Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems

Quarterly Technical Progress Report

April 1, 2003 – June 30, 2003

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ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-01NT41185, "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," during the time-period April 1, 2003 through June 30, 2003. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-01NT41185. EPRI, Great River Energy (GRE), and City Public Service (CPS) of San Antonio are project co-funders. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates with the byproducts from the FGD system. The current project is testing previously identified, effective catalyst materials at a larger, pilot scale and in a commercial form, to provide engineering data for future full-scale designs. The pilot-scale tests will continue for approximately 14 months at each of two sites to provide longer-term catalyst life data.

This is the seventh full reporting period for the subject Cooperative Agreement. During this period, project efforts included continued operation of the first pilot unit, conducting catalyst activity measurements, installing sonic horns for on-line catalyst cleaning, and installing the fourth catalyst, all for the GRE Coal Creek site. CPS began installation of the second mercury oxidation catalyst pilot unit at their Spruce Plant during the quarter. Laboratory efforts were conducted to support catalyst selection for that second pilot unit. This technical progress report provides an update on these efforts.

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INTRODUCTION

This document is the quarterly Technical Progress Report for the project "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," for the time-period April 1, 2003 through June 30, 2003. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-01NT41185. EPRI, Great River Energy (GRE) and City Public Service (CPS) of San Antonio are project co-funders. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. The oxidizing species are already present in the flue gas, and may include chlorine, hydrochloric acid (HCl) and/or other species. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates with the byproducts from the FGD system. The objective of this project is to test previously identified effective catalyst materials at a larger scale and in a commercial form to provide engineering data for future full-scale designs. The pilot-scale tests will continue for approximately 14 months at each of two sites to provide longer-term catalyst life data. After successful completion of the project, it is expected that sufficient full-scale test data will be available to design and implement demonstration-scale or commercial-scale installations of the catalytic mercury oxidation technology.

The two utility team members are providing co-funding, technical input, and host sites for testing. GRE is providing the first test site at their Coal Creek Station (CCS), which fires a North Dakota lignite, and CPS is providing the second site at their J.K. Spruce Plant, which fires a Powder River Basin (PRB) subbituminous coal. These two host sites each have existing wet FGD systems downstream of high-efficiency particulate control devices, an ESP at CCS and a reverse-gas fabric filter at Spruce**.**

The remainder of this report is divided into five sections: an Executive Summary followed by a section that describes Experimental procedures, then sections for Results and Discussion, Conclusions, and References.

EXECUTIVE SUMMARY

Summary of Progress

The current reporting period, April 1, 2003 through June 30, 2003, is the seventh full technical progress reporting period for the project. Efforts over the current period included continued operation of the first mercury oxidation catalyst pilot unit with three catalysts installed, conducting catalyst activity measurements, installing sonic horns for on-line catalyst cleaning, and installing the fourth catalyst, all at the CCS site. Installation began on the second pilot unit, which was built with EPRI funding, at CPS' Spruce Plant. A limited number of laboratory evaluations of catalyst materials for the Spruce Plant pilot tests were also conducted.

The first pilot unit is installed at the outlet of an induced draft fan and downstream of the cold-side electrostatic precipitator on Unit 1 at CCS. An SCR catalyst and a palladium-based catalyst (Pd #1) have been in operation since October 3, 2002. A third, subbituminous ash-based catalyst, SBA #5, was installed in the pilot unit the first week in December. The fourth, Carbon #6 (C #6) catalyst was installed during the current quarter, and placed in service on June 5, 2003.

Two catalyst activity measurement trips were conducted, one in late April and one in mid-June. As described in previous quarterly technical progress reports[1,2], an increase in pressure drop has been seen over time across the three catalysts in service at CCS. In January, it was determined that the pressure drop increase and a corresponding reduced mercury oxidation activity were due to buildup of fly ash within the catalysts. The catalysts were cleaned of fly ash and measurements showed that their activity was restored. After some investigation, it was decided that a sonic horn might allow continued catalyst operation with minimal fly ash buildup. A horn was procured and installed on one compartment (Pd #1) in March. After about two months of operation with the horn in service, it appeared to be effective in limiting fly ash buildup. After two months, the pressure drop across the Pd #1 catalyst remained at about 0.3 in. H_2O, and measurements in April showed that the Pd #1 catalyst maintained high activity for elemental mercury oxidation (>90% oxidation at a 2000 acfm flue gas flow rate).

Based on this success, three more sonic horns were procured during the quarter, and were installed on the pilot unit by GRE personnel the week of June 2. At the same time, the three catalysts were cleaned of fly ash buildup (the buildup was very minor in the Pd #1 catalyst with the operating horn), and the fourth catalyst (C #6) was installed. The pilot unit was started back up on June 5 with all four catalysts in service and sonic horns operating on all four compartments. A catalyst activity measurement trip was conducted the following week, and showed high activity (>90% Hg^0 oxidation) for the Pd #1 and new C #6 catalysts but significantly lower activity (about 50% oxidation) for the SCR and SBA #5 catalysts.

Also during this reporting period, CPS began installation of the second catalyst pilot unit at their Spruce Plant. Laboratory testing continued during the quarter to support the selection and sizing of catalyst materials for pilot-scale evaluation at Spruce. No subcontracts were issued or completed during the current reporting period.

Problems Encountered

There were no significant new problems encountered during the reporting period.

Plans for Next Reporting Period

The next reporting period covers the time-period July 1 through September 30, 2003. The pilot unit at CCS will remain in operation with all four catalysts in service and sonic horns operating in each compartment to prevent fly ash buildup. Routine sampling trips will be conducted to evaluate catalyst activity at CCS. An intensive flue gas sampling trip (Ontario Hydro measurements across each catalyst chamber) is scheduled to occur in late July. The original project schedule called for these measurements to have been made after seven months of pilot unit operation (~May 2003). However, the schedule for this trip was adjusted to ensure the fly ash buildup problems had been resolved and that the C #6 catalyst had been installed and reached mercury adsorption equilibrium.

