

Full-Scale Testing of a Mercury Oxidation Catalyst Upstream of a Wet FGD System

Final Technical Report

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ABSTRACT

This document presents and discusses results from Cooperative Agreement DE-FC26-06NT42778, “Full-scale Testing of a Mercury Oxidation Catalyst Upstream of a Wet FGD System,” which was conducted over the time-period July 24, 2006 through June 30, 2010. The objective of the project was to demonstrate at full scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in pulverized-coal-fired flue gas. Oxidized mercury is removed downstream in wet flue gas desulfurization (FGD) absorbers and collected with the byproducts from the FGD system. The project was co-funded by EPRI, the Lower Colorado River Authority (LCRA), who also provided the host site, Great River Energy, Johnson Matthey, Southern Company, Salt River Project (SRP), the Tennessee Valley Authority (TVA), NRG Energy, Ontario Power and Westar. URS Group was the prime contractor and also provided co-funding.

The scope of this project included installing and testing a gold-based catalyst upstream of one full-scale wet FGD absorber module (about 200-MW scale) at LCRA’s Fayette Power Project (FPP) Unit 3, which fires Powder River Basin coal. Installation of the catalyst involved modifying the ductwork upstream of one of three wet FGD absorbers on Unit 3, Absorber C. The FGD system uses limestone reagent, operates with forced sulfite oxidation, and normally runs with two FGD modules in service and one spare. The full-scale catalyst test was planned for 24 months to provide catalyst life data. Over the test period, data were collected on catalyst pressure drop, elemental mercury oxidation across the catalyst module, and mercury capture by the downstream wet FGD absorber.

The demonstration period began on May 6, 2008 with plans for the catalyst to remain in service until May 5, 2010. However, because of continual increases in pressure drop across the catalyst and concerns that further increases would adversely affect Unit 3 operations, LCRA decided to end the demonstration early, during a planned unit outage. On October 2, 2009, Unit 3 was taken out of service for a fall outage and the catalyst upstream of Absorber C was removed. This ended the demonstration after approximately 17 months of the planned 24 months of operation. This report discusses reasons for the pressure drop increase and potential measures to mitigate such problems in any future application of this technology.

Mercury oxidation and capture measurements were made on Unit 3 four times during the 17-month demonstration. Measurements were performed across the catalyst and Absorber C and “baseline” measurements were performed across Absorber A or B, which did not have a catalyst upstream. Results are presented in the report from all four sets of measurements during the demonstration period. These results include elemental mercury oxidation across the catalyst, mercury capture across Absorber C downstream of the catalyst, baseline mercury capture across Absorber A or B, and mercury re-emissions across both absorbers in service. Also presented in the report are estimates of the average mercury control performance of the oxidation catalyst technology over the 17-month demonstration period and the resulting mercury control costs.

TABLE OF CONTENTS

	Page
Disclaimer	i
Abstract.....	ii
Executive Summary	1
Introduction	1
Experimental Approach	2
Results and Discussion.....	8
Engineering Design and Construction	8
Design	8
Construction.....	10
Field Testing of Mercury Oxidation Catalyst Followed by Wet FGD System in PRB Flue Gas	14
Catalyst Pressure Drop Performance	14
Catalyst Oxidation and Absorber C Mercury Removal Performance	25
May 2008 Results	26
November 2008 Results.....	43
June 2009 Results	53
September 2009 Results.....	61
Plant Restoration	72
Mercury Control Process Metrics.....	74
Mercury Removal Performance.....	74
Cost of Mercury Control.....	76
Mass of Mercury Captured	77
Control Costs	78
Mercury Control Cost per Pound Estimates	81
Conclusions.....	83
Catalyst Pressure Drop.....	83
Mercury Oxidation Performance	83
Mercury Capture by the Downstream Wet FGD System	84
Mercury Control Process Metrics.....	84
List of Graphical Materials	86
References.....	87
List of Acronyms and Abbreviations.....	88
Appendix A – CFD Modeling Results Summary	90
Appendix B – OH Individual Run Results from the Four Measurement Periods	101
Results from First Measurement Period, May 2008.....	101
Results from Second Measurement Period, November 2008.....	102
Results from Third Measurement Period, June 2009.....	103
Results from Fourth Measurement Period, September 2009.....	104

EXECUTIVE SUMMARY

This document presents and discusses results from Cooperative Agreement DE-FC26-06NT42778, “Full-scale Testing of a Mercury Oxidation Catalyst Upstream of a Wet FGD System,” which was conducted over the time-period July 24, 2006 through June 30, 2010. The objective of the project was to demonstrate at full scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury (Hg^0) in flue gas from coal combustion. The project was co-funded by EPRI, the Lower Colorado River Authority (LCRA), who also provided the host site, Great River Energy, Johnson Matthey, Southern Company, SRP, TVA, NRG Energy, Ontario Power and Westar. URS Group was the prime contractor and also provided co-funding.

The mercury control process under development uses a catalyst to promote oxidation of elemental mercury in flue gas from coal-fired power plants that are equipped with wet flue gas desulfurization (FGD) systems. Oxidized mercury (Hg^{2+} , presumably in the form of mercuric chloride [HgCl_2]) is removed in the wet FGD absorbers and collected with the byproducts from the FGD system. The scope of this project included installing and testing a previously identified catalyst material (gold) upstream of one full-scale wet FGD absorber module (about 200-MW scale) at LCRA’s Fayette Power Project (FPP) Unit 3, which fires Powder River Basin (PRB) coal. Installation of the catalyst involved modifying the ductwork upstream of one of three wet FGD absorber modules on Unit 3, Absorber C. The FGD system uses limestone reagent, operates with forced sulfite oxidation, and normally runs with two FGD modules in service and one spare. The full-scale catalyst test was planned for 24 months to provide catalyst life data. Over the test period, data were collected on catalyst pressure drop, elemental mercury oxidation across the catalyst module, and mercury capture by the downstream wet FGD module.

The demonstration began when flue gas flow commenced through the catalyst and Absorber C on May 6, 2008. The original plan was for the catalyst to remain in service until May 5, 2010, other than during Unit 3 outages. However, because of continual increases in pressure drop across the catalyst and concerns that further increases would adversely affect Unit 3 operations, LCRA decided to end the demonstration early during a planned unit outage. On October 2, 2009, Unit 3 was taken out of service for a fall outage and the catalyst upstream of Absorber C was removed. This ended the demonstration after approximately 17 months of the planned 24 months of operation.

The pressure drop increase mentioned above was caused by deposition of fly ash in the small flow channels of the honeycomb-style catalyst, in spite of the fact that the catalyst was installed downstream of a high-efficiency electrostatic precipitator (ESP). Sonic horns were employed as part of the catalyst installation to provide for acoustic cleaning of fly ash from the catalyst, but were not effective at preventing fly ash buildup. It is speculated that the lack of effectiveness of the sonic horns resulted from a non-ideal flue gas velocity distribution at the front face of the first catalyst layer and sonic horn placement that was not optimal. However, it may be that more energetic cleaning devices, such as air soot blowers, and/or a larger catalyst pitch would be required to avoid such problems in any future application of this technology.

Four times over the course of the 17-month demonstration, mercury oxidation and capture measurements were made on Unit 3 by the Ontario Hydro method. These efforts included

mercury concentration and speciation measurements across the catalyst and Absorber C and “baseline” measurements across Absorber A or B, which did not have a catalyst upstream. Results from the initial measurement effort, conducted shortly after the catalyst was first placed in service, showed 80% oxidation of elemental mercury across the catalyst. These measurements agreed favorably with design calculations which predicted 81% oxidation across the catalyst. The initial results also showed a 69% reduction in total mercury concentration at the Absorber C outlet compared to that at the outlet of Absorber A, without a catalyst upstream. This result compared favorably with a requirement of the DOE solicitation that led to the funding of this cooperative agreement, which called for a 50 to 70% reduction in flue gas total mercury concentration compared to baseline operation.

Over time the oxidation of elemental mercury across the catalyst decreased, partly because of an expected loss of catalyst activity with time and partly because of buildup of fly ash in portions of the catalyst. The mercury removal across Absorber C was also intermittently limited by mercury re-emissions. In the last set of measurements conducted in September 2009, shortly before the catalyst was taken out of service, the elemental mercury oxidation across the catalyst averaged 57%, although with only two of the three original layers in service, compared to a predicted performance of 70% for two fresh catalyst layers. However, in spite of the 57% elemental mercury oxidation across the catalyst, the Absorber C outlet total mercury concentration was actually 27% higher than the Absorber B (baseline) module outlet. This increase was due to significant mercury re-emission across Absorber C, whereas only minimal re-emission was measured across baseline Absorber B. Several reasons for the intermittent re-emissions across the Unit 3 FGD absorbers were investigated. The best explanation is that low weight percent (wt%) solids in the absorber slurry coupled with low iron concentrations in the slurry solids limited the adsorption of mercury into the solids where re-emission reactions are less likely to occur. To fully realize the benefits of a mercury oxidation catalyst installed upstream of the Unit 3 wet FGD system, the absorber slurry may have to be controlled at higher wt% solids levels, and/or a limestone with higher iron content may be necessary. Alternately, iron or FGD re-emission additives may need to be added to the FGD system.

INTRODUCTION

This document present and discusses results from Cooperative Agreement DE-FC26-06NT42778, “Full-scale Testing of a Mercury Oxidation Catalyst Upstream of a Wet FGD System,” which was conducted over the time-period July 24, 2006 through June 30, 2010. The objective of the project has been to demonstrate at full scale the use of solid honeycomb catalysts to promote oxidation of elemental mercury in pulverized-coal-fired flue gas. The project was co-funded by EPRI, LCRA, who also provided the host site, Great River Energy, Johnson Matthey, Southern Company, SRP, TVA, NRG, Ontario Power and Westar. URS Group was the prime contractor and also provided co-funding.

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This report presents and discusses results from the project over its entire duration. The remainder of this report is divided into three sections: Experimental Approach, Results and Discussion, and Conclusions, followed by a List of Graphical Materials included in the report, References, and a List of Acronyms and Abbreviations. Two appendices are attached at the end of the report. Appendix A illustrates computational fluid dynamics run results for the catalytic reactor design, while Appendix B reports individual Ontario Hydro run measurement results from the catalyst demonstration period.

EXPERIMENTAL APPROACH

The project was conducted on Unit 3 at LCRA's FPP, a 460-MW unit that fires PRB. The unit has a tangentially fired, Alstom pulverized coal boiler with low-NO_x burners, a cold-side ESP for particulate control, and a limestone/forced oxidation FGD system for SO₂ control. The Alstom FGD system includes three spray absorbers, of which two normally operate to achieve greater than 90% SO₂ removal on the flue gas treated. About 5-15% of the flue gas is bypassed to maintain about 85% overall SO₂ removal and a stack temperature of at least 145°F (63°C). The PRB blend typically contains approximately 0.3 wt% sulfur, 20 ppm Cl, and 0.1 ppm Hg. Figure 1 is a schematic of the flue gas path for FPP Unit 3.

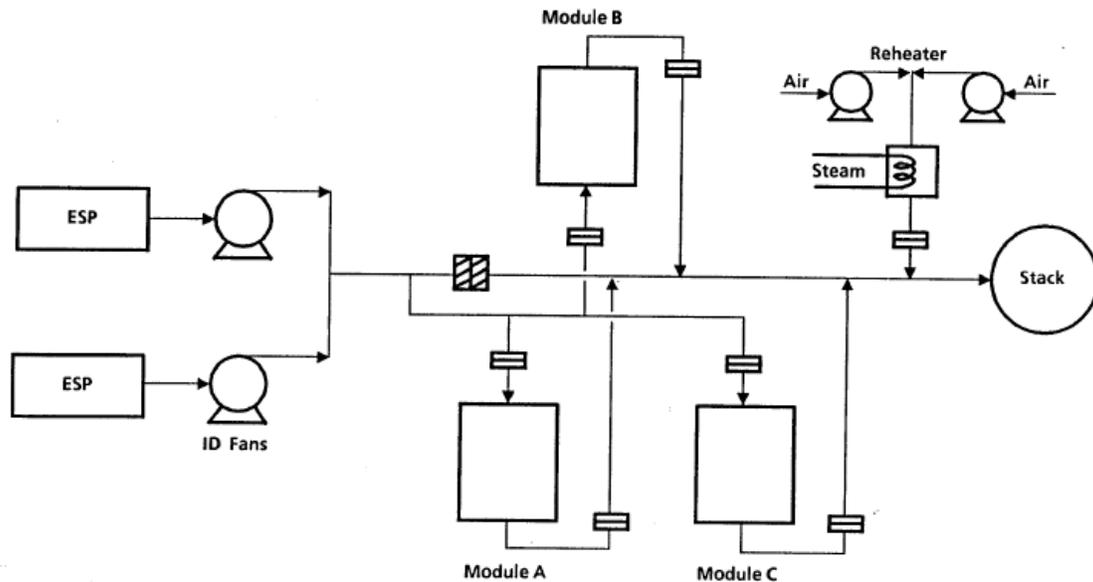


Figure 1. Schematic of FPP Unit 3 Configuration

In a unit with a cold-side ESP, the oxidation catalyst technology would likely be installed in the ESP outlet nozzle, where the flue gas velocity is already relatively low and minimal plant modifications would be required for catalyst installation. However, for this project the catalyst treated the flue gas going to only one of two operating FGD modules. At FPP, as in most plants, the flue gas exiting the ESPs combines before going to the FGD system. To treat the flue gas going to only one FGD module, the catalyst was installed in the duct run that provides flue gas flow only to that module. The flue gas velocity was higher than desired for catalyst operation in that existing absorber inlet duct. The project therefore involved removing the Absorber C inlet duct from the inlet isolation damper to the absorber inlet expansion joint, and replacing that short section with an oxidation catalyst reactor of larger cross section to lower the flue gas velocity. Because the installation was downstream of the absorber inlet isolation damper, a unit outage was not required to install the new reactor. However, some modifications had to be made during a unit outage in Spring 2007, including removal of a perforated plate flue gas flow distribution device upstream of the Absorber C isolation damper, relocation of the Absorber C isolation damper seal air fan, and relocation of the Absorber C ductwork purge air fan.

Figure 2 shows the FPP FGD duct configuration, noting where the catalytic reactor module was installed, and Figures 3 and 4 show sketches of the new reactor compared to the existing duct.

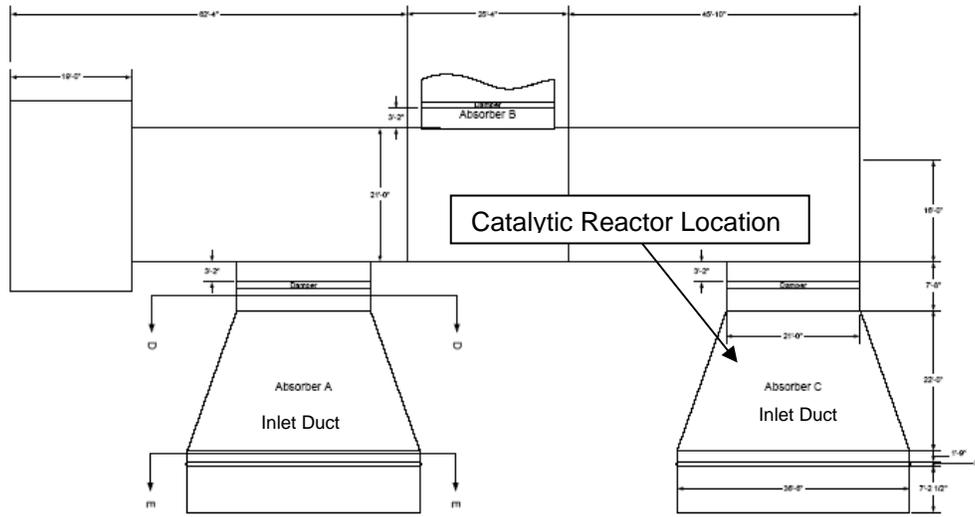


Figure 2. FGD Duct Configuration Showing Location of New Catalytic Reactor

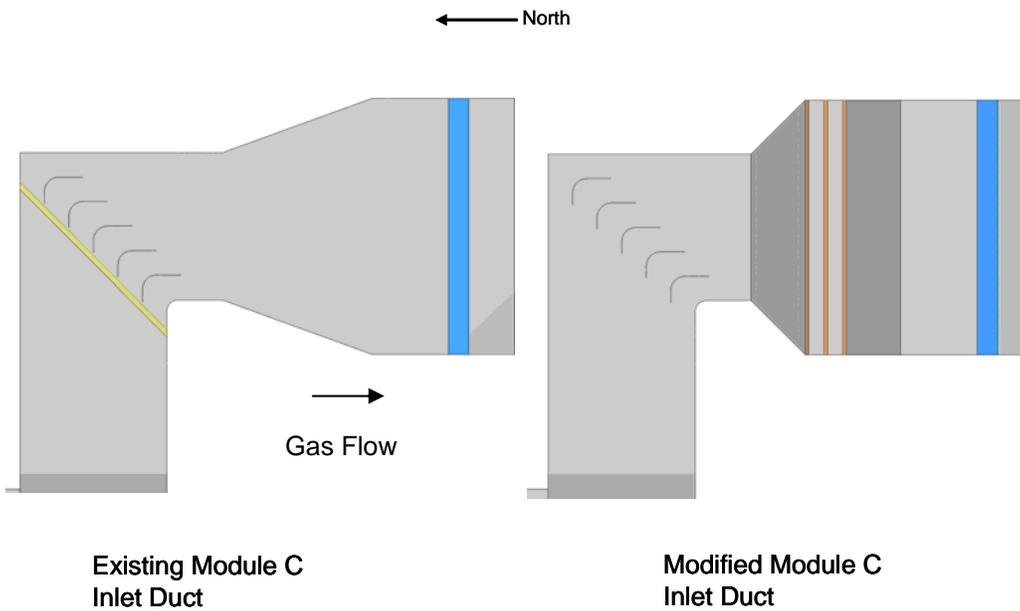


Figure 3. Sketch of Reactor Compared to Previous Inlet Duct (plan view)

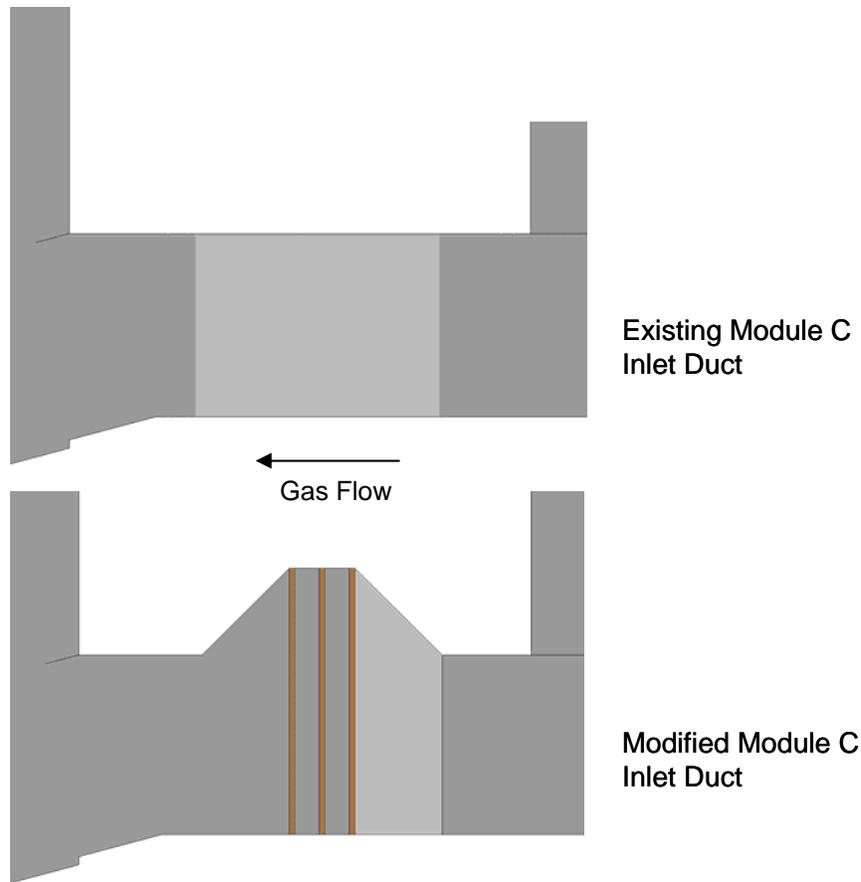


Figure 4. Sketch of New Reactor Compared to Previous Inlet Duct (side elevation)

With flue gas to one of two operating FGD modules being treated and with 5-15% flue gas bypass around the FGD system, the scale of the integrated catalyst/FGD testing was about 200 MW. The size of the new reactor was limited in this location by existing structural steel, scrubber slurry piping and cable trays, and by the relatively short length of duct run in which it was installed. Therefore the superficial flue gas velocity through the catalyst was about 15 ft/s (4.6 m/s), considerably higher than a velocity of about 5 ft/s (1.5 m/s) if the catalyst were installed at the outlet of an ESP. These space limitations also lead to less catalyst being installed than originally desired. The original plan was to install enough catalyst to achieve greater than 90% oxidation of the elemental mercury in the inlet flue gas, but with the limits imposed by the available space, the quantity of catalyst was predicted to achieve only 81% oxidation.

A gold catalyst was supplied by team member Johnson Matthey at reduced cost. They prepared approximately 8700 catalyst “bricks,” each of which are 150-mm by 150-mm in cross-section and either 6-in. (152-mm) or 8-in. (203-mm) deep. The bricks were assembled by a Johnson Matthey subcontractor into 36 modules, and these modules were placed in three layers in the reactor. The total installed catalyst depth at startup was 20 inches (508 mm). Some details of the catalyst installed are summarized in Table 1. An example catalyst block or brick is shown in Figure 5.

Table 1. Details of Gold-based Catalyst Tested

Parameter	Value
Catalyst Type	Gold on gamma alumina, ceramic substrate
Supplier	Johnson Matthey (Cormetech subcontractor)
Cell Pitch	64 cpsi (3.2-mm cell width, center to center of wall)
Catalyst Depth	20 in. [508 mm] (two 6-in. [152-mm] layers and one 8-in. [203-mm] layer)
Design Superficial Velocity	15 ft/s (4.6 m/s)
Total Catalyst Volume	1,174 ft ³ [33.3 m ³] (8712 pieces, each 150 mm x 150 mm in cross section)
Design Space Velocity	21,300 ^{-hr} (referenced to 32°F, 0°C)
Design Oxidation of Inlet Elemental Mercury across Catalyst	81% (based on empirically corrected mass transfer calculations)

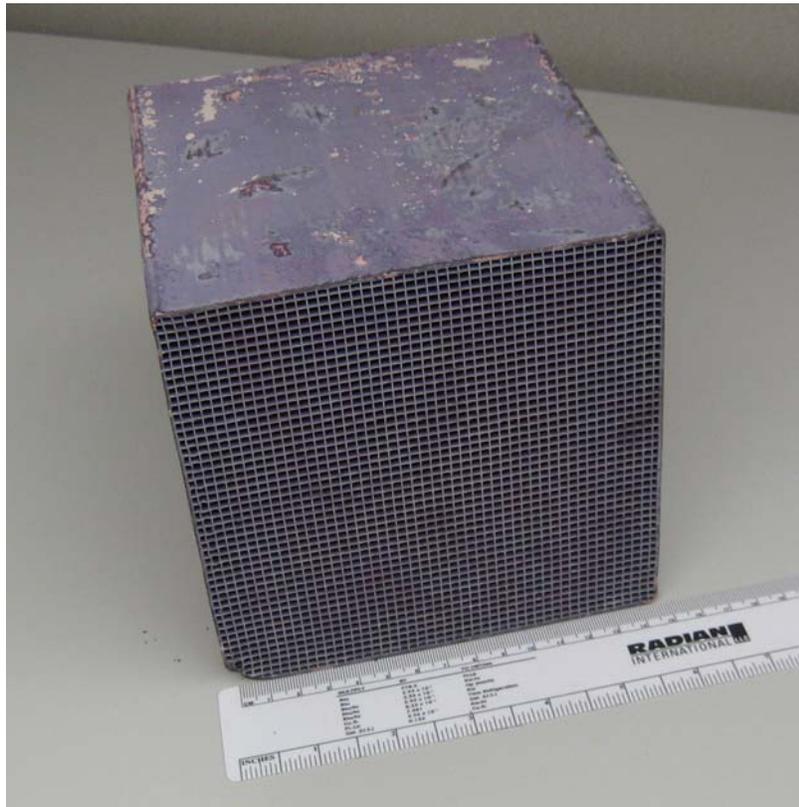


Figure 5. Example Catalyst Block (one of approximately 8700 installed upstream of Absorber C)

The main cost of a catalytic oxidation process is replacing catalysts to maintain high elemental mercury oxidation and high overall removal percentages. A two-year catalyst life is the minimum required to make the process viable, therefore, a 24-month test period was planned. LCRA made every reasonable effort to keep the catalytic reactor and FGD Absorber C in operation over the demonstration period. The demonstration period was ended early, after approximately 17 months of operation, because of pressure drop issues across the catalyst.

The catalyst operated with normal operation of FGD Absorber C. LCRA FGD operators regularly observed the reactor to ensure proper operation, particularly of the sonic horns installed to prevent fly ash buildup. LCRA and URS monitored parameters such as unit load, flue gas flow rate and temperature, and catalyst pressure drop via regular downloads from the plant data historian.

The original plan was for URS personnel to travel to FPP approximately every other month to measure catalyst elemental mercury oxidation performance and oxidized mercury capture by FGD Absorber C. Two mercury semi-continuous emissions monitors (Hg SCEMs) were to be used to measure mercury concentration and speciation at the inlet and outlet of the catalyst, while total mercury concentrations were to be measured at the Absorber C FGD outlet by a sorbent trap method. Periodic measurements of baseline mercury capture were to be made at the outlet of the other FGD module in service as well. The operation of the Hg SCEMs has been described in previous reports.¹ Ontario Hydro (OH) measurements² were also to be conducted on three occasions to verify SCEM results, near the beginning, mid-point, and end of the 24-month period. Additional OH tests were planned to characterize baseline Hg removal by the other FGD module in service.

However, during initial catalyst performance characterization measurements in May 2008, the Hg SCEM and sorbent trap measurements did not agree well with simultaneous OH measurements. For this reason, the plan was changed to rely primarily on OH measurements rather than using Hg SCEMs and sorbent traps to determine catalyst performance over time. The three planned OH measurement periods were to be supplemented with additional measurement periods, nominally making measurements every six months.

OH measurements of mercury capture by FGD Absorber C were used to determine whether mercury re-emissions were limiting capture of the catalytically oxidized elemental mercury. Mercury re-emission describes a phenomenon where oxidized mercury is removed from the flue gas by the FGD absorber, but then reduced back to the elemental form by species such as sulfite in the wet FGD slurry liquor. Elemental mercury, being relatively insoluble in the wet FGD liquor, is then released back into the FGD outlet flue gas. Measurements were also made across the other absorber in service without a catalyst upstream.

Catalyst inlet flue gas was characterized to determine halogen and trace element concentrations. The inlet and outlet of the catalyst was also characterized by the Controlled Condensation method to determine whether it oxidizes SO₂ to SO₃, producing vapor-phase sulfuric acid (H₂SO₄) in the flue gas. Appreciable oxidation could increase plume opacity due to the presence of sub-micron-diameter sulfuric acid mist in the wet FGD outlet flue gas.

