Oxidation of Mercury Across SCR Catalysts in Coal-Fired Power Plants Burning Low Rank Fuels

Quarterly Progress Report

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Disclaimer

Abstract

This is the first Quarterly Technical Report for DOE Cooperative Agreement No: DE-FC26-03NT41728. The objective of this program is to measure the oxidation of mercury in flue gas across SCR catalyst in a coal-fired power plant burning low rank fuels using a slipstream reactor containing multiple commercial catalysts in parallel. The Electric Power Research Institute (EPRI) and Ceramics GmbH are providing co-funding for this program. This program contains multiple tasks and good progress is being made on all fronts. During this quarter, analysis of the coal, ash and mercury speciation data from the first test series was completed. Good agreement was shown between different methods of measuring mercury in the flue gas: Ontario Hydro, semi-continuous emission monitor (SCEM) and coal composition. There was a loss of total mercury across the commercial catalysts, but not across the blank monolith. The blank monolith showed no oxidation. The data from the first test series show the same trend in mercury oxidation as a function of space velocity that has been seen elsewhere. At space velocities in the range of 6,000-7,000 hr^{-1} the blank monolith did not show any mercury oxidation, with or without ammonia present. Two of the commercial catalysts clearly showed an effect of ammonia. Two other commercial catalysts showed an effect of ammonia, although the error bars for the no-ammonia case are large. A test plan was written for the second test series and is being reviewed.

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Executive Summary

This project received funding from the Department of Energy under Cooperative Agreement No: DE-FC26-03NT41728. The Electric Power Research Institute (EPRI) and Ceramics GmbH are providing co-funding for this program. This project has a period of performance that started February 19, 2003 and continues through August 18, 2003.

Under a separate program (cooperative agreement DE-FC26-00NT40753), Reaction Engineering International (REI) has been funded by the Department of Energy to carry out research and development on NO_x control options for coal-fired utility boilers. The objective of one of the tasks in the NO_x-control program is to evaluate and model SCR catalyst deactivation. REI will be responsible for six-month testing of multiple commercial catalysts simultaneously in a power plant slipstream reactor. This multi-catalyst reactor provides an ideal test bed for advancing the state of knowledge regarding mercury oxidation by SCR catalysts, with a focus on low rank fuels.

In this program, REI is using the multi-catalyst slipstream reactor to determine oxidation of mercury across six separate SCR catalysts at AEP's Rockport Unit 1. During the six-month testing under the existing NO_x-control program, two weeklong sampling campaigns for mercury speciation will be carried out: at the beginning of the six-month period and at an intermediate point. URS will conduct the one-week campaigns to measure gaseous mercury speciation at the inlet and at the outlet of each catalyst chamber.

The specific project tasks are:

- Task 1   Test Preparation
- Task 2   Test Plan
- Task 3   Field Measurements of Mercury Speciation
- Task 4   Data Analysis and Validation
- Task 5   Management and Reporting

During the last three months, our accomplishments include the following:
- Analysis of the mercury sampling carried out by URS was completed.
- Good agreement was shown between different methods of measuring mercury in the flue gas: Ontario Hydro, semi-continuous emission monitor (SCEM) and coal composition.
- Mercury in the flue gas was predominantly elemental. The Ontario Hydro measurement corresponded to 81% of gaseous mercury as elemental. The SCEM values for elemental mercury tended to be lower than the Ontario Hydro value, though it is hard to generalize since the Ontario Hydro measurement was only made on one day.
- The SCEM reading when sampling a given port seemed to need several minutes to come to a steady state value. This may have been due to partial clogging of the ash filters, which reduced the amount of flue gas sample going to the analyzer.
- There was a loss of total mercury across the commercial catalysts, but not across the blank monolith. This suggests that the loss was not in the sampling system, but rather associated with active catalyst. Over the time period of the testing, the amount of time that the catalyst was exposed to flue gas did not seem to influence the loss of mercury.

- The blank monolith showed no oxidation. One of the monolith catalysts and one of the plate catalysts showed considerable oxidation at high space velocities, but the other commercial catalysts did not. At typical space velocities for full-scale SCR catalysts and with excess ammonia relative to NO, the oxidation was 60-80%. Other slipstream work has shown that mercury oxidation decreases with increasing space velocity (that is, decreasing residence time). The data from the first test series show the same trend that has been seen elsewhere.

- At space velocities in the range of 6,000-7,000 hr^{-1} the blank monolith did not show any mercury oxidation, with or without ammonia present. Two of the commercial catalysts clearly showed an effect of ammonia. Two other commercial catalysts showed an effect of ammonia, although the error bars for the no-ammonia case are large. The amount of oxidation without ammonia was about the same for all the catalysts (approximately 80%), but when ammonia was present, there was a much larger range of mercury oxidation values.

- A test plan for the second test series was written and reviewed by team members.

Experimental Methods

Within this section we present in order, brief discussions on the different tasks that are contained within this program. For simplicity, the discussion items are presented in the order of the Tasks as outlined in our original proposal.

Task 1 – Test Preparation

Site Description

The Rockport plant consists of two 1300 MW_e B&W opposed wall-fired boilers. These are supercritical boilers that burn a blend of bituminous and subbituminous coals. The average mix is 87% Powder River Basin sub-bituminous and 13% bituminous coal. 100% PRB is burned during off-peak periods and on weekends when the unit is not generally required to operate at full load.

Slipstream Reactor Description

The slipstream reactor designed to test the deactivation of SCR catalysts in the field is operational and collecting data at the AEP Rockport plant. The reactor contains six SCR catalysts in parallel and is designed to withdraw a flue gas sample at the exit of the economizer. The reactor contains five commercial catalysts, both plate and honeycomb type, and one blank ceramic monolith. Details of the catalysts' phsyical properties are given in Table 1. The six catalysts, four monolith and two plate, are configured as shown in Figure 2.

Table 1. Catalyst Properties

Chamber:	1 (Blank)	2	3	4	5	6
Catalyst type:	Monolith	Monolith	Plate	Plate	Monolith	Monolith
Chamber porosity:	58.7%	70.0%	85.0%	86.9%	70.0%	68.3%
Length of catalyst in chamber (inch):	24.40	21.50	39.25	43.25	20.06	19.75

Anhydrous ammonia is injected into the flue gas stream near the entrance to the reactor, and blended with a static mixer. For the first test series, the molar ratio of NH_3/NO_x was set at approximately 1.1 in order to ensure that NO_x destruction was not limited by stoichiometry and to give margin for swings in NO_x levels.
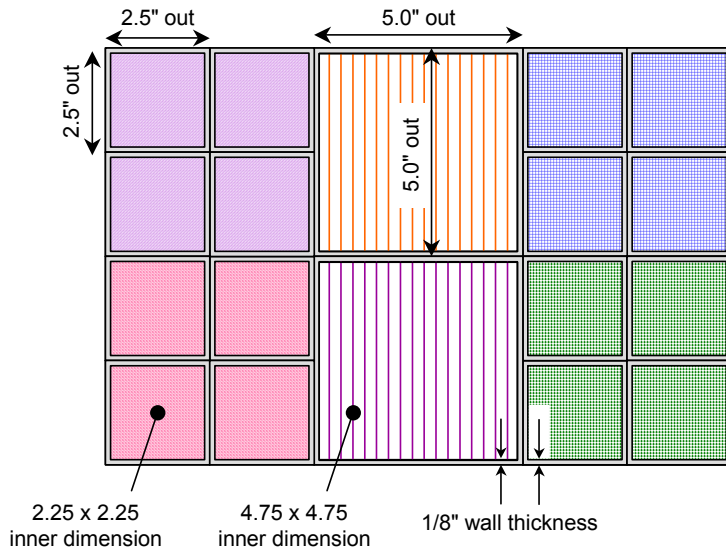
Figure 2. Arrangement of catalysts (plan view)

The system has seven sampling ports, one before the catalyst chambers and one after each of the six catalyst sections. The ports themselves consist of thin tubes that enter the channel and bend downward, in line with gas flow.   There are sintered metal filters at the point where the individual samples are withdrawn; these can be blown back with compressed air. The inlet sample has a 30-foot heated line (upstream of the sample conditioning unit), ¼" SS; the six outlet samples have 10-ft heated lines, ¼" SS. The sample lines are heated to about $250^{o}F$. In the sample conditioning and switching unit, seven lines come in from the reactor and one line goes out to the NO_x/O_2 analyzer. The switching valves are in a heated box, heated to $175^{o}F$. There is blowback air for these valves. For the mercury testing, URS took a sample at the exit of the heated switching valve.