One project team member, EPRI, funded the construction of a second oxidation catalyst pilot unit that will be used for testing at CPS' Spruce Plant. During the coming quarter, CPS will complete the installation of that pilot unit, and startup of the pilot unit should commence near the end of the quarter. Catalyst procurement activities will also occur during the quarter.

Prospects for Future Progress

During the subsequent reporting period (October 1 through December 31, 2003), and likely continuing into calendar year 2004, the first pilot unit is to remain in operation at CCS, and be evaluated for elemental mercury oxidation activity through routine (~monthly) evaluation trips. A final intensive flue gas sampling trip will occur at the end of the long-term catalyst evaluation period at CCS (~first quarter of calendar year 2004). Pilot testing should be completed at CCS approximately at the end of the first quarter of 2004.

Catalyst testing should commence at the second site, CPS' Spruce Plant, late in the next reporting period (July 1 through September 30, 2003). An initial intensive gas characterization effort for the Spruce Plant site should occur early in the subsequent quarter (October 1 through December 31, 2003).

EXPERIMENTAL

The work described in this technical progress report was conducted using two different experimental apparatuses. One is an elemental mercury catalyst oxidation pilot unit (8000 acfm of flue gas treated) located at GRE's CCS Station in North Dakota. The pilot unit has four separate compartments that allow four different catalysts to treat flue gas from downstream of the host plant's particulate control device and upstream of its FGD system. Details of the pilot unit design, construction, catalyst preparation and pilot unit operation have been discussed in previous quarterly technical progress reports[2, 3, 4, 5]. The activity of these catalysts is being determined by measuring the change in elemental mercury concentration across each catalyst, while ensuring that the total mercury concentrations do not change significantly across the catalyst. These measurements are primarily being conducted using a mercury semi-continuous emissions monitor (SCEM) developed with funding from EPRI. The analyzer has been described in a previous report[6]. Periodically, the analyzer results are being verified by conducting manual flue gas sampling efforts in parallel across each catalyst chamber by the Ontario Hydro method.

The second experimental apparatus is a bench-scale test unit that is used to evaluate the activity of candidate catalyst cores under simulated flue gas conditions. The testing is being conducted at simulation gas flow rates of approximately 1 to 2 nl/min. The simulation gases contain a mixture of compressed gases intended to approximate flue gas compositions at the pilot unit host sites. The simulation gases include nitrogen, oxygen, carbon dioxide, water vapor, sulfur dioxide, nitrogen oxides, hydrochloric acid, elemental mercury, and a small amount of mercuric chloride. As for the pilot units, an EPRI SCEM is used to measure catalyst activity for oxidizing elemental mercury in the simulation gases. The bench-scale catalyst oxidation test apparatus has also been previously described in quarterly technical progress reports[4, 5].

During the current quarter, an additional type of measurement was conducted. During the April catalyst activity measurement trip to CCS, an impinger filled with recycle slurry from the full-scale wet lime FGD system at CCS was inserted into the sample gas path to the mercury SCEM used to quantify catalyst performance. Results with the slurry impinger in the sample gas path were compared to results without the impinger in line to provide an indication of the potential effectiveness of the FGD absorbers at CCS for removing catalytically oxidized mercury from the flue gas.

Figure 1 is a schematic of the sample gas configuration for these tests. The 500-ml stainless steel impinger was filled about half way with a fresh sample of the FGD slurry, sealed, and heated to about 55^{o}C with heat tape and insulation. Flue gas flow through the impinger was the same as that going to the mercury SCEM, 1 nl/min. The slurry samples were changed after a few analyzer measurement cycles to limit pH drop in the impinger slurry. In the FGD system, the pH of the recycle slurry is maintained at a constant value by lime slurry makeup, but in the impinger the pH drops with time due to absorption of SO_2 from sample gas.

The results of the impinger tests conducted in April are presented in the following section of this report.