Another experimental apparatus used as part of this project was a bench-scale test unit that was used to evaluate the activity of catalyst samples under simulated flue gas conditions. The bench-scale catalyst oxidation test apparatus was previously described in quarterly technical progress reports for Cooperative Agreement DE-FC26-01NT41185^{3,4}.

RESULTS AND DISCUSSION

Engineering Design and Construction

As described in the previous section, part of the project scope was to design and implement modifications to the ductwork going to one of three wet FGD modules on FPP Unit 3, to allow the installation of the oxidation catalyst upstream of that FGD module. These design and construction efforts are described below.

Design

As part of the design effort, computational fluid dynamics (CFD) modeling of gas flow through the modified ductwork and catalysts was conducted. Visual representations of the model results are appended to this document. Table 2 summarizes key results from the CFD model runs. The main findings of the CFD modeling were:

- The best choice for which FGD module to retrofit the oxidation catalyst reactor upstream of was Absorber C;
- An existing perforated plate flow distribution device in the ductwork upstream of the Absorber C isolation damper should be removed during an upcoming Unit 3 outage;
- No gas flow distribution devices would be required to achieve acceptable gas flow distribution across the face of the installed catalyst layers (although fly ash buildup on the catalyst during the demonstration call this conclusion into question);
- Installation of three 6-in. (152-mm) layers of catalyst upstream of Absorber C should result in improved flue gas velocity distribution at the inlet of Absorber C compared to current operation (later modified to two 6-in. [152-mm] layers and one 8-in. [203-mm] layer to maximize the amount of catalyst installed);
- Installation of three 6-in. (152-mm) layers of catalyst upstream of Absorber C would be expected to alter the scrubbed flue gas flow distribution between the two FGD modules in service from a current value of about 49% to Absorber C and 51% to the other module to modified values of about 45% to Absorber C and 55% to the other module (based on clean catalyst); and
- If Absorber C were to be operated between the time when the existing perforated plate was removed and when the catalyst was installed, the flue gas flow distribution at the inlet to Absorber C would be slightly worse than during previous operation.

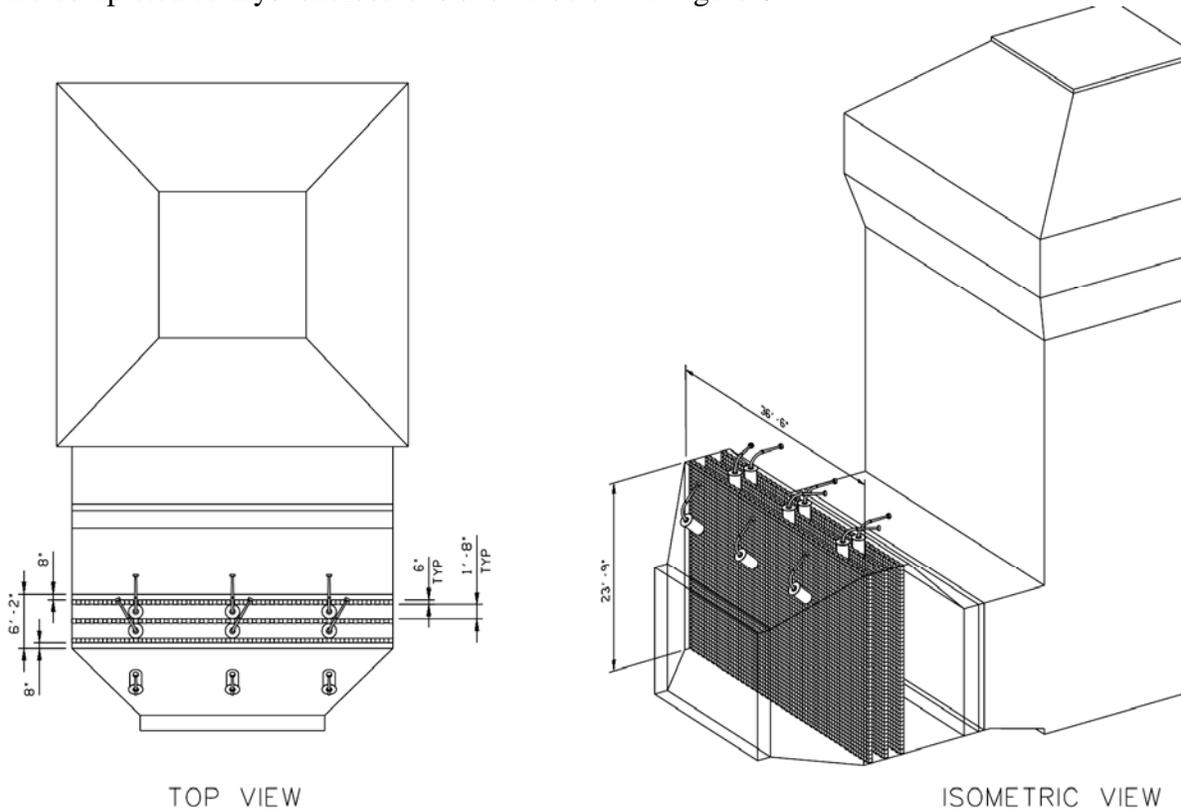
Based on these findings, the project team commenced with detailed design of ductwork modifications to add a catalytic reactor upstream of FGD Absorber C. The plant felt the change in flue gas flow distribution between Absorber C and either Absorber A or B once the catalyst was installed would be manageable, and could perhaps be adjusted by varying the number of spray headers in service in the two operating FGD modules.

Table 2. Key Results from CFD Modeling Conducted as Part of Design Effort

Case Description	Absorbers in Service	Gas Flow Split to FGD Absorbers, % of Scrubbed Flue Gas			Perforated Plate Pressure Drop, in. H ₂ O [kPa]	Catalyst Pressure Drop, in. H ₂ O [kPa]	Average Superficial Velocity at Front Face of Catalyst, ft/s [m/s]
		A	B	C			
Existing Operation	A and C	50.5	-	49.5	0.8 [0.2]	-	-
	B and C	-	51.0	49.0	0.8 [0.2]	-	-
After Catalyst Installation	A and C	54.8	-	45.2	-	1.4 [0.35]	13.2 [4.02]
	B and C	-	55.1	44.9	-	1.4 [0.35]	13.1 [3.99]

The plant did not plan to, and in fact did not operate Absorber C during the time period between when the existing perforated plate was removed and when the catalyst was installed, so no adverse effect of removing the existing perforated plate prior to catalyst installation was expected.

Detailed design efforts were largely completed during calendar year 2006. An isometric drawing of the completed catalytic enclosure is shown below in Figure 6.



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Figure 6. Isometric and Plan Drawing of Catalytic Reactor Design, Showing Sonic Horn Placement

Construction

During the first quarter of calendar year 2007, two requests for proposals were sent to a number of candidate subcontractors, one for shop fabrication of new structural steel members and ductwork components, and a second for all associated construction activities at the FPP Unit 3 site. The subcontract for the structural steel and ductwork modification components was awarded to Skotz, Inc. This work was completed in October 2007.

However, the request for proposals for site construction activities had only one bidder out of three candidates, CCC Group. That bidder's proposal was for approximately twice the budgeted amount. Consequently, only a portion of the subcontract was awarded. Part of the scope of the subcontract needed to be completed during a Unit 3 Spring outage and therefore was awarded to CCC Group to keep the project schedule viable (it would be 18 to 24 months before another Unit 3 scheduled outage) and was completed as planned in the spring of 2007. Those scope items included removal of a perforated plate flue gas flow distribution device upstream of the Absorber C isolation damper, relocation of the Absorber C isolation damper seal air fan, and relocation of the Absorber C ductwork purge air fan.

The remainder of the site construction scope, which could be conducted with Unit 3 on line, was rebid and awarded to subcontractor FL Smidth Airtech. This work commenced on October 22, 2007. The major remaining items included:

- Demolition of the existing duct between the isolation damper and the FGD inlet expansion joint;
- Installation of the new duct section and support steel, which had to be hoisted into position piece by piece and welded together in place because of limited access to this area;
- Installation of the catalyst support structure;
- Modification of work platforms external to the reactor to conform to the new duct shape,
- Installation of a new expansion joint between the reactor and the absorber inlet flange;
- Installation of the sonic horns to be used for acoustic cleaning of the catalyst, including a control cabinet and instrument air supply;
- Installation of other instrumentation for catalyst pressure drop and flue gas temperature, and new electrical circuits; and
- Insulation and lagging of the new duct run and the lids which are removed to load and unload catalyst in the reactor.

Some final welding and insulation and lagging of the lids was deferred until after the catalyst was installed in March 2008, while the balance of the site construction effort was completed by January 19, 2008.

Team member Johnson Matthey fabricated and delivered 36 catalyst modules to FPP. The modules arrived and were unloaded at the site March 3, 2008. Although the gold-based catalyst was received in early March, it could not be loaded into the new catalytic reactor until later in the month because of a problem with the hoist installed to support catalyst loading. The hoist had operated acceptably during earlier construction efforts in January, but by March it was not thought to be safe to use to load the catalyst because of issues related to the chain that coils up just below the hoist as the load is lifted. These issues were resolved by replacing the bucket into which the chain coils with a deeper bucket; the replacement was made by the hoist manufacturer under warranty and the hoist worked properly during catalyst loading later in March. The catalyst was loaded by FL Smidth and remaining mechanical construction activities (primarily reinstalling the reactor lids and insulating and lagging them) were completed by March 27th.

The oxidation catalyst was not immediately put into service because the downstream FGD Absorber C module was not ready to go back into service. Since Absorber C was scheduled to be off line for a considerable period of time during this construction effort, LCRA began overhaul activities on that absorber module. Many of the overhaul activities could not be conducted safely with construction activity overhead so these overhaul items were completed in April 2008. Startup of Absorber C and the oxidation catalyst occurred on May 6, 2008. Several photographs taken during the construction effort are attached as Figures 7 through 12 below.



Figure 7. New Duct Run with Expanded Cross Section for Catalyst during Trial Fit-up at Fabricator's Shop



Figure 8. Side Three-quarter View of Absorber C and Inlet Duct after Construction



Figure 9. One of 36 Catalyst Modules Being Unloaded from Shipping Crate Prior to Being Installed in Catalytic Reactor



Figure 10. Catalyst Module Being Lifted into Place to Install in Catalytic Reactor



Figure 11. View from Above Catalytic Reactor Showing Catalyst Module Being Installed by Sliding Down Support Structure



Figure 12. View from Inside of New Catalytic Reactor Showing One Layer of Catalyst Installed (3 of 12 panels per layer in view)

Field Testing of Mercury Oxidation Catalyst Followed by Wet FGD System in PRB Flue Gas

Absorber C with the catalyst installed upstream was put back into service on May 6, 2008 to begin the planned 24-month demonstration period. Over the demonstration period, catalyst pressure drop was tracked continually over time, and periodic measurements were made of elemental mercury oxidation across the catalyst and mercury removal across Absorber C. Additionally, flue gas and FGD system characterization measurements were made.

The following subsections report the catalyst pressure drop results and the catalyst oxidation and Absorber C mercury capture performance data, respectively.

Catalyst Pressure Drop Performance

During the design phase of the project, the flue gas pressure drop across the clean catalyst at full unit load was estimated at 1.4 in. H₂O (0.35 kPa). As described above, because of the pressure drop across the catalyst, a perforated plate flow distribution device upstream of Absorber C was removed since it was no longer necessary. That device had a full-load pressure drop of approximately 0.8 in. H₂O (0.2 kPa), so the net pressure drop increase due to the catalyst retrofit was expected to be only 0.6 in. H₂O (0.15 kPa).

A concern at the beginning of the project was whether or not the nine sonic horns installed would be adequate to prevent fly ash buildup in the catalyst cells, which would result in a

corresponding increase is flue gas pressure drop. Over the first two months of operation, the sonic horns appeared to adequately prevent fly ash buildup. They were programmed to each sound every 10 minutes, with each bank of three (upstream of each catalyst layer) sounding for 10 seconds. With this acoustic cleaning cycle, the full-load flue gas pressure drop across the catalyst remained at approximately 1.4 to 1.6 in. H₂O (0.35 to 0.40 kPa), which is very near the predicted value, with no indication of increase. This is illustrated in Figure 13 below.

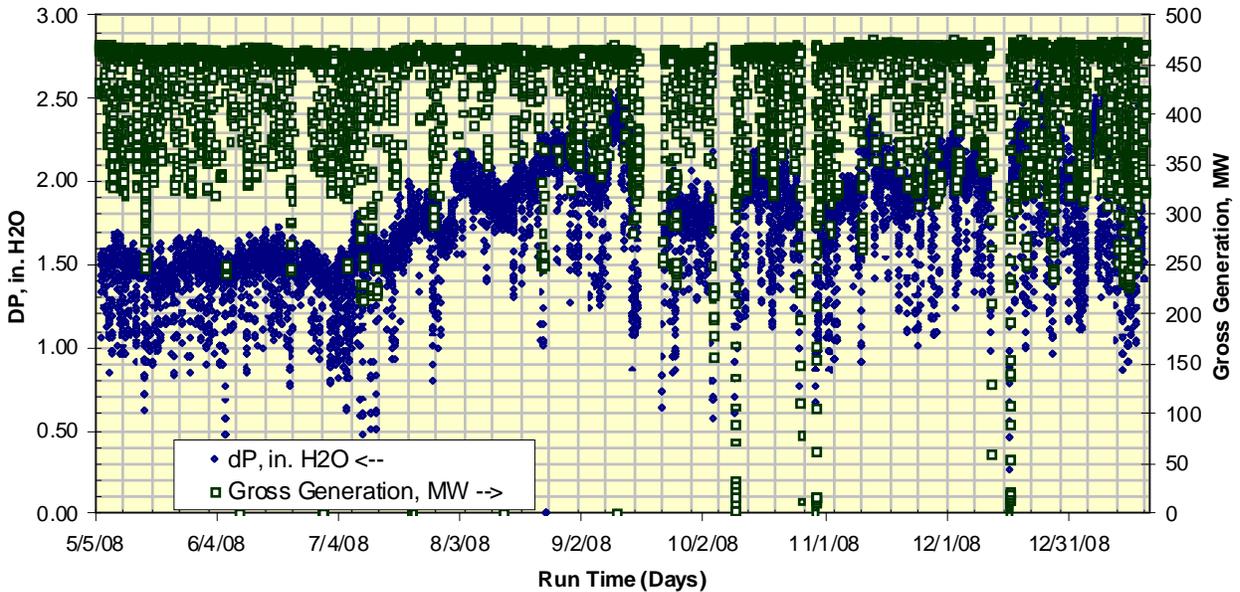


Figure 13. Flue Gas Pressure Drop across the Catalyst over the First Seven Months of Operation (note: 1.00 in. H₂O equals 0.249 kPa)

However, after approximately two months of operation the pressure drop across the catalyst began to increase. On August 6, after three months of operation, the sonic horn operation was increased from 10 seconds every 10 minutes to 15 seconds every 5 minutes. However, this had little effect on the pressure drop increase.

By mid-September 2008 (4+ months of operation) the full-load pressure drop had increased from an average of about 1.5 in. H₂O (0.37 kPa) at startup to about 2.4 in. H₂O (0.60 kPa). An unscheduled Unit 3 outage occurred, which provided the opportunity to open the ductwork and observe the catalysts. Only the front face of the first layer and the back face of the third layer could be observed with all three catalyst layers in place. The back face of the third layer was relatively clean, but fly ash was observed to be attached to the leading edges of the cell walls in the first layer. In the upper portion of the catalyst enclosure (where the duct is expanded in the vertical direction) and along the sidewalls of the enclosure, this buildup on the leading edges had bridged over to block the cell openings. Photos of open and plugged cells in the first layer are shown in Figures 14 and 15, while a photo of the relatively clean back side of the third layer is shown in Figure 16.



Figure 14. Photo of the Lower Middle Section of the First Catalyst Layer Showing Fly Ash Buildup on the Leading Edges but Few Plugged Cells



Figure 15. Photo of a Catalyst Block Near the Sidewall of the Enclosure Showing Nearly All of the Cells Blocked with Fly Ash



Figure 16. Photo of Back Side of Third Catalyst Layer, Showing Little Fly Ash Buildup

While the unit was down, the plant used a vacuum truck and long hose to clean as much of the fly ash as possible off of the leading edge of the first layer. As was shown in Figure 13, after the outage and this cleaning, the pressure drop across the catalyst recovered to 1.8 in. H₂O (0.45 kPa), only 0.3 in. H₂O (0.07 kPa) greater than the clean catalyst pressure drop.

Over the next three months, the pressure drop across the catalyst increased slowly with time in operation. As shown in Figure 13, the full-load pressure drop was in the range of 2.2 to 2.4 in. H₂O (0.55 to 0.60 kPa) by the end of December 2008. The increase with time appeared to be slower than was observed in the July to September timeframe, possibly because of the increased sonic horn operating frequency implemented in August.

Because of the increases in catalyst pressure drop, two efforts were made to mitigate the effects of pressure drop increases. The first was a series of velocity traverse measurements to see how varying the number of slurry recycle pumps/spray header levels in service in Absorbers A and C could be varied to maintain SO₂ removal compliance while offsetting some of the catalyst pressure drop. Four tests were conducted over a two-day period, October 21-22, 2008. The test conditions are summarized in Table 3.

The following data were collected for each test:

- Flue gas velocity in each module outlet duct, by multi-port pitot traverse,
- Absorber A and C outlet gas pressures,
- Absorber A and C outlet gas temperatures, by thermocouple, and
- Various Unit 3 process data (from plant data historian).

Table 3. Velocity Test Conditions

Test Number	No. of Pumps in Service, Absorber A	No. of Pumps in Service, Absorber C
1 (baseline)	3	3
2	4	3
3	4	2
4 (typical operation at low coal sulfur conditions)	3	2

These data were used to calculate the percentage of flue gas flowing through each absorber as a function of number of pumps/spray header levels in service, and any impacts on the percent flue gas bypass and/or overall SO₂ removal percentage.

The test results are summarized in Table 4, which focuses on the results of the manual gas measurements, and Table 5, which primarily summarizes the Unit 3 process data.

The process data show that Unit 3 operating conditions were relatively stable during these tests, with full unit load and nearly constant flue gas flow rate and bypass damper percent opening. No Jacobs Ranch coal, a higher-sulfur-content PRB coal, was fired during these tests.

The velocity data and calculated percentage flow split between Absorbers A and C did not vary as much as expected when the number of pumps in service was changed over the first three tests. Adding a fourth pump in service on Absorber A during Test 2 had almost no measurable effect compared to Test 1, while taking the third pump out of service in Absorber C for Test 3 decreased the percent of scrubbed flue gas flow through Absorber A by less than 2 percentage points compared to Test 2.

However, it should be noted that the instantaneous pitot-tube pressure differential readings varied over a relatively wide range during these measurements, indicating pulsation in the flow in the absorber outlet ducts. The samplers recorded the high and low values observed on a digital differential pressure readout over approximately 15 seconds and the average of these two values was used in the flow rate calculations. These fluctuations most likely impacted the accuracy of the flow rate measurements, particularly for Absorber A versus Absorber C, and particularly in Test 1, where only three pumps were in service on Absorber A. The flow pulsations were likely less severe on Absorber C because of the additional pressure drop of the catalyst upstream. Having four pumps in service on Absorber A for Tests 2 and 3 helped dampen the pulsation across that absorber. For Test 4, pinch clamps were used to constrict the flexible lines between the pitot and the digital pressure readout, which slowed the variation in the pressure differential readings and may have improved the measurement accuracy.

Table 4. Summary of Velocity Test Flue Gas Measurements

Test No.	Pumps in Service		Absorber Outlet Duct Flue Gas Velocity, ft/s [m/s]		% of Scrubbed Flue Gas Flow Through Absorber A	Absorber Outlet Flue Gas Temperature, °F [°C]	
	A	C	A	C		A	C
1	3,4,5 (3 total)	3,4,5 (3 total)	73 [22]	48 [15]	60	136 [58]	139 [59]
2	2,3,4,5 (4 total)	3,4,5 (3 total)	74 [23]	48 [15]	61	141 [61]	140 [60]
3	2,3,4,5 (4 total)	4,5 (2 total)	71 [22]	50 [15]	59	138 [59]	138 [59]
4	3,4,5 (3 total)	4,5 (2 total)	71 [22]	39 [12]	64	140 [60]	133 [56]

Table 5. Summary of Velocity Test Results including Unit 3 Process Conditions Recorded from Plant Instrumentation

Test Condition	Abs. C Catalyst Diff. Press.	Abs. C Catalyst Inlet. Press.	Stack Gas Temp	Stack Inlet Temp	Stack Temp	Stack Gas Flow	Stack Gas SO ₂	Stack Inlet Gas SO ₂	Calculated SO ₂ Removal	FGD Bypass Damper Position	Gross Generation	Abs. A Additive Slurry Flow	Abs. C Additive Slurry Flow	Abs. A	Abs. C	Flow Through Abs. A	Limestone Slurry to Absorber A
	In. H ₂ O	In. H ₂ O	°F	°F	°F	kscfm	lb/MM BTU	lb/MM BTU	%	%	MW	gpm	gpm	pH	pH	%	%
1	1.88	4.03	145	322	144	1151	0.09	0.66	86.9	22	467	61.7	32.4	6.01	6.04	60	66
2	2.01	4.32	145	327	143	1140	0.09	0.70	87.9	20	467	45.2	27.8	6.01	6.01	61	62
3	2.16	4.08	145	329	144	1149	0.10	0.71	86.6	20	466	44.5	27.1	6.01	6.05	59	62
4	2.00	3.73	145	322	144	1149	0.10	0.68	85.0	21	464	66.3	27.0	6.01	6.04	64	71

Note: 1.00 in. H₂O equals 0.249 kPa;
 (°F - 32) ÷ 1.8 equals °C;
 1.00 kscfm equals 26.4 nM³/min;
 1.0 lb/MMBtu equals 0.43 kg/GJ;
 1.00 gpm equals 0.227 M³/h.

Test 4 represented normal operation when the unit is firing relatively low-sulfur coal blend (three pumps on Absorber A and two pumps on Absorber C). Comparing the Test 4 and Test 3 results, it appears that adding a fourth pump in service in Absorber A (Test 3) can decrease the percentage of scrubbed flue gas flow through Absorber A by over 5 percentage points.

An attempt was made to use the flow rates of limestone slurry to the absorbers to provide another estimate of the relative flue gas flow rates to each. However, the limestone makeup rates vary widely over time, in on-off fashion, and the duration of each test was not long enough to develop reliable averages for both absorbers.

Both the inlet flue gas pressure data and the SO₂ removal data show that these parameters are controlled primarily by the total number of pumps in service between the two absorbers, with little difference between operating two in one absorber and four in the other versus three pumps in each.

The preferred mode of operation as the pressure drop across the catalyst upstream of Absorber C increases was determined to be to operate with four pumps in service in Absorber A (or B) and two pumps in service in Absorber C. This mode of operation was expected to provide nearly equal SO₂ removal performance to operating three pumps on both absorbers, but to reduce the percentage of scrubbed flue gas treated in Absorber A by about 5 percentage points.

The second effort to mitigate the pressure drop increase was to have a representative from GE Energy, the vendor of the horns, review the sonic horn installation and operation. The GE Energy representative, Jake Shelton, visited FPP Unit 3 on December 15, 2008. His objectives were to subjectively determine if the horns were performing with the proper sonic energy output and to review the details of how the horns were installed. He had four major findings:

- 1) The horns were producing the expected level of sonic energy based on his experience and listening to several horn cycles;
- 2) The bells of the horns should be insulated to minimize corrosion and/or solids deposition due to moisture condensation;
- 3) The horns were not spaced optimally across the width of the catalyst reactor; and
- 4) The horns for the first catalyst layer were not oriented to take full advantage of the acoustic cleaning energy produced.

The following paragraphs explain his findings for items 2 through 4 above.

Insulation of Horn Bells – Mr. Shelton commented that they had learned over the years that horn life is promoted by insulating the bell (the part below the diaphragm) where it extends up beyond the insulation and lagging on the duct wall or ceiling. During periods when a horn is not sounding, hot flue gas diffuses up into the bell and cools, and the moisture in the flue gas condenses. This condensation leads to corrosion on the internal surfaces of the cast iron bell material. Also, some fly ash is contained in the flue gas that migrates up the bell, so fly ash

deposition and cementation can occur. Eventually the horn can fail due to penetration of the walls of the bell by corrosion and/or blockage of the sound pathway by scale and ash deposition. He did not think this would be an issue over the planned two-year demonstration period, but could become a problem with longer operation.

Horn Placement across the Reactor Width – One thing that Mr. Shelton noted is that the effective coverage volume of the horns is nominally a cylinder with a diameter of about 15 feet (4.6-m), with the horn in the center. The catalytic reactor is 36.5-ft (11.1-m) wide, which is somewhat more than two horns could cover effectively (30 ft [9.1-m]), hence three horns per layer were recommended and installed. GE Energy recommended that the horns be equally spaced across the top of the reactor. This meant that the horns should have been installed such that each horn was installed at the center of approximately 12 ft (3.7 m) of reactor width. However, the mechanical designer incorrectly interpreted “equal spacing” as allowing for equal spacing between the wall and the first horn, between the first and second horn, etc. As a result, the center horns are installed at the center of the reactor, as they should be, but the outboard horns are installed too close to the center and too far from the outside wall. This is illustrated in Figure 17 below.

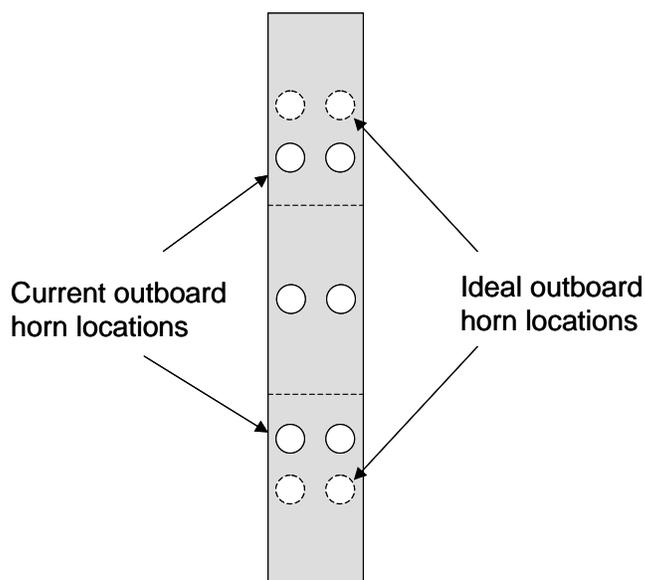


Figure 17. Illustration of Recommended and Actual Spacing of Sonic Horns across Top of Reactor (horns for catalyst layers 2 and 3 are depicted; not to scale)

Based on the inspection of the catalyst made in mid-September 2008, it appeared that the second and third catalyst layers were being effectively cleaned in spite of the outboard horns being placed a bit too far from the walls. Consequently, it was primarily the placement of the horns upstream of the first catalyst layer that appeared to be an issue. The placement of the first row of horns is further discussed below.

Placement of the First Row of Horns on the Upslope of the Catalytic Reactor Inlet Transition – Mr. Shelton commented that this row of horns should have been oriented perpendicular to the gas flow as it goes through the catalyst (i.e., the centerline of the bell discharge oriented

vertically), with the downstream edge of the bell only about one foot upstream of the first layer. Instead, based on input from other GE Energy staff members at the time the horns were installed, the horns were placed perpendicular to the upslope of the reactor roof as it transitions from the original duct height of 16 ft (4.9 m) to the full reactor height of 23.75 ft (7.2 m). That is, the centerline of the bell discharge was installed 45° from vertical, or at a 45° angle to the gas flow as it goes through the catalyst. This had the effect of reducing the percentage of the front face of the first catalyst layer that was effectively cleaned by the horns. The actual and recommended orientations are illustrated in Figure 18.