The SCR slipstream reactor was installed in the flue gas duct downstream of the economizer and upstream of the air preheater on Unit 1. Figure 3 is a schematic of the slipstream SCR reactor as installed at Rockport. A sampling probe was inserted through an existing port in the duct wall. The probe extends approximately three feet into the duct and has a 2-ft long slot, oriented 90° from the direction of flow in the duct. An isolation valve was placed on the inlet line just outside the duct wall. This valve is coupled to the control system, and closes automatically if the flue gas becomes too cold in order to prevent condensation in the catalyst units. The reactor exhaust line is connected to the horizontal duct downstream of the air preheater. As shown in Figure 3, the slipstream reactor is fitted with a 3-inch port for Ontario Hydro measurements, one SCR inlet heated sample line and an outlet heated sample line for each of the six catalyst chambers. Each one of the sample lines feeds into a heated chamber, housing selector valves in a unit called the sequencer. With this arrangement any sampling sequence can be performed using REI's custom-made software.

One SCR Inlet
Heated Sample Line

Pneumatic Isolation Valve

Flue Gas

Ammonia Injector

Ontario Hydro
Sample Port

Duct Wall

SCR Reactor

Six SCR Outlet Heated
Sample Lines to Sequencer

Duct Wall

Flue Gas
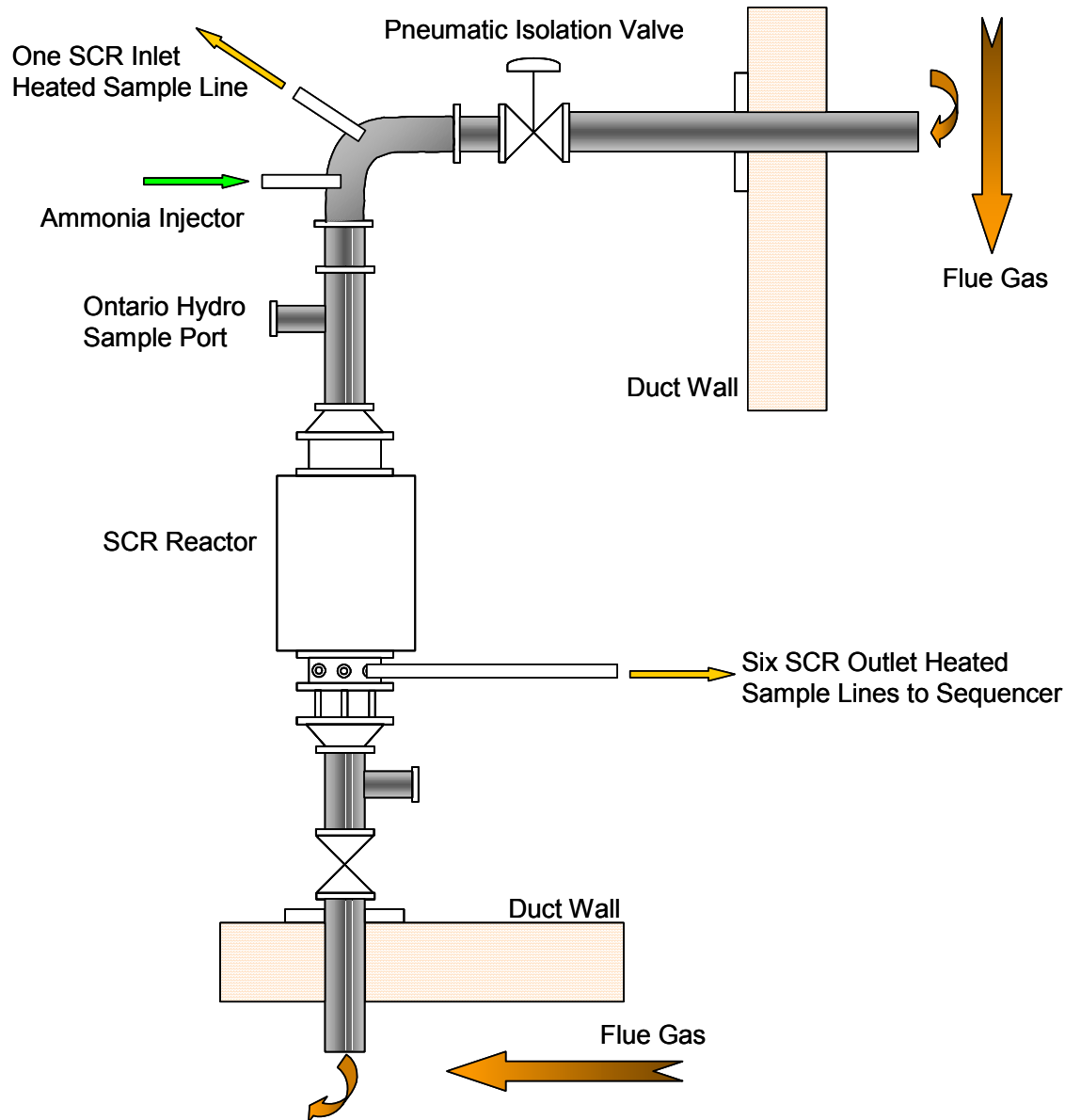
Figure 3. SCR Slipstream Reactor

Task 3 - Field Measurements of Mercury Speciation

The first test series was begun at the end of March; data were taken between 28 March and 2 April, 2003. The test crew from URS used a semi-continuous mercury emissions monitor (SCEM) to provide near real-time feedback during catalyst evaluations. To minimize fluctuations in mercury in the flue gas, the plant was run at constant load throughout the mercury tests. The start of the mercury tests was plagued by problems with the mercury SCEM. Eventually these were resolved and testing could start. The tests conducted included an Ontario

Hydro sampling train at the inlet to the SCR and elemental and total mercury measurements using the SCEM at the inlet and outlet of the catalyst chambers.

There were six catalyst chambers consisting of two plate-type catalysts and four monolith or honeycomb catalyst catalysts (as discussed above). The sampling was controlled automatically by the slipstream reactor control system; the sequence was: inlet, chamber one, chamber two, chamber three, inlet, chamber four, chamber five, chamber six, inlet. Tests conducted in the first day (28 March) were sampled for thirty minutes for each sample line. In subsequent tests, the sampling time was limited to twenty minutes.

During the tests, the temperature in the boiler duct was approximately 720^oF. Temperature in the catalyst chambers was controlled to 650^oF, based on thermocouples located on the outside of the chambers. Stable flow and temperature conditions were generally achieved. Table 2 shows a summary of the test conditions. Ammonia and flue gas flow rate set points in the catalyst chambers are shown in Table 3. The ammonia flow was the equivalent of 1.1:1 ammonia to NO, (molar basis), assuming that the NO concentration in the flue gas was 400 ppm.

Table 2. Mercury Oxidation Test Conditions

Test Day	Run No.	Mercury Measured	Target Space Velocity (hr^{-1})*	Ammonia Flow Status
03-28-03	1-1	elemental	6000	on
	1-2	elemental	6000	off
	1-3	total	6000	on
03-31-03	2-1	elemental	6000	on
	2-2	total	6000	off
04-01-03	3-1	total	6000	on
	3-2	elemental	3000	on
	3-3	total	3000	on
04-02-03	4-1	elemental	3000	off
	4-2	elemental	10000	on

*At 650^oF

Table 3. Target Flue Gas Flow Rate in the Catalyst Chambers

SV, 1/hr	1	2	3	4	5	6	TOTAL	NH_3, ml/min
3000	4.19	8.88	9.80	10.02	4.04	3.94	40.88	0.509
6000	8.38	17.77	19.61	20.05	8.08	7.88	81.8	1.019
10000	13.97	29.62	32.68	33.42	13.47	13.13	136.29	1.698

Table 4 Test Data Collected During Mercury Testing

Parameter	Sample/Signal/Test	Frequency
Coal	Batch sample to pulverizer, as fired. Ultimate, proximate, ash composition, Hg, Cl analyses.	Daily
Fly ash	Batch sample from ESP silos 3 & 4 and from economizer hopper. LOI, Hg, Cl, ash composition analyses.	Daily

Unit operation	Plant PI Data:
	    Boiler load
	    Flow rates and temperatures
	    O_2 (air preheater)
	    NO_x, SO_2 (stack)
		At least several times per day

Mercury (total and speciated)	Inlet and outlet of catalyst chambers (SCEM)	Per test plan
Mercury (total and speciated)	Ontario Hydro, inlet of APH	Once, three repeat measurements

Table 4 shows a list of samples collected during the tests for further analysis. Coal and ash samples were analyzed by Microbeam Technologies, Inc. (Grand Forks, ND). During the test run on March 28, 2003 both the Ontario Hydro and the SCEM were run simultaneously. The Ontario Hydro sample was taken through the three-inch port upstream of the catalyst chambers indicated in Figure 3. Analysis of the Ontario Hydro filters and impinger solutions was carried out by URS.