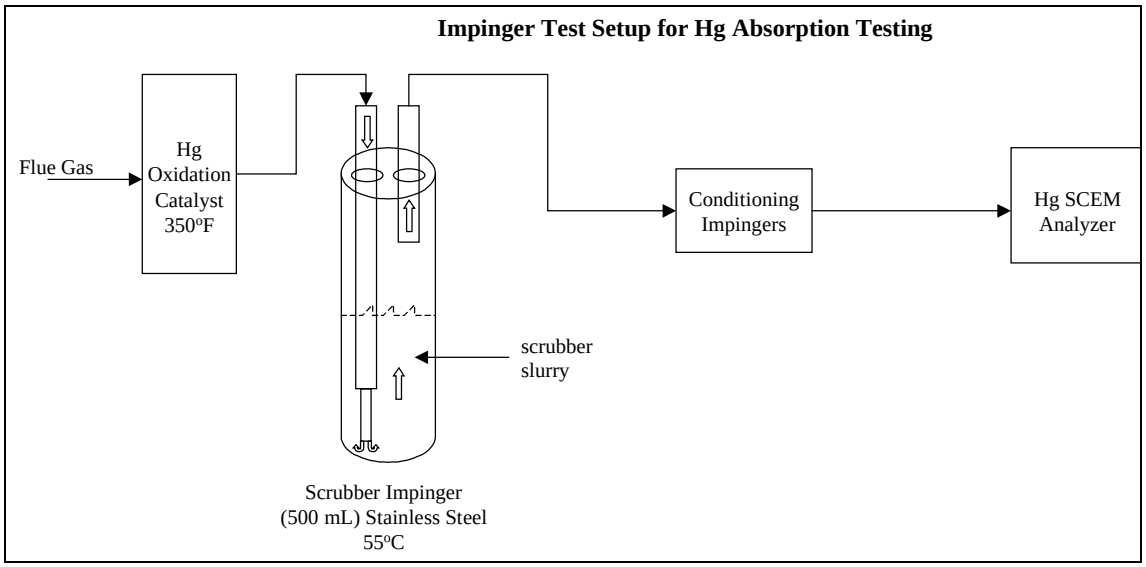

Figure 1. Schematic of Test Apparatus with Impinger Scrubber

RESULTS AND DISCUSSION

This section provides details of technical results for the current reporting period (April 1, 2003 through June 30, 2003). The technical results presented include a discussion of the data from pilot unit testing at CCS and results of laboratory evaluations of catalyst materials. There are no results yet to report for the second pilot unit at CPS' Spruce Plant.

Pilot Unit Operation at CCS

As described in the previous quarterly reports, the first pilot unit was started up at CCS with the SCR and Pd #1 catalysts the first week of October 2002. The other two catalysts (SBA #5 and C #6) were not yet available, so testing began with only two of the four catalysts installed. Initial catalyst activity measurements were made using the EPRI mercury SCEM, which has been described in earlier progress reports. The October results showed high activity for the Pd#1 catalyst, over 90% of elemental mercury across the catalyst, as was expected based on previous laboratory and field testing with this material. The SCR catalyst results showed significantly lower oxidation percentages at the same flue gas flow rates, in the range of 60 to 70% oxidation of elemental mercury across the catalyst. Throughout this report, the elemental mercury oxidation percentages across catalysts are reported based on the drop in elemental mercury concentration across the catalyst, and do not just reflect the total flue gas mercury oxidation percentage at the catalyst outlet.

By December 2002, activity measurement results showed a marked decrease in activity for both catalysts. The percentage oxidation of elemental mercury across Pd #1 dropped from greater than 90% in October to 50-70% in December, and across the SCR catalyst dropped from 60-70% in October to 20-30% in December. Follow-up testing in January determined that the catalyst surfaces were becoming plugged due to a buildup of fly ash, in spite of the catalyst being installed downstream of a high-efficiency ESP. This was confirmed by observed pressure drop increases across the catalyst chambers, and by physically inspecting the catalysts to observe and clean out the fly ash buildup.

The third catalyst, SBA #5, was installed in December, 2002. The January trip provided the first opportunity to measure the activity of the SBA #5 catalyst after it had time to achieve adsorption equilibrium. However, it too was adversely affected by fly ash buildup.

It was decided that a method of mechanical cleaning should be implemented on the pilot unit. Both air soot blowers and sonic horns were considered. After reviewing full-scale SCR experience with on-line catalyst cleaning and talking to a number of soot blower and sonic horn vendors, it was decided that a sonic horn would be the easiest field retrofit at CCS and would offer a good probability of success. A small, 17-inch horn produced by Analytec Corporation of Pagosa Springs, Colorado appeared to be the best solution based on price, availability, and probability of success. During the last week of March 2003, an Analytec sonic horn was installed on the Pd #1 catalyst box to provide an occasional pulse of acoustic energy to the catalysts to dislodge accumulated particulate matter. The horn was installed on the top wall of the catalyst housing inlet transition, approximately 1.5 feet upstream of the first catalyst module. The horn was programmed to sound for 10 seconds every half hour.

At the time the sonic horn was installed, the catalyst housing was opened and the Pd #1 catalyst modules were cleaned. Thus, the sonic horn test on the Pd #1 catalyst was begun with a relatively clean (of fly ash buildup) catalyst charge.

The plan was that, if effective, a horn would be installed on each of the other catalyst chambers. After the pilot unit was placed back in service on March 27, it was clear that the horn was effective at controlling the pressure drop across the Pd #1 catalyst. Figure 2 illustrates the pilot unit pressure drop data for all three catalysts from October 2002 (December 2002 for the SBA #5 catalyst) through May 27, 2003.