Recommended first layer horn location

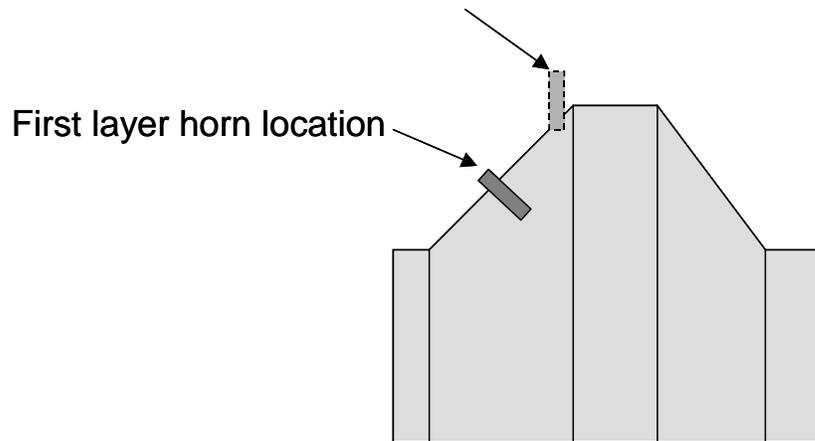


Figure 18. Illustration of Actual and Currently Recommended Location and Orientation of First Layer Sonic Horns (not to scale)

Had the horns been placed as Mr. Shelton recommended, each horn would have effectively cleaned an area nearly 15-ft (4.6-m) wide and the entire 23.75-ft (7.2-m) of reactor height, as the “cylinder” of effective cleaning can readily span the 23.75-ft height. If spaced optimally, each horn would only need to clean about 12-ft (3.7-m) of catalyst width, so the three horns would have provided about 115% coverage of the front face of the first layer.

Installed as they were at 45° to the front face, each horn projected an ellipse of most effective cleaning area onto the catalyst face approximately 15-ft (4.6-m) wide and 21-ft (6.4-m) high. This is illustrated in Figure 19. With optimal spacing across the reactor width, the three horns would effectively cover approximately 86% of the catalyst front face. However, since the outboard horns were mounted too close to the reactor centerline, the effective coverage was somewhat less than the theoretical value of 86%. The approximate coverage is illustrated in Figure 19.

Two options were discussed for improving the acoustic cleaning of the first catalyst layer. One was to relocate the first-layer horns as described above (perpendicular to the gas flow and closer to the first layer). A second was to install a fourth horn on the side of the reactor towards the top, to help clean the top sections of catalyst in the first layer that appeared to be most prone to plugging. One horn mounted perpendicular to the gas flow through the catalyst should effectively clean the entire 36.5-ft (11.1-m) width.

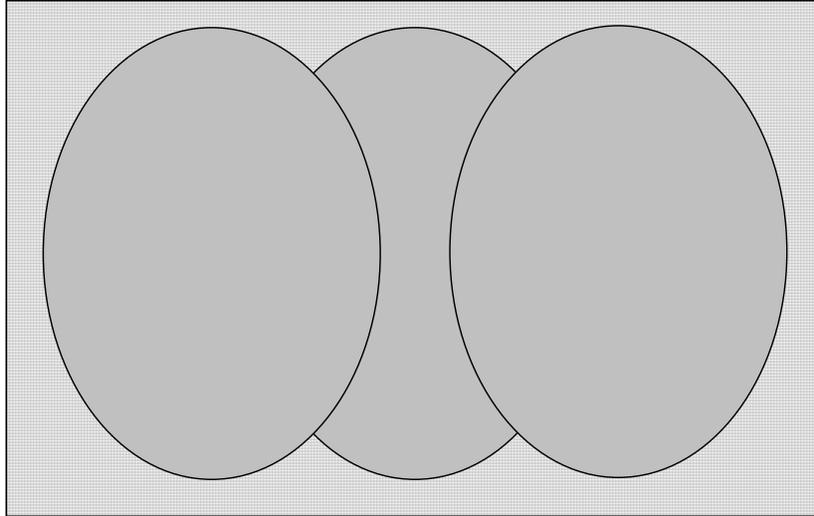


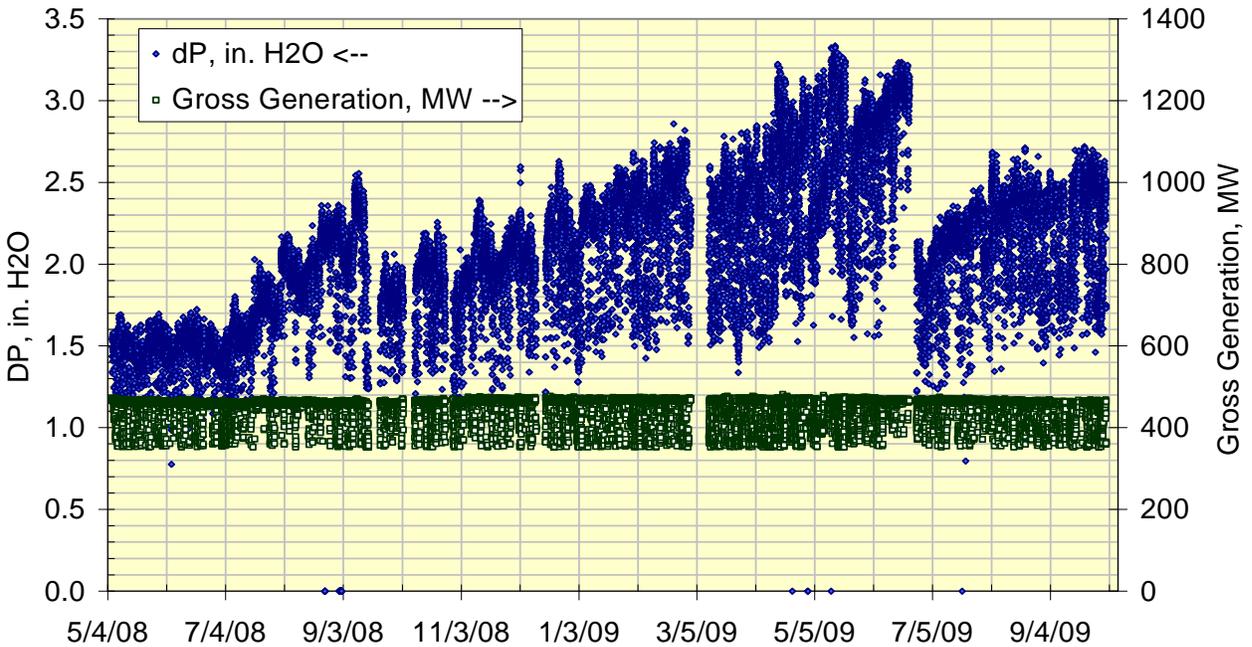
Figure 19. Illustration of Projected Area of Most Effective Cleaning Energy for First Catalyst Layer (not to scale)

However, it was considered possible that neither of these options would improve the catalyst pressure drop performance, taking into account two potential issues:

- 1) In spite of the non-ideal horn locations, it is possible that sonic wave reflection in this confined installation results in relatively effective acoustic cleaning. Thus, relocating the horns might not yield a significant improvement, and other factors may limit the effectiveness of the cleaning.
- 2) Since this is a horizontal gas flow installation, the acoustic cleaning relies on gas velocity to sweep fly ash through the catalyst once the sonic energy re-entrains it. The observed areas of fly ash buildup tend to correlate with areas of lower gas velocity upstream of the first layer, as indicated by previous CFD modeling. Thus, it is possible that even with a more optimal horn placement there would still be fly ash buildup in the areas previously observed.

Unfortunately, either of the potential solutions considered would have to be implemented during a unit outage, and no Unit 3 outages were planned. In the interim, URS and LCRA continued to track the pressure drop across the catalyst versus time.

Figure 20 shows the catalyst pressure drop data for the entire demonstration period for high unit load operation (>300 MW gross unit load). The pressure drop continued to increase with time after the September 2008 off-line cleaning, in spite of the increased acoustic cleaning frequency and duration.



**Figure 20. Flue Gas Pressure Drop Across the Catalyst over 17 Months of Operation
(note: 1.00 in. H₂O equals 0.249 kPa)**

By early March 2009, the full-load pressure drop had increased into the range of 2.5 to 2.8 in. H₂O (0.62 to 0.70 kPa). An unscheduled unit outage brought a second opportunity to inspect the catalyst and vacuum clean the leading edge of the first layer. The fly ash buildup on the first layer was generally in the same locations as was observed in September 2008 (upper portion of reactor, and near the reactor side walls) although qualitatively heavier and covering a greater percentage of the front face. After vacuum cleaning the leading edge, the pressure drop recovered by only a few tenths of an inch of water (0.1 kPa or less). By mid-April 2009 the pressure drop had increased back into the range of 2.3 to 2.8 in. H₂O (0.57 to 0.70 kPa).

By mid-May 2009 the pressure drop had increased further to as high as 3.3 in. H₂O (0.82 kPa). A brief unit outage in the latter half of May provided an opportunity to manually clean the leading edge of the first layer for a third time since startup. After vacuum cleaning the front face of the first layer, an attempt was made to use compressed air at 90 psig (6.2 bar) flowing from a 3/8-in. (9.5-mm) diameter nozzle to dislodge fly ash from further within the catalyst flow channels. However, the force of the compressed air as it exited the nozzle caused damage to the leading edges of some of the first layer catalyst blocks, so this more aggressive cleaning was stopped and the reactor was put back in service. This cleaning lowered the pressure drop to approximately 2.8 in. H₂O (0.70 kPa) immediately after the catalyst was put back in service. However, by mid-June the pressure drop was back up to 3.2 in. H₂O (0.80 kPa).

Because of the increases in catalyst pressure drop observed, plant operating personnel were concerned about the ability to continue reliable operation of Unit 3 throughout the peak summer demand period. Although Unit 3 has adequate induced draft fan capacity, the added pressure drop of the catalyst caused an imbalance of flue gas flow between Absorber C and the other absorber in service (Absorber B at that time). With the catalyst pressure drop above 3 in. H₂O (0.75 kPa), only 30-35% of the scrubbed flue gas went through Absorber C while 65-70% went through Absorber B. With such a flow mismatch, the high flue gas velocity in Absorber B could lead to operating problems such as a plugged mist eliminator and/or solids deposition in the absorber outlet duct. The third absorber that would normally have been a spare, Absorber A, was off line and unavailable with ongoing overhaul and upgrade work. Thus, the ability to scrub a high percentage of the flue gas during full-load operation through the summer came into question.

One of the options considered was to improve the acoustic cleaning of the first catalyst layer by relocating the three sonic horns upstream of the first catalyst layer, as described above. This option would relocate the first-layer horns from the upslope of the reactor roof to place them closer to the front face of the first layer and perpendicular to the gas flow. However, this would have required a forced unit outage. After observing the tenacity of the buildup in the first layer catalyst, and removing a catalyst sample block from the first layer and observing fly ash buildup on the second layer through the opening, it was judged that sonic horn relocation at this time would not be adequate to lower and control the pressure drop at acceptable levels.

During an unscheduled Unit 3 outage late in June, LCRA plant management made a decision to remove the first layer of the catalyst installation while the unit was off line. This inherently lowered the pressure drop by removing 30% of the catalyst depth, with the added benefit that the layer with the most buildup was removed. As shown in Figure 20, this layer removal at the end of June 2009 lowered the full-load catalyst pressure drop to approximately 2.0 in. H₂O (0.5 kPa). It was expected that this decrease in pressure drop would allow successful operation until the Unit 3 Fall 2009 outage. As discussed elsewhere in this report, LCRA made a decision to end the demonstration at that fall outage and remove the remaining two catalyst layers.

At the beginning of the unit outage on October 2, 2009, the mercury oxidation catalyst had been in service for nearly 17 months. At the end of the demonstration period, the catalyst pressure drop for the two of three original layers that remained in service was in the range of 2.5 to 2.7 in. H₂O (0.62 to 0.67 kPa). The catalyst was removed from the ductwork upstream of Absorber C during that outage.

Catalyst Oxidation and Absorber C Mercury Removal Performance

The gold-based oxidation catalyst was first placed in service upstream of Absorber C on the morning of May 6, 2008. The initial flue gas characterization and catalyst performance measurement effort was conducted the following week, starting May 12, 2008. The original plan for mercury measurements for this program included approximately bi-monthly mercury SCEM measurement trips. However, because of poor SCEM agreement with OH method results seen in results from May 2008 and the fact that the OH method is a reference method, the mercury oxidation and removal results for the rest of the program were obtained using only the OH

method. Note that for many mercury control technologies, sorbent trap methods such as Appendix K or Method 30B are now commonly used to measure control performance. However, for characterizing the performance of mercury oxidation catalysts and evaluating mercury re-emission levels across wet FGD systems, speciated mercury concentrations must be measured and the OH method remains the only reference method which speciates mercury.

A total of four OH measurement trips were conducted over the course of the 17-month demonstration period. Results from each of the four trips are presented and discussed in separate subsections below. The OH results are shown as mean values for three measurement runs in this section; individual run results are shown in tables in Appendix B.

May 2008 Results

Mercury Oxidation and Removal

During the week of May 12, 2008, initial mercury oxidation and FGD capture data were measured for both Absorber C with the catalyst upstream and Absorber A without. The OH mercury concentration results are summarized in Table 6 below and in Table 7 these concentration data have been used to calculate performance metrics. The total mercury concentration data in Table 6 are shown in units of $\mu\text{g}/\text{dNm}^3$ and as a mercury emission rate in pounds of mercury per trillion Btu of heat input to the boiler (lb Hg/TBtu). The latter is based on a conversion calculated from the F factor for subbituminous coal, 9780 dry standard cubic feet of flue gas at 0% excess oxygen per million Btu of heat input.

Table 6. May 2008 Gas-phase Mercury Concentration Data by the Ontario Hydro Method (mean value for three measurement runs \pm 95% confidence interval of mean)

Location	Hg ⁰ Concentration ($\mu\text{g}/\text{dNm}^3$ at 3% O ₂)	Hg ²⁺ Concentration ($\mu\text{g}/\text{dNm}^3$ at 3% O ₂)	Total Hg Concentration, includes particulate Hg	
			($\mu\text{g}/\text{dNm}^3$ at 3% O ₂)	(lb Hg/TBtu)
Absorber C (Catalyst Upstream) Data (5/16/2008):				
Catalyst Inlet	9.2 \pm 0.4	5.0 \pm 1.8	14.2 \pm 1.5	9.4 \pm 1.0
Catalyst Outlet/ Absorber C Inlet	1.8 \pm 0.8	11.8 \pm 2.2	13.7 \pm 1.8	9.1 \pm 1.2
Absorber C Outlet	2.4 \pm 0.8	0.3 \pm 0.1	2.9 \pm 0.7	1.9 \pm 0.5
Absorber A (No Catalyst) Data (5/13-5/14/2008):				
Absorber A Inlet	7.3 \pm 0.9	7.1 \pm 1.0	14.4 \pm 1.1	9.6 \pm 0.7
Absorber A Outlet	8.9 \pm 2.7	0.4 \pm 0.1	9.5 \pm 2.7	6.3 \pm 1.8

Table 7. Mercury Oxidation and FGD Capture Data by the Ontario Hydro Method

Parameter	Value (mean \pm 95% confidence interval for three measurement runs)
Catalyst Inlet Hg Oxidation (%)	35 \pm 9*
Predicted Hg Oxidation across catalyst (% , empirically corrected)	81
Measured Hg Oxidation across catalyst (%)	80 \pm 9
% Oxidized Hg at Catalyst Outlet	86 \pm 6
Hg Removal Across Absorber C Wet FGD, %	80 \pm 5
Absorber C Hg ⁰ Re-emissions, % of FGD Inlet Hg ²⁺	5 \pm 11
Baseline (Absorber A) Inlet Hg Oxidation (%)	49 \pm 6*
Absorber A Hg Removal (%)	34 \pm 18
Absorber A Hg ⁰ Re-emissions, % of FGD Inlet Hg ²⁺	23 \pm 45
Absorber C Hg Removal Increase over Absorber A (%)	69 \pm 13

*These baseline mercury oxidation percentages were measured on different days

One thing apparent in these data is that the mercury oxidation percentage at the south induced draft (ID) fan outlet/FGD inlet varies from day to day on Unit 3, with 35% oxidation measured one day and 49% measured on another. This is the reason why the catalyst inlet elemental mercury concentration in Table 6 was higher than the Absorber A inlet elemental concentration. Furthermore, there was substantial run-to-run variability in the results, as seen in the relatively high 95% confidence intervals about the mean values shown in Tables 6 and 7. This is discussed further for the Absorber A outlet flue gas data later in this subsection.

The mean elemental mercury oxidation across the catalyst was 80%, very near the value of 81% predicted from empirically corrected mass transfer calculations. Including the baseline mercury oxidation upstream of the catalyst, the mean catalyst outlet mercury oxidation percentage was 86%.

As described earlier, re-emission describes a phenomenon where a portion of the oxidized mercury removed across the wet FGD absorber is chemically reduced back to the elemental form which, being relatively insoluble, is released back into the absorber outlet flue gas. Re-emissions across both Absorber A and Absorber C appeared to limit mercury capture, with a mean value of 23% of the inlet oxidized mercury being re-emitted across Absorber A and a less significant 5% being re-emitted across Absorber C. However, the difference in re-emission percentages could be affected by day-to-day variations, since the Absorber A and Absorber C performance was measured on different days. For both absorbers, these results indicate that overall mercury

capture might be improved through the use of FGD mercury re-emission additives or perhaps changes in FGD operation. The re-emission values for Absorber A are discussed further below.

The mean overall mercury capture across the FGD system improved from 34% across baseline Absorber A to 80% across Absorber C because of the catalyst upstream. This represents a mean 69% increase in mercury capture compared to the baseline removal, which is at the upper end of the increase required by the DOE-NETL solicitation that led to funding of this project. The solicitation required a 50 to 70% increase beyond baseline mercury removal, or, stated differently, a 50 to 70% reduction from baseline mercury emissions.

However, the baseline (Absorber A) mercury removal measured may have been overstated in this comparison because of the higher baseline FGD inlet mercury oxidation when the Absorber A data were taken compared to when the Absorber C data were taken. Note that the Absorber A inlet data and the catalyst inlet data were taken at the same measurement ports in the south induced draft (ID) fan outlet duct on the two days, so this is clearly day-to-day variation and not a sampling location artifact.

On the other hand, as seen in Table 7, for the calculated percent mercury re-emission across Absorber A the 95% confidence interval about the mean (45%) was much greater than the mean itself (23% of the Absorber A inlet oxidized mercury). Looking at the individual OH run results, the first and third runs showed little or no re-emissions across Absorber A (3% and -8%, respectively) while the second run showed extremely high re-emissions at 66% of the Absorber A inlet oxidized mercury. A Q test was run on these results and it was not possible to disregard the results of the second run as an outlier at 90% confidence. Thus, the results of all three runs are included in the mean and confidence intervals shown in Table 7. Given the concerns about the data from Run 2, the re-emission levels and outlet mercury from Absorber A may be overstated in these data because of questionable results from Run 2. The overall mercury capture across Absorber A may be correspondingly understated as well.

Additional measurement methods were also conducted during the week of May 12. Figure 21 shows the locations and types of mercury measurements performed. Mercury measurements were performed at the inlet and outlet of the catalyst with Hg SCEMs, at the outlet of both absorbers with Appendix K (App K) systems, and compared to results across the catalyst and across both absorber modules by the OH method, as reported above.

The Hg SCCEM and App K measurement method results showed generally poor agreement when compared to the OH results. The results and comparisons of the flue gas mercury measurements are shown in Tables 8 and 9 and discussed below.

As shown in Tables 8 and 9, the mercury measurements obtained with Hg SCCEM and OH methods at the catalyst inlet (equivalent to Absorber A inlet) and catalyst outlet/Absorber C inlet did not agree well. With the exception of the total mercury measurement at the catalyst outlet, which showed good agreement with the OH result, the total mercury measured by the Hg SCCEM was only 47% to 56% of the mercury measured by the OH method.

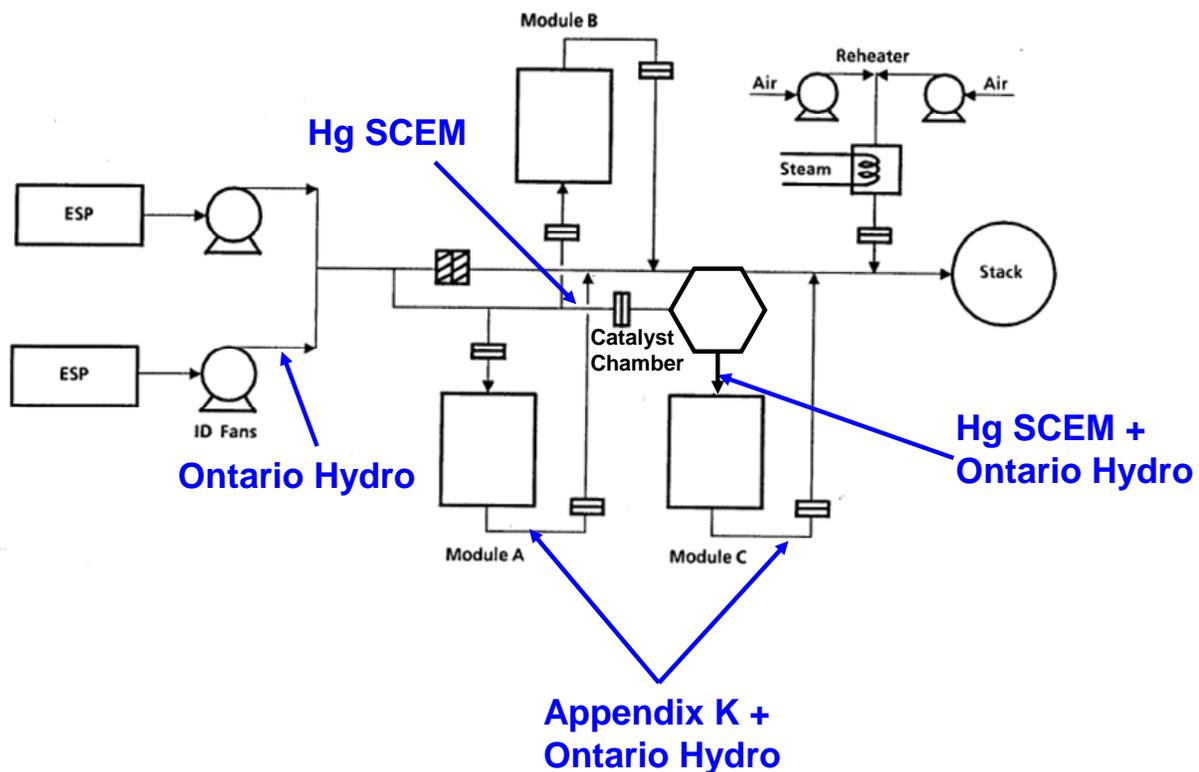


Figure 21. Schematic of Mercury Sampling Locations at Fayette Power Plant Unit 3 in May 2008 Measurements

Table 8. Comparison of Mercury Measurements across Catalyst and FGD Absorber C in May 2008

Catalyst Inlet Flue Gas ($\mu\text{g}/\text{Nm}^3$ @ 3% O_2):	
Hg^{T} (SCEM)	7.9 ± 0.6
Hg^0 (SCEM)	3.4 ± 0.1
Hg^{2+} (SCEM, by difference)	4.5 ± 2.2
Catalyst Outlet/Absorber C Inlet Flue Gas ($\mu\text{g}/\text{Nm}^3$ @ 3% O_2):	
Hg^{T} (SCEM)	14.1 ± 1.0
Hg^0 (SCEM)	0.2 ± 0.1
Hg^{2+} (SCEM, by difference)	13.9 ± 1.8
% Oxidation at Catalyst Outlet (SCEM)	98 ± 1
% Oxidation across Catalyst (SCEM)	94 ± 4

Absorber C Outlet Flue Gas ($\mu\text{g}/\text{Nm}^3$ @ 3% O_2):	
Hg ^T (Appendix K)	29.4 ± 22.8
Catalyst Inlet Flue Gas ($\mu\text{g}/\text{Nm}^3$ @ 3% O_2):	
Hg ^T (OH, by addition)	14.2 ± 1.5
Hg ⁰ (OH)	9.2 ± 0.4
Hg ²⁺ (OH)	5.0 ± 1.8
Catalyst Outlet/Absorber C Inlet Flue Gas ($\mu\text{g}/\text{Nm}^3$ @ 3% O_2):	
Hg ^T (OH, by addition)	13.6 ± 1.8
Hg ⁰ (OH)	1.8 ± 0.8
Hg ²⁺ (OH)	11.8 ± 2.2
Absorber C Outlet Flue Gas ($\mu\text{g}/\text{Nm}^3$ @ 3% O_2):	
Hg ^T (OH, by addition)	2.7 ± 0.7
Hg ⁰ (OH)	2.4 ± 0.8
Hg ²⁺ (OH)	0.3 ± 0.1
% Oxidation at Catalyst Outlet (OH)	86 ± 6
% Oxidation across Catalyst (OH)	80 ± 9
% Removal of Hg ^T across Absorber C (OH)	80 ± 5
% Removal of Hg ²⁺ across Absorber C (OH)	97 ± 3
Hg ⁰ Re-emissions, % of inlet Hg ²⁺ (OH)	5 ± 11
Calculated Relative Accuracy Results (alternate method result, percentage of OH result):	
Catalyst Inlet: Hg ^T Relative Accuracy, SCEM vs OH	56%
Catalyst Inlet: Hg ⁰ Relative Accuracy, SCEM vs OH	37%
Catalyst Outlet: Hg ^T Relative Accuracy, SCEM vs OH	104%
Catalyst Outlet: Hg ⁰ Relative Accuracy, SCEM vs OH	11%
Absorber C Outlet: Hg ^T Relative Accuracy, App K vs OH	1088%

Table 9. Comparison of Mercury Measurements across Absorber A in May 2008

Absorber A Inlet Flue Gas ($\mu\text{g}/\text{Nm}^3$):	
Hg ^T (Hg SCEM)	6.8 ± 0.5
Hg ⁰ (Hg SCEM)	2.8 ± 0.1
Hg ²⁺ (Hg SCEM, by difference)	4.0 ± 1.1
Absorber A Outlet Flue Gas ($\mu\text{g}/\text{Nm}^3$):	
Hg ^T (Appendix K)	3.6 ± 3.3
Absorber A Inlet Flue Gas ($\mu\text{g}/\text{Nm}^3$):	
Hg ^T (OH, by addition)	14.4 ± 1.1
Hg ⁰ (OH)	7.3 ± 0.9
Hg ²⁺ (OH)	7.1 ± 1.0
Absorber A Outlet Flue Gas ($\mu\text{g}/\text{Nm}^3$):	
Hg ^T (OH, by addition)	9.3 ± 2.7
Hg ⁰ (OH)	8.9 ± 2.7
Hg ²⁺ (OH)	0.4 ± 0.1
% Removal of Hg ^T across Absorber A (OH)	34 ± 18
% Removal of Hg ²⁺ across Absorber A (OH)	95 ± 1
Hg ⁰ Re-emissions, % of inlet Hg ²⁺ (OH)	23 ± 45
Calculated Relative Accuracy Results (alternate method result, percentage of OH result):	
Absorber A Inlet: Hg ^T Relative Accuracy, Hg SCEM vs OH	47%
Absorber A Inlet: Hg ⁰ Relative Accuracy, Hg SCEM vs OH	38%
Absorber A Outlet: Hg ^T Relative Accuracy, App K vs OH	39%

The percentage mercury oxidation across the catalyst as measured by the Hg SCEMs was 94%. This measurement is suspect because mass transfer modeling shows that the catalyst should achieve a maximum of 91% oxidation based on instantaneous reaction rates at the catalyst surface, and 81% oxidation when empirically corrected for reaction rate using pilot-scale data. The OH mercury oxidation results agree well with the empirically adjusted model results, showing 80% oxidation across the catalyst.