For the SCEM measurements, a sample gas from the sequencer was directed to a train of impingers (see Figure 4). For elemental mercury measurement, the flue gas was passed through impingers containing potassium chloride solution (KCl) followed by a set of impingers containing caustic soda, NaOH. KCl captures oxidized mercury while allowing elemental mercury to flow through. NaOH was used for removing acid gases in the flue gas (SO_2, HCl). For total mercury measurements, the KCl impingers were replaced with a set of impingers containing stannous chloride ($SnCl_2$). Stannous chloride reduces oxidized mercury to elemental mercury. Thus downstream mercury measurement equipment detects total mercury in the sample gas (elemental mercury + oxidized mercury).

After passing through the impingers, the flue gas was directed to an amalgamation unit (gold trap) that adsorbs mercury at a temperature slightly below room temperature. After a predetermined amount of time, the gold trap is heated to release the concentrated mercury, which is conveyed in a carrier gas to a cold-vapor atomic absorption accessory for quantitative analysis.
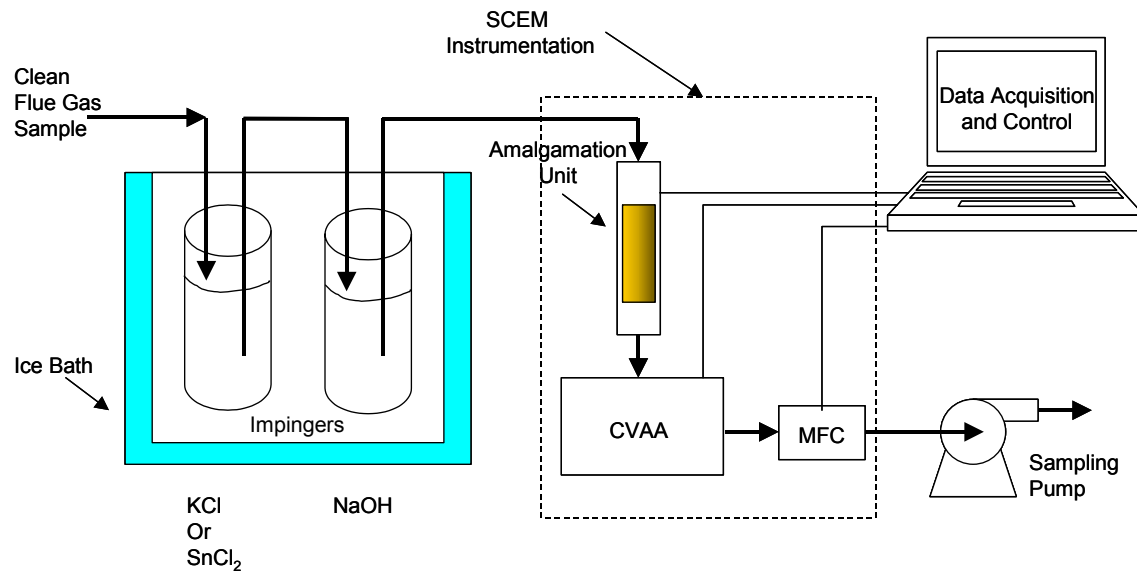
Figure 4. Field setup of the SCEM and impingers

Results and Discussion

Task 3 - Field Measurements of Mercury Speciation

Coal and Ash Data

Coal samples were obtained at the inlet to the pulverizers. The samples were pulverized; ultimate and proximate analyses were carried out by Microbeam Technologies, as well as measurement of Hg and Cl. The Hg and Cl measurements were made at the University of North Dakota Energy & Environmental Center (EERC). Table 5 presents the coal data on both as-received and dry bases.

The coal blend is nominally 87% subbituminous (from the Powder River Basin or PRB) and 13% bituminous. The heating value of the coal is commensurate with the blend, as is the coal chlorine content. The mercury content of the coal is equivalent to 8-11 $\mu g/nm^3$ of mercury, if all the mercury were in the flue gas at 5% O_2.

Table 5. Coal Data

MTI ID	03-055	03-056	03-057		03-055	03-056	03-057
Date	3/28/03	4/1/03	4/2/03		3/28/03	4/1/03	4/2/03
ULTIMATE ANALYSIS (As Received):				ULTIMATE ANALYSIS (Dry):			
Carbon	50.67	51.80	51.75	Carbon	71.11	70.43	70.3
Hydrogen	3.51	3.64	3.46	Hydrogen	4.92	4.95	4.7
Oxygen	10.89	11.04	11.18	Oxygen	15.28	15.01	15.19
Nitrogen	0.76	0.78	0.75	Nitrogen	1.07	1.06	1.02
Sulfur	0.32	0.30	0.37	Sulfur	0.45	0.41	0.5
Ash	5.12	5.99	6.10	Ash	7.18	8.14	8.29
Moisture	28.74	26.45	26.39				
Hg, $\mu g/g$	0.063	0.087	0.067	Hg, $\mu g/g$	0.0881	0.118	0.0911
Cl, $\mu g/g$	86	118	147	Cl, $\mu g/g$	120	160	200
HHV, Btu/lb	8,723	8,989	8,989	HHV, Bty/lb	12,241	12,222	12,092
SO$_2$, lb/MBtu	0.74	0.67	0.82	Hg, $\mu g/g$ ash	19.6	28.8	18.2
Ash, lb/MBtu	5.87	6.66	6.79	Cl, $\mu g/g$ ash	1,671	1,966	2,413
Hg, lb/TBtu	7.20	9.66	7.46				
Hg, ug/dnm^3 (5%O$_2$)	8.02	10.82	8.46				

The ash composition of the coal was measured using the standard ASTM Ash Chemistry method. This composition is shown in Table 6 for one day, calculated on an SO_3-free basis. The ash compositions were also measured in the economizer ash and the ESP ash; these are shown

Table 6. Ash composition: Major elements as wt% oxides, SO₃-free basis

	Coal 3/28/03	Economizer Ash 3/28/03	ESP Ash 3/38/03
Ash composition, wt%			
SiO_2	46.7	47.9	47.5
Al_2O_3	19.9	19.5	20.1
TiO_2	1.4	1.3	1.3
Fe_2O_3	6.4	6.3	5.8
CaO	16.3	16.3	16.6
MgO	4.9	4.9	4.6
K_2O	1.1	0.9	1.0
Na_2O	1.6	1.3	1.4
P_2O_5	1.0	0.8	1.0
SrO	0.25	0.25	0.27
BaO	0.46	0.44	0.49
MnO	0.03	0.03	0.02

for comparison with the coal ash in Table 6. As expected from the blend, the ash contains significant calcium (about 16 wt% as CaO) and more iron than might be found in a typical PRB coal. The sodium content of coal was about 1.5 wt% Na_2O.

Ash samples were analyzed for loss on ignition (LOI), Hg and Cl, as shown in Table 7. The LOI of these samples was generally low. Since the ash was a pale tan color, the carbon content of the ash is probably even lower than the LOI indicates. In any case, the ash has a very low amount of unburned carbon. The ESP ash has 15-20 times more mercury than the economizer ash sample; this suggests that there is some adsorption of mercury by the ash that takes place between the economizer and the ESP (probably post-air preheater). However, the amount of mercury adsorbed on the ESP ash is less than 0.5% of the mercury in the coal. Thus, the fly ash from Rockport is very unreactive toward mercury.

Table 7. Composition of Ash

Ash sample	Date	MTI-ID	LOI, wt%	Hg, µg/g	Cl, µg/g	% Hg in Ash	%Cl in Ash
Economizer	3/28/03	03-058	0.08%	0.0053	28.6	0.03%	1.71%
ESP, silos 3&4	3/28/03	03-061	0.31%	0.0809	20.2	0.41%	1.21%
ESP, silos 3&4	3/31/03	03-062	0.37%	0.118	24.6	--	--
ESP, silos 3&4	4/1/03	03-060	0.31%	0.127	23.6	0.44%	1.20%
ESP, silos 3&4	4/2/03	03-059	0.34%	0.101	26.8	0.55%	1.11%

The chlorine content of the ash was fairly constant from the economizer to the ESP sample, suggesting that any reaction of gaseous chlorine compounds with ash takes place at temperatures above the economizer exit temperatures. Very little of the chlorine in the coal ended up in the

Table 8. Flue gas composition estimated from coal composition, except as noted.

	3/28/03	4/1/03	4/2/03
Excess Air	35%	35%	35%
O_2	4.0%	4.0%	4.0%
CO_2	13.3%	13.4%	13.5%
H_2O	10.6%	10.2%	10.0%
N_2	72.0%	72.3%	72.4%
SO_2 [ppm]	317	292	360
HCl [ppm]	7.5	10.1	12.8
NO_x [ppm]*	400	400	400
Hg, ug/dnm^3 (5%O_2)	8.02	10.82	8.46

*Estimated from previous measurements

ash, from 1.2% to 1.7% of the total chlorine was in the ash. This means that most of the chlorine in the coal was found in the gas phase.