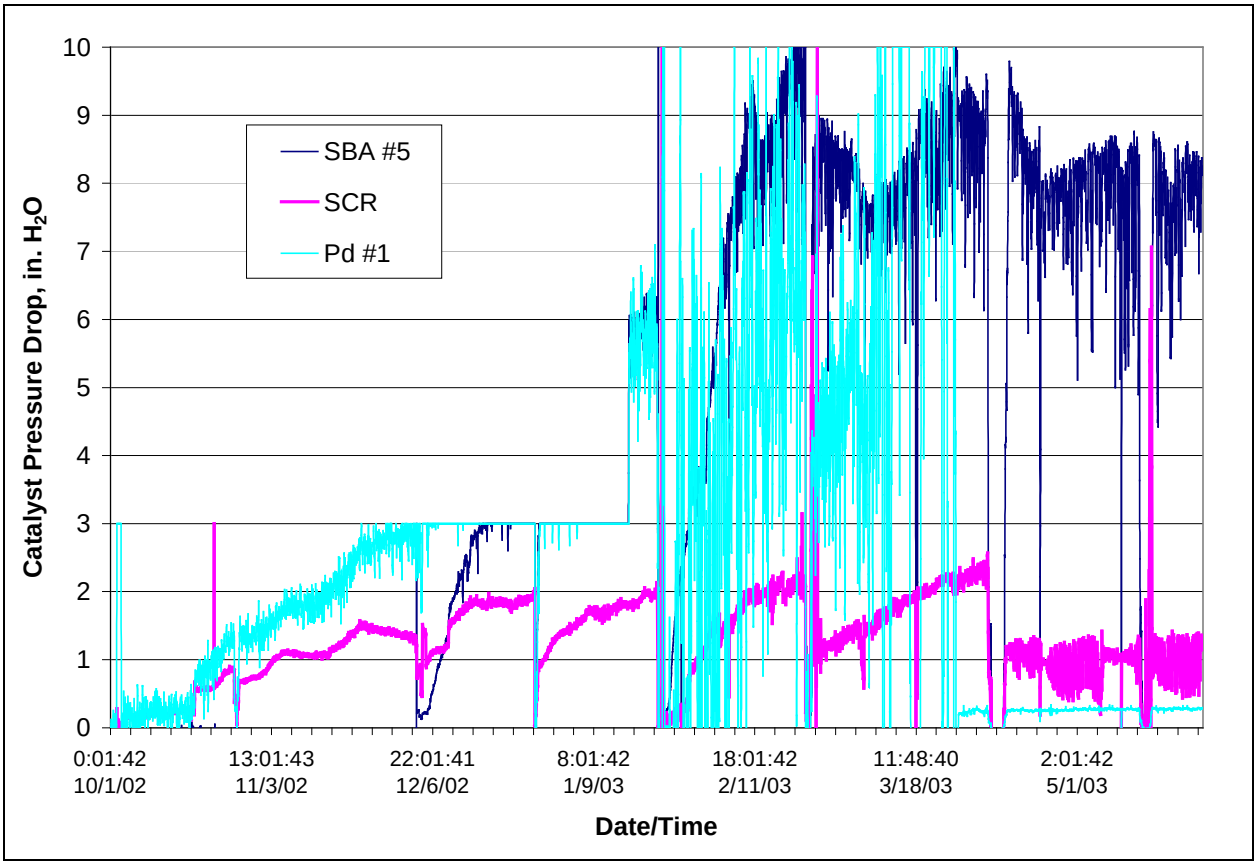

Figure 2. Pressure Drop Data for the Three Catalysts in Service at CCS through May 27.

The data for Pd #1 (the lightest shaded line on the figure) show the pressure drop pegged at over 3 in. H_2O from early December 2002 through late January 2003. In January, the pressure differential transducers were recalibrated to measure up to 10 in. H_2O differential, and the differential across the Pd #1 chamber was measured at 5 to 6 in. H_2O. Shortly thereafter, the pilot unit was taken off line and the catalyst was cleaned of fly ash. After the catalyst was cleaned and the pilot unit was put back into service, the signal from the pressure differential transducer on the Pd #1 catalyst was producing a noisy signal. However, on average the pressure drop across the Pd #1 catalyst increased to 6 or 7 in. H_2O within three weeks of operation. After a host unit trip the pressure drop was reduced to about 4 to 5 in. H_2O, then increased again until the pilot unit was brought off line in late March to install the sonic horn. Between the time when the catalyst

came back on line with the horn was installed and the end of May (a period of two months), the pressure drop across the Pd #1 catalyst increased by only 0.1 in. H_2O, ending at 0.3 in. H_2O.

However, the effectiveness of the horn could not be confirmed until it could be verified that the Pd #1 catalyst also retained high activity. A catalyst activity measurement trip was conducted the week of April 23 to determine whether the horn also allowed the Pd #1 catalyst to remain at high activity for elemental mercury oxidation.

When the URS samplers arrived the morning of April 23, the pilot unit was found off-line due to a station power outage on April13. The unit did not restart when power was restored, as it was intended to, apparently due to a problem with an "uninterruptible power supply" (UPS) used as a power conditioner for the pilot unit control computer. The power outage was long enough to run down the battery backup in the UPS, and the UPS did not reset automatically after power was restored. The pilot unit was restarted on April 23, and ran overnight while total mercury concentrations were measured at the outlet of each catalyst.

On April 24, the oxidation performance was measured for the three installed catalysts. The results of these measurements are summarized in Table 1.

Table 1. Summary of Catalyst Activity Results from CCS, April 2003

Flue Gas Sample	Total Hg Concen-tration ($\mu g/Nm^3$)	Elemental Hg Concen-tration ($\mu g/Nm^3$)	Overall Hg Oxidation (% of total)	Observed Hg Adsorption across Catalyst (%)	Hg^0 Oxidation across Catalyst (%)	Flue Gas Flow Rate (acfm)	Catalyst Area Velocity (sft/hr)
Inlet to Pilot Unit	18.62	8.92	52	NA*	NA	NA	NA
SBA #5 Out	18.74	8.04	57	0	10	2000	33
SCR Out	18.39	7.89	57	1	12	1500	14
Pd #1 Out	9.45	1.01	89	49	89	2000	49

*NA – not applicable

After being off line for over a week, the Pd #1 catalyst appeared to have renewed mercury adsorption capacity – the catalyst outlet total mercury concentration was about half of the inlet value. Oxygen concentration measurements on the sample gas from the Pd #1 outlet showed normal O_2 levels, so there was no indication of a leak in the sample from that box. Such a leak could have introduced a low bias in the outlet total mercury measurements. The catalyst and SBA #5 catalyst were not adsorbing any mercury according to these results.

Activity results showed that the Pd #1 catalyst, after being kept clean with the sonic horn, was achieving about 90% oxidation of elemental mercury while the "dirty" SCR and SBA #5 catalysts were relatively inactive (10-12% elemental mercury oxidation). However, the Pd #1 results are confounded by the apparent mercury adsorption (i.e., some of the drop in elemental mercury concentration across the Pd #1 could be due to adsorption rather than oxidation).