Because of the high mercury oxidation across the catalyst observed during the Hg SCEM measurements, the sampling configurations at both the inlet and outlet were changed to include only Teflon parts instead of a mixture of stainless steel and Teflon. This option was investigated because it was thought the stainless steel could possibly be oxidizing the mercury in the sample gas. The Teflon sampling system was tested at two depths into the duct horizontally and did not show any differences compared to the original stainless steel and Teflon sampling system. However, there were some spatial differences in comparing the measurements at different depths (i.e., the results varied by where in the duct the end of the probe was situated).

The gas for the SCEM sampling system was obtained from a single point in the duct whereas the OH method was conducted by traversing the entire width of the duct at depths representing the average velocity for each port (a full traverse of each port was not feasible). Because the duct is quite large (36.5-ft [11.1-m] width) it is likely that much of the observed measurement difference between the Hg SCEM and OH methods is a result of single point versus multiple point gas sampling.

The App K measurements at the Absorber A and C outlets also did not agree well with the OH total mercury measurements. The Absorber C outlet App K measurements averaged almost eleven times higher than the OH mercury measurements, and the individual run results were quite variable (the 95% confidence interval was nearly as large as the mean value). The sorbent tubes had noticeable amounts of dried FGD slurry solids on them when they were analyzed. The slurry would have had mercury in it which is thought to be the reason for the high recovery of mercury on these samples relative to OH results.

In contrast, the average Absorber A outlet App K mercury concentration was only 39% of the OH mercury concentration result. It is not apparent why the Absorber A sorbent tubes did not have the same apparent slurry carryover bias as Absorber C. The gas velocity data showed that Absorber A treats more flue gas than Absorber C because of the additional pressure drop associated with the catalyst upstream of Absorber C. About 58% of the scrubbed gas was measured to go through Absorber A and 42% through Absorber C. Correspondingly, Absorber A was operating at a higher gas velocity and was more likely to carry over slurry from its mist eliminator. Similar to the Absorber C outlet, there was a high degree of uncertainty with the App K measurements at the Absorber A outlet. The 95% confidence interval is $\pm 92\%$ of the mean concentration whereas the 95% confidence interval for the OH measurements conducted over the same time period at this location is only $\pm 29\%$ of that mean concentration.

The sampling issues with both the SCEM and App K methods persuaded the project team to modify the project plan to only sample with the OH mercury measurement method for the rest of the sampling efforts at FPP Unit 3. Further investigation of the reasons for the discrepancies with either the SCEM or App K mercury measurement methods were not conducted. Such investigations would have been expensive, requiring multiple instances of simultaneous measurements by the two methods, and might not have provided the information needed to determine how to successfully employ these lower cost measurement methods.

Flue Gas and FGD Sample Characterization Results

One objective of the initial intensive sample effort conducted in May 2008 was to characterize the flue gas and FGD system on FPP Unit 3, and to make measurements of whether any of the flue gas SO₂ content is oxidized to SO₃ across the catalyst. These results are reported below.

Gas-phase Halogen Concentrations

A URS-designed “mini-impinger” setup was used to measure flue gas halogen content, pulling a gas sample off of the inertial gas separator (IGS) filter for the catalyst inlet mercury SCEM. The impinger solutions used and analytical techniques are the same as those used in EPA Method 26a. The mini-impinger approach therefore measures halogen concentrations in the same manner as does Method 26a. The results of these measurements are shown in Table 10.

Table 10. Results of May 2008 Measurements of Gas-phase Halogen Concentrations at the Catalyst Inlet by Mini-impinger Method

Run No.	1	2	3
Date	5/13/2008	5/13/2008	5/13/2008
Sample Start Time	12:02	13:09	14:16
Sample End Time	13:02	14:09	15:16
HCl, ppmv dry @ 3% O ₂	1.52	1.66	1.67
HBr, ppmv dry @ 3% O ₂	0.03	0.03	0.03
Cl ₂ , ppmv dry @ 3% O ₂	0.01*	0.01*	0.01*
Br ₂ , ppmv dry @ 3% O ₂	<0.01	<0.01	<0.01
Oxygen, vol% dry	8.5	7.5	7.0
Moisture, vol%	12.2	12.1	12.2

*Measured value was below lowest analytical standard run during instrument calibration

The results show about 1.6 ppmv of HCl in the catalyst inlet flue gas (dry, 3% O₂ basis), with trace amounts of HBr and Cl₂. These measurements agree very well with the coal chloride concentration measured in the 5/13 coal sample of 19 ppm by weight (see Table 15 later in this section). This coal concentration was used to estimate a flue gas concentration based on the EPA F-factor, and the resulting estimate was very close to the measured values at 1.52 ppmv (dry, 3% O₂ basis). It is believed this small amount of halogen content is what contributes to mercury oxidation across the catalyst.

Gas-phase Trace Element Concentrations by Method 29

EPA Method 29 was used to quantify vapor-phase concentrations of trace elements in the flue gas other than mercury at the Absorber A inlet/catalyst inlet location (south ID fan outlet). The results from these measurements are summarized in Table 11. For most of the elements, the

amounts detected in the Method 29 impinger solutions were not much higher than was measured in field blank impinger solutions, suggesting that the flue gas concentrations of these elements were very low. The trace elements that were clearly present in the flue gas vapor phase in measurable concentrations included arsenic (As), barium (Ba) and selenium (Se). Selenium is a suspected mercury oxidation catalyst poison, so these concentrations are of particular interest.

Table 11. Results of May 2008 Measurements of Gas-phase Metal Concentrations at Catalyst Inlet by Method 29 (all values reported in $\mu\text{g}/\text{Nm}^3$ @ 3% O_2)

Location	Catalyst Inlet		
	1	2	3
Run No.	1	2	3
Date	5/15/2008	5/15/2008	5/15/2008
Sample Start Time	8:15	11:56	15:18
Sample End Time	11:13	13:20	16:55
As	1.31*	1.57	1.72
Ag	0.11*	0.09*	0.08*
Ba	35.0	32.7	42.5
Be	0.02	0.02	Not Detected
Cd	0.18*	0.22*	0.18*
Co	0.49	0.29*	0.28*
Cr	45.1	5.50*	5.55*
Cu	11.6*	14.8	8.65*
Mn	9.55*	5.96*	3.57*
Ni	32.0	6.55*	6.41*
Pb	1.51*	1.90*	1.59*
P	55.4*	54.5*	58.4*
Sb	0.12*	0.12*	0.10*
Se	146	143	159
Zn	38.1*	44.3*	34.5*

*Impinger concentration result was less than five times the field blank concentration for this analyte

Gas-phase SO_3 Concentration Measurements across Mercury Oxidation Catalyst

Because the catalyst installed is an oxidation catalyst, it could possibly oxidize other species present in the flue gas such as SO_2 . Oxidation of a significant fraction of the SO_2 in the flue gas

upstream of the wet FGD system to SO₃ or vapor-phase sulfuric acid (H₂SO₄) would be undesirable because of potentially adverse effects on duct corrosion and plume opacity. To determine if such oxidation is occurring, the Controlled Condensation System (CCS) method was used to measure flue gas SO₃/H₂SO₄ concentrations at the catalyst inlet and outlet locations. The results of these measurements are shown in Table 12.

Table 12. Results of May 2008 Flue Gas SO₃/H₂SO₄ Concentration Measurements across Mercury Oxidation Catalyst

Location	Catalyst Inlet	Catalyst Outlet
Flue Gas SO ₃ /H ₂ SO ₄ Concentration, ppmv (dry basis at actual O ₂):		
Run No. 1	0.04	0.01
Run No. 2	0.03	0.03
Run No. 3	0.04	0.43
Run No. 4	0.13	0.02
Average	0.06	0.12
Other Flue Gas Parameters Measured:		
O ₂ , vol%	7.0	7.1
Moisture, vol%	10.4	10.9
SO ₂ , ppmv (dry basis)	501	447

The results in Table 12 show very low SO₃/H₂SO₄ concentrations at both the catalyst inlet and outlet locations. Although the four-run average for the catalyst outlet concentration is higher than for the inlet location, that average is driven by one result (Run 3) that appears to be an outlier (0.43 ppmv dry basis). The practical lower method detection limit for the CCS method is generally regarded to be approximately 0.2 ppmv, and the other three measurements at the catalyst outlet were well below this value. In spite of the one outlier result, it appears that both the catalyst inlet and outlet SO₃/H₂SO₄ concentrations are at or below the practical method detection limit. Even taking the one 0.43 ppmv measurement at face value, this would represent less than 0.1% conversion of the catalyst inlet SO₂, which is an insignificant percentage. Consequently, SO₂ oxidation across the catalyst does not appear to be an issue.

FGD Slurry Analyses

FGD slurry samples were collected from the pH measurement pots on both Absorber A and Absorber C, to determine the Unit 3 FGD chemistry and to observe whether there were any significant differences between the chemistries of Absorbers A and C. As the samples were collected the pH, oxidation-reduction potential (ORP) and temperature of the slurry liquor were also measured. Portions of the samples were filtered right at the sampling location into

preserving solutions, which diluted and cooled the liquor and added chemicals to preserve the FGD liquor species of interest in its current chemical form. The sampling and preservation protocols used were from the EPRI *FGD Chemistry and Analytical Methods Handbook, Volume 2, Revision 2*.⁵ A whole slurry sample was also collected for a gravimetric weight percent solids determination, and the solids recovered from this determination were digested and analyzed for acid insoluble inert content, calcium, magnesium, sulfite, sulfate and carbonate. Finally, a slurry sample was collected and returned to the EPRI onsite mobile laboratory trailer, where it was filtered and preserved for offsite mercury analyses. The results from these analyses are presented in Table 13.

Table 13. Results of May 2008 FGD Slurry Analyses

Description	Absorber A		Absorber C	
	5/13/2008	5/14/2008	5/14/2008	5/16/2008
Time	15:50	11:15	14:25	13:40
pH	5.96	5.89	5.94	5.85
Temperature, °C	55.3	55.0	55.9	55.2
ORP, mV (relative to SHE)*	670	814	612	621
Solid Results:				
Ca, mg/g	225	224	225	224
Mg, mg/g	0.5	0.5	0.9	0.7
SO ₃ , mg/g	<0.7	<0.7	<0.7	<0.7
SO ₄ , mg/g	533	536	531	534
CO ₃ , mg/g	5	5	6	5
Inerts, wt%	2.70	2.27	2.58	2.47
Solids, wt%	10.3	11.4	10.1	10.0
Sulfite Oxidation, %	100	100	100	100
Limestone Utilization, %	98.5	98.8	98.1	98.6
Solid Analytical Closures				
Weight, %	-0.9	-1.0	-1.2	-1.2
Molar, %	0.0	-0.5	0.2	0.0
Liquid Results:				
Ca ⁺⁺ , mg/L	560	476	605	632

Description	Absorber A		Absorber C	
	5/13/2008	5/14/2008	5/14/2008	5/16/2008
Mg ⁺ , mg/L	1,610	1,450	2,310	2,070
Na ⁺ , mg/L	4,340	5,480	6,360	5,930
Cl ⁻ , mg/L	6,000	6,090	7,830	7,780
Br ⁻ , mg/L	69	84	105	97
F ⁻ , mg/L	58	67	98	88
CO ₃ ⁻ , mg/L	140	140	39	48
SO ₃ ⁻ , mg/L	<4	<4	<3	<3
SO ₄ ⁻ , mg/L	8,910	10,800	13,500	12,900
Total Hydrolyzable Sulfur, mg/L as SO ₄ ⁻ , net after subtracting sulfite and sulfate	1,480	-463	-680	20
Charge Imbalance Calculated, %	-3.5	-1.9	-0.4	-3.5

*SHE – standard hydrogen electrode, defined as 0 mV electrode potential. Measurements made against silver/silver chloride electrode saturated with potassium chloride, 197 mV electrode potential relative to SHE.

The results in the top half of the table show that URS measured absorber slurry pH values of 5.85 to 5.96, which were in reasonable agreement with plant instrumentation. The ORP showed highly oxidizing conditions, with values in the range of +600 to +800 mV relative to a standard hydrogen electrode (+400 to +600 mV as measured relative to a silver/silver chloride electrode saturated in potassium chloride). The slurry wt% solids were 10 to 11 wt% for all of the samples. Sulfite oxidation remained at 100% in all of the slurry solid samples, and the limestone utilization was consistently high, ranging from 98.1% to 98.8%. The analytical closures on the solid samples were all acceptable from both a weight and molar recovery basis, which provides some confidence in the accuracy of the analyses. There was no significant difference in solid chemistry between the Absorber A and Absorber C samples.

The liquid results show that Absorber C was operating at slightly higher concentrations of dissolved, highly soluble species (e.g., magnesium, sodium, and chloride) than Absorber A. This difference does not seem to be significant.

There is a value in the table called “total hydrolyzable sulfur” that represents possible “sulfur-nitrogen” species in the FGD liquor. Sulfur-nitrogen species are generally chemically reducing species, and as such they can impact sulfur oxidation efficiencies and mercury re-emission reactions. The total hydrolyzable sulfur analysis is conducted by subjecting a liquor sample to very strong oxidizing and hydrolyzing conditions, to break down the complex sulfur-containing

molecules, then analyzing the resulting sample for sulfate concentration. The original sulfite and sulfate concentration measurements, such as are shown in the table, are then subtracted from the total sulfate in the hydrolyzed sample. If there are significant quantities of sulfur-nitrogen species present in the FGD liquor, the total hydrolyzable sulfur concentration can be significantly higher than what was previously determined to be present in the form of sulfite or sulfate. However, the total hydrolyzable sulfur can also include sulfur-only species such as dithionate ($S_2O_6^-$) and peroxydisulfate ($S_2O_8^-$). The values in Table 13 for total hydrolyzable sulfur concentrations for these liquor samples vary from positive to negative, which suggests that there was not much sulfur-nitrogen species or other sulfur-containing species other than sulfite or sulfate present in this FGD liquor.

The last row in the table, the calculated charge imbalance in the liquor analytical results, compares the total cations to total anions analyzed in the liquor, and shows acceptable closure for these samples (i.e., very close to electroneutrality). This indicates there is no major cation or anion missing from the analysis and/or suggests that the anion and cation concentrations are reasonably accurate.

Mercury Analyses of FGD Samples

Table 14 summarizes the results of slurry solid and liquor mercury analyses. Also shown in the table are the results of “reagent blank” and “field blank” analyses, the latter conducted on deionized water treated through the same filter apparatus and recovered in sample bottles from the same source and with the same preserving solutions as the FGD samples. The blank results show mercury concentrations below the effective analytical detection limits, which provides some confidence that there was no contamination of the actual slurry samples.

The results show relatively low liquor mercury concentrations of 0.2 to 1.0 $\mu\text{g/L}$ (~ppb) of mercury in both the Absorber A and Absorber C slurries during these sampling periods. When compared to the amount of mercury found in the slurry solids, the liquid-phase mercury represents only 0.1 to 0.3% of the total mercury in the slurry. Thus, 99.9 to 99.7% of the mercury found in these slurry samples was present with the slurry solid phase.

Mercury re-emissions are known to be caused by reactions between absorbed oxidized mercury (Hg^{2+}) and sulfite/bisulfite and/or other reducing species in FGD liquors. For a given FGD chemistry, higher concentrations of Hg^{2+} in the liquor generally result in higher re-emission levels. The observed low liquor mercury concentrations (all of the measured Hg in the liquor are expected to be Hg^{2+}) may account for the relatively minor mercury re-emissions measured by the OH method across the wet FGD Absorber C (see Tables 6 and 7). However, the reason for the higher average re-emissions measured across Absorber A on May 13 and 14 is less clear, as the liquor mercury concentrations were slightly lower in Absorber A than in Absorber C. However, as mentioned above, only one of three OH measurements at the Absorber A outlet showed significant re-emissions, and this result is somewhat suspect.

Table 14. Results of May 2008 FGD Sample Mercury Analyses

Sample Location	Date	Time Sampled	Hg in Solids (µg/g)	Liquor Hg (µg/L)	wt% Solids	% of slurry Hg in liquor
Field Blank	5/13/2008	12:25	-	<0.155	-	-
Reagent Blank	5/13/2008	15:05	-	<0.155	-	-
Absorber A	5/13/2008	16:12	2.18	0.628	10.3	0.2%
Absorber A	5/14/2008	10:47	1.96	0.240	11.4	0.1%
Absorber C	5/14/2008	13:45	3.24	0.267	10.1	0.1%
Absorber A	5/15/2008	15:05	1.96	0.331	NA*	NA
Absorber C	5/15/2008	10:00	3.26	0.987	NA	NA
Gypsum	5/15/2008	14:40	2.08	-	-	-
Field Blank	5/16/2008	-	-	<0.155	-	-
Absorber C	5/16/2008	13:40	2.96	1.05	10.0	0.3%

*NA – not analyzed

Since nearly all of the mercury in the slurry was found with the solids, it would be expected that an increase in mercury capture across Absorber C due to the oxidation of mercury by the catalyst upstream would be reflected in higher mercury concentrations in the Absorber C slurry solids. This is indeed the case. The Absorber A slurry solids were observed to contain about 2 µg/g (ppm) of mercury while the Absorber C slurry solids contained 3 µg/g or greater. On days where the mercury concentration was measured in both the Absorber A and Absorber C slurry solids (May 14 and 15), the mercury concentration in the Absorber C solids was 65 to 66% higher than in the Absorber A solids. This increase agrees well with the OH results, which showed approximately a 69% mean increase in mercury capture across Absorber C due to the effects of the mercury oxidation catalyst, or a 64% increase when compared to only OH Runs 1 and 3 at the Absorber A outlet.

The dewatered gypsum produced by the Unit 3 wet FGD system is a mixture of byproduct solids produced in Absorbers A and C. As such, it was expected that the gypsum would have a mercury content about halfway between that of the Absorber A and C slurry solids. The gypsum sample from May 15 actually had a mercury concentration closer to that of Absorber A than Absorber C. However, the Unit 3 FGD system has a thickener for primary dewatering. Because of the solids residence time in the thickener and filter feed tank, the gypsum sample may be reflective of operation several days earlier, perhaps during a time that the baseline mercury oxidation percentage and mercury capture by Absorber A was lower than on May 13-15.

Mercury Mass Balances Around the Unit 3 FGD System

Mercury balance calculations were conducted based on the data collected around the Unit 3 FGD system the week of May 12th. Good mercury balance closure would add credibility to the flue gas mercury concentration measurements made, and would help support the decision that the OH method results provided the best measure of flue gas mercury concentrations. Three types of mass balances were conducted. Each type is described below along with the calculation results.

Coal Mercury versus ESP Outlet Flue Gas Mercury Concentrations

Coal analyses were used to calculate the concentration of mercury expected in the flue gas downstream of the ESP, taking into account the amount of mercury found in the fly ash sample. The flue gas flow rate was estimated using a fuel-specific F factor (EPA Method 19), and the coal mercury content was taken from analyses of a single coal sample from each day that OH method measurements were made. The gross unit load and gross plant heat rate were also used in these calculations. The fly ash mercury content was taken from a single fly ash sample collected each day, and the fly ash quantity was estimated by assuming the fly ash represents 80% of the coal ash. The coal and fly ash analysis data used for these calculations are shown in Table 15.

Table 15. May 2008 Coal and Fly Ash Sample Analysis Results

Date	5/13/2008	5/14/2008	5/16/2008
Coal:			
Total Moisture (wt%)	32.26	32.36	30.72
Ash (dry wt%)	7.82	6.10	8.82
Carbon (dry wt%)	68.16	68.58	67.35
Hydrogen (dry wt%)	5.44	5.09	5.29
Nitrogen (dry wt%)	1.43	1.42	1.36
Sulfur (dry wt%)	0.80	0.80	0.86
Chlorine (dry wt%)	0.0019	0.0007	0.0037
Heating Value (dry BTU/lb) [kJ/kg]	11,936 [27,760]	11,706 [27,230]	11,783 [27,410]
Mercury (ppm, dry basis)	0.13	0.14	0.18
Fly Ash (first field sample):			
Mercury (ppm, dry basis)	0.08	0.07	0.12
Loss on Ignition (dry wt%)	0.38	0.16	0.31

Comparisons between the ESP outlet mercury based on coal and ash sample analyses and the OH measurement at the catalyst inlet/Absorber A inlet (south ID fan outlet) are shown in Table 16.

The results show reasonable agreement between the coal mercury and the flue gas OH measurements performed on May 13th and 14th, with the mean OH value representing 83% of what would be expected based on the coal mercury. However, for the ESP outlet/catalyst inlet values measured on May 16th, the agreement was only 66%. It appears that the poorer agreement is a result of relatively high mercury content in the coal sample from May 16th. The coal mercury concentration was measured to be considerably higher in the grab sample from May 16th compared to the other days, and higher than what the plant reported for routine coal train samples from May. It is likely that the grab sample from May 16th represented a portion of the coal with higher than average mercury content, and thus biased the results of this comparison.

Table 16. Mercury Balance for ESP Outlet Flue Gas, May 2008

	Absorber A Inlet Measurements	Catalyst Inlet Measurements
Date	5/13-5/14/2008	5/16/2008
Hg in Coal Fired, g/h	21.6	29.2
Hg in Fly Ash, g/h	0.6	1.4
Net Hg from Coal in ESP Outlet Gas, g/h	20.0	27.8
Hg in ESP Outlet Gas as measured by OH (mean for 3 runs), g/h	17.3	17.9
OH Recovery of Hg in Coal (mean for 3 OH runs), % \pm 95% Confidence Interval of Mean	83 \pm 3	66 \pm 6

Given that the SCEM results for the ESP outlet/catalyst inlet location showed even lower total mercury concentrations than the OH results, and by a considerable margin (mean values 47% to 56% of the OH result), these mass balances showed the OH measurements were the better measure of flue gas mercury concentrations. This comparison supported the decision to conduct only OH measurements in the future.

Recovery of Flue Gas Mercury in Gypsum Byproduct

A second mercury balance calculation determined the extent to which the mercury measured in the gypsum byproduct samples reflects the amount of coal mercury that appeared to have been removed by the FGD absorbers. As shown earlier in this section of the report, the amount of mercury in the liquor was very low in the FGD slurry samples (0.1 to 0.3% of the total mercury in the slurry), so only the mercury in the gypsum solids was used in the calculations. The amount of mercury recovered in the gypsum was calculated from the absorber slurry solids sample mercury concentration and the estimated gypsum production in each FGD absorber. The latter was estimated based on the percentage of the flue gas scrubbed in each absorber, the coal sulfur, and the percent SO₂ removal across the wet FGD system (corrected for the amount of flue gas bypass around the FGD system). At steady state, the apparent removal of the coal mercury in the gypsum should match the observed percent mercury removal across the FGD modules as measured by the OH method.

The results of these calculations are shown in Table 17. The results show that the apparent removal of the coal mercury in Absorber A is higher than predicted based on the OH results across the absorber, while the apparent removal of coal mercury in Absorber C is very near what the OH results indicate. The 95% confidence intervals of the two types of measurements overlap for both absorbers.

Table 17. Recovery of Coal Mercury in FGD Gypsum, May 2008

	Absorber A Inlet Measurements	Catalyst Inlet Measurements
Date	5/13-5/14/2008	5/16/2008
Net Hg from Coal in ESP Outlet Gas, g/h	20.0	27.8
Hg in Flue Gas to Absorber, g/h	11.5	11.0
Hg in Gypsum Produced in FGD Absorber, g/h	7.3	8.5
Gypsum Recovery of Hg in Coal (mean for 3 OH run periods), %, \pm 95% Confidence Interval of Mean	64 \pm 15	77 \pm 1
Observed Hg Removal across Absorber by OH Method (mean for 3 OH runs), %	34 \pm 18	80 \pm 5

However, in the case of the Absorber A data, the confidence intervals for both measurement types are very large, indicating considerable uncertainty in the mean values. For the OH results, recall that the Absorber A outlet data for the second of three runs were suspect, and led to the high 95% confidence intervals to the mean of three values. If the data from only Runs 1 and 2 are averaged, the observed mercury removal across Absorber A by the OH method increases to 43%, which is closer to but still not a good match with the 64% mean value indicated by the mercury in the gypsum

A second mass balance was calculated using the catalyst inlet OH values rather than the coal mercury content as the FGD inlet mercury concentration. The results of these calculations are shown in Table 18. Using the inlet OH run data as the basis for the amount of mercury entering the FGD system, the mercury in the gypsum was calculated to over-recover the amount of mercury measured to have been removed from the flue gas. For both Absorber A and Absorber C, the gypsum mercury recovery was over 40 percentage points higher than the measured mercury removal across these absorbers. There was no overlap in the 95% confidence intervals of the means.

Table 18. Recovery of ESP Inlet Mercury in FGD Gypsum, May 2008

	Absorber A Inlet Measurements	Catalyst Inlet Measurements
Date	5/13-5/14/2008	5/16/2008
Hg in Flue Gas to FGD Absorber by OH, g/h	9.5	6.8
Hg in Gypsum Produced in FGD Absorber, g/h	7.3	8.5
Gypsum Recovery of Hg in FGD Inlet Gas (mean for 3 OH runs), % ± 95% Confidence Interval of Mean	77 ± 16	125 ± 17
Observed Hg Removal across Absorber by OH Method, % ± 95% Confidence Interval of Mean	34 ± 18	80 ± 5

There are several possible explanations for this high recovery, including (but not limited to):

- The Absorber A and catalyst inlet OH total mercury concentrations were biased low (this was already indicated as a possibility in Table 11 above);
- The Absorber A and C outlet OH total mercury concentrations were biased high, which would understate the mercury capture by each module;
- The gypsum production estimates were biased high (e.g., the actual SO₂ removal was lower than indicated, or the amount of flue gas bypass around the FGD system was higher than indicated); and/or
- The gypsum mercury concentrations measured were biased high.

The actual reason(s) for the high recovery were not determined as part of this project. However, it was concluded that the FGD slurry mercury analyses tend to support the OH results, in spite of the poor closure of some of these mass balance calculations. As shown earlier in Table 14, Absorber A slurry solids were observed to contain about 2 µg/g (ppm) of mercury while the Absorber C slurry solids contained 3 µg/g or greater. On days where the mercury concentration was measured in both the Absorber A and Absorber C slurry solids (May 14 and 15), the mercury concentration in the Absorber C solids was 65 to 66% higher than in the Absorber A solids. This increase agrees well with the OH method results, which showed 69% greater mercury capture across Absorber C than Absorber A (64% using only the OH results from Runs 1 and 2 at the Absorber A outlet).

November 2008 Results

Flue Gas Mercury Oxidation and Capture

During the week of November 17, 2008, a second round of OH mercury oxidation and FGD capture data were measured across Absorber C and the catalyst upstream, and across Absorber

A. Figure 22 illustrates the measurement locations. All four measurement locations were sampled simultaneously during three test periods over two days. In the previous, May 2008 test period, the performance of baseline Absorber A and the performance of Absorber C with the catalyst upstream were measured on separate days.