The composition of the flue gas can be estimated from the coal composition. Based on the ash composition, we assume that all of the chlorine in the coal is present as HCl. NO_x was not measured during the mercury test period, but just prior to the test period, NO_x was about 400 ppm at full load. Table 8 gives the estimated flue gas composition.

Mercury Speciation Data

Mercury speciation data were obtained for a wide range of space velocities, from 1,000 to 10,000 hr^{-1}. At a single space velocity, data were obtained with and without ammonia.

Control of flow through the test chambers was achieved using the eductors on each, individual chamber; the compressed air flow to the eductors was regulated by the control system, based on the desired set points. Because the flow rates needed for the mercury testing are about ten times lower than those needed for the catalyst deactivation experiments, modifications were made to the operation of the system to achieve those flow rates. The manual gate valve on the outlet of the reactor was partially closed, which restricted the flow through the reactor and increased the pressure. This allowed the eductors to control flow in the desired range. This method promoted ash build-up in the reactor, however. During the tests, some of the catalyst chambers became blocked and had to be cleaned. During the tests, problems were also experienced with limitation of flow rates from the catalyst chambers caused by blocked ash filters. This was manifested by high oxygen content in the gas being sampled by the SCEM, indicating that the sample pump was pulling in outside air because of the partial blockage of the ash filters.

The catalyst was relatively new, with only about 300 hours on flue gas at the start of the mercury testing. Prior to beginning the test, the reactor was taken off-line for ash removal for several days. Therefore, at the start of the mercury measurements on 28 May, the catalyst had not been exposed to flue gas for several days.

The SCEM data consist of multiple measurements (of either elemental or total mercury). The sample period was twenty minutes for most of the test period. Figure 5 shows one test series.

In some cases, the initial points for a given sample location were not used to compute the average value. The average values and the standard deviation (of the data points used) are shown in Figure 6. The Appendix contains the complete set of measurements (average values) for all the tests. The standard deviation of the individual measurements taken at a given data point was reasonable. The average inlet concentration of elemental mercury (or total mercury) appeared stable, when inlet measurements were repeated over a period of several hours. There were some problems with excessive pressure in the catalyst chamber and sample lines due to ash blockage. This resulted in leaks in the sample line and, occasionally, unstable mercury readings.

01-April-2003: with ammonia, ~3000 hr-1
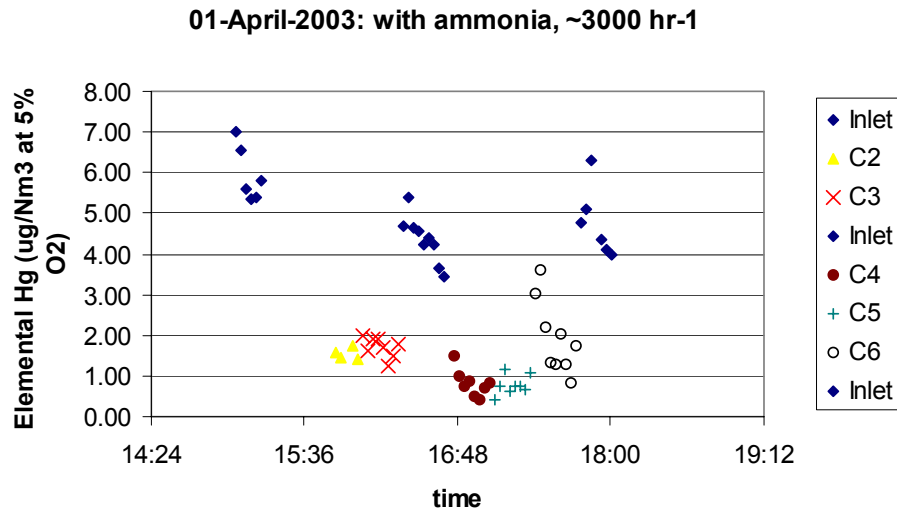
Figure 5. Mercury SCEM data (µg/Nm^3 at 5% O$_2$) for elemental mercury at 3000-7000 hr^{-1} space velocity with ammonia

01-April-2003: with ammonia, ~3000 hr-1

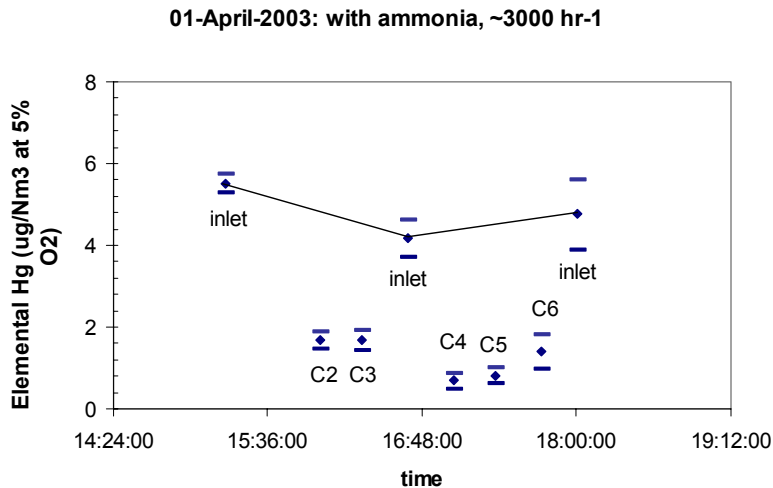**Figure 6. Average values of mercury SCEM data (µg/Nm^3 at 5% O$_2$) for elemental mercury at 3000-7000 hr^{-1} space velocity with ammonia**

On the first day of testing, Ontario Hydro measurements were made. Table 9 summarizes the three Ontario Hydro measurements, with an average value. The amount of particulate mercury was very low, about 1.7% of the total mercury measured. The ESP ash had about 0.4% of the total mercury, based on the coal composition. Both of these measurements suggest that the fly ash does not adsorb any significant amount of mercury. Figure 7 compares the average Ontario Hydro total mercury with the total gaseous mercury (averaged from the test period) from the SCEM and the total mercury based on the coal composition, all corrected to 5% O_2. There was good agreement between the total mercury measurement by SCEM, Ontario Hydro and coal composition.

Table 9. Ontario Hydro Measurements (28 March 2003); mercury concentrations in µg/Nm^3 at 5% O_2.

Gas Vol. Sampled (dscf)	Gas Vol. Sampled (Liters - dry)	Oxidized Hg (µg)	Elemental Hg (µg)	Total Hg (µg)	Oxidized Hg (µg/Nm^3)	Elemental Hg (µg/Nm^3)	Particulate (µg/Nm^3)	Total Hg (µg/Nm^3)
62.153	1760.71	1.50	11.78	13.28	0.86	6.78	0.12	7.76
62.992	1784.48	1.88	10.03	11.91	1.06	5.69	0.13	6.89
60.351	1709.66	1.97	10.18	12.15	1.17	6.03	0.13	7.33
61.83	**1751.61**	**1.78**	**10.66**	**12.45**	**1.03**	**6.17**	**0.13**	**7.33**

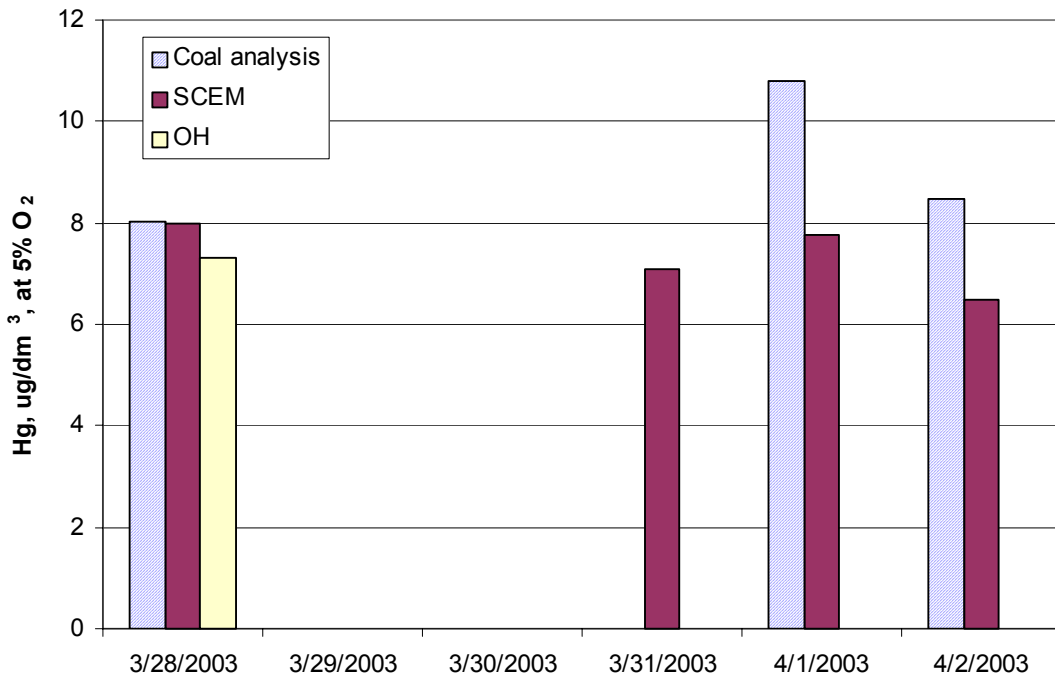**Figure 7. Total mercury measurements, μg/Nm3, corrected to 5% O₂**

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The Ontario Hydro measurement corresponded to 81% of gaseous mercury as elemental. Table 10 compares the Ontario Hydro mercury speciation with the average values of the gas-phase speciation as measured by the SCEM at the inlet to the slipstream reactor. The SCEM values for elemental mercury tend to be lower than the Ontario Hydro value, though it is hard to generalize, since the Ontario Hydro measurement was only made on one day.