In spite of this confounding effect, the Pd #1 results were taken to be quite encouraging. Elemental mercury concentrations of nearly 10 μg/Nm^3 at the inlet were lowered to an average of 1.0 μg/Nm^3 at the outlet of that catalyst, with some measurements as low as 0.6 μg/Nm^3. Based on the relatively high activity and low pressure drop values for Pd #1, efforts to procure and install similar Analytec sonic horns on the other three boxes were begun.

It was also planned that the fourth catalyst (C #6) would be installed at the same time as the sonic horn installation. Since the sonic horn installed on that compartment should prevent fly ash buildup, this catalyst should be able to avoid operation with substantial fly ash plugging or fouling.

The sonic horns were installed by CCS plant personnel the first week of June. On June 2, the pilot unit was again found to be off line, this time apparently due to a station power outage the evening of May 27. After two such occurrences within a period of two months, the problematic UPS was replaced with a new unit. The new unit was first tested to ensure that it will start back up automatically when power is restored after an extended power outage.

The catalyst chambers were opened on June 2nd and 3rd without first restoring flue gas flow, and fly ash buildup was cleaned out with compressed air. For the Pd #1 catalyst, none of the catalyst cells were plugged, but some fly ash was observed to blow out of each cell when it was cleaned.

The fly ash buildup was more substantial in the SCR and SBA #5 catalysts. For the SCR catalyst, it appeared that a circle of cells about 18 inches in diameter was all that remained open for flue gas flow; all of the outboard cells appeared to be plugged with fly ash. The fly ash was relatively dry and free flowing, and the SCR catalyst was readily cleaned out.

The fly ash buildup on the SBA #5 catalyst was more substantial and appeared to be more tenacious. It was not clear how flue gas was flowing through the SBA #5, as virtually all of the cells on the front face of the first catalyst layer looked to be plugged. The ash seemed to have been partially “set up,” and it took more effort to blow the fly ash deposits loose with compressed air than was required with the SCR catalyst. This apparent setting up may have been a result of the pilot unit being off line for several days prior. This allowed the catalyst chambers to cool, and they were not purged of moist flue gas at the time of the unplanned power outage.

Not all of the plugged catalyst cell openings on the first layer of catalyst could be cleaned with compressed air. Some buildups were too tenacious, so the plugs were left in place. It was estimated that approximately 2% of the cells in the first catalyst layer were left plugged. Also, the screens that hold the catalyst blocks in place in the catalyst “cans” had become bowed over time. This bowing reduced the clearance between catalyst layers, which made it difficult to get the compressed air probe in position to clean all of the cells in the second and third layers. The buildup in the second and third layers appeared to be much more dry and free flowing than on the face of the first layer, though.

The horns were installed on the other three compartments (the initial horn remained on the Pd #1 compartment), and the fourth catalyst (C #6) was installed. Figure 3 shows a typical sonic horn installation on a catalyst chamber inlet transition duct.

Figure 3. Typical Sonic Horn Installation on the Pilot Unit at CCS.

The pilot unit was restarted on June 5 with all four catalysts installed and the sonic horns in service on each compartment (10 seconds each every 30 minutes). A catalyst performance measurement trip was conducted the next week (June 11-12) after nearly one week in operation. The results from this trip (using the EPRI Hg SCEM for measurements) are summarized in Table 2.

The results show that the Pd #1 remains highly active (90% elemental mercury oxidation at 2000 acfm) and that the new catalyst (C #6) appears to be very active (97% oxidation). Both of these catalysts were still adsorbing some Hg at the time of these measurements (~15% adsorption by the Pd, 25% by the C #6), so these results could be biased slightly.

The SCR catalyst and SBA #5 fly ash catalyst results were less encouraging. These catalysts were measured to achieve about 30% elemental mercury oxidation at their normal flue gas flow rates. The performance of these catalysts will be monitored to see if their activity decreases further with time. If so, catalyst replacement or regeneration may need to be considered. A follow up trip is planned for July to conduct Ontario Hydro method measurements to verify analyzer results for all four catalysts and to continue tracking changes in activity with time.

With the horns in service, the pressure drop across the four catalysts is staying very low. The pressure drop values for the month of June are plotted in Figure 4. By the end of June, all four

Table 2. Summary of Catalyst Activity Results from CCS, June 2003

Sample Location	Total Hg Concen-tration ($\mu g/Nm^3$)	Elemental Hg Concen-tration ($\mu g/Nm^3$)	Overall Hg Oxidation (% of total)	Observed Hg Adsorption across Catalyst (%)	Hg^0 Oxidation across Catalyst (%)	Flue Gas Flow Rate (acfm)	Catalyst Area Velocity (sft/hr)
Normal Flow Rate Results:							
Pilot Unit Inlet	10.2	7.29	29	NA*	NA	NA	NA
SBA #5 outlet	9.88	4.76	52	3.0	35	2005	33
SCR outlet	10.0	5.26	48	1.7	28	1480	14
C #6 outlet	7.74	0.22	97	24	97	1994	30
Pd #1 outlet	8.60	0.75	91	16	90	2011	49
Alternate Flow Rate Results:							
Pilot Unit Inlet	10.4	7.29	30	NA	NA	NA	NA
SBA #5 outlet	9.88	3.79	62	4.7	48	1509	25
SCR outlet	10.0	5.44	46	3.4	25	955	9.1
C #6 outlet	7.74	0.21	97	25	97	2490	38
Pd #1 outlet	8.60	1.09	87	17	85	2456	61

*NA – Not applicable.