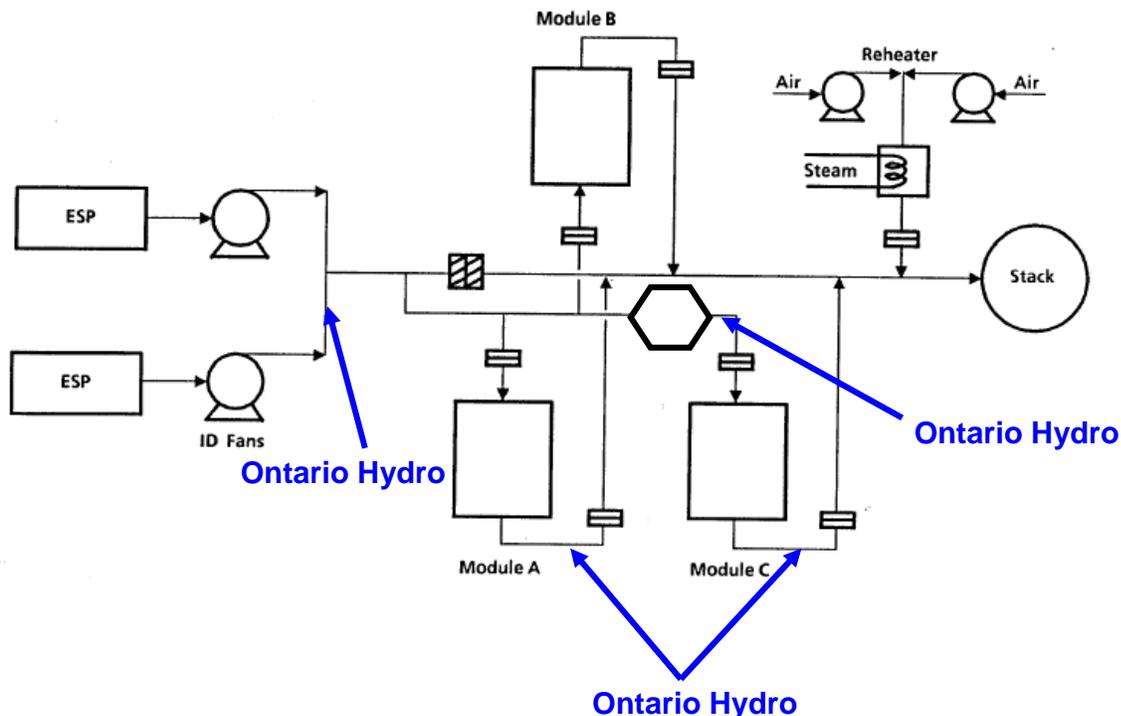


Figure 22. Schematic of Mercury Sampling Locations at FPP Unit 3, November 2008

The OH mercury concentration results are summarized in Table 19. These data were used to calculate mercury oxidation and FGD capture percentages, which are reported in Table 20. The corresponding May 2008 results are repeated in the table for comparison.

As a reminder, the previous, May 2008 OH results showed an average of 80% oxidation of elemental mercury across the catalyst, 86% oxidized mercury at the catalyst outlet and 80% total mercury removal across Absorber C. Absorber A showed 49% mercury oxidation at the inlet and 34% total mercury removal. The corresponding improvement in mercury capture by Absorber C compared to Absorber A outlet was 69%.

In comparison, the November 2008 OH results showed an average of 77% oxidation of mercury across the catalyst, a 3-percentage-point decrease compared to the May data. Some loss of mercury oxidation activity is expected over time because of fly ash buildup and adsorption of species such as selenium from the flue gas which can block active catalyst sites. This drop of 3% oxidation represents a relatively small decrease over more than six months of service. However, given the potential for measurement error in both sets of measurements (see the 95% confidence intervals for the means for each set of measurements) it was clear that it would take additional OH measurements over time to accurately assess the rate of activity loss for this installation.

Table 19. November 2008 Gas-phase Mercury Concentration Data by the Ontario Hydro Method (mean value for three measurement runs \pm 95% confidence interval of mean, corrected to 3% O₂) see discussion in text about O₂ correction for November data

Location	Hg ⁰ Concentration (µg/Nm ³ at 3% O ₂)	Hg ²⁺ Concentration (µg/Nm ³ at 3% O ₂)	Total Hg Concentration, includes particulate Hg	
			(µg/Nm ³ at 3% O ₂)	(lb Hg/TBtu)
Absorber C (Catalyst Upstream) Data (11/19-11/20/2008):				
Catalyst Inlet*	4.6 \pm 0.3	5.1 \pm 1.2	9.7 \pm 0.9	6.4 \pm 0.6
Catalyst Outlet/ Absorber C Inlet	1.0 \pm 0.1	9.0 \pm 0.1	10.0 \pm 0.2	6.6 \pm 0.1
Absorber C Outlet	4.7 \pm 0.3	0.3 \pm 0.1	5.0 \pm 0.2	3.3 \pm 0.1
Absorber A (No Catalyst) Data (11/19-11/20/2008):				
Absorber A Inlet*	4.6 \pm 0.3	5.1 \pm 1.2	9.7 \pm 0.9	6.4 \pm 0.6
Absorber A Outlet	6.0 \pm 0.3	0.2 \pm 0.2	6.0 \pm 0.2	4.0 \pm 0.1

*These numbers represent the same measurements, made at the outlet duct of the south Unit 3 ID fan

Table 20. Mercury Oxidation and FGD Capture Data by the Ontario Hydro Method, May 2008 and November 2008 Data (mean \pm 95% confidence interval for 3 measurement runs)

Parameter	May 2008	November 2008
Catalyst Inlet Hg Oxidation (%)	35 \pm 9*	52 \pm 7*
Predicted Hg Oxidation across catalyst (% , empirically corrected)	81	81
Measured Hg Oxidation across catalyst (%)	80 \pm 9	77 \pm 4
% Oxidized Hg at Catalyst Outlet	86 \pm 6	90 \pm 1
Hg Removal Across Absorber C Wet FGD, %	80 \pm 5	49 \pm 4
Absorber C Hg ⁰ Re-emissions, % of FGD inlet Hg ²⁺	5 \pm 11	41 \pm 3
Baseline (Absorber A) Inlet Hg Oxidation (%)	49 \pm 6*	52 \pm 7*
Absorber A Hg Removal (%)	34 \pm 18	37 \pm 9
Absorber A Hg ⁰ Re-emissions, % of FGD inlet Hg ²⁺	23 \pm 45	28 \pm 9
Absorber C Hg Removal Increase over Absorber A (%)	69 \pm 13	18 \pm 6

*Measurements for Absorber A versus Absorber C were made on separate days in May 2008, but were conducted simultaneously over a two-day period in November 2008

Since the baseline mercury oxidation percentage was higher at the catalyst inlet in November 2008 than was measured in May, the overall mercury oxidation percentage was higher at the catalyst outlet/Absorber C inlet in November than in May, 90% versus 86%. However, this did not correspond with greater mercury removal across Absorber C; only 49% removal was measured in November compared to 80% in May. The reason for the lower removal in November appears to be greater elemental mercury re-emissions across Absorber C. In May, it was calculated that only 5% of the Absorber C inlet oxidized mercury content was re-emitted, whereas in November 41% was re-emitted.

Absorber A was observed to remove an average of 37% of the total inlet mercury in November compared to 34% in May. This is a result of slightly higher inlet mercury oxidation in November (52% versus 49%) and similar levels of mercury re-emissions (28% of the inlet oxidized mercury re-emitted in November compared to 23% in May). However, there were concerns about the results of Run 2 at the Absorber A outlet in May, so the May Absorber A average mercury removal may have been understated while the re-emission percentage may have been overstated.

Because of the relatively high re-emission level measured across Absorber C, the observed improvement in mercury capture over Absorber A resulting from the oxidation catalyst was only 18% on average, compared to 69% in May 2008. It is apparent that the re-emission levels across these FGD absorbers vary over time, and may be exacerbated for Absorber C by the relatively high percentage of oxidized mercury going it. To fully realize the benefits of the oxidation catalyst in enhanced mercury capture by the downstream FGD system, modifications to the FGD chemistry and/or the use of re-emission additives may be required.

There is one issue with the November 2008 OH measurement results regarding how the flue gas oxygen concentration corrections to 3% O₂ were made. Normal procedure during OH measurements is to measure the sample gas O₂ concentration during each run. The run data are corrected to a common O₂ concentration, typically 3%, to account for flue gas leakage to the duct and/or in the OH sampling train for each location and run. Normally, in a positive-pressure duct such as upstream of the FGD modules at FPP, and with the host unit operating at full load, the O₂ concentrations measured from run to run and from location to location should show only minor variation. Thus, the amount of correction of each measured concentration to a 3% O₂ basis should be relatively consistent for each measurement at each location.

However, in November 2008 the O₂ measurements made during each run at each location (by the Fyrite method) show a wide range of variation. Individual measurements ranged from 3.2% to 11.0% O₂ across the four measurement locations. This much variation does not appear to be technically possible. As an example, the 11% O₂ measurement was made at the catalyst outlet location, which averaged 9.5% O₂ for the three OH measurement runs. In comparison, the ID fan outlet location averaged 6.5% O₂ for the same three run periods. The flue gas duct is at positive pressure between these two measurement locations, so air leakage is very unlikely and a 3% O₂ increase in flue gas oxygen concentration does not seem possible. The 3.2% O₂ measurement was made at the Absorber A FGD outlet, which averaged 4.8% O₂ for the three OH runs. This location runs slightly negative pressure relative to ambient because of the draft from the Unit 3 stack, so if anything a small amount of air leakage could be possible. However, the average O₂

concentration measured went down compared to the Absorber A inlet flue gas, which for these measurements was the South ID fan outlet gas. This again does not seem technically possible. Other evidence shows that the actual sample gas O₂ concentrations could not have varied by as much as the Fyrite measurements showed, including:

- Sample gas moisture and CO₂ concentrations were consistent from run to run, and did not support that there were significant variations in air dilution from run to run or location to location,
- Unit 3 stack and furnace monitors showed very consistent CO₂ and O₂ concentrations (respectively) from run to run, and very similar values compared to what was measured in May 2008,
- The uncorrected total mercury concentrations for the catalyst inlet (ID fan outlet) and catalyst outlet location showed much better agreement (i.e., little loss or gain of total mercury across the catalyst) before any O₂ correction than after correcting to 3% O₂ with the as-measured Fyrite data.

For these reasons, it was decided to use the average flue gas O₂ concentration measured in May 2008 for all runs at all locations (7.3%) to correct the as-measured flue gas mercury concentrations to a 3% O₂ basis. It was felt that this value provided the best estimate of the actual flue gas O₂ concentrations with Unit 3 at full load, and was consistent with the stack CO₂ concentrations measured in May and November. One might consider that the O₂ concentrations are higher at the FGD outlet locations than at the upstream locations, because the FGD outlet ducts tend to run at negative pressure and because of the effects of forced oxidation air in the absorbers. However, the outlet duct pressure tends to run only slightly negative, and the oxidation air is introduced in a separate, vented (to atmosphere) reaction tank rather than in an integral reaction tank as in most newer absorber designs. Furthermore, since this is a low-sulfur FGD system, the amount of oxidation air added is minimal compared to the flue gas oxygen. Thus, little if any increase in flue gas O₂ would be expected across the absorbers. Using an assumed common O₂ concentration for all runs at all locations essentially uses the as-measured mercury concentrations to calculate performance and only corrects to the 3% O₂ level for comparison with the May data.

FGD Sample Analyses

During the November 2008 measurement period, FGD samples were collected, preserved, and subsequently analyzed for routine FGD analytes. These results are presented below in Table 21. The results in the top half of the table show that absorber slurry pH values of 5.72 to 5.84 were measured, which were in reasonable agreement with plant instrumentation and close to the values measured in May 2008. The ORP values were in the range of +450 to +480 mV relative to SHE (~250 to 280 mV as measured). The slurry wt% solids values were 7 to 8 wt%, which were lower than were measured in May (10 to 11 wt%). Sulfite oxidation remained at 100% in all of the slurry solid samples, and the limestone utilization was high, ranging from 98.3% to 98.8%. The analytical closures on the solid samples were all acceptable from both a weight and molar

recovery basis. There was no significant difference in solid chemistry between the Absorber A and Absorber C samples.

Table 21. Results of November 2008 FGD Slurry Analyses

Description	Absorber A	Absorber C
Date	11/20/2008	11/20/2008
Time	-	10:55
pH	5.72	5.84
ORP, mV relative to SHE*	480	450
Temperature, °C	55.5	55.5
Solid Results:		
Ca, mg/g	225	226
Mg, mg/g	1.2	1.0
SO ₃ , mg/g	<0.7	<0.7
SO ₄ , mg/g	530	536
CO ₃ , mg/g	4	3
Inerts, wt%	2.19	1.78
Solids, wt%	6.94	7.62
Sulfite Oxidation, %	100.0	100.0
Limestone Utilization, %	98.3	98.8
Solid Analytical Closures		
Weight, %	-2.0	-1.6
Molar, %	0.7	0.6
Liquid Results:		
Ca ⁺⁺ , mg/L	635	724
Mg ⁺ , mg/L	2,498	2,518
Na ⁺ , mg/L	7,224	7,149
Br ⁻ , mg/L	120	117
Cl ⁻ , mg/L	9,131	8,826

Description	Absorber A	Absorber C
Date	11/20/2008	11/20/2008
CO ₃ ⁼ , mg/L	44	44
SO ₃ ⁼ , mg/L	<3	<3
SO ₄ ⁼ , mg/L	14,674	14,397
Charge Imbalance Calculated, %	-2.1	0.7

*SHE – standard hydrogen electrode

The liquid results show that Absorber C was operating at similar concentrations of dissolved, high solubility species (e.g., magnesium, sodium, and chloride) compared to Absorber A. The last row in the table, the calculated charge imbalance in the liquor analytical results, compares the total cations to total anions analyzed in the liquor, and shows acceptable closure for these samples (i.e., electroneutrality). This indicates there is no major cation or anion missing from the analysis and/or suggests that the anion and cation concentrations are reasonably accurate. Total hydrolyzable sulfur analyses were not conducted for the November 2008 samples, but the fact that the liquor charge imbalance calculations come so close to electroneutrality suggests that there could be few, if any, sulfur-nitrogen species or other sulfur-containing species present.

Table 22 summarizes the results of absorber slurry solid and liquor mercury analyses, and also shows the results of field blank analyses. The blank results show mercury levels below the effective analytical detection limits, as expected.

Table 22. Results of November 2008 FGD Sample Mercury Analyses

Sample Location	Date	Time Sampled	Hg in Solids (µg/g)	Liquor Hg (µg/L)	wt% Solids	% of Slurry Hg in Liquor
Field Blank	11/19/2008	16:00	-	<0.132	-	-
Mod A Absorber	11/19/2008	14:09	1.52	0.851	7.21	0.6%
Mod C Absorber	11/19/2008	16:05	1.65	2.15	7.80	1.3%
Field Blank	11/20/2008	14:00	-	<0.133	-	-
Thickener Overflow	11/20/2008	9:15	93.3	1.80	0.004	31.9%
Mod A Absorber	11/20/2008	12:45	1.79	0.404	6.94	0.3%
Mod C Absorber	11/20/2008	12:45	1.70	0.605	7.62	0.4%
Gypsum	11/19/2008	9:30	1.52	-	-	-

The FGD sample results show liquor mercury concentrations of 0.40 to 0.85 µg/L (~ppb) of mercury in Absorber A and 0.61 to 2.15 µg/L in Absorber C during these sampling periods. The

mercury concentrations in the Absorber C liquor are generally higher than the 0.2 to 1.0 µg/L values measured in May 2008 whereas the Absorber A mercury liquor concentrations are similar to what was measured in May. When compared to the amount of mercury found in the slurry solids, the liquid-phase mercury represents 0.3 to 0.6% of the total mercury in the slurry for Absorber A and 0.4 to 1.3% of the total mercury in the slurry for Absorber C. In May 2008, the percentage of the mercury in the slurry liquor in both modules was generally lower, representing 0.1 to 0.3% of the total mercury in the slurry (i.e., 99.7 to 99.9% of the mercury was in the solids in May).

The higher liquor mercury concentrations may account for the higher mercury re-emissions measured by the OH method across Absorber C in November as compared to May 2008 (41% of the inlet Hg²⁺ re-emitted versus only 5%). The re-emission levels were also slightly higher across Absorber A in November compared to May (28% versus 23%).

The reason for the higher liquor mercury concentrations and the corresponding higher re-emission levels in November versus May might be related to the wt% solids levels in the absorber slurry. There is growing evidence showing that oxidized mercury changes phase from the FGD liquor to the slurry solids due to adsorption on and/or co-precipitation with fine ferric hydroxide precipitates in the slurry. The iron is introduced from the limestone reagent, from fly ash carryover into the FGD system, and from attrition of iron-based grinding media in the limestone ball mill. Once the mercury is in the solid phase, it is less likely to be chemically reduced and re-emitted.

In an FGD system with a thickener for primary solids dewatering, fine solids are almost quantitatively separated from the FGD liquor in the thickener, so there is virtually no recycle of fine solids back to the absorbers. For example, in Table 23 it can be seen that the thickener overflow had only 0.004 wt% solids content. Thus, the amount of the iron hydroxide solids present in an FGD system with a thickener is a function of the rate at which the solids enter the system and the wt% solids in the absorber slurry. In contrast, in a system with hydrocyclones for primary dewatering, there can be considerable recycle of fine solids back to the absorber, so iron hydroxide concentrations in the absorber slurry can cycle up over time.

As discussed above, the wt% solids in the absorber slurry was considerably lower in November than in May 2008, which most likely means there were fewer iron hydroxide solids present to adsorb/co-precipitated mercury from the liquor. It is possible that if the slurry wt% solids level were increased, the mercury re-emissions would have decreased. This potential effect is discussed later in this section.

Although the amount of mercury found in the liquor was higher in November than in May, nearly all of the mercury in the slurry was still found with the solids (98.7% to 99.7%). Thus, it would be expected that an increase in mercury capture across Absorber C as a result of the oxidation of mercury across the catalyst upstream would be reflected in higher mercury concentrations in the Absorber C slurry solids compared to Absorber A solids. Based on the November 2008 OH results, this increase in concentration should amount to about 18% on average. However, unlike the May results where the FGD solids mercury concentrations showed agreement with the OH results, the November solids results do not agree. In the November 19

samples, the Absorber A slurry solids were observed to contain 1.52 $\mu\text{g/g}$ (ppm) of mercury while the Absorber C slurry solids contained 1.65 $\mu\text{g/g}$. Thus, the observed increase in concentration was only 9%. In the November 20 samples, the Absorber C slurry solids actually had a lower measured mercury concentration than the Absorber A solids (1.70 versus 1.79 $\mu\text{g/g}$).

There are three potential reasons why the absorber solids analyses did not show the expected 18% higher mercury concentration in Absorber C compared to Absorber A. One is that the digested absorber solids did not run well on the cold-vapor atomic absorption (CVAA) analyzer used to measure their mercury concentrations. There were issues with both repeatability of duplicate analyses and poor recovery of matrix spikes (i.e., mercury spiked into the original solids prior to digestion). The samples were analyzed several times in an attempt to resolve these issues, with no clear resolution. The numbers shown in Table 23 represent an average of all of the measurements for each sample. Because of this, the accuracy of these analyses may not be adequate to distinguish an 18% difference in mercury concentration. In retrospect, these samples perhaps should have been analyzed using atomic fluorescence, where they could have been run at higher dilution to minimize matrix interferences that may have been affecting the CVAA results.

A second potential reason for this apparent discrepancy between the OH and solids analysis results is that the absorber solids are taken from the absorber reaction tank, which at FPP has a very long residence time (several days). Thus, the solids may not be truly reflective of the conditions at the time the OH measurements were made.

A third potential reason is that mercury may have been lost from the vent on the reaction tanks. As mentioned earlier in this report, the reaction tanks on the Unit 3 FGD system are separated from the absorber vessel and have separate vent stacks to the atmosphere to release excess forced oxidation air. It is possible that in addition to the mercury re-emissions measured in the Absorber C outlet flue gas, there were mercury re-emissions occurring while the slurry was in the reaction tanks and being emitted from the vent stacks. In such a case, this mercury loss would not have been measured in the flue gas, and the mercury in the reaction tank slurry solids would be lower than predicted from the flue gas measurements.

The thickener overflow and byproduct gypsum solids were also sampled and analyzed for mercury concentration. The dewatered gypsum produced by the Unit 3 wet FGD system was at the time a mixture of solids produced in Absorbers A and C. As such, it was expected that the gypsum would have a mercury content about halfway between that of the Absorber A and C slurry solids. The single gypsum sample collected November 19 had a mercury concentration nearly identical to that of Absorber A, and lower than in the Absorber C sample. However, as a result of the solids residence time in the thickener and vacuum filter feed tank, the gypsum sample may be reflective of operation several days earlier, during a time where perhaps the baseline mercury oxidation percentage and mercury capture by Absorber A was lower than on November 19.

The thickener overflow sample shows that the thickener is very effective at removing suspended solids from the liquor that is returned to the FGD absorbers. As mentioned above, the suspended solids concentration was measured at only 0.004 wt%. These solids are very fine particles, most

likely rich in iron hydroxides, and have a very high mercury concentration (93 µg/g). The thickener overflow liquor mercury concentration was measured as 1.8 µg/L, which is between the values measured for the two absorbers as might be expected.

Coal and Ash Analysis Results

Each day of OH measurements, plant personnel collected grab samples of the coal feed to Unit 3 at representative coal feeders. These samples were analyzed for moisture, heating value, and the concentrations of ash, sulfur, chlorine, and mercury. The results are summarized in Table 23. Compared to the coal analyses for the May 2008 samples, as shown previously in Table 15, the November coal samples show somewhat lower moisture content, similar ash content, lower sulfur content, higher chlorine content and lower mercury concentration.

Table 23. Results of Coal Analyses for November 2008 OH Measurement Dates

Date	Total Moisture (wt %)	Analytical Result, dry basis				
		Heating Value (Btu/lb) [kJ/kg]	Ash (wt%)	Sulfur (wt%)	Chlorine (ppm)	Mercury (ppm)
11/19/2008	29.32	11,805 [27,460]	7.40	0.43	138	0.12
11/20/2008	30.68	11,789 [27,420]	6.89	0.43	174	0.10

The lower mercury concentration helps explain why the flue gas total mercury concentrations measured in November were lower than in May; the November coal sample analyses averaged 0.11 ppm of mercury, while the May coal samples averaged 0.15 ppm. The ratio of coal mercury concentrations in November versus May is almost identical to the ratio of flue gas total mercury concentrations (~10 µg/Nm³ at 3% O₂ in November versus 14 µg/Nm³ at 3% O₂ in May).

Furthermore, the higher coal chlorine concentrations in November versus May (approximately 150 ppm versus 21 ppm) may explain the higher baseline mercury oxidation upstream of the catalyst and the minimal loss of activity measured after six months of flue gas service. Coal chloride concentration is a key factor in native mercury oxidation in coal-fired boilers and in mercury oxidation across low-temperature catalysts such as installed upstream of Absorber C. However, it should be noted that the coal chlorine concentrations measured in the November samples are high relative to other measurements for PRB coals and are therefore suspect.

Table 24 summarizes the results of fly ash sample analyses from the November 2008 OH measurement trip. The November samples showed relatively low concentrations of mercury (0.09 to 0.12 µg/g) and LOI (<0.5 wt%) as did the May 2008 fly ash sample results,.

Table 24. Results of Fly Ash Analyses for November 2008 OH Measurement Dates

Date	Time	Sample Location	Hg ($\mu\text{g/g}$)	LOI (%)
11/19/2008	10:30	A1-2 & A1-4	0.123	0.46
11/20/2008	13:30	A1-2 & A1-4	0.092	0.15

June 2009 Results

During the week of June 1, 2009, a third round of OH mercury oxidation and FGD capture data were measured across Absorber C and the catalyst upstream, and across the baseline (no catalyst upstream) absorber. Between November 2008 and June 2009, Absorber A was taken out of service and the baseline absorber became Absorber B. The sampling locations are shown below in Figure 23. As during the previous measurement periods, FGD samples were collected and preserved, and subsequently analyzed for mercury concentration and other routine FGD analytes. Unit 3 coal and fly ash samples were collected; coal samples were sent to a subcontracted laboratory for short proximate, chloride and mercury analyses, and fly ash samples were analyzed for loss on ignition and mercury. Results from this measurement effort are presented and discussed below.

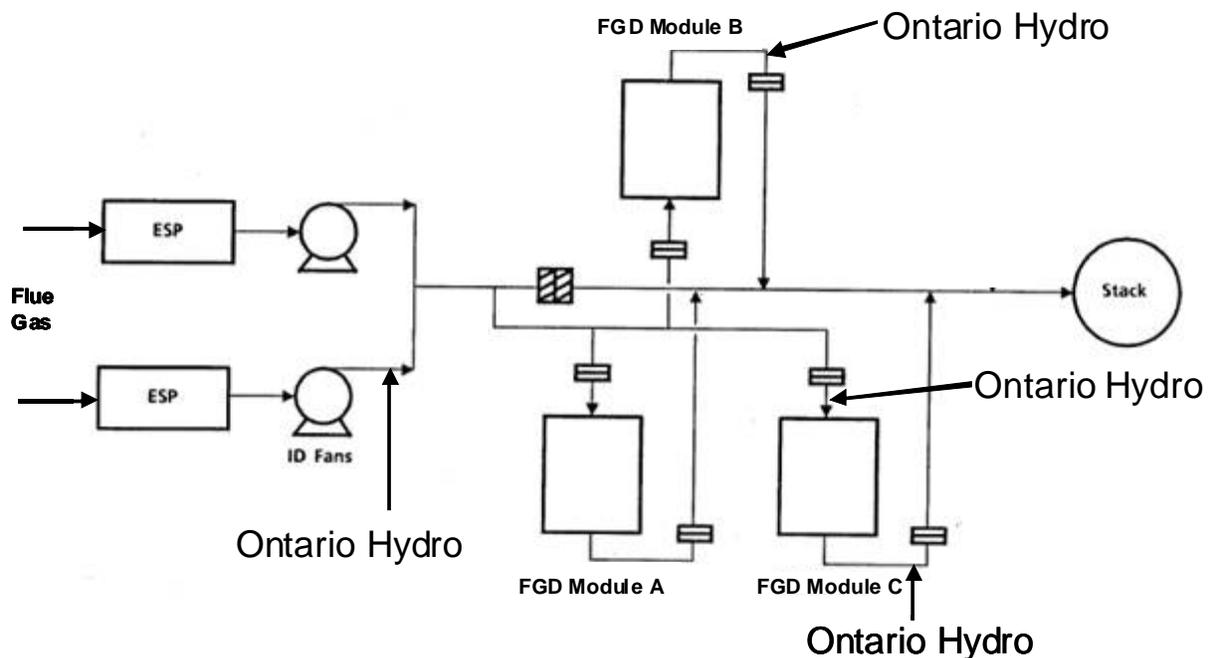


Figure 23. Schematic of Ontario Hydro Method Measurement Locations, June and September 2009

Flue Gas Mercury Oxidation and Removal Measurement Results

Simultaneous OH method flue gas measurements were made at the Unit 3 South ID fan outlet, catalyst outlet, Absorber C outlet, and Absorber B outlet duct locations. Results from these measurements are summarized in Table 25, and calculated values are compared to previous results from May 2008 and November 2008 in Table 26. The original plan had been to conduct these OH measurements in May 2009, after 12 months of catalyst operation, but an unscheduled Unit 3 outage and URS staffing constraints resulted in the measurements being delayed until June. These measurements represent performance after nearly 13 months of catalyst operation.