Table 10. Experimental conditions and speciation of gaseous mercury, average values measured by SCEM, unless otherwise noted.

| Date | Temperatures, ^{o}F | | | Space Velocity | NH$_3$ (avg) ppm | Inlet Mercury | | |
	Boiler Duct	Entrance	Chamber			Hg^0, µg/Nm^3, 5% O$_2$	Hg$_T$, µg/Nm$_3$, 5% O$_2$	%Elemental Hg
3/28/03[1]						6.17	7.64[2]	81%
3/28/03	727	651	657	medium	408	5.88	8.00	74%
3/31/03	719	631	657	medium	452	5.00	7.00	71%
4/1/03	719	602	657	low	555	4.82	7.75	56%
4/1/03	717	625	656	medium	523		7.82	
4/2/03	724	641	662	medium	0	6.04	6.47	93%
4/2/03	726	658	667	high	435	4.81	6.47	80%

1 Ontario Hydro measurement
2 Gaseous mercury only

From the SCEM data on mercury at the inlet and outlet of the chambers, we can calculate the loss of total mercury across the chamber and the loss of elemental mercury across the chamber. The inlet value (either Hg^0 or total Hg$_T$) was measured periodically when the chamber outlet values were being measured (see Figure 6 for an example). In general, inlet value was fairly constant during a measuring period. In order to calculate the loss of elemental or total mercury across individual chambers, the inlet value was interpolated at the appropriate time.

Figure 8 shows that some loss of total mercury was observed across the commercial catalysts, but not across the blank monolith. The values shown in the figure were calculated from average values of inlet and outlet mercury. The error bars on the figure were computed from the standard deviation of the average measured values using a quadratic formula. Note that errors in the measurement itself have not been included.

There was no loss of total mercury across the blank monolith, but there was loss of mercury across the commercial catalysts. It is important to note that the inlet sample line is approximately three times longer than the outlet sample lines; all are heated stainless steel. There are Teflon lines inside the heated switching valve assembly. If there were a significant loss of mercury in the samples lines, there would be less mercury measured from the inlet line as compared to the outlet line from the blank monolith. That was not observed.
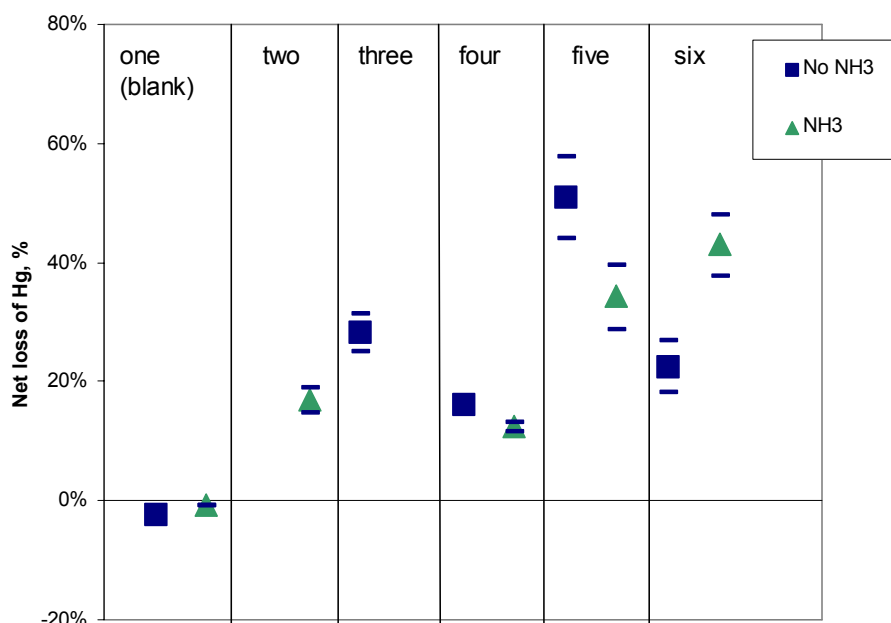
Figure 8. Calculated loss of total mercury across catalyst chambers for space velocity of approximately 7,000 hr^{-1}, with and without ammonia

There are several possible explanations for the observed loss of mercury on the commercial catalysts and the absence of such loss across the blank monolith. There could be adsorption of mercury by the commercial catalysts. This has been observed by URS and others on fresh catalyst. In the first test series, the catalysts had been exposed to flue gas in total for only 200-300 hours. Furthermore, the catalysts were off-line for cleaning right before the mercury testing began. Thus, if there were a transient adsorption of mercury, it might have been more pronounced at the start of the testing. In Figure 9, the loss of total mercury across the catalysts is plotted as a function of time from the start of flue gas flow; this graph starts at zero, corresponding to the time when the slipstream reactor was brought back on line after cleaning. There is no clear effect of time in the range of 0 to 80 hours.

One of the problems that could occur in the sampling system is preferential loss of oxidized mercury. Elemental mercury is expected to be less reactive with surfaces in the sampling system than oxidized mercury. If oxidized mercury were preferentially being removed in the sampling system, one would expect to see larger losses of total mercury as the amount of oxidized mercury at the outlet of the reactor increased (or the amount of elemental mercury decreased). Instead, the opposite trend was observed in Figure 10: the loss of mercury across the commercial catalysts was greatest when there was more elemental mercury leaving the catalyst. Note that this was not true for the blank monolith, which had a lot of elemental mercury leaving the catalyst but no loss of total mercury across the catalyst.
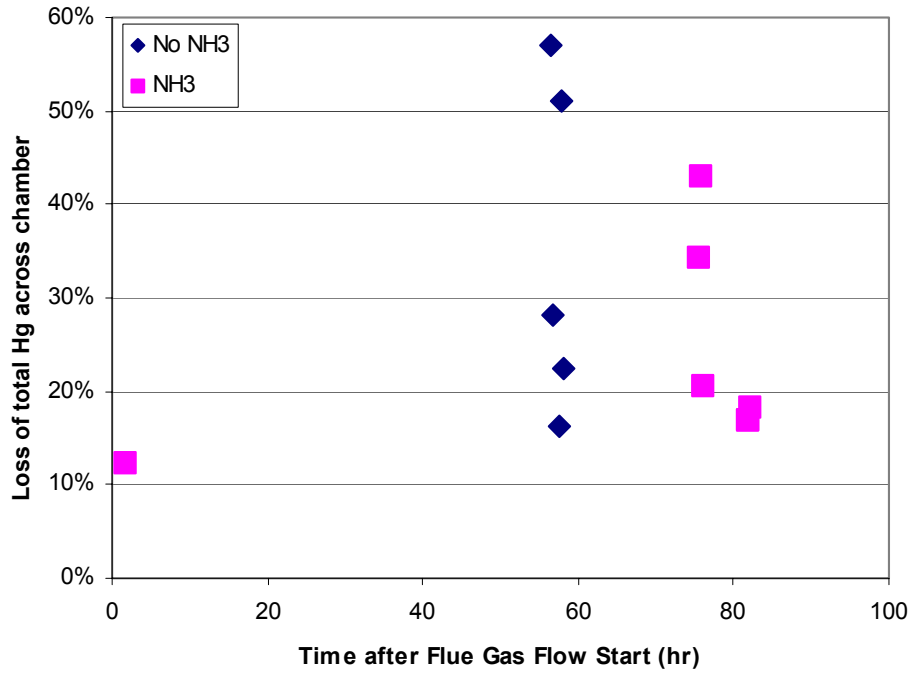
Figure 9. Loss of total mercury across commercial catalysts as a function of time since last start-up of reactor.
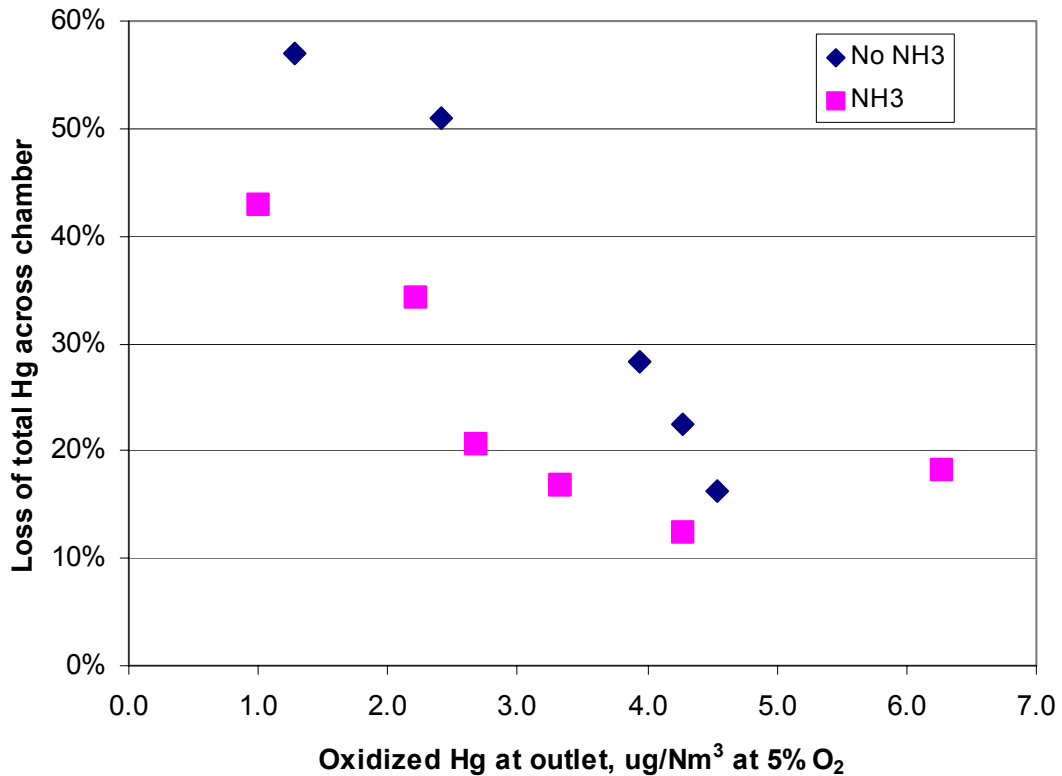
Figure 10. Loss of total mercury across commercial catalysts as s function of oxidized mercury at outlet (estimated from separate elemental mercury measurements)

