 1998.

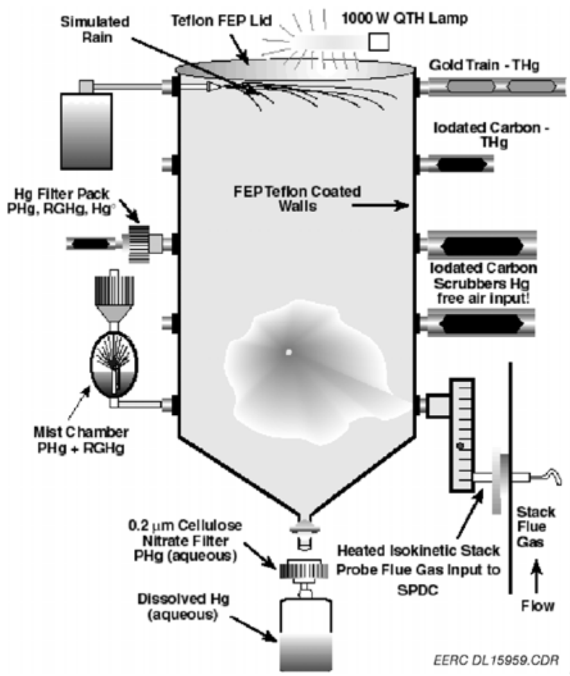

Figure 1. Schematic of the Frontier Geosciences SPDC

project were to perform controlled tests at the pilot scale using dynamic spiking of known mercury compounds (i.e., Hg^0 and $HgCl_2$) to prove the ability of the SPDC to determine the following:

- Whether mercury condenses onto particulate matter (PM) in a cooling plume
- Whether there is reduction of Hg^{2+} to Hg^0 occurring in hygroscopic aerosols
- Whether condensed Hg^{2+} on particles is photochemically reduced to Hg^0
- Whether or not the Solid Ontario Hydro (SOH) mercury speciation method provides the same results as the Ontario Hydro (OH) mercury speciation method.

Rationale

Techniques are available to measure the various forms of mercury at the stack as well as in ambient air. However, clearly the next step is to attempt to understand the mercury transformations that occur in a plume. Currently, very few data exist as to the mercury chemistry that can occur in flue gas plumes. The SPDC, developed by Frontier Geosciences, has the potential to simulate plume and atmospheric effects on mercury that may help researchers understand the mercury chemistry that occurs immediately following a power plant stack.

Approach

The evaluation of the SPDC was carried out by using the relatively controlled (and very well characterized) environment of the EERC pilot-scale particulate test combustor (PTC) flue gas. The test matrix for the SPDC experiments is shown in Table 1. For the pilot-scale tests, the SPDC was located well downstream of the particulate control device (either the tubular electrostatic precipitator [ESP] or the high-efficiency pulse-jet baghouse). The test variables for the SPDC included PM concentration (based on whether the baghouse or ESP was used), simulated rain, duration, ozone concentration, and mercury form and concentration. Very extensive measurements were made on the device to determine total mercury, particulate-phase mercury, and gas-phase mercury (i.e., Hg^0 and Hg^{2+}).

As shown in Table 1, known amounts of Hg^0 and/or $HgCl_2$ were spiked into the flue gas stream, using mercury-spiking systems previously developed at the EERC. These systems have been shown to accurately spike either Hg^0 or $HgCl_2$ into the PTC.

Table 1. Test Matrix[a,b,c]

Test No.	Fuel	Particulate Control Device	Hg Spike[d]	Light	Simulated Rain	Ozone, ppb
1	Natural gas	Baghouse	Hg^0	No	No	0
2	Natural gas	Baghouse	$HgCl_2$	No	No	0
3	Blacksville	ESP	None	No	No	0
4	Blacksville	ESP	None	Yes	Yes	0
5	Blacksville	ESP	None	Yes	No	0
6	Blacksville	ESP	$HgCl_2 + Hg^0$	No	No	0
7	Blacksville	ESP	$HgCl_2 + Hg^0$	Yes	Yes	0
8	Blacksville	ESP	$HgCl_2 + Hg^0$	No	Yes	0
9	Blacksville	ESP	$HgCl_2 + Hg^0$	Yes	No	0
10	Blacksville	ESP	$HgCl_2 + Hg^0$	Yes	No	200
11	Blacksville	Baghouse	None	No	No	0
12	Blacksville	Baghouse	None	Yes	Yes	0
13	Blacksville	Baghouse	$HgCl_2 + Hg^0$	No	No	0
14	Blacksville	Baghouse	$HgCl_2 + Hg^0$	Yes	Yes	0
15	Blacksville	Baghouse	$HgCl_2 + Hg^0$	No	Yes	0
16	Blacksville	Baghouse	$HgCl_2 + Hg^0$	Yes	No	0

[a] The dilution ratio for the chamber was between 140:1 and 200:1 for all runs.
[b] Hg^0 was monitored continuously (every 3–5 minutes).
[c] Hg^{2+} and particulate-bound mercury were sampled at 6, 30, 60, and 120 minutes for each test.
[d] The $HgCl_2$ and Hg^0 spikes were nominally 12 or 15 $\mu g/dm^3$.

For each test, the speciated flue gas mercury was measured using the OH and the SOH methods. After a known volume of flue gas was injected into the SPDC, speciated vapor-phase mercury measurements were made as a function of time using a Tekran mercury continuous emission monitor with a KCl denuder. The test was then conducted based on the test matrix shown above. Following each test, rinses were made of the unit, and the mercury was measured in the rinses.

Progress

The pilot-scale testing for this project was carried out during March 2000. The OH data for the test runs are shown in Table 1, and a final report for the project was issued November 2001.