The results show a considerably lower percentage oxidation of inlet elemental mercury across the catalyst than was previously measured in May and November 2008, at 52%. This includes an expected loss of activity after 13 months of operation in the PRB flue gas, but also represents adverse effects of fly ash buildup in the catalyst cells, which blocked catalyst surface area, making it inactive. Furthermore, blocked cell tends to increase the flue gas velocity through the remaining active cells and adversely affect flue gas flow in the downstream catalyst layers. During the May 2008 measurements, conducted right after catalyst startup, the average pressure drop across the catalyst was 1.5 in. H₂O (0.37 kPa) and during the November 2008 measurements it was approximately 2.0 in. H₂O (0.50 kPa). In contrast, in June 2009 the average pressure drop had increased to nearly 3 in. H₂O (0.75 kPa).

Table 25. Results from June 2009 Ontario Hydro Method Flue Gas Sampling

Location	Hg ⁰ Concentration (µg/Nm ³ at 3% O ₂)	Hg ²⁺ Concentration (µg/Nm ³ at 3% O ₂)	Total Hg Concentration, includes particulate Hg	
			(µg/Nm ³ at 3% O ₂)	(lb Hg/TBtu)
Absorber C (Catalyst Upstream) Data (6/2-6/3/2009):				
Catalyst Inlet*	6.1 ± 1.6	4.8 ± 0.4	11.0 ± 1.8	7.3 ± 1.2
Catalyst Outlet/ Absorber C Inlet	2.9 ± 0.7	8.1 ± 2.2	11.0 ± 2.9	7.3 ± 1.9
Absorber C Outlet	3.1 ± 0.6	<0.2 ± 0.0	3.2 ± 0.5	2.1 ± 0.3
Absorber B (No Catalyst) Data (6/2-6/3/2009):				
Absorber B Inlet*	6.1 ± 1.6	4.8 ± 0.4	11.0 ± 1.8	7.3 ± 1.2
Absorber B Outlet	6.2 ± 1.8	<0.1 ± 0.0	6.2 ± 1.8	4.1 ± 1.2

*Sampled at South ID fan location

Table 26. June 2009 Ontario Hydro Results Compared to May 2008 and November 2008 Results (all values mean \pm 95% confidence interval for three measurement runs)

Parameter	May 2008	November 2008	June 2009
Catalyst Inlet Hg Oxidation (%)	35 \pm 9*	52 \pm 7*	44 \pm 7*
Predicted Hg Oxidation across catalyst (%; empirically corrected)	81	81	81
Measured Hg Oxidation across catalyst (%)	80 \pm 9	77 \pm 4	52 \pm 5
% Oxidized Hg at Catalyst Outlet	86 \pm 6	90 \pm 1	74 \pm 1
Hg Removal Across Absorber C Wet FGD, %	80 \pm 5	49 \pm 4	71 \pm 5
Absorber C Hg ⁰ Re-emissions, % of FGD inlet Hg ²⁺	5 \pm 11	41 \pm 3	3 \pm 9
Baseline (Absorber A or B) Inlet Hg Oxidation (%)	49 \pm 6*	52 \pm 7*	44 \pm 7*
Absorber A or B Hg Removal (%)	34 \pm 18	37 \pm 9	44 \pm 8
Absorber A or B Hg ⁰ Re-emissions, % of FGD inlet Hg ²⁺	23 \pm 45	28 \pm 9	2 \pm 7
Absorber C Hg Removal Increase over Absorber A or B (%)	69 \pm 13	18 \pm 6	48 \pm 11

*Sampled at South ID fan location

A mass transfer model was used to estimate how much of the catalyst cross-section would have to be plugged to result in a pressure drop of nearly 3 in. H₂O (0.75 kPa). Gas velocity measurements taken during the OH runs indicated that Absorber C was treating only 33% of the total Unit 3 scrubbed flue gas, so this flow percentage was also considered. The model predicted that approximately 60% of the catalyst cross-sectional area would have to be plugged with fly ash to reach this pressure drop, and that the face velocity of the flue gas entering the remaining open catalyst cells would be nearly 29 ft/s (8.8 m/s). The model also predicted that at these conditions, the remaining unplugged catalyst cells would only achieve 66% elemental mercury oxidation (down from 81% in the original prediction for clean catalyst). Thus, much of the observed loss of activity seen in the June 2009 measurements could be due to fly ash buildup which plugged some catalyst cells, and the subsequent increase in face velocity across the remaining unplugged cells.

The mean results of the three sets of measurements of elemental mercury oxidation across the catalyst from May 2008 through June 2009 are plotted in Figure 23. The 95% confidence intervals of each mean of three OH measurements during each measurement trip are shown as bars above and below each value. Also shown in the plot is a linear least squares fit through the three means; a linear relationship of activity loss versus time would normally be expected. The linear fit is not good; the line is passing below the 95% confidence interval of the November 2008 mean value.

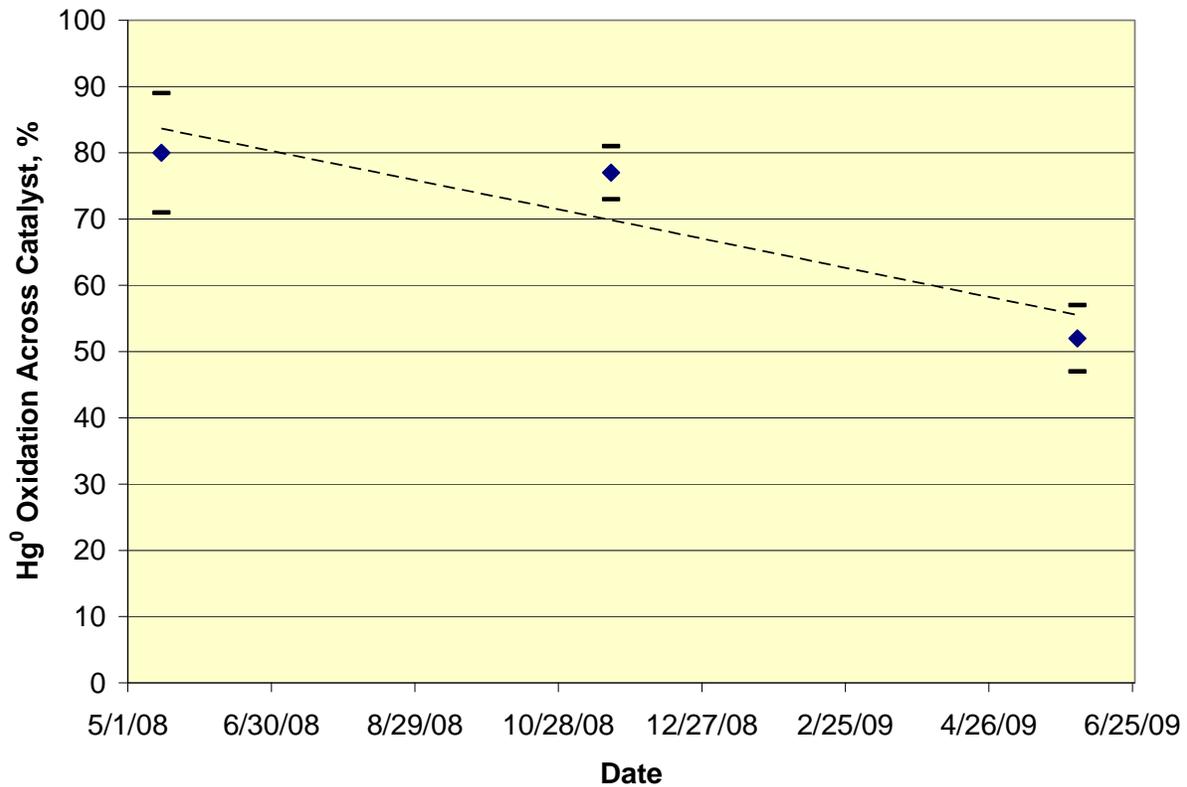


Figure 24. Plot of Measured Hg⁰ Oxidation across Catalyst vs. Time, Through June 2009

It is possible to get a linear fit that passes within the 95% confidence intervals. Such a line passes through the upper ends of the confidence intervals of the May 2008 and June 2009 means and the lower end of the confidence interval of the November 2008 mean. This could be interpreted as indicating that all of the three mean values are biased, and that the true means lie at the extremes of the 95% confidence intervals. However, it is more likely that the buildup of fly ash across the catalyst over time has resulted in a curved relationship of activity versus time, or an accelerated loss of measured activity over the past seven months. With only three data points, it was not possible to discern the true shape of this relationship. The fourth and final set of OH measurements, discussed later in this section, provides a better indication of the shape of this relationship.

In reviewing the results in Table 26, it is interesting to note that the overall FGD capture of mercury by Absorber C was considerably higher in June 2009 than was measured in November 2008 (71% versus 49%) in spite of the absorber inlet mercury oxidation percentage being lower (74% versus 90%). The data indicate that the FGD capture of mercury was greatly limited by re-emissions across Absorber C in November 2008 (41%) but much less so in June 2009 (3%). Both the November and June results showed lower capture of mercury across Absorber C than in May 2008 (80%), during which relatively high inlet mercury oxidation (86%) and low re-emissions (5%) were measured. Possible reasons for the variable re-emission levels seen in these measurements are discussed later in this section.

FGD Slurry Analysis Results

FGD slurry and liquor samples were collected from both operating FGD absorber modules during the June OH measurements. These samples were subjected to routine FGD chemistry analyses as summarized below in Table 27, and slurry mercury analyses as summarized in Table 28.

Table 27. Results of June 2009 FGD Slurry Analyses

Description	Absorber B		Absorber C	
	6/2/2009	6/3/2009	6/2/2009	6/3/2009
Time	12:30	11:00	10:00	9:40
pH	5.71	5.73	5.81	5.96
ORP, mV relative to SHE*	402	405	472	474
Temperature, °C	57.7	56.4	57.6	56.9
Solid Results:				
Ca, mg/g	229	226	226	227
Mg, mg/g	0.716	0.767	0.529	0.495
SO ₃ , mg/g	<0.60	<0.60	<0.60	<0.60
SO ₄ , mg/g	523	525	528	531
CO ₃ , mg/g	3.95	4.43	2.13	2.43
Inerts, wt%	1.79	2.26	2.31	2.12
Solids, wt%	9.03	8.55	8.65	8.71
Sulfite Oxidation, %	100	100	100	100
Limestone Utilization, %	97.4	97.9	98.7	98.5
Solid Analytical Closures:				
Weight, %	-3.0	-2.4	-2.2	-1.8
Molar, %	2.1	1.2	1.1	1.2
Particle Size Distribution:				
D ₁₀ , μm**	17.9	16.2/15.2	15.2/14.7	14.8
D ₅₀ , μm**	46.3	43.6/42.7	37.5/36.5	36.9

Description	Absorber B		Absorber C	
	6/2/2009	6/3/2009	6/2/2009	6/3/2009
D ₉₀ , μm**	80.0	75.8/74.2	64.6/63.4	63.3
Liquid Results:				
Ca ⁺⁺ , mg/L	642	685	635	670
Mg ⁺ , mg/L	2,550	2,450	1,800	1,810
Na ⁺ , mg/L	6,520	6,400	5,210	4,850
Br ⁻ , mg/L	125	122	90	91
Cl ⁻ , mg/L	8,800	8,550	6,180	6,150
CO ₃ ⁼ , mg/L	137	116	120	156
SO ₃ ⁼ , mg/L	1.18	1.00	<0.80	<1.00
SO ₄ ⁼ , mg/L	13,900	13,700	10,400	10,500
Charge Imbalance Calculated, %	-1.3	-1.4	1.6	-0.2

*SHE – standard hydrogen electrode

**D₁₀ – the particle size where 10% of the particles, by volume (roughly proportional to mass), are smaller; D₅₀ – the particle size where 50% of the particles, by volume, are smaller; D₉₀ – the particle size where 90% of the particles, by volume (roughly proportional to mass), are smaller. Where two sets of numbers are entered in a cell separated by a forward slash, the second number represents the result for a duplicate sample analysis.

Table 28. Results of June 2009 FGD Sample Mercury Analyses

Sample Location	Date	Time Sampled	Hg in Solids (μg/g)	Liquor Hg (μg/L)	wt% Solids	% of Slurry Hg in Liquor
Absorber B	6/2/2008	12:30	2.17	0.769	9.03	0.4
Absorber C	6/2/2008	14:30	2.26	0.362	8.65	0.2
Unit 3 Gypsum	6/2/2008	20:00	1.43	-	-	-
Field Blank	6/3/2008	09:10	-	<0.282	-	-
Absorber B	6/3/2008	11:04	2.25	0.901	8.55	0.4
Absorber C	6/3/2008	09:20	2.26	<0.262	8.71	<0.2
Unit 3 Gypsum	6/3/2008	11:55	1.50	-	-	-

The results in the top half of Table 27 show that URS measured absorber slurry pH values of 5.71 to 5.96, which were in reasonable agreement with plant instrumentation and similar to the

values measured in May and November 2008. . The ORP values were around +400 mV for Absorber B and +470 mV relative to SHE for Absorber C (~200 and 270 mV as measured, respectively). These values are considerably lower than were measured in May 2008, but close to the November 2008 values. The slurry wt% solids values were 8 to 9%, which were slightly higher than the values measured in November 2008 (7 to 8 wt%), but lower than values measured in May 2008 (10 to 11 wt%).

Sulfite oxidation remained at 100% in all of the slurry solid samples, and the limestone utilization was relatively high, ranging from 97.4% to 98.7%. The Absorber C limestone utilization values were slightly higher than for Absorber B. This is possibly because Absorber C was treating less flue gas than Absorber B due to the catalyst pressure drop, and hence the slurry residence time in the reaction tank was longer. The analytical closures on the solid samples were all acceptable from both a weight and molar recovery basis. Other than the slight difference in limestone utilization noted above, there was no significant difference in chemistry between the Absorber B and Absorber C samples.

Absorber slurry solid samples were also analyzed for particle size distribution using a Microtrac laser-based particle size analyzer. The results show that the Absorber B solids were slightly larger than the Absorber C solids, at 43-46 μm volume-mean particle size versus ~37 μm for Absorber C. At first, this result seems surprising. Because Absorber C was treating less flue gas than Absorber B, the average solids residence time in the Absorber C reaction tank was longer than for Absorber B, and thus gypsum particles should have had time to grow larger. However, in low-sulfur-coal FGD systems such as on Unit 3, the solids residence times in the absorber reaction tanks tend to be long enough that particle sizes become limited by attrition. This attrition is caused by shearing during the numerous passes through the slurry pumps and nozzles. This appears to be the case for Absorber C – the longer residence time resulted in slightly smaller mean particle sizes.

The liquid results in Table 27 show that Absorber C was operating at similar concentrations of dissolved, highly soluble species (e.g., magnesium, sodium, and chloride) compared to Absorber B. The values are very similar to those measured in November 2008. The last row in the table, the calculated charge imbalance in the liquor analytical results, shows acceptable closure for these samples (i.e., close to electroneutrality). This indicates there is no major cation or anion missing from the analysis and/or suggests that the anion and cation concentrations are reasonably accurate. The total hydrolyzable sulfur results for these samples (not shown in the table) were very close to (actually slightly lower than) the total of sulfite and sulfate in the liquor. This indicates that there were no additional sulfur-containing anions, such as sulfur-nitrogen species, dithionates or persulfates in these samples.

Table 28 summarizes the results of slurry liquor mercury analyses. Also shown in the table are the results of a “field blank” analysis. As in the data from the previous measurement trips, the blank results show mercury levels below the effective analytical detection limits. The results in Table 28 show liquor mercury concentrations of 0.77 to 0.90 $\mu\text{g/L}$ (~ppb) in Absorber B and <0.26 to 0.36 $\mu\text{g/L}$ in Absorber C during these sampling periods. The mercury concentrations in the Absorber C liquor are lower than were measured in November 2008 (0.61 to 2.15 $\mu\text{g/L}$) or May 2008 (1.05 $\mu\text{g/L}$). The Absorber B mercury liquor concentrations are in the same range as

those measured in Absorber A in November 2008 (0.40 to 0.85 µg/L) but higher than were measured in Absorber A in May 2008 (0.24 to 0.63 µg/L).

As described earlier, mercury re-emissions are known to be caused by reactions between absorbed Hg^{2+} and sulfite/bisulfite and/or other reducing species in FGD liquors. Higher concentrations of Hg^{2+} in the liquor generally appear to result in higher re-emission levels (all of the measured Hg in FGD liquor is presumed to be Hg^{2+}). Previously in this section it was theorized that higher liquor mercury concentrations in Absorber C in November 2008 accounted for the higher mercury re-emissions measured across that absorber in November compared to May 2008; 41% of the inlet Hg^{2+} re-emitted in November versus only 5% in May. The June 2009 Absorber C liquor concentration measurements were the lowest of the three measurement periods conducted at the time, and the June 2009 Absorber C re-emissions were also the lowest of the three (3% of the inlet Hg^{2+} re-emitted), so these data generally support the previous theory.

The re-emission levels were also lower across Absorber B in June 2009 (only 2%) than were measured across Absorber A in November 2008 (28%) or May 2008 (23%). However, there was no clear trend for lower absorber liquor mercury concentration in the June 2009 Absorber B results compared with the concentrations that were measured for Absorber A in May and November 2008.

The June 2009 solids mercury concentration data are somewhat anomalous. The June OH results showed considerably greater mercury capture across Absorber C than Absorber B, yet the absorber slurry solids from the two absorbers were measured to have nearly the same mercury concentrations. One would expect higher mercury concentrations in the Absorber C slurry solids. Furthermore, both were measured to have a higher mercury concentration than the product gypsum on both days, but the gypsum should have a mercury content near those of the absorber samples. It is not clear why these solid sample analyses do not show the expected trends. It is possible that the different gypsum mercury content is attributable to residence time effects. Considering the solids residence time in the thickener, the gypsum solids may have represented operation several days earlier, when the coal mercury may have been lower. The fact that the gypsum mercury concentration was slightly higher on June 3 than on June 2 suggests that the concentration was slowly increasing over time.

Coal and Fly Ash Analyses

Each day of OH measurements, plant operations personnel collected grab samples of the coal feed to Unit 3 at representative coal feeders. These samples were analyzed for moisture, heating value, and the concentrations of ash, sulfur, chlorine, and mercury. The results are summarized in Table 29. Compared to the coal analyses for the May 2008 and November 2008 samples, the June 2009 coal samples showed similar heating values, similar to slightly higher moisture content, and similar ash content. The June sulfur content was lower than in May 2008 but slightly higher than in November 2008, while the June chlorine content was considerably higher than in May 2008 but lower than was measured in November 2008. The chlorine content of the November 2008 coal samples was considered suspect, though. Finally, the June 2009 mercury concentration was higher than was measured in November 2008, but within the range measured in the May 2008 samples.

Table 29. Results of June 2009 Coal Analyses for OH Measurement Dates

Date	Total Moisture (wt %)	Analytical Result, dry basis				
		Heating Value (Btu/lb) [kJ/kg]	Ash (wt%)	Sulfur (wt%)	Chlorine (ppm)	Mercury (ppm)
6/02/2009	34.55	11,871 [27,610]	6.45	0.59	61	0.15
6/02/2009	31.55	11,662 [27,130]	7.16	0.45	110	0.17

Fly ash samples were collected from Unit 3 ESP hoppers and analyzed for LOI and mercury concentration. These measurements were used to indicate whether there was any significant capture of the coal mercury with the fly ash. Two samples were typically collected each day of measurements, representing first-field and second-field ash. The June 2009 fly ash results are shown in Table 30. The results show relatively low LOI and low mercury concentrations in the fly ash, as expected.

Table 30. Results of Fly Ash Analyses for June 2009 OH Measurement Dates

Date	Time	Sample Location	Hg (µg/g)	LOI (%)
6/02/2009	16:15	A1-2	0.124	0.46
6/02/2009	16:15	A1-4	0.211	0.30
6/03/2009	13:00	A1-2	0.095	0.59
6/03/2009	13:00	A1-4	0.196	0.30

September 2009 Results

The fourth catalyst performance measurement effort was conducted the week of September 7, 2009, and included OH measurements of mercury oxidation across the catalyst and FGD capture of mercury across Absorbers B and C. Also during this measurement period, FGD samples were collected, preserved, and subsequently analyzed for mercury concentration and for other routine FGD analytes. Unit 3 coal and fly ash samples were collected; coal samples were sent to a subcontracted laboratory for short proximate, chloride and mercury analyses, while the fly ash samples were analyzed for LOI and mercury.

These results are presented and discussed below. As described elsewhere in this report, because of concerns over pressure drop increases, the first catalyst layer was removed from service in late June 2009, shortly after the June 2009 OH measurement effort was completed. Thus, the fourth and last measurement trip reflected operation with only two catalyst layers in service, those which had originally been the second and third layers.

Mercury Oxidation and Removal Measurement Results

OH method flue gas measurements were made at the Unit 3 South ID fan outlet, catalyst outlet, Absorber C outlet, and Absorber B (no catalyst) outlet duct locations. These locations were previously shown schematically in Figure 23. Results from these measurements are summarized in Table 31, and compared to previous results in Table 32.

The original plan had been to conduct the fourth set of OH measurements in early November of 2009, after 18 months of operation. However, a planned Unit 3 outage in October and the decision to remove the remaining two catalyst layers at that time led to the need to move these measurements up to September 2009. These measurements represent approximately 16 months of catalyst operation. The results from September 2009 actually show a higher percentage oxidation of inlet elemental mercury across the catalyst than was measured in June 2009, at 57% (versus 52% in June), in spite of the first layer having been removed between the two sets of measurements. In June 2009 the average full-load pressure drop across the three layers of catalyst had been nearly 3 in. H₂O (0.75 kPa), while in September 2009 the pressure drop across the remaining two layers was approximately 2.3-2.4 in. H₂O (0.57-0.60 kPa).

A mass transfer model was used to extrapolate the performance of the two layers of catalyst measured in September to a corresponding performance with three layers. The model predicted that with two layers achieving a mean of 57% elemental mercury oxidation across the catalyst, a third, 6-inch (152-mm) layer with the same performance level would have increased the oxidation across the catalyst to 70%.

Table 31. Results from September 2009 Ontario Hydro Method Flue Gas Sampling

Location	Hg ⁰ Concentration (µg/Nm ³ at 3% O ₂)	Hg ²⁺ Concentration (µg/Nm ³ at 3% O ₂)	Total Hg Concentration, includes particulate Hg	
			(µg/Nm ³ at 3% O ₂)	(lb Hg/TBtu)
Absorber C (Catalyst Upstream) Data (9/9-9/10/2009):				
Catalyst Inlet*	6.5 ± 0.9	7.8 ± 1.4	14.2 ± 0.6	9.4 ± 0.4
Catalyst Outlet/ Absorber C Inlet	2.8 ± 0.7	10.5 ± 2.1	13.3 ± 2.0	8.8 ± 1.3
Absorber C Outlet	8.7 ± 1.1	<0.4 ± 0.1	8.9 ± 1.2	5.9 ± 0.8
Absorber B (No Catalyst) Data (9/9-9/10/2009):				
Absorber B Inlet*	6.5 ± 0.9	7.8 ± 1.4	14.2 ± 0.6	9.4 ± 0.4
Absorber B Outlet	7.0 ± 0.6	<0.3 ± 0.0	7.0 ± 0.5	4.7 ± 0.3

*Sampled at South ID fan outlet location

Table 32. September 2009 Ontario Hydro Results Compared to Previous Results (all values mean \pm 95% confidence interval for three measurement runs)

Parameter	May 2008	November 2008	June 2009	September 2009
Catalyst Inlet Hg Oxidation (%)	35 \pm 9*	52 \pm 7*	44 \pm 7*	55 \pm 8*
Predicted Hg Oxidation across catalyst (%; empirically corrected)	81	81	81	81
Measured Hg Oxidation across catalyst (%)	80 \pm 9	77 \pm 4	52 \pm 5	57 \pm 4
% Oxidized Hg at Catalyst Outlet	86 \pm 6	90 \pm 1	74 \pm 1	79 \pm 5
Hg Removal Across Absorber C Wet FGD, %	80 \pm 5	49 \pm 4	71 \pm 5	37 \pm 8
Absorber C Hg ⁰ Re-emissions, % of FGD inlet Hg ²⁺	5 \pm 11	41 \pm 3	3 \pm 9	57 \pm 5
Baseline (Absorber A or B) Inlet Hg Oxidation (%)	49 \pm 6*	52 \pm 7*	44 \pm 7*	55 \pm 8*
Absorber A or B Hg Removal (%)	34 \pm 18	37 \pm 9	44 \pm 8	51 \pm 5
Absorber A or B Hg ⁰ Re-emissions, % of FGD inlet Hg ²⁺	23 \pm 45	28 \pm 9	2 \pm 7	7 \pm 5
Absorber C Hg Removal Increase over Absorber A or B (%)	69 \pm 13	18 \pm 6	48 \pm 11	-27 \pm 12

*Sampled at South ID fan outlet location

The results of the four measurements of elemental mercury oxidation across the catalyst are plotted in Figure 25. The 95% confidence intervals of each mean of three OH measurements are shown as bars above and below each measurement. Also shown in the plot is the extrapolated performance from September 2009 with three rather than two layers of catalyst in service. A dashed line is shown fit through the means of the first two sets of measurements in May and November 2008. The June 2009 results fall well below this line, while the September 2009 results, extrapolated to three-layer performance, fall very near this line.

This plot suggests that the fly ash plugging seen in the first catalyst layer removed in June 2009 was adversely affecting the performance of the two downstream layers (i.e., flue gas was not redistributing to cells downstream of plugged cells in the first layer). It appears that once the first layer was removed, the two remaining layers saw an improved inlet flue gas velocity distribution and the performance of those two remaining layers returned to nearly match the linear activity loss relationship seen in the first two measurements.