Finally, we looked at the effect of space velocity on loss of total mercury in Figure 11. There was no discernible effect of space velocity, although that might be expected if the loss of mercury represented an adsorption phenomenon.

In conclusion, there was a loss of total mercury across the commercial catalysts, but not across the blank monolith. This suggests that the loss was not in the sampling system, but rather associated with active catalyst. Over the time period of the testing, the amount of time that the catalyst was exposed to flue gas did not seem to influence the loss of mercury.
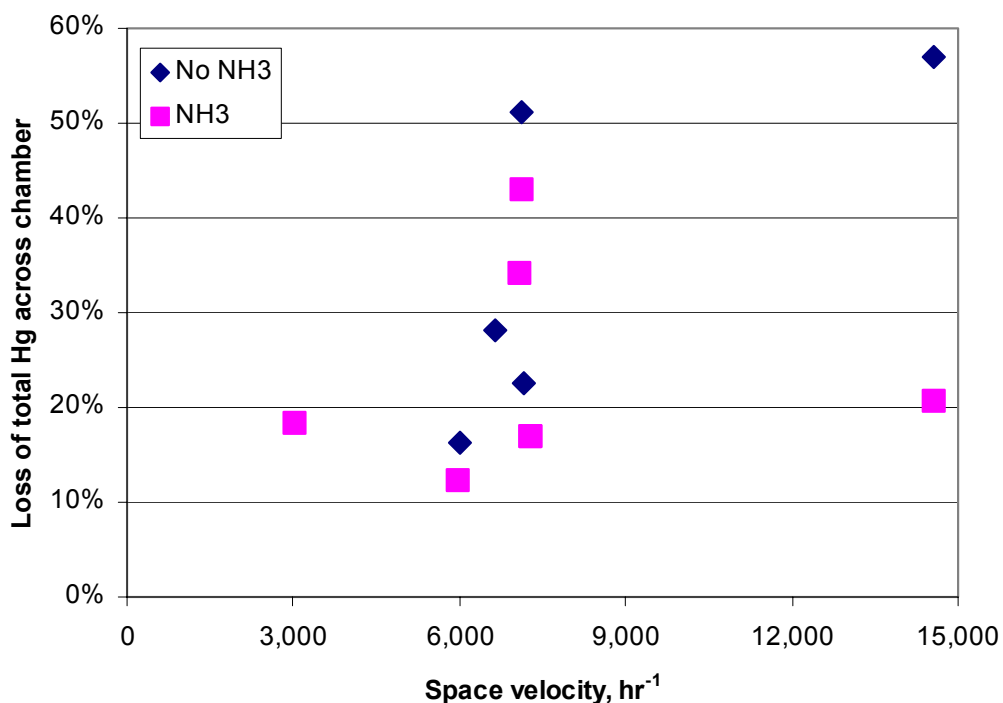
Figure 11. Loss of total mercury across commercial catalysts as a function of space velocity

If the loss of total mercury were due to adsorption of elemental mercury by the catalyst, the product of that adsorption would almost certainly be oxidized mercury. Thus, if the loss of total mercury across the catalyst were due to adsorption of elemental mercury (as suggested), then the change in elemental mercury across the catalyst should be a valid measure of mercury oxidation, even if there are losses of total mercury.

The effect of space velocity on mercury oxidation is shown in Figure 12. The points in Figure 12 are calculated from the measured outlet elemental mercury and the interpolated value of the inlet elemental mercury. The values shown in the figure were calculated from average values of inlet and outlet mercury. The error bars on the figure were computed from the standard deviation of the average measured values using a quadratic formula. Note that errors in the measurement itself have not been included.
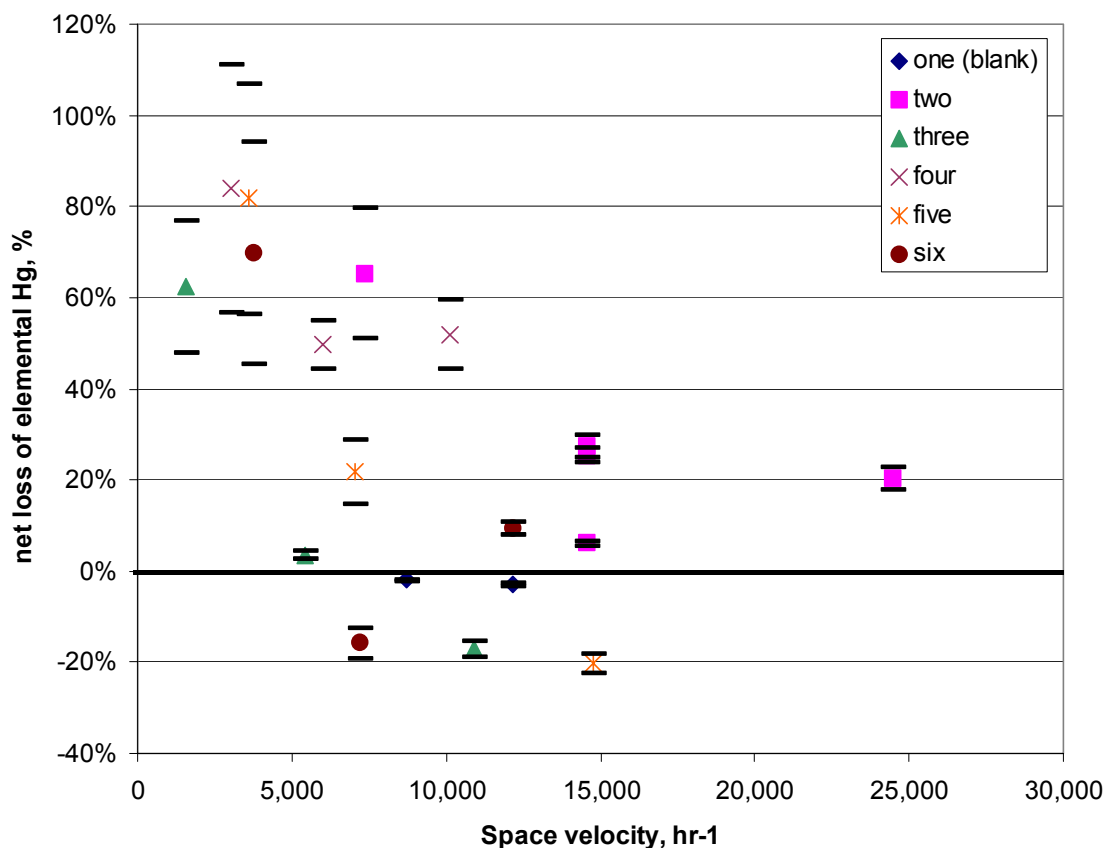
Figure 12. Oxidation (net loss of elemental mercury) at 650°F as a function of space velocity for excess ammonia

Other slipstream work, particularly that done by URS, has shown that mercury oxidation decreases with increasing space velocity (that is, decreasing residence time). The data from the first test series show the same trend that has been seen elsewhere.