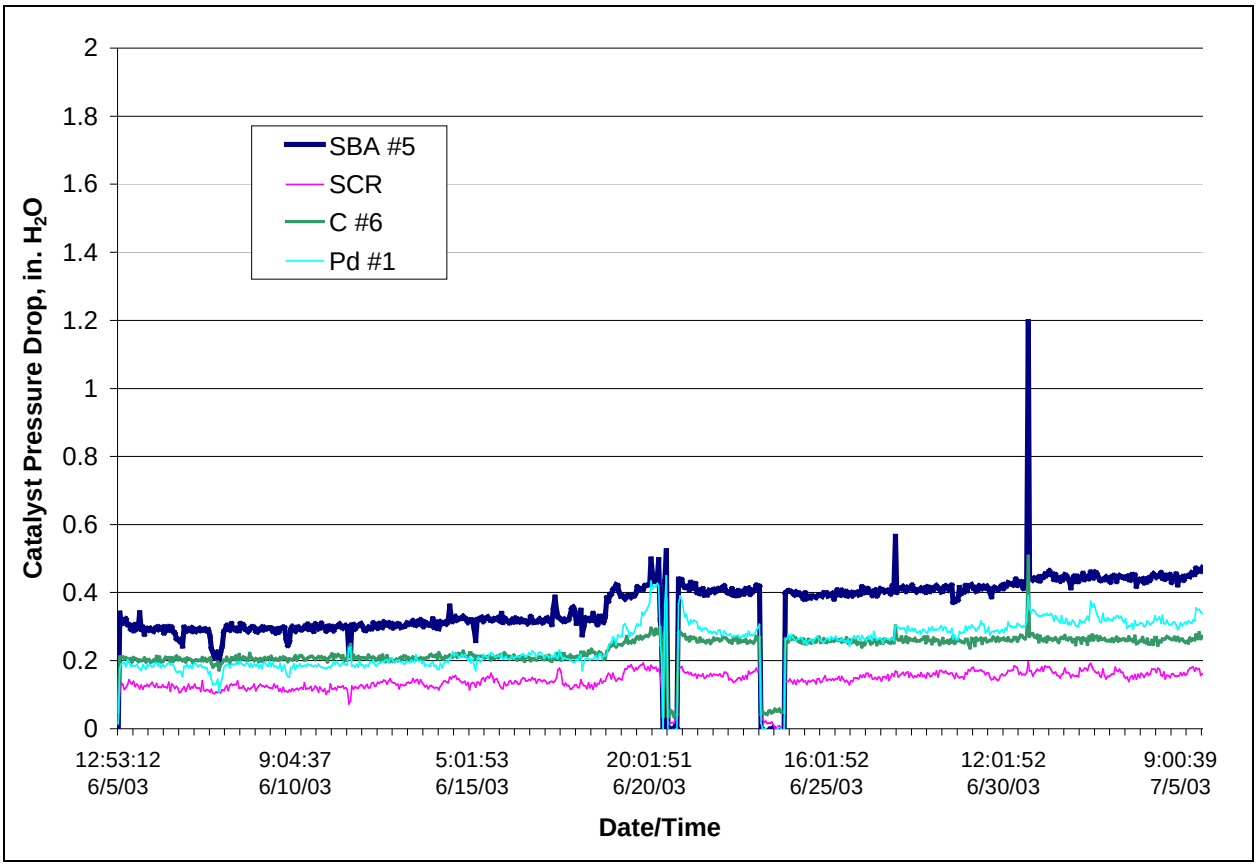

Figure 4. Pressure Drop Data for the Catalysts in Service at CCS, June 5 through July 5.

catalyst chambers measured within about 0.1 in. H_2O of the initial pressure drop from when they were restarted on June 5. At the end of June, the SBA #5 pressure drop was about 0.4 in. H_2O, the Pd #1 and C #6 was about 0.3 in. H_2O, and the SCR catalyst (larger pitch and 1500 acfm flow rate) was less than 0.2 in. H_2O.

In Figure 4, the two periods of near zero pressure drop across all four catalysts are due to a loss of compressed air to the pilot unit. The pilot control valves are operated with compressed air from the CCS Station "non-essential" air system. The station lost air pressure in the non-essential air system twice in June, and the "fail closed" control valves shut off flue gas flow until air pressure was restored. There are two other upset periods seen on the plot that remain unexplained. There was an apparent increase in pressure drop across all four catalysts that began the afternoon of June 19. CCS personnel are not aware of any coincident upsets on Unit 1 that may have been related to these pressure drop increases. Also, there was a large spike in the measured pressure drop values across three of the four compartments on July 1. This is apparently just a glitch in the recorded data.

Scrubber Simulation Test Results

During the April measurement trip, scrubber simulation tests were conducted using an impinger filled with Coal Creek FGD slurry placed in the sample line between the pilot unit and Hg SCEM, as described in the previous section. The results of these tests are summarized in Table 3.

Table 3. Results of Scrubber Simulation Tests Conducted at CCS, April 2003

Flue Gas Sample Location	Impinger Inlet Concentrations (µg/Nm^3)		Impinger Outlet Concentrations (µg/Nm^3)		Impinger Inlet Hg Oxidation (% of Total)	Impinger Outlet		Changes Across Impinger:			
	Total Hg	Hg^0	Total Hg	Hg^0		Apparent Hg^{+2} Reduction to Hg^0 (%)	Hg Oxidation (% of total)	Increase in Hg^0 (%)	Hg^{+2} Removal (%)	Total Hg Removal (%)	Hg^0 Removal (%)
Pilot Inlet	15.5	9.47	9.66	9.49	61	0	2	0	97	38	0
Pd#1 Out	7.64	0.86	2.33	2.12	89	19	9	147	97	70	-147

These results showed that the impinger simulated baseline (no oxidation catalyst) scrubber mercury removal well - about 97% removal of oxidized Hg, and virtually no increase in elemental mercury concentration across the FGD absorber. This is exactly what was measured across the full-scale scrubber by Ontario Hydro last October.[2] However, the results on the Pd #1 outlet gas appear to show evidence of "re-emissions" of elemental mercury across the impinger when treating the catalytically oxidized mercury. The elemental mercury concentration in the sample gas from downstream of the Pd #1 catalyst increased from less than 1 µg/Nm^3 to a little more than 2 µg/Nm^3 across the impinger. However, the overall mercury removal across the impinger was measured at 70% in spite of this apparent "re-emission". This control level exceeds DOE's control objectives for mercury controls for both lignite (55%+) and subituminous (65%+) coals.