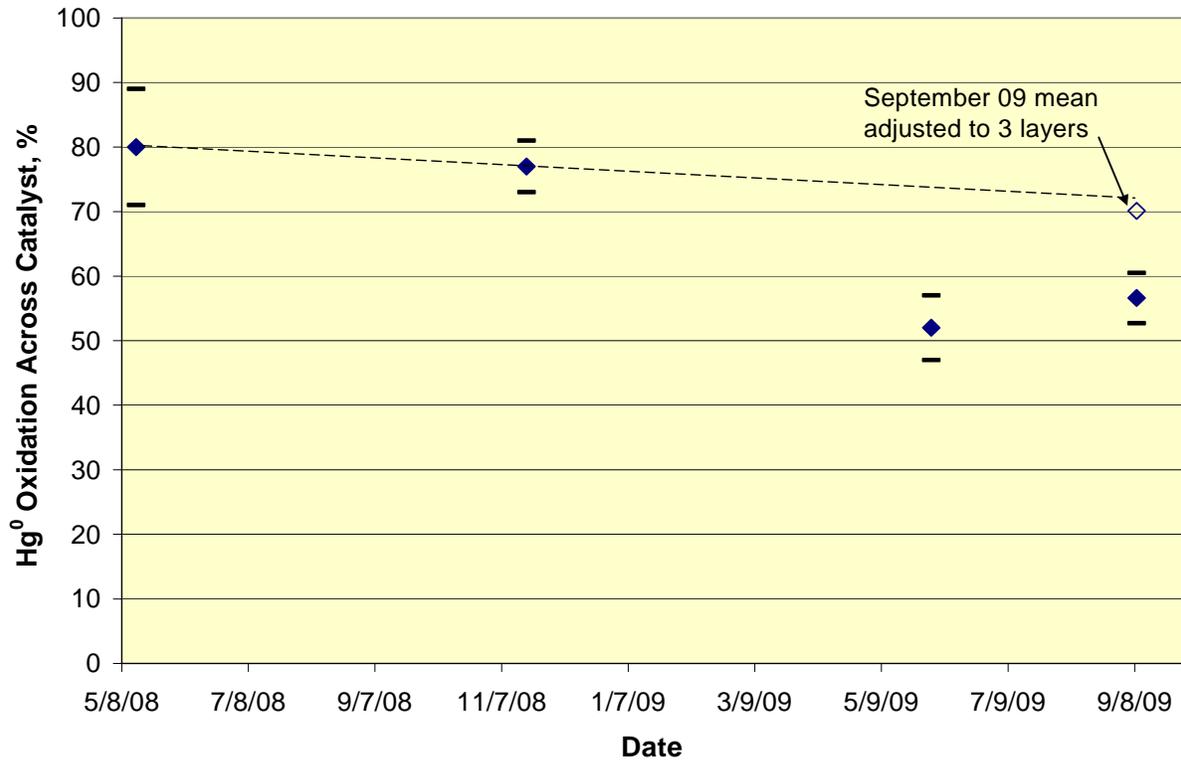


Figure 25. Plot of Measured Hg⁰ Oxidation across Catalyst vs. Time

The mercury capture by FGD Absorber C was considerably lower in September 2009 (37%) than was measured in June 2009 (71%) in spite of the absorber inlet mercury oxidation percentage being higher (79% in September versus 74% in June). The data indicate that the capture of mercury was greatly limited by re-emission across Absorber C in September 2009 (57% of FGD inlet oxidized mercury re-emitted) whereas it had been much less limited by re-emission in June 2009 (3%). The September 2009 results showed the lowest percentage capture of mercury across Absorber C and the highest re-emissions compared to the three previous sets of measurements. Possible reasons for the re-emission levels seen in these September measurements are discussed below with the FGD slurry sample results.

FGD Slurry Analysis Results

As mentioned above, URS collected FGD slurry and liquor samples from both operating FGD absorber modules on Unit 3 during the September OH measurements. These samples were subjected to routine FGD chemistry analyses, as summarized in Table 33.

Table 33. Results for September 2009 FGD Slurry Analyses

Description	Absorber B		Absorber C	
	9/9/2009	9/10/2009	9/9/2009	9/10/2009
Date	9/9/2009	9/10/2009	9/9/2009	9/10/2009
Time	13:30	9:37	14:00	10:10
pH	5.85	5.80	5.95	5.59
ORP, mV relative to SHE*	532**	432	545**	436
Temperature, °C	56.0	55.1	56.5	55.9
Solid Results:				
Ca, mg/g	222	222	222	224
Mg, mg/g	0.5	0.5	0.4	0.5
SO ₃ , mg/g	<0.7	<0.7	<0.7	<0.7
SO ₄ , mg/g	537	519	529	524
CO ₃ , mg/g	2.0	2.3	1.6	2.0
Inerts, wt%	2.46	2.55	2.55	2.51
Solids, wt%	9.90	10.23	7.62	7.94
Sulfite Oxidation, %	100.0	100.0	100.0	100.0
Limestone Utilization, %	99.7	98.5	99.4	98.7
Solid Analytical Closures:				
Weight, %	-1.2	-3.6	-2.3	-2.8
Molar, %	-0.5	1.3	0.1	1.1
Liquid Results:				
Ca ⁺⁺ , mg/L	609	598	581	604
Mg ⁺ , mg/L	1,321	1,293	1,183	1,281
Na ⁺ , mg/L	3,385	2,998	3,395	3,417
Br ⁻ , mg/L	69	67	72	72
Cl ⁻ , mg/L	4,549	4,254	4,822	4,802
CO ₃ ⁼ , mg/L	136	156	122	110
SO ₃ ⁼ , mg/L	<3	<3	<3	<3

Description	Absorber B		Absorber C	
	9/9/2009	9/10/2009	9/9/2009	9/10/2009
SO ₄ ²⁻ , mg/L	7,414	7,168	8,050	7,187
Total Hydrolyzable Sulfur, mg/L as SO ₄ ²⁻	7,444	7,005	7,678	7,689
Total Hydrolyzable Sulfur, mg/L as SO ₄ ²⁻ , net after subtracting sulfite and sulfate	30	-160	-370	500
Charge Imbalance Calculated, %	-1.3	-1.4	1.6	-0.2

*SHE – standard hydrogen electrode

**Value is suspect because of poor probe/meter agreement with standard ORP solution in post sampling check

The results in the top half of the table show that URS measured absorber slurry pH values of 5.59 to 5.95, which were in reasonable agreement with plant instrumentation and similar to the values measured previously during this project. The ORP values for September 9 are suspect, but the values for September 10 were between +432 and +436 mV relative to SHE (232 to 236 mV as measured relative to silver/silver chloride reference electrode in saturated potassium chloride). These values are within the same general range as was measured in November 2008 and June 2009, but lower than was measured in May 2008. The Absorber C slurry wt% solids was 7 to 8%, which was slightly lower than URS measured in June 2009 (8 to 9%), similar to the values measured in November 2008 (7 to 8 wt%), but substantially lower than values measured in May 2008 (10 to 11 wt%). Mercury re-emissions across Absorber C were highest in November 2008 and September 2009, the two time periods where the wt% solids in Absorber C were lowest. The Absorber B wt% solids levels in September 2009 were higher than in Absorber C, at around 10 wt%. As shown above in Table 32, mercury re-emissions were correspondingly measured to be much lower across Absorber B than across Absorber C in September.

Sulfite oxidation remained at 100%, and the limestone utilization was high, ranging from 98.5% to 99.7%. The Absorber C limestone utilization values were very similar to those for Absorber B. The analytical closures on the solid samples were all acceptable from both a weight and molar recovery basis, which provides some confidence in the accuracy of the analyses. There was no significant difference in solid chemistry between the Absorber B and Absorber C samples.

The liquid results in Table 33 show that Absorber C was operating at similar concentrations of dissolved, highly soluble species (e.g., magnesium, sodium, and chloride) compared to Absorber B. The values are generally lower than were measured in November 2008 and June 2009, indicating that the FGD system was operating in a more dilute mode (more fresh water makeup). The lower chloride concentrations may have contributed to the higher re-emissions seen across Absorber C in September 2009, as chloride is known to form strong aqueous complexes with mercury that can limit re-emissions. The last row in the table, the calculated charge imbalance in the liquor analytical results, compares the total cations to total anions analyzed in the liquor, and

shows acceptable closure for these samples (i.e., close to electroneutrality). The total hydrolyzable sulfur results for these samples were close to (+7% to -5%) the total of sulfite and sulfate in the liquor. This indicates that there were few, if any, additional sulfur-containing anions such as sulfur-nitrogen (S/N) species in these samples.

The mercury analysis results for these FGD samples are shown in Table 34. Included in the table are the results of “field blank” analyses which, as in the previous three measurement trip data sets, show mercury levels below the effective analytical detection limits.

Table 34. Results of September 2009 FGD Slurry Mercury Analyses

Sample Location	Date	Time Sampled	Hg in Solids (µg/g)	Liquor Hg (µg/L)	wt% Solids	% of Slurry Hg in Liquor
Absorber B	9/9/2009	13:45	1.46	<0.78	9.90	<0.5%
Absorber C	9/9/2009	14:00	0.57	<0.73	7.62	<1.5%
Absorber C	9/9/2009	18:25	0.59	<0.65	NA	-
Field Blank	9/9/2009	-	-	<0.65	-	-
Absorber B	9/10/2009	9:57	1.52	<0.65	10.2	<0.4%
Absorber C	9/10/2009	10:27	0.65	<0.66	7.94	<1.2%
Unit 3 Thickener Overflow	9/10/2009	11:00	NA	<0.65	-	-
Unit 3 Gypsum	9/10/2009	11:00	0.96	-	-	-
Field Blank	9/10/2009	-	-	<0.65	-	-

*NA – not analyzed

The results in Table 34 show liquor mercury concentrations generally below detection limits, or <0.65 to <0.78 µg/L (~ppb) in Absorber B and <0.65 to <0.73 µg/L in Absorber C during the September sampling periods. The mercury concentrations in the Absorber C liquor were lower than were measured in November 2008 (0.605 to 2.15 µg/L) or May 2008 (1.05µg/L), and similar to those measured in June 2009. The Absorber B mercury liquor concentrations were approximately in the same range as those measured in Absorber A in November 2008 (0.40 to 0.85 µg/L) and in May 2008 (0.24 to 0.63 µg/L), but slightly lower than was measured in Absorber B in June 2009 (0.77 to 0.90 µg/L). Varying analytical detection limits from measurement period to measurement period confound this comparison, though.

Mercury re-emissions are known to be caused by reactions between absorbed Hg²⁺ and sulfite/bisulfite and/or other reducing species in FGD liquors. Higher concentrations of Hg²⁺ in the liquor generally result in higher re-emission levels (all of the measured Hg in FGD liquor is presumed to be Hg²⁺). Previously in this section it was theorized that higher liquor mercury concentrations in Absorber C in November 2008 accounted for the higher mercury re-emissions measured across that absorber in November than in May 2008 (41% of the inlet Hg²⁺ re-emitted

in November versus only 5% in May). The June 2009 Absorber C liquor concentration measurements were the lowest of the three measurement periods conducted to that date, and the June 2009 Absorber C re-emissions were also the lowest of the three sets of measurements (3% of the inlet Hg^{2+} re-emitted), so these data generally supported the previous theory. This trend is not seen in the September 2009 Absorber C data, which correspond with the highest re-emission levels measured across Absorber C. However, again the variable analytical detection limits confound this comparison at these relatively low mercury concentrations.

Table 34 also shows the mercury concentrations in the FGD absorber solids and product gypsum solids. In the September 2009 data, the Absorber B samples were measured with much higher mercury concentrations than in Absorber C samples ($\sim 1.5 \mu\text{g/g}$ versus $\sim 0.6 \mu\text{g/g}$). This supports the flue gas OH data, which indicate that Absorber C was limited in mercury capture by re-emissions. The gypsum samples from September show a mercury concentration between those of the two absorbers, as would be expected.

Other variables can impact the amount of re-emissions from an FGD absorber other than dissolved Hg^{2+} concentrations. For example, pH, chloride concentration and sulfite concentration can all impact re-emission rates. Previously in this section, the potential impacts of slurry weight percent solids level on liquor mercury concentrations and re-emission levels were also discussed. The September 2009 results tend to support this hypothesis, as the weight percent solids level was lower in Absorber C than in Absorber B, and correspondingly the mercury re-emission levels were higher across Absorber C.

Table 35 summarizes the values measured for a number of parameters that are thought to affect absorber liquor mercury concentrations and mercury re-emission levels. In reviewing the values in the table, few consistent trends are observed. One expected result might be a correlation with FGD liquor chloride concentrations. Chloride is known to form stable complexes with Hg^{2+} and thus higher chloride concentrations could tend to limit re-emission levels. However, there is no consistent trend in the chloride data; high and low re-emission levels are seen with both high and low chloride concentrations in the two absorbers.

One apparent trend is that the Absorber C slurry wt% solids levels were low in November 2008 and September 2009 when re-emissions were high, and higher in both May 2008 and June 2009 when re-emission levels were low. However, such trends are not consistently seen in the Absorber A and B data. The wt% solids levels in Absorber A were also low in November 2008 when re-emissions across that absorber were high, but during the other period with apparently high re-emissions from Absorber A, in May 2008, the wt% solids were relatively high.

However, as noted earlier in this section the high mean re-emissions percentage seen in May 2008 represents the results of three Ontario Hydro runs conducted simultaneously at two locations, the catalyst inlet/Absorber A inlet and at the Absorber A outlet. Of the three paired runs, the first and last showed negligible re-emission levels of +3% and -8% of the Absorber A inlet oxidized mercury while the middle run showed a re-emission level of 66% of the inlet oxidized mercury. The mean re-emission percentage was 23%, but the 95% confidence interval was $\pm 45\%$ about the mean. Thus, the 95% confidence interval for the mean of three measurements included low or even zero re-emissions.

Table 35. Summary of Parameters that Might have Impacted Re-emissions across Unit 3 FGD Absorbers

	Baseline Absorber Data				Absorber C (with Catalyst Upstream) Data			
Date	May 08	Nov. 08	June 09	Sept. 09	May 08	Nov. 08	June 09	Sept. 09
Absorber	A	A	B	B	C	C	C	C
Slurry wt% solids	10.3 - 11.4	6.9	8.6 - 9.0	9.9 - 10.2	10.0 - 10.1	7.6 - 7.8	8.7	7.6 - 7.9
FGD Liquor Hg Concentration, µg/L	0.24 - 0.63	0.40 - 0.85	0.77 - 0.90	<0.65 - <0.78	1.05	0.61 - 2.15	<0.28 - 0.36	<0.65 - <0.73
pH	5.89 - 5.96	5.72	5.71 - 5.73	5.80 - 5.85	5.85	5.84	5.81 - 5.96	5.59 - 5.95
Oxidation-Reduction Potential (ORP), mV relative to SHE	605 - 814	394 - 480	302 - 305	432	621 - 740	376 - 450	472 - 474	436
Liquor Chloride, mg/L	6,000 - 6,090	9,130	8,550 - 8,800	4,250 - 4,550	7,780	8,830	6,150 - 6,180	4,800 - 4,820
Liquor Sulfite, mg/L	<4	<3	1.0-1.2	<3	<3	<3	<0.8 - <1.0	<3
Absorber Solids Hg, µg/g	1.96 - 2.18	1.52 - 1.79	2.17 - 2.25	1.46 - 1.52	2.96 - 3.26	1.65 - 1.70	2.26	0.57 - 0.65
Absorber Solids Iron, µg/g	629 - 710	579 - 713	723 - 777	642-645	769-818	488 - 579	772 - 805	642 - 653
Iron Solids in Absorber Slurry, µg/g of slurry	72 - 73	40 - 51	62 - 70	64 - 66	77 - 83	38 - 44	67 - 70	49 - 52
Measured Hg Re-emissions across Absorber, % of inlet Hg ²⁺	23 ± 45* (-3)	28 ± 9	2 ± 7	7 ± 5	5 ± 11	41 ± 3	3 ± 9	57 ± 5

*This result is suspect because of the large 95% confidence interval. Value in parentheses is average of Runs 1 and 3 only.

A Q test was conducted to determine if the middle run result could be discarded as an outlier, but it was acceptable to remain in the data set at 90% confidence. With a data set of only three measurements, it is difficult to discard a value as an outlier based on a Q test. However, based on the first and third run results only, the May 2008 re-emission results would follow the apparent trend noted with wt% solids in the absorber slurry. The higher wt% solids level of 10 to 11 wt% in Absorber A would go along with the low re-emissions measured in two of the three runs.

The trend for higher re-emissions as the wt% solids in the absorber slurry goes down may be related to the amount of iron fines present in the absorber slurry. There is increasing evidence that adsorption or co-precipitation on iron hydroxide fines accounts for the mercury phase change from the liquor to the solids in FGD absorber slurry. The iron comes into the FGD system with the limestone reagent and/or with fly ash carryover. At the pH and ORP conditions of most wet FGD systems, the iron is oxidized to the +3 valence state and precipitates as ferric hydroxides.

In wet FGD systems that have hydrocyclones for primary dewatering of the absorber blow down slurry, fine particles are often recycled with the low-wt%-solids hydrocyclone overflow stream that is returned to the absorber. The hydrocyclone underflow is further dewatered to produce the byproduct gypsum. In such FGD systems, the amount of iron in the absorber slurry is less sensitive to the wt% solids in the slurry because of the recycle of iron-rich fines that occurs. However, in the FPP Unit 3 FGD system, a thickener is used for primary dewatering of the absorber blow down slurry. Thickeners typically effect a near quantitative removal of solids from the slurry, so very few solids are recycled to the absorber; nearly 100% of the solids report to the thickener underflow and are further dewatered to produce the gypsum byproduct. As an example, hydrocyclones used for primary dewatering typically produce an overflow stream that contains 1 wt% to 4 wt% solids, whereas the thickener overflow at FPP Unit 3 was measured in November 2008 to contain only 0.004 wt% solids (40 ppm). At FPP Unit 3, the amount of iron in the absorber slurry solids is strictly a function of how much enters the system with the limestone or other sources, and the wt% solids in the absorber slurry.

To further investigate the apparent correlation between wt% solids and measured re-emission levels, absorber slurry solids from both absorbers in service during each of the four Ontario Hydro measurement trips were analyzed for iron concentration. These results are also included in Table 35. For Absorber C, a trend is apparent in that for the test periods where re-emissions were high, the wt% solids were less than 8 wt% and the absorber solid iron concentrations were 653 µg/g or lower, while for test periods where re-emissions were low the wt% solids were 8.7 wt% or greater and the iron concentrations were 769 µg/g or greater. For Absorbers A or B, such a trend is a bit less clear cut (e.g., the iron concentration ranges overlap for high versus low re-emission periods).

Since both the wt% solids and the concentration of iron in the solids affect the amount of iron hydroxide fines present in absorber slurry, the wt% solids and iron concentration were multiplied to calculate an iron solids concentration in the slurry, in µg of iron solids (as Fe) per g of slurry. These values are shown in Table 35, and were plotted versus average re-emission percentages (percent of absorber inlet oxidized mercury concentration) in Figure 26.

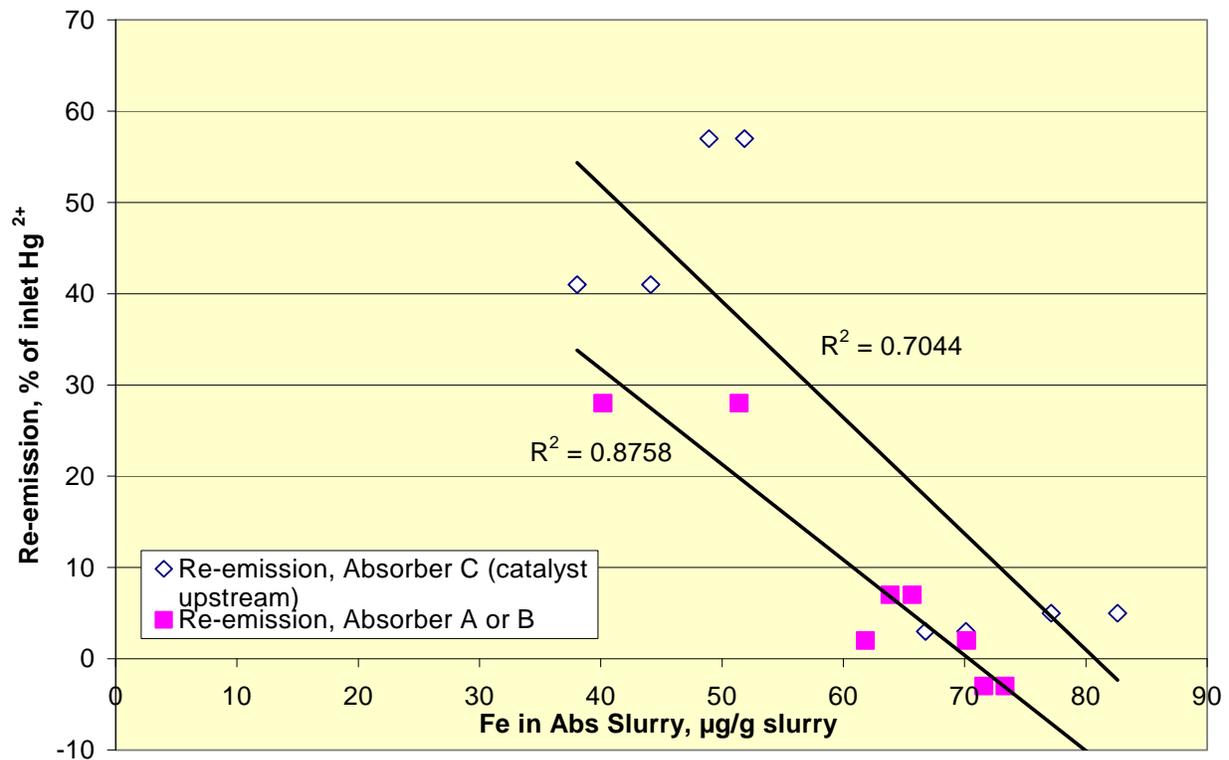


Figure 26. Re-emissions across the FPP Unit 3 Absorbers versus Iron in Absorber Slurry

The data for the two absorbers in service are plotted separately in the figure because of the difference the catalyst makes in the amount of oxidized mercury going to each of the two absorbers. Also, for May 2008, the re-emission results for Absorber A do not include the results for Run 2; if Run 2 results had been included in the average plotted the linear fit of the Absorber A/B data would not have been as good.

Apart from the one data edit mentioned above, the data plot and the linear least-squares fits of the data for the two absorbers support the theory that the amount of iron hydroxide fines present in the absorber slurry impacts whether or not significant re-emissions occur. The R^2 values for the two linear least-squares fits of 0.70 and 0.88 show reasonably good correlations, and the slopes of the correlations are nearly parallel, as would be expected.

In summary, the cause of the variable re-emission levels seen across the Unit 3 FGD absorbers remains uncertain, but there is convincing evidence that high re-emissions tend to occur when the amount of iron present in the absorber slurry, presumably as iron hydroxide fines, is low. These data suggest that operation at higher wt% solids in the absorber slurry and/or with higher iron content in the limestone reagent could maintain low re-emission levels across the absorbers. Based on the plots in Figure 26, it appears that a somewhat higher iron concentration in the slurry is required downstream of the oxidation catalyst, perhaps due to the higher percentage of oxidized mercury in the FGD inlet flue gas.

Coal and Fly Ash Analyses

Each day of OH measurements, plant operations personnel collected grab samples of the coal feed to Unit 3 at representative coal feeders. These samples were analyzed for moisture, heating value, and the concentrations of ash, sulfur, chlorine, and mercury. The results are summarized in Table 36. The results in Table 36 are generally within the ranges seen in previous coal samples from Unit 3.

Table 36. Results of Coal Analyses for September 2009 OH Measurement Dates

Date	Time	Total Moisture (wt %)	Analytical Result, dry basis				
			Heating Value (Btu/lb) [kJ/kg]	Ash (wt%)	Sulfur (wt%)	Chlorine (ppm)	Mercury (ppm)
9/09/2009	08:15	30.62	11,826 [27,510]	7.05	0.54	33	0.13
9/10/2009	07:30	30.90	11,779 [27,400]	7.15	0.61	25	0.12

Fly ash samples were collected from Unit 3 ESP hoppers and analyzed for LOI and mercury concentration. These measurements indicate whether there was any significant capture of the coal mercury with the fly ash. Two samples were collected each day of measurements, representing first-field and second-field ash. The September fly ash results are shown in Table 37. The results for fly ash samples show relatively low LOI and low mercury concentrations in the fly ash, as do the fly ash samples from previous OH measurement trips.

Table 37. Results of Fly Ash Analyses for September 2009 OH Measurement Dates

Date	Time	Sample Location	Hg (µg/g)	LOI (%)
9/09/2009	14:45	1 st Field South Header	0.134	0.15
9/09/2009	14:45	2 nd Field South Header	0.090	0.20
9/10/2009	10:00	1 st Field South Header	0.054	0.22
9/10/2009	10:00	2 nd Field South Header	0.043	0.16

Plant Restoration

After the demonstration period ended, LCRA removed the catalyst from the ductwork upstream of Absorber C and installed a new perforated plate system designed by URS as part of the demonstration project. The perforated plate is intended to replace a previously existing perforated plate that was removed when the catalyst was installed as well as to restore a nearly ideal flue gas velocity distribution at the inlet to Absorber C. The new perforated plate was installed on the existing catalyst framework after all three layers of catalyst were removed. A

staggered void area design was employed to account for the raised roof of the catalytic reactor, which CFD modeling showed would otherwise have created a high velocity area at the top of the scrubber outlet duct downstream of the reactor vessel. According to the model, a staggered design with 27%-open-area plate in the top half of the reactor and 58%-open-area plate in the bottom half compensates for the raised roof.

Also, after all 36 catalyst modules were removed from the ductwork upstream of Absorber C, efforts began to find a subcontractor to recycle the used catalyst to recover its gold content. Two catalyst recycling contractors were contacted, Johnson Matthey, the original catalyst supplier, and Metal and Catalyst Resources of Bellaire, Texas.

To facilitate hiring a recycling subcontractor, two individual catalyst pieces (blocks) from the first layer, which was removed late June 2009, were sent to a third-party laboratory to be leached for trace elements in a strong acid environment (20% nitric acid and 20% hydrochloric acid). The leachate was subsequently analyzed for concentrations of the eight RCRA metals, plus gold (to provide an indication of the amount of gold present on the blocks). These concentration data were then extrapolated to estimate the quantities of each of these metals present in the entire inventory of approximately 8700 blocks in the catalyst installation at FPP. The results of these analyses and calculations are summarized in Table 38. The sample panels A and B in the table refer to where in the first catalyst layer the block samples were taken.

Table 38. Estimated Gram Quantities of Selected Elements in 8700 Catalyst Pieces

Sample Identification	Ag	As	Ba	Cd	Cr	Hg	Pb	Se	Au
Sample Panel A	0.442	14.9	105	0.214	41.8	2.67	18.7	1,045	7,765
Sample Panel B	0.539	18.8	97.3	0.292	51.8	1.45	21.6	4,267	8,256

Bids were received from both potential catalyst recycling contractors. The catalyst recyclers proposed fees based on the number of modules (36), the net weight of the catalyst blocks in the modules (estimated at 46,800 lb [21,300 kg] total by URS), and the total amount of gold contained (estimated by URS at 8,000 g based on the catalyst block elemental analyses shown above). In each bid, the revenue from the recycling effort was the market value of a proposed recoverable percentage of the total amount of gold assayed in the blocks processed, with the market value to be determined at an agreed-upon date (the current value as this report is being prepared is about \$1,200 per troy ounce, or about \$39 per gram). The net proceeds from the recycling effort, which are to be refunded to DOE, will be the revenue minus the recycler's fees and other expenses related to the recycling effort. Based on the estimated quantities shown above, the bid from Metals and Catalyst Resources was predicted to provide a higher dollar return to DOE, so the recycling award was made to them. The eventual settlement with Metals and Catalyst Resources will be made based on actual catalyst block total weight and a more thorough assay of the catalyst pieces after they are ground for processing.

On March 10th and 11th, the 36 modules were loaded by LCRA staff onto flatbed semi-trailers at FPP, and were hauled to Metal and Catalyst Resources' dismantling contractor. A number of catalyst blocks were removed from sample holders in modules in the first and third catalyst layers, after the modules were removed and before they were shipped. These used sample blocks are being reserved for possible regeneration testing, third-party assays, etc. As this report is being prepared the recycling process is underway.

Mercury Control Process Metrics

This cooperative agreement was funded as an award in Funding Opportunity Announcement Number DE-PS26-05NT42510 under Area of Interest 2, additional (Round 3) Phase II field testing of advanced post combustion mercury control technologies capable of achieving 50-70% mercury removal. The goal for Area of Interest 2 was to reduce mercury control costs to 50% or less of the baseline cost, which was stated as an estimated \$60,000/lb (\$27,000/kg) of mercury removed. Now that the demonstration period has been completed, the actual performance of the oxidation catalyst technology can be compared to the performance and cost metrics detailed in the Funding Opportunity Announcement. The mercury removal performance and cost per pound of mercury removed are discussed in separate subsections below.