The blank monolith showed no oxidation. One of the monolith catalysts and one of the plate catalysts showed considerable oxidation at high space velocities, but the other commercial catalysts did not. At typical space velocities for full-scale SCR catalysts, the oxidation was 60-80%.

The presence of ammonia has been demonstrated to inhibit oxidation of mercury in some cases. Figure 13 compares oxidation with and without ammonia for space velocities in the range of 6,000 to 7,000 hr^{-1}. This is higher than the range for full-scale catalysts, but serves to better illustrate the effect of ammonia. Catalyst C1 (blank monolith) does not show any mercury oxidation, with or without ammonia present. Catalysts C3 and C6 (plate and monolith, respectively) clearly show an effect of ammonia. Catalysts C4 and C5 (plate and monolith, respectively) appear to show an effect of ammonia, although the error bars for the no-ammonia case are large. The amount of oxidation without ammonia was about the same for all the catalysts (approximately 80%), but when ammonia was present, there was a much larger range of mercury oxidation values.
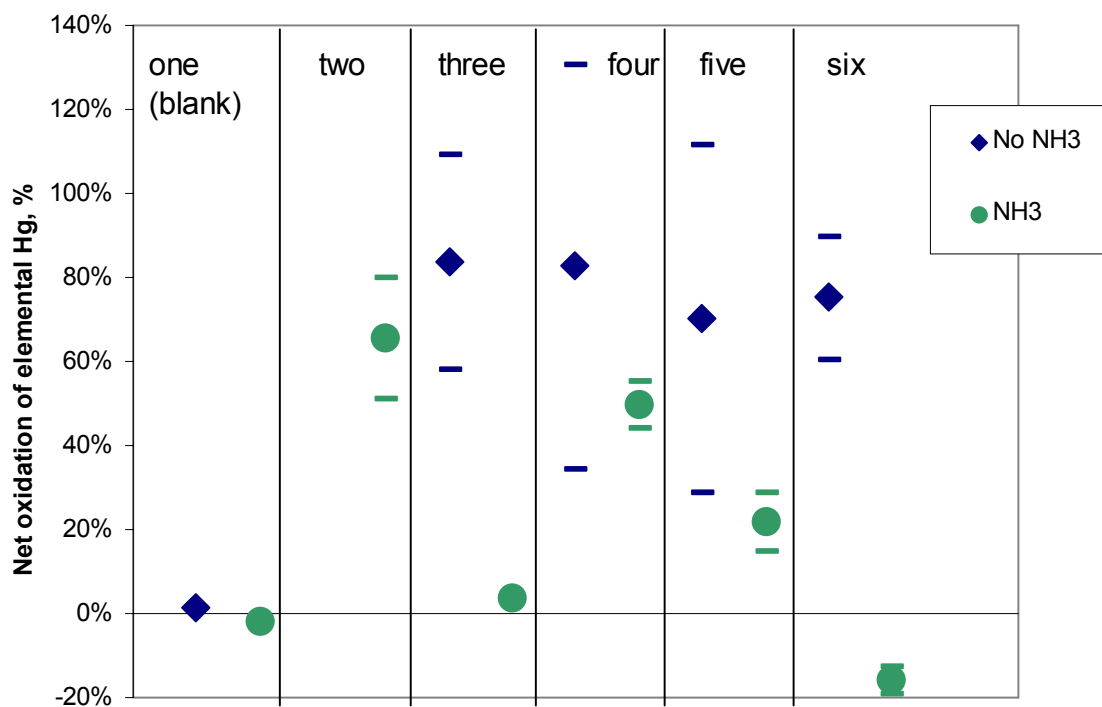
Figure 13. Calculated loss of elemental mercury across catalyst chambers for space velocity of approximately 7,000 hr^{-1}, with and without ammonia

Plans for Second Test Series

Issues were raised by the results of the first test series regarding the quality of the data. The SCEM reading when sampling a given port seemed to need several minutes to come to a steady state value. This may have been due to the ash filters being partially clogged (as shown by high O_2 readings at the SCEM), which reduced the amount of flue gas sample going to the analyzer. The sample lines did not appear to react with mercury nor did the catalyst chambers themselves, based on the good agreement between inlet and outlet mercury measurements of the blank monolith. In addition to paying more attention to the ash filters during the second test series, we plan to investigate the transient behavior of the sampling system and analyzer when switching between channels to make sure that the SCEM gives a stable reading reliably.

The loss of mercury across the catalyst appeared to be related to the presence of active catalyst. Over the period of the first test series (about 80 hours) there was no effect of time on the mercury loss across the commercial catalysts. Adsorption of elemental mercury is suspected to be the underlying phenomenon, but it is not clear what influences this. During the second test series, we plan to examine the loss of mercury across the catalysts as a function of changes in space velocity and ammonia flow.

After analyzing the data from the first test series and discussing it with team members, the following additional issues were raised:

- Coal samples should be taken from the weigh belt feeders; some help from AEP will be required to do that correctly.

- The best way to sample the ESP ash is to empty the hoppers before the test; some help from AEP will be required to do that correctly. For the first test, ESP ash was taken from silos 3&4.

- We should make NO_x measurements at the same time as Hg measurements. URS will have to bring a more powerful sample pump in order to do that.

- Can we build a manual valve array (heated) to vent the other lines to the atmosphere while not being sampled?

- Regarding loss of Hg across catalyst, Lynn Brickett from NETL noted that turning the ammonia off and then turning it back on again produced a big slug of Hg at the outlet in full-scale sampling.

- Substoichiometric ammonia (~0.9 NH_3/NO) would be better for the next test.

- We determined that we could not get the plant to run 100% PRB because that would mean dropping load too much.

A test plan for the second test series has been prepared and is being reviewed by team members.

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Conclusions

Good progress has been made on several fronts during the last three months. In particular:

- Good agreement was shown between different methods of measuring mercury in the flue gas: Ontario Hydro, semi-continuous emission monitor (SCEM) and coal composition.
- Mercury in the flue gas was predominantly elemental.
- The SCEM reading when sampling a given port seemed to need several minutes to come to a steady state value. This may have been due to the ash filters being partially clogged, which reduced the amount of flue gas sample going to the analyzer.
- There was a loss of total mercury across the commercial catalysts, but not across the blank monolith.
- The blank monolith showed no oxidation. The data from the first test series show the same trend in mercury oxidation as a function of space velocity that has been seen elsewhere.
- At space velocities in the range of 6,000-7,000 hr^{-1} the blank monolith did not show any mercury oxidation, with or without ammonia present. Two of the commercial catalysts clearly showed an effect of ammonia. Two other commercial catalysts showed an effect of ammonia, although the error bars for the no-ammonia case are large.

During the next quarter, the second test series will be completed and preliminary data analysis will be carried out.

Appendix:

Mercury Measurements from Semi-Continuous Monitor

Table A-1. SCEM Data from 28 March 2003

chamber	Time	Elapsed time, minutes	T-duct	T-entr	T-cab (avg)	SV, hr^{-1} (avg)	NH$_3$, avg ppm	End time	Elapsed	species	Hg (@5% O2)	St.Dev
inlet	9:17											
	9:47	29.98	727	652	657		386	9:49:15	32.03	elemental	5.68	0.19
one	9:48											
	10:18	29.97	732	657	659	8,718	383	10:17:35	25.97	elemental	5.77	0.34
two	10:18											
	10:48	29.97	735	660	661	14,599	382	10:48:16	28.33	elemental	4.21	0.16
three	10:48											
	11:18	29.97	731	660	662	6,640	385					
inlet	11:20											
	11:50	29.97	723	655	660		385	11:52:16	33.03	elemental	5.53	0.20
four	11:51											
	12:21	29.98	721	652	658	6,021	388					
five	12:21											
	12:51	29.98	726	654	657	12,899	387					
six	12:51											
	13:21	29.98	727	654	658	10,821	389					
inlet	13:23											
	13:53	29.98	728	655	658		390	13:54:18	28.75	elemental	5.62	0.30
inlet	13:57											
	14:16	19.53	726	654	659		427	14:17:10	20.02	elemental	5.10	0.24
two	16:18											
	17:03	44.97	726	643	657	14,565	432	17:07:11	45.80	elemental	3.77	0.26
inlet	17:05											
	17:20	14.45	728	646	654		422	17:21:29	11.43	total	7.63	0.23
one	17:20											
	17:35	14.72	730	647	654	7,177	421	17:35:47	11.43	total	7.68	0.36
three	17:35											
	17:50	14.72	727	647	654	6,545	426					
four	17:50											
	18:05	14.72	726	647	654	5,988	441	18:08:17	14.30	total	6.69	0.37