The ability of the FGD system to scrub catalytically oxidized Hg requires more investigation. It is not known to what extent the "static" nature of the impinger filled with FGD slurry simulates the actual fate of Hg in a dynamic, operating FGD absorber, particularly for the catalytically oxidized Hg case. The impinger solutions were changed before each set of measurements, which limited the pH drop to about 0.5 units over the course of a set of measurements, so hopefully this relatively small change in pH did not skew the results. However, it is not known to what extent the impinger test simulated other factors that may influence mercury “re-emissions” across full-scale wet FGD absorbers. Such factors could include absorber interfacial surface area, pH drop across the absorber, gas and liquid phase mass transfer coefficients, etc.

Laboratory Evaluation of Candidate Catalysts

Testing of catalyst cores in the laboratory for mercury oxidation activity continued during this quarter, under simulated PRB (Spruce) flue gas conditions.

In previous technical progress reports for this project, data scatter was reported in laboratory results that appears to have been caused by an interference between some component in the sample gas exiting Pd #1 cores and the Tris-(hydroxymethyl)aminomethane (Tris) solution used to remove oxidized mercury from the sample gas. This apparent interference caused a high degree of variability in the measured catalyst outlet elemental mercury concentrations, and thus caused previous catalyst performance results for some sample cores to be suspect.

As a workaround for this apparent interference, the laboratory analyzer was run with KCl impinger solutions rather than Tris solutions. However, late last year it was determined that the KCl impinger solutions were being depleted very rapidly during some laboratory runs. The result of this depletion was a low bias in the indicated elemental mercury concentration. Thus, there was concern that laboratory results could be biased by depleted KCl impinger solutions.

Because of concern over depletion of the KCl impinger solutions and interferences with Tris, since early this year the laboratory run procedures were modified once again. Now, the performance of each catalyst core is measured both with fresh Tris and fresh KCl solutions. Good agreement between results with the two impinger solution types is taken as an indicator that potential biases with each solution type were avoided. If the results with the two impinger solution types do not agree well, the test is repeated.

This procedure has been used to evaluate candidate catalyst materials for the pilot testing to be conducted at Site 2, CPS’ Spruce Plant, which fires PRB coal. Table 4 compares the simulation gas compositions for CCS versus Spruce Plant simulations.

Table 5 summarizes the results of laboratory tests conducted during the current quarter at simulated Spruce Plant conditions. Figure 4 shows the results of all of the catalyst testing conducted in the laboratory at simulated Spruce conditions, including results from previous quarters for Pd #1, SBA #5 and gold catalysts.

Table 4. Gas Conditions for Host Site Simulations

Species	CCS Conditions	Spruce Conditions
SO_2 (ppm)	500	200
NO_x (ppm)	200	200
HCl (ppm)	6	6
O_2 (%)	5	5
CO_2 (%)	12	12
H_2O (%)	9	7
N_2 (%)	Balance	Balance
Temperature (^oF)	350	300

Table 5. Laboratory Simulation Results at Spruce Conditions from the Current Quarter (average using KCl and Tris impingers for measuring elemental mercury concentrations)

Catalyst	Gas Flow Rate (l/min)	Inlet Hg^0 ($\mu g/Nm^3$)	Outlet Hg^0 ($\mu g/Nm^3$)	Hg^0 Oxidation (%)
SCR catalyst; 1” core	0.94	31.0	5.37	82.7
SCR catalyst; 1" core	1.3	21.1	4.18	76.1
SCR catalyst; 1" core	1.7	16.1	4.38	77.2
C #6; 1" core	0.94	27.0	3.68	86.4
C #6; 1" core	1.3	19.6	3.97	79.7
C #6; 1" core	1.7	15.0	3.17	78.8