Mercury Removal Performance

The mercury removal performance capability of the technology was required to be 50 to 70% removal relative to baseline performance. In this project, baseline performance was measured for each OH measurement period. The mercury removal performance of the oxidation catalyst technology was calculated by comparing the Absorber C outlet mercury concentration to that of baseline Absorber A or B, whichever was in service. This comparison was made for each of the four OH measurement periods in Table 32 above.

The actual improvement in mercury capture (reduction in outlet total mercury concentration) when comparing Absorber C to Absorber A or B outlet concentrations ranged from 69% in May 2008 to -27% (higher outlet concentration) in September 2009. The May 2008 improvement drops to 64% if the one Absorber A outlet measurement that is in question is not included in the mean. Either way, the May 2008 result was well within the performance range required for Area of Interest 2, but none of the three later OH measurement period results showed 50% or greater mercury capture relative to baseline operation.

The three later performance numbers reflect an expected decrease in mercury oxidation performance of the catalyst over time in operation, but as described earlier in this section that decrease was exacerbated by extensive fly ash buildup in the first catalyst layer in June 2009 and by removal of the first layer prior to the September 2009 measurements. Furthermore, variable mercury re-emission levels across Absorber C and either Absorber A or B greatly influenced the relative effectiveness of the mercury oxidation technology. The fact that none of three OH measurement period results after May 2008 showed greater than 50% mercury capture relative to baseline is primarily a result of 1) high mercury re-emissions across Absorber C in November 2008 and September 2009, and 2) low catalyst oxidation performance because of fly ash buildup in June 2009.

Since there are only four sets of mercury removal performance measurements available from this 17-month period, the only way to estimate the overall mercury removal performance for the demonstration is to merely average the four sets of numbers. The average performance data are summarized in Table 39. However, a straight numerical average likely introduces a low bias in the results since two of the four sets of measurements were conducted during the final four months of operation, when the effects of fly ash buildup were most prevalent. Thus, these averages likely under-predict the actual performance of the oxidation catalyst system over the 17-month demonstration.

Table 39. Average Results from the Four OH Measurement Periods

Parameter	Average	Average w/o Absorber A Run 2, May 2008
Absorber A or B Inlet Total Mercury, $\mu\text{g}/\text{dNm}^3$ @3% O ₂	12.3	12.3
Absorber A or B Outlet Total Mercury, $\mu\text{g}/\text{dNm}^3$ @3% O ₂	7.2	6.9
Catalyst/Absorber C Inlet Total Mercury, $\mu\text{g}/\text{dNm}^3$ @3% O ₂	12.3	12.3
Absorber C Outlet Total Mercury, $\mu\text{g}/\text{dNm}^3$ @3% O ₂	5.0	5.0
Absorber A or B Total Mercury Removal, %	41	44
Absorber C Total Mercury Removal, %	59	59
Absorber C Improvement over Absorber A or B, %	30	27
Absorber A or B Average Inlet Hg Oxidation, %	50	50
Absorber C Average Inlet Hg Oxidation, %	80	80

It is not possible to use other means to estimate the mercury oxidation and removal performance over the demonstration period. The change in oxidation across the catalyst is relatively predictable, with a steady decrease in performance over time that was compounded by fly ash buildup. However, the adverse effects of mercury re-emissions on mercury control performance in Absorber C and in baseline Absorber A or B are much less predictable. The re-emission levels were possibly related to absorber slurry wt% solids levels and iron concentrations in the solids, but it is not possible to retroactively track these parameters over time. Iron analyses were not routinely conducted on absorber slurry solids. The slurry density was tracked by plant instrumentation as an indicator of wt% solids. It appears that low wt% solids levels occurred because the plant instrumentation went out of calibration, so the plant instrument readings do not provide a reliable indication of periods where low wt% solids occurred. Consequently, averages for the four measurement periods are the only available indicators of mercury oxidation and removal performance.

The averages in the table show that the catalyst inlet and Absorber A or B inlet total mercury concentration averaged $12.3 \mu\text{g}/\text{Nm}^3$, while the Absorber C outlet averaged $5.0 \mu\text{g}/\text{Nm}^3$ and the

Absorber A or B outlet averaged $7.2 \mu\text{g}/\text{Nm}^3$, all values adjusted to a dry, 3% O_2 flue gas basis. The Absorber A or B outlet average drops to $6.9 \mu\text{g}/\text{Nm}^3$ if the questionable results from the second run at the Absorber A outlet in May 2008 are dropped. These averages correspond with 59% total mercury removal across the catalyst and Absorber C, with a baseline value of 41% removal across Absorber A or B (44% with the one May 2008 result removed). Comparing the absorber outlet concentrations, the catalyst/Absorber C outlet concentrations averaged 30% lower than the Absorber A or B outlets (27% with the one May 2008 result removed), which falls well short of the target range of 50 to 70% reduction relative to baseline.

As mentioned above, this shortfall in performance is attributable to three effects: 1) a decrease in catalyst mercury oxidation performance over time due to aging effects, 2) a further decrease due to excessive fly ash buildup, particularly in the first catalyst layer, leading to operation with only two catalyst layers for the final three months, and 3) variable mercury re-emissions across the absorbers. The first effect was expected at the outset of the demonstration period, while the second effect was not expected. However, even with the first two effects limiting mercury oxidation performance later in the demonstration, the Absorber C inlet total mercury oxidation percentage averaged 80%, as shown in the table. This value reflects both the baseline mercury oxidation at the ID fan outlet and the elemental mercury oxidation that occurred across the catalyst. In comparison, the Absorber A or B inlet total mercury oxidation averaged 50%. Were it not for the third effect listed above, variable mercury re-emissions across the absorbers, it is likely that the mercury control metrics for Area of Interest 2 would have been met.

It was apparent during periods where low mercury re-emissions were measured across each of the three absorbers that it is possible to operate with re-emission levels of 5% or less (percentage of the absorber inlet oxidized mercury). Two sets of measurements each for Absorbers C and B with low re-emissions (plus one set for Absorber A if the suspect absorber outlet OH run from May 2008 is excluded) averaged between 4 and 5% re-emissions. These results also averaged greater than 92% net capture of inlet oxidized mercury after considering the absorber outlet oxidized mercury concentration and elemental mercury re-emission levels.

This observation suggests that it could have been possible to operate the absorbers to achieve 92% or greater net removal of oxidized mercury (after re-emission effects), such as by ensuring that the absorber slurry wt% solids levels were maintained above 10 wt%. With 92% net removal of inlet oxidized mercury and with the average inlet oxidation percentages shown in Table 39, it is possible that an average of 74% mercury removal could have been achieved across Absorber C and 46% across Absorbers A or B. These estimates correspond with an average 52% reduction in outlet mercury concentration at Absorber C compared to Absorber A or B. Had the demonstration gone to the full 24-month duration, it would have been desirable to conduct the fifth OH measurement period while controlling the Absorber C and Absorber A or B slurry wt% solids level above 10% to see if low re-emission levels resulted.

Cost of Mercury Control

The mercury control performance results discussed above were used as the basis for calculating demonstration costs in dollars per pound of mercury removed. The amount of mercury removed was limited by fly ash buildup and the resulting early end to the demonstration, and by variable

mercury re-emissions across the wet FGD absorbers, so the smaller denominator in this calculation makes the result larger. This is particularly the case for this, a catalytic process, where the operating costs are relatively minor and most of the costs are associated with capital modifications and initial catalyst purchase.

Mass of Mercury Captured

The pounds of mercury removed were estimated from the mercury removal results discussed above and the measured flue gas flow rates during the four OH measurement periods. These flow rate results are summarized below in Table 40. The results show that at the beginning of the demonstration with clean catalyst, the flow was split evenly between Absorbers A and C. After fly ash buildup began the split was closer to one-third to Absorber C and two-thirds through the other absorber in service. This inequity in flow limited the amount of mercury captured downstream of the mercury oxidation catalyst.

Table 40. Summary of Flue Gas Flow Rate Data for OH Measurement Periods

Measurement Period	Flue Gas Flow Rate, Absorber C Outlet, dscfm [0°C] (Nm ³ /h @3% O ₂)	Flue Gas Flow Rate, Absorber A or B Outlet, dscfm [0°C] (Nm ³ /h @3% O ₂)	Absorber C % of Scrubbed Flue Gas Flow	Unit Load, Net MW
May 2008	611,100 (628,900)	620,800 (627,300)	50.1%	440
November 2008	571,600 (615,100)	1,100,000 (1,176,00)	34.3%	446
June 2009	400,700 (477,800)	841,200 (851,600)	35.9%	441
September 2009	355,500 (369,500)	725,400 (818,000)	31.1%	372

These flow rate data were combined with the difference between the Absorber A or B outlet mercury concentration and the Absorber C outlet concentration to quantify the amount of mercury removed due to the oxidation technology, and the resulting amounts were averaged. An average unit load for the four measurement periods of 425 net MW was also developed from the data in Table 40. The average mass of mercury removed during these four periods was used to estimate a total for the entire demonstration period. This was calculated by multiplying the average hourly rate by the following ratio: total net generation for Unit 3 during the demonstration period divided by the average hourly generation during the four measurement periods.

The results of these calculations are shown in Table 41. The results show an estimate of only 34.0 lb (15.4 kg) of mercury removed beyond baseline performance during the 17-month demonstration. This amount drops even lower if the one Absorber A outlet measurement that is in question for the May 2008 measurement trip is dropped. Correspondingly the May 2008 mercury concentration reduction for Absorber C is lowered to 5.26 µg/Nm³ and the mass removal rate to 3.31 g/hr, and the total mercury capture estimate for the demonstration period is lowered to 28.8 lb (13.1 kg).

Table 41. Estimate of Total Mercury Removed during Oxidation Catalyst Demonstration

Measurement Period	Hg Removed		
	$\mu\text{g}/\text{Nm}^3$ @3% O ₂	g/hr	Total lb (kg) of Hg over Demonstration Period
May 2008	6.62	4.16	-
November 2008	1.09	0.67	-
June 2009	2.97	1.42	-
September 2009	-1.9	-0.70	-
Average	2.20	1.39	34.0 (15.4)

A further estimate was made of what this quantity could have been if the both operating absorbers were operated in a mode such that mercury re-emissions were limited to 5% of the inlet oxidized mercury concentration. This possibly could have been achieved by maintaining the wt% solids in the absorbers above 10 wt%. That estimate was 44.7 lb (20.3 kg).

This estimate was further extrapolated to what might have been achieved if fly ash buildup was better controlled and the demonstration had gone the full 24 months, with a result of 63.6 lb (28.9 kg). Thus, with better control of fly ash buildup in the catalyst and of re-emissions across the absorbers (including the baseline absorber) the amount of mercury captured could have been nearly doubled. This estimate does not account for further benefits such as the possibility of improved catalyst performance and/or higher flue gas flow rates through the catalyst (hence, more mercury treated and removed) if there had been less fly ash buildup.

Control Costs

The costs for the mercury capture demonstration (the numerator in the dollar per pound calculation) consist of 1) the amortized capital cost for the ductwork modifications to allow the catalyst to be installed upstream of Absorber C, 2) the cost of the catalyst itself, 3) increased power consumption by the Unit 3 ID fans because of the catalyst pressure drop, and 4) the compressed air usage by the sonic horns used for acoustic cleaning of the catalyst. These costs are summarized in Table 42 and discussed below.

The capital cost and catalyst cost were well documented as project expenses. The capital cost included the engineering design for the duct modifications; demolition of the old duct; fabrication and field construction of the new ductwork, structural steel and catalyst support frames; sonic horns; various instrumentation; and catalyst delivery and installation. This totaled \$1.88 million. To be consistent with a previous DOE report,⁶ this capital cost was amortized to a levelized, current-dollar annual cost assuming a 20-yr asset life (15.7% annual capital recovery factor), or \$415,000 over the life of the demonstration period. This amortization assumes the process would continue to operate over a typical remaining asset life, not just during the demonstration period.

Table 42. Summary of Oxidation Catalyst Demonstration Costs

Cost Item	Cost Basis	Cost over 17-Month Demonstration Period
Capital Modifications to Ductwork	Actual, tracked costs (\$1.882 million) levelized and reported over demonstration period	\$0.415 million
Catalyst Purchase	Actual, tracked costs, including cost shared amount	\$1.660 million
Catalyst Recycle Credit	Estimated net revenue	\$0.175 million
ID Fan Power	Estimate	(\$0.148 million)
Compressed Air Usage	Estimate	\$0.005 million
TOTAL Net Cost	-	\$2.053 million
Fly Ash Sales Value	Tracked sales over demonstration period, pro-rated to 200 MW	\$0.253 million
Avoided Landfill Costs	Estimate	\$0.254 million

The catalyst cost was \$1.66 million, although the catalyst supplier, Johnson Matthey, cost shared 25% of this amount. However, at the end of the project the used catalyst has economic value because of its gold content. After considering the costs associated with transporting, recovering, and refining the catalyst pieces, the three layers of catalyst are estimated to have a net positive value of \$175,000 based on 2010 gold prices. The actual value is not known as this report is being written because the recycling effort is still underway. This is one area where the change in economic conditions from when the project began until the end of the project – a period of nearly five years – benefited the project economics. At the time the catalyst was originally priced the value of gold was in the range of \$450 to \$500 per troy ounce, while it is currently valued at over \$1,200 per troy ounce. This increase in the price of gold greatly benefited the value of the recycled catalyst; at \$450 per troy ounce the catalysts would have had little net value after recycling costs.

The cost of power was estimated from the average flue gas flow rate based on the data shown in Table 40 and the average pressure drop across the catalyst of 1.96 in. H₂O (0.488 kPa) over the 488 days that Unit 3 operated during the demonstration period. Based on fan/motor efficiencies of 75% and 95%, respectively, and an assumed cost of internal power of \$0.066/kW-h, this equates with increased fan power costs of \$148,000 over the demonstration period.

The cost of plant compressed air used to operate the sonic horns was estimated based on the horn operating cycle: nine horns each operated for 15 seconds every 5 minutes, and the manufacturer’s rating of horn air consumption: 80 scfm (130 Nm³/h) at 80 psig (550 kPa).

Assuming 488 days of operation, this amounts to 25 million scf (0.67 million Nm³) of compressed air usage and approximately \$5,000 of compressor power costs.

There are avoided costs that should also be considered in the economics for this process, including the value of fly ash sales that would likely have been lost if an approach such as activated carbon injection was used for mercury control. Unit 3 produces a high quality Class C fly ash. The location of FPP within 100 miles of the Austin, Houston and San Antonio metropolitan areas results in the fly ash being used extensively as cement replacement in concrete sold in those markets. One of the drivers for LCRA to participate in this demonstration was that they were seeking a mercury control technology that would not jeopardize their fly ash sales, as might implementation of activated carbon injection. Even so-called ash-compatible carbons can affect fly ash quality and may jeopardize sales or lower sales prices in competitive markets.

In the year prior to the beginning of the demonstration, LCRA sold 100% of the ash from Unit 3 for a total revenue stream of approximately \$1.8 million dollars. For the 200 MW of generating capacity that was to be treated by the oxidation catalyst technology during the demonstration, these sales corresponded with revenues of approximately \$800,000 per year. However, shortly after the demonstration began in mid-2008, the U.S. economy slowed significantly and home, commercial, and road building was curtailed. Correspondingly the demand for concrete and for Class C fly ash as a cement replacement was greatly reduced. As a result, during the demonstration period LCRA was able to sell less than 43% of the fly ash from Unit 3, at an average price about 35% lower than the year prior to the demonstration. This greatly reduced the economic benefit of employing the oxidation catalyst technology rather than conventional activated carbon injection during the demonstration period. The revenue stream associated with fly ash from the portion of the flue gas treated by the oxidation catalyst amounted to only \$180,000 per year rather than the anticipated \$800,000. Although this benefit of the oxidation catalyst technology is greatly reduced, it still should be considered when comparing the economics of this technology to other candidate technologies.

A corresponding benefit is more difficult to quantify – the avoided cost of disposing of fly ash with activated carbon content. LCRA has only limited permitted landfill area available at FPP, and does not have a fully developed estimate for the costs associated with a new landfill should all of the fly ash have to be disposed. The ash not sold during the demonstration period is being stored on site and sold into low value markets such as road base as a means of reducing inventories. However, this is not a viable option for long term operation. If a technology such as activated carbon injection were implemented at FPP and rendered the fly ash unsaleable, it would result in a significant operating cost to permit, develop and operate a landfill operation. To put a dollar figure on the value of this benefit in Table 42, a landfill disposal cost of \$17/ton was used to be consistent with the previous DOE report.⁶

Together, the fly ash sales revenue and avoided landfill costs represent 25% of the levelized mercury control costs for this demonstration. As discussed above, this percentage could have been considerably greater had fly ash sales been more robust, and therefore could have represented a larger benefit of using this technology compared to technologies that adversely affect fly ash reuse.

Mercury Control Cost per Pound Estimates

Table 43 summarizes the calculations of mercury control costs in dollars per pound, based on the total net cost of the demonstration of \$2.053 million as shown in Table 42 above. Three cases are shown in Table 43. One uses the data from all four OH measurement trips during the demonstration at face value and the second was adjusted to disregard the suspect results for Run 2 at the Absorber A outlet location in the May 2008 trip. The third case is an estimate for how the cost effectiveness might have been improved if the FGD system could be operated to minimize mercury re-emissions at 5% of the inlet oxidized mercury concentration.

Table 43. Mercury Control Costs for Demonstration of Catalytic Oxidation Technology

Cost Basis	Mercury Removed, %	Mercury Removed, lb	Mercury Control Cost, \$/lb	% Reduction from DOE \$60,000/lb Baseline
Base Case	30	34.0	\$60,300	-1
Base Case without Absorber A Run 2 Data, May 2008	27	28.8	\$71,300	-19
Estimated Case Assuming Re-emissions Limited to 5% of FGD Inlet Hg ²⁺	55	44.7	\$45,900	24

As might have been expected since the mercury control target was not met, the mercury control cost target of 50% or greater reduction from the estimated baseline cost of \$60,000/lb was also not met. Depending on how the May 2008 data were treated, the cost relative to the DOE baseline ranged from essentially equal to DOE's \$60,000/lb to representing a 19% increase. Even the case where costs were estimated for re-emissions being held to a low level in both operating FGD absorbers showed only a 24% reduction.

However, the costs per pound of mercury removed are not greatly different than DOE estimates of costs for using activated carbon injection on PRB coal-fired units with cold-side ESPs for particulate control at the 50% control level,⁶ roughly the same control level as at FPP. The DOE estimates ranged from \$44,000/lb to \$60,500/lb when byproduct impacts are considered, on units in the same size range as the demonstration conducted in this project, ranging from 140 to 240 MW. Since LCRA does sell as much of the fly ash from Unit 3 as possible, up to 100% in a robust economy, and the catalytic oxidation technology does not have any impact on the fly ash, it is appropriate to compare these technologies on an equal basis with respect to byproducts.

Another set of mercury control cost per ton estimates was made based on the assumption that fly ash buildup in the catalyst could be controlled and that the demonstration period had gone the full 24 months. Because the capital levelization and power costs are prorated to the time of operation, these values would not be impacted when assuming a longer operating period. However, the catalyst cost does go down on a dollars per pound basis when assuming a 24-month rather than a 17-month life. Assuming successful operation for 24 months, the mercury

control cost estimates were lowered to \$47,400/lb for the base case in Table 43 and \$36,000/lb for the low re-emission case. The latter represents a 40% cost reduction compared to DOE's estimated \$60,000/lb baseline mercury control cost in the Funding Opportunity Announcement.

CONCLUSIONS

The demonstration period was ended after 17 months of the planned 24-month duration. A few conclusions are apparent, and are discussed below.

Catalyst Pressure Drop

The sonic horns as installed were not effective at controlling fly ash buildup in the fine-pitched catalyst, and the pressure drop continually increased over time. Changes to the sonic horn installation were recommended by the acoustic cleaning system vendor, GE Energy, but would not likely have been effective in cleaning up the fly ash buildup already experienced after seven months of operation.

It is now believed that it is primarily poor flue gas velocity distribution in the upper portion and side walls of the catalytic reactor chamber that limited the ability of the horns to control fly ash buildup. The horns are intended to re-entrain fly ash particles off of the catalyst surfaces, but rely on adequate flue gas velocity to carry re-entrained particles away. The fly ash buildup was clearly worst in the upper and sidewall areas described above, which see lower-than-average flue gas velocity because of the rapid duct cross section expansion between the Absorber C inlet damper and the first catalyst layer. The fact that the sonic horns installed on Unit 3 were not placed optimally may have exacerbated this effect.

Acoustic cleaning may be more effective in a situation where enough space is available to use lesser angles to expand the duct cross section, the horns are placed optimally, and turning vanes are installed (if needed) to produce an even velocity distribution across the catalyst face. It may also prove that more energetic cleaning devices, such as air soot blowers, and/or a less fine catalyst pitch (fewer than 64 cells per square inch, or larger than 3.2-mm cells) are needed to ensure that fly ash buildup does not become an issue.

Mercury Oxidation Performance

The catalyst initially performed very near projected values for mercury oxidation percentage. Even after six months of operation, the elemental mercury oxidation percentage across the catalyst was only 3 percentage points below what was measured immediately after the catalyst was placed in service and only 4 percentage points below the predicted new-catalyst performance. However, after 13 months of operation a substantial loss of activity was measured; the June 2009 elemental mercury oxidation across the catalyst dropped by 25 percentage points from measurements taken seven months earlier in November 2008. It is believed that some of this activity loss was real, but that a substantial portion was “artificial” in that it was caused by the buildup of fly ash in the catalyst, which blocked otherwise active catalyst surface area. In fact, after removing the heavily plugged first catalyst layer from the reactor in late June, the September 2009 OH measurement results with only two layers in place showed better mercury oxidation results than the June 2009 measurements with three layers. This suggests that gas flow to portions of the second and third layers had been blocked by fly ash buildup in the first layer.

Mercury Capture by the Downstream Wet FGD System

The mercury removal performance of the FGD absorber immediately downstream of the catalyst was initially measured to be at the upper end of the percentage improvement required by the DOE solicitation, showing up to a 69% percent reduction in mercury emissions compared to an FGD module without a catalyst upstream. However, six months later in November 2008 measurements, the improvement in mercury capture resulting from the catalyst installation was only 18%. In June 2009, the improved mercury capture relative to the baseline absorber was restored to 48% in spite of greatly reduced elemental mercury oxidation across the catalyst. However, the September 2009 results showed less mercury removal across Absorber C than across the baseline absorber, Absorber B.

Mercury concentration measurements indicate that the mercury capture performance of Absorber C, with the catalyst installed upstream, was greatly limited by mercury re-emissions in November 2008 and September 2009, but that re-emissions were minimal in May 2008 and June 2009. This suggests that mercury re-emissions across this FGD system are variable over time, and may be influenced by factors such as coal and limestone characteristics and/or FGD operating conditions. In particular, the weight percent solids levels in the absorber slurry were lower than normal in the November 2008 and September 2009 testing, and may have contributed to higher FGD liquor mercury concentrations and higher re-emissions in Absorber C. This effect appears to be exacerbated by low iron concentrations in the absorber slurry solids during the periods of low wt% solids in the slurry. Changes to FGD operating conditions to maintain higher wt% solids levels, the use of a limestone with a higher iron content, and/or the use of FGD re-emission additives may be required to continually realize the benefits of a mercury oxidation catalyst on FGD mercury capture by the Unit 3 FGD system.

Mercury Control Process Metrics

The goals of this demonstration were to operate successfully for 24 months, achieve a 50 to 70% reduction in Absorber C outlet mercury concentration compared to the baseline absorber, all at a cost of \$30,000/lb of mercury removed or less. Unfortunately none of these objectives were met. As described throughout this report, a buildup of fly ash in the catalyst led to an early end to the demonstration, after nearly 17 months of operation. The adverse effects of the fly ash buildup on oxidation catalyst performance along with variable mercury re-emissions across the Unit 3 wet FGD absorbers led to the increase in mercury removal averaging only 27 to 30% during the demonstration, rather than the desired 50 to 70%. Had re-emissions been continually controlled to a low percentage as was sometimes measured across the Unit 3 FGD absorbers, it is likely that an increase of greater than 50% mercury removal would have been realized.

It should be noted that these average mercury removal estimates are likely biased low by the fact that two of the four sets of measurements were conducted during the last four months of the 17-month demonstration. Thus, half of the available data reflect the adverse effects of substantial fly ash buildup in the catalyst layers, including having to conduct the final set of measurements with only two of three original catalyst layers still in service.

Because the demonstration did not go for the planned 24 months and the mercury removal performance metrics were not met, the mercury control cost metrics were also not met. The

calculated, levelized cost of mercury capture was in the range of \$60,300 to \$71,300/lb of mercury in current dollars, so no improvement was realized over the DOE estimated baseline of \$60,000/lb. However, analysis of the cost data indicated that if the fly ash buildup could be limited to allow at least 24 months of catalyst operation and FGD absorber operation could be controlled to limit mercury re-emissions to low levels, a control cost of \$36,000/lb or lower could have been achieved.

Further reductions in cost per pound of mercury removed might be realized if the catalyst could be regenerated to allow an operating life longer than 24 months. However, the effectiveness of regeneration was not investigated as part of this demonstration because of the size of the demonstration and corresponding budget constraints.

LIST OF GRAPHICAL MATERIALS

Figure 1. Schematic of FPP Unit 3 Configuration.....	2
Figure 2. FGD Duct Configuration Showing Location of New Catalytic Reactor.....	3
Figure 3. Sketch of Reactor Compared to Previous Inlet Duct (plan view)	3
Figure 4. Sketch of New Reactor Compared to Previous Inlet Duct (side elevation)	4
Figure 5. Example Catalyst Block (one of approximately 8700 installed upstream of Absorber C)	5
Figure 6. Isometric and Plan Drawing of Catalytic Reactor Design, Showing Sonic Horn Placement.....	9
Figure 7. New Duct Run with Expanded Cross Section for Catalyst during Trial Fit-up at Fabricator’s Shop.....	11
Figure 8. Side Three-quarter View of Absorber C and Inlet Duct after Construction.....	12
Figure 9. One of 36 Catalyst Modules Being Unloaded from Shipping Crate Prior to Being Installed in Catalytic Reactor.....	12
Figure 10. Catalyst Module Being Lifted into Place to Install in Catalytic Reactor	13
Figure 11. View from Above Catalytic Reactor Showing Catalyst Module Being Installed by Sliding Down Support Structure.....	13
Figure 12. View from Inside of New Catalytic Reactor Showing One Layer of Catalyst Installed (3 of 12 panels per layer in view)	14
Figure 13. Flue Gas Pressure Drop across the Catalyst over the First Seven Months of Operation (note: 1.00 in. H ₂ O equals 0.249 kPa)	15
Figure 14. Photo of the Lower Middle Section of the First Catalyst Layer Showing Fly Ash Buildup on the Leading Edges but Few Plugged Cells.....	16
Figure 15. Photo of a Catalyst Block Near the Sidewall of the Enclosure Showing Nearly All of the Cells Blocked with Fly Ash	16
Figure 16. Photo of Back Side of Third Catalyst Layer, Showing Little Fly Ash Buildup.....	17
Figure 17. Illustration of Recommended and Actual Spacing of Sonic Horns across Top of Reactor (horns for catalyst layers 2 and 3 are depicted; not to scale).....	21
Figure 18. Illustration of Actual and Currently Recommended Location and Orientation of First Layer Sonic Horns (not to scale)	22
Figure 19. Illustration of