Table A-2. SCEM Data from 31 March 2003

chamber	Time	Elapsed time, minutes	T-duct	T-entr	T-cab (avg)	SV (avg)	NH3 (avg) ppm	End time	Elapsed	species	Hg (@5% O₂)	St.Dev
one	12:10											
	12:11	0.80	721	650	656	7,286	417					
two	12:11											
	12:14	2.23	721	648	655	14,538	422					
inlet	12:37											
	12:57	20.08	719	637	655		480	12:53:20	13.20	elemental	5.16	0.51
one	12:57											
	13:17	19.80	718	631	657	7,284	450	13:18:57	15.37	elemental	8.03	0.16
two	13:17											
	13:37	19.80	721	629	658	14,588	460	13:36:53	12.80	elemental	4.85	0.25
three	13:37											
	13:57	20.07	720	628	657	5,417	461	13:57:23	15.37	elemental	4.99	1.02
inlet	13:59											
	14:19	20.08	719	627	655		460	14:17:53	17.93	elemental	5.19	0.54
four	14:20											
	14:39	19.80	719	627	655	6,006	455	14:40:56	17.93	elemental	2.56	0.08
five	14:40											
	15:00	19.80	721	626	655	7,054	454	14:58:52	15.37	elemental	3.90	1.20
six	15:00											
	15:20	20.08	718	626	655	7,216	455	15:21:55	17.92	elemental	5.67	1.00
inlet	15:22											
	15:42	20.07	716	624	655		455	15:42:25	15.37	elemental	4.64	0.26
inlet	16:01											
	16:20	19.80	720	634	656		0	16:22:27	12.82	total	7.33	0.15
one	16:21											
	16:40	19.82	719	632	658	7,310	0	16:42:56	17.93	total	7.37	0.42
two	16:41											
	17:00	19.80	719	630	658	14,572	0	17:00:52	12.80	total	2.92	0.38
three	17:01											
	17:21	19.82	722	630	658	6,627	0	17:21:22	15.38	total	4.63	0.50

chamber	Time	Elapsed time, minutes	T-duct	T-entr	T-cab (avg)	SV (avg)	NH3 (avg) ppm	End time	Elapsed	species	Hg (@5% O$_2$)	St.Dev
inlet	17:23											
	17:43	20.08	719	630	657		0	17:44:25	20.50	total	6.18	0.53
four	17:43											
	18:03	19.80	717	628	659	6,003	0	18:04:55	15.38	total	5.40	0.28
five	18:03											
	18:23	19.82	718	629	659	7,122	0	18:22:50	10.23	total	3.30	0.43
six	18:23											
	18:43	19.87	720	629	658	7,181	0	18:43:20	15.37	total	5.49	1.05
inlet	18:46											
	19:06	19.80	722	633	656		0	19:01:16	12.82	total	7.48	0.27

Table A-3. SCEM Data from 1 April 2003

chamber	Time	Elapsed time, minutes	T-duct	T-entr	T-cab (avg)	SV hr^{-1} (avg)	NH$_3$, avg ppm	End time	Elapsed	species	Hg (@5% O$_2$)	St.Dev
inlet	8:37											
	8:57	19.82	716	638	657		483	8:59	12.72	total	7.48	0.68
one	8:57											
	9:17	19.80	715	631	657	1,080	520	9:20	19.17	total	9.50	0.22
two	9:17											
	9:38	20.07	714	627	656	14,559	512	9:37	11.97	total	6.07	0.33
three	9:38											
	9:58	19.82	717	625	656	4,886	520					
inlet	10:00											
	10:20	19.80	718	623	656		533	10:22	14.37	total	8.02	0.28
four	10:20											
	10:40	19.82	718	622	656	6,009	541	10:39	9.58	total	4.90	0.49
five	10:40											
	11:00	19.80	717	621	655	7,068	542	11:00	9.58	total	5.26	0.82
six	11:00											
	11:20	20.08	718	621	655	7,141	540	11:22	7.18	total	4.56	0.53
inlet	11:22											
	11:39	16.32	715	620	654		520	11:34	7.18	total	7.97	0.11
inlet	14:58											
	15:18	19.80	720	637	661		547	15:15	7.17	elemental	5.52	0.21
one	15:18											
	15:38	20.08	718	613	662	0	677					
two	15:38											
	15:58	19.80	720	607	663	7,338	654	16:00	19.17	elemental	1.69	0.21
three	15:58											
	16:18	19.82	722	604	663	1,563	582	16:19	16.77	elemental	1.70	0.25
inlet	16:21											
	16:40	19.82	718	599	661		571	16:41	14.37	elemental	4.16	0.46
four	16:41											
	17:01	19.80	720	596	656	3,036	547	17:02	14.37	elemental	0.69	0.19

chamber	Time	Elapsed time, minutes	T-duct	T-entr	T-cab (avg)	SV hr^{-1} (avg)	NH$_3$, avg ppm	End time	Elapsed	species	Hg (@5% O$_2$)	St.Dev
five	17:01											
	17:21	20.07	722	596	649	3,591	541	17:22	14.37	elemental	0.82	0.21
six	17:21											
	17:41	19.80	721	597	648	3,771	514	17:43	14.37	elemental	1.41	0.42
inlet	17:43											
	18:03	19.80	717	595	652		529	18:00	14.37	elemental	4.76	0.85
two	18:03											
	18:23	19.82	719	594	657	7,281	511	18:24	11.97	total	6.94	0.77
four	18:24											
	18:43	19.80	718	595	657	3,008	501	18:43	11.98	total	6.82	0.50
inlet	18:46											
	19:06	19.80	714	595	657		484	19:00	9.58	total	8.35	0.35

Table A-4. SCEM Data from 2 April 2003

chamber	Time	Elapsed time, minutes	T-duct	T-entr	T-cab (avg)	SV hr^{-1} (avg)	NH$_3$, avg ppm	End time	Elapsed	species	Hg (@5% O$_2$)	St.Dev
inlet	9:09											
	9:29	19.82	723	651	671		0	9:29	16.77	elemental	6.55	0.98
one	9:30											
	9:49	19.82	724	646	662	7,409	0	9:51	14.37	elemental	6.31	0.51
two	9:50											
	10:10	20.10	725	643	659	14,601	0	10:10	14.38	elemental	2.57	0.75
three	10:10											
	10:30	19.82	723	639	660	6,588	0	10:32	16.75	elemental	0.99	0.28
inlet	10:32											
	10:52	19.82	723	638	661		0	10:51	16.77	elemental	5.98	0.76
four	10:52											
	11:12	19.83	724	638	661	6,056	0	11:12	16.77	elemental	1.03	0.59
five	11:12											
	11:32	19.82	726	638	660	7,182	0	11:33	18.32	elemental	1.72	0.99
six	11:32											
	11:53	20.08	725	637	659	7,237	0	11:52	14.37	elemental	1.41	0.21
inlet	11:55											
	12:15	19.85	726	637	659		0	12:14	16.77	elemental	5.59	0.60
inlet	12:41											
	13:00	19.82	723	655	666	11,919	432	13:00	16.75	elemental	4.77	0.47
one	13:01											
	13:21	19.83	725	656	666	12,146	431	13:22	14.37	elemental	4.95	0.24
two	13:21											
	13:41	19.83	727	658	666	24,482	433	13:41	14.37	elemental	3.84	0.25
three	13:41											
	14:01	19.82	727	659	667	10,928	435	14:02	16.77	elemental	5.63	0.23
four	14:01											
	14:21	20.10	725	658	667	10,097	435	14:22	16.77	elemental	2.31	0.24
five	14:22											
	14:41	19.82	727	659	667	14,762	434	14:41	16.77	elemental	5.79	0.25

chamber	Time	Elapsed time, minutes	T-duct	T-entr	T-cab (avg)	SV hr^{-1} (avg)	NH$_3$, avg ppm	End time	Elapsed	species	Hg (@5% O$_2$)	St.Dev
six	14:42											
	15:01	19.82	726	659	668	12,179	436	15:00	14.35	elemental	4.36	0.41
inlet	15:04											
	15:24	19.80	724	658	668		438	15:21	16.77	elemental	4.86	0.54
inlet	15:26											
	15:46	19.85	726	659	668		436	15:45	16.77	total	6.47	0.35