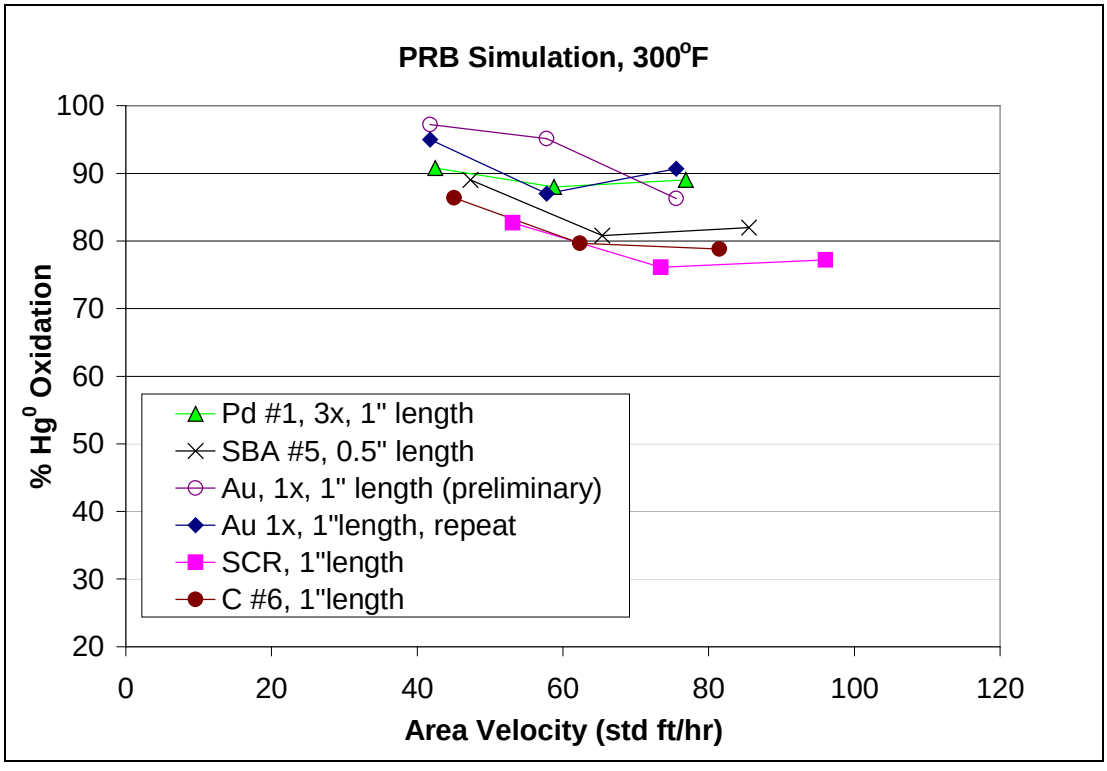

Figure 5. Effect of Area Velocity on Catalytic Oxidation of Hg^0 at Simulated Site 2 Conditions

When the results are plotted as a function of area velocity, the Pd and Au catalysts show the highest elemental mercury oxidation performance. The SCR, SBA #5 and C #6 catalyst types show lower performance, but the results very similar for these three catalysts at the simulated PRB flue gas conditions.

Catalyst Supply

During the quarter, the fourth, C #6 catalyst was installed in the pilot unit at CCS. Catalyst supply efforts are now focused on the second pilot unit, at CPS' Spruce Plant, which is expected to be operational by the end of July.

As shown above, of the five candidate catalysts, the Pd #1 and Au catalysts showed the highest elemental mercury oxidation activity in the laboratory evaluations. The SCR, SBA #5 and C #6 catalysts show similar elemental mercury oxidation performance in the laboratory when treating simulated flue gas at PRB conditions. However, of these three less active candidate catalysts, the SBA #5 material is the least likely to be available to produce commercial quantities of catalyst, as it is a unique fly ash byproduct from a single power plant. Consequently, the four catalysts to be tested in the second pilot unit at Spruce will include Pd #1, Au, SCR and the C #6 catalyst.

During July, the required catalyst dimensions will be determined based on laboratory and CCS activity results, and all four catalysts will be ordered from their respective suppliers. It is expected that the Pd #1 and Au catalysts will become available in August. The SCR catalyst may not become available until late September, due to Argillon production facilities shutting down in August for summer vacation. The C #6 catalyst will most likely take the longest time to procure because of the multiple process steps by several subcontractors that have to take place to produce this material in honeycomb catalyst form.

CONCLUSION

In the initial six plus months of pilot unit operation, it became apparent that the potential for adverse effects from the ash remaining in the flue gas downstream of a high-efficiency ESP was underestimated at the beginning of the project. After two months of operation, the Pd #1 and SCR catalysts had seen a significant loss of activity for Hg^0 oxidation and a significant increase in pressure drop. Both of these effects were attributed to fly ash buildup within the catalyst chambers and within the flow channels of the catalyst honeycomb cells. Fortunately, the collected fly ash remained dry and free flowing, and was readily removed by blowing compressed air through the catalyst cells and vacuuming up loose fly ash.

Because of the observed ash accumulation on the catalysts at CCS, provisions had to be made to help keep catalyst surfaces cleaner. Sonic horns are commonly used to clean catalysts on line in utility SCR applications for NO_X control, and appear to be similarly be effective in this application (lower dust loading but horizontal gas flow). A trial application of a sonic horn was installed on the Pd #1 catalyst chamber in late March, and was effective in limiting fly ash build up during two months of operation. Based on this success, similar sonic horns were installed on each of the other three chambers. In one month of operation, the four horns appear to be effective at limiting fly ash buildup, as evident from low pressure drop values across the catalysts. Catalyst activity measurements in July will provide an indication if the horns have also been effective in maintaining high catalyst activity.

After eight months of operation, the Pd #1 catalyst has not seen a significant loss in activity for elemental mercury oxidation, although recent results have been confounded by mercury adsorption after the catalyst was out of service for short periods. The SCR catalyst has dropped from 67% to less than 30% oxidation over the same period. The SBA #5 catalyst has dropped from 75% oxidation to 35% oxidation over a five-month period. However, all of these results are confounded by the fly ash buildup experienced prior to the sonic horn installations. The fly ash buildup could have had beneficial or negative effects on catalyst activity. If the catalysts can be deactivated by species in the flue gas, the honeycomb cells that were blocked by fly ash buildup may have been “protected” from deactivation by flue gas species. Conversely, the fly ash buildup could have directly affected catalyst activity in an adverse manner through physical blockage or chemical reactions at active sites.

Laboratory results during the quarter showed the Pd #1 and Au catalyst types are most active, while the other three candidate catalysts for the pilot unit at Spruce Plant show similar but lower elemental mercury oxidation activity in simulation gas. Of these three, the SBA #5 is least available to produce commercial quantities of catalyst. Consequently, the second pilot unit will test these four catalysts – Pd #1, Au, C #6, and the SCR catalyst from Argillon.

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