The average flue gas analyses during the runs using coal were 1280 ppm SO_2, 5.0% O_2, and 13.8% CO_2. The average particulate loading during the runs was 0.305 gr/dscf using the ESP (Runs 3–10) and 0.006 gr/dscf using the baghouse (Runs 11–16).

To ensure valid results, reasonable mercury balances were obtained around the SPDC. For purposes of these tests, mercury balances ±25% were considered reasonable. Except for the first test on the natural gas, all the mercury balances were within acceptable limits.

The SPDC results show a very rapid decrease in both Hg^{2+} and particulate-bound mercury. It appears the rate of decease is so fast that it occurs even before the first real measurement can be made. Two explanations are possible for the rapid decrease. First, the Hg^{2+} could have been reduced to Hg^0; secondly, the Hg^{2+} may have collected along the walls of the SPDC and been removed by the rinses. If there was a reduction of Hg^{2+} to Hg^0, then a corresponding increase in Hg^0 should have been observed. In fact, there was a corresponding increase in Hg^0 for almost all the tests. However, the increase in the mass of Hg^0 is substantially less than the decrease in the mass of Hg^{2+}. Although it appears there is some reduction of Hg^{2+} to Hg^0, there are also clearly substantial wall effects within the SPDC chamber. The overall change in Hg species within the SPDC chamber for each of the tests is shown in Table 2. An example of these results is shown graphically in Figure 2.

As part of the SPDC testing, a comparison of the SOH method was made to the OH method sampling for speciated mercury. Paired sampling trains were run. The statistical comparison for each mercury species from the methods is shown in Table 3. Comparing the two methods, the calculated t-statistic is less than the t-value for each of the measured mercury species. Therefore, the two methods are statistically similar not only for total mercury, but Hg^{2+}, Hg^0, and particulate-bound mercury as well.

Status

The project is complete, and a final report has been submitted to all team members.

Potential Users/Technology Transfer

Although it was initially anticipated that the results from these experiments would be used by EPA, EPRI, DOE, and others in ongoing modeling efforts, results seem to indicate a limited commercial application because of the high wall effects.

Table 2. Change in Mercury Species in the SPDC

Test No.	Hg^{2+} Mass Change, μg	Hg^0 Mass Change, μg	Difference, μg
3	47.08	6.79	40.29
4	43.67	8.19	35.48
5	37.33	6.59	30.74
6	77.38	10.07	67.31
7	79.89	11.14	68.75
8	75.88	7.9	75.09
9	97.42	10.16	87.26
10	60.01	17.79	42.22
11	56.86	−2.93	59.79
12	56.17	2.3	53.87
13	88.55	9.62	78.93
14	87.05	11.54	75.51
15	82.45	12.7	69.75
16	104.72	0.04	104.68

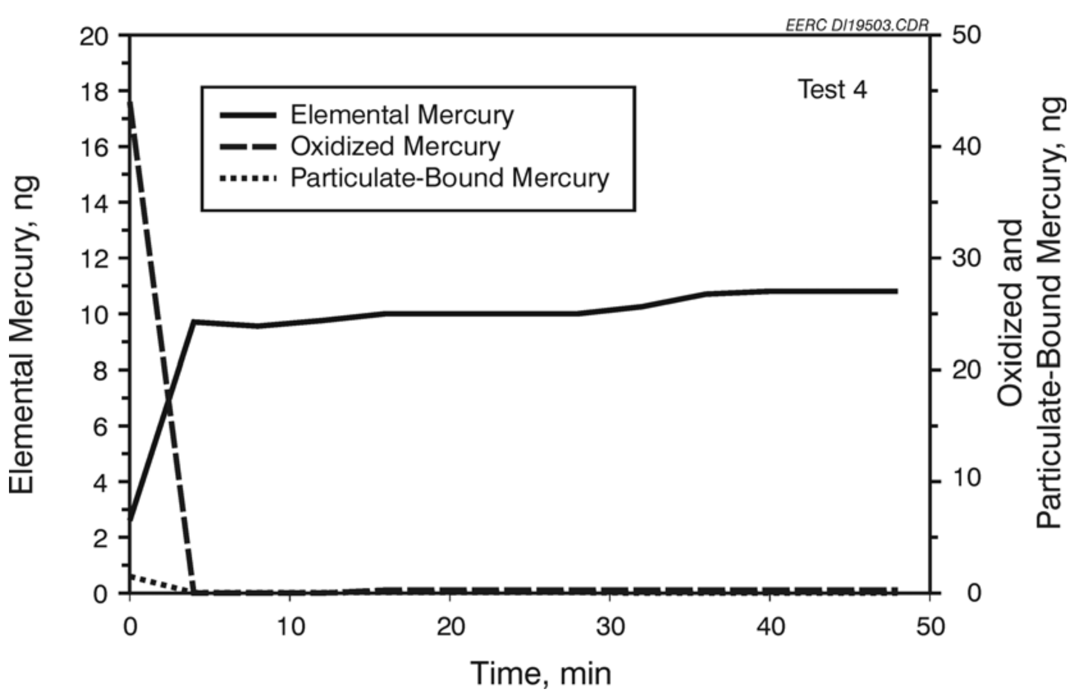

Figure 2. The Change in Mercury Speciation as a Function of Time for SPDC Test 4

Table 3. Statistical Comparison between the OH and SOH Mercury Sampling Methods

Statistical Component	Total Hg	Hg^0	Hg^{2+}	Particulate-Bound Hg
Mean Difference, µg	1.2500	0.2425	0.5188	0.6229
Mean Standard Deviation, µg	3.2490	1.0826	3.2486	1.1667
Calculated t-statistic	1.539	1.4125	0.8958	0.6388
t-statistic (95% confidence)	1.753	1.753	1.753	1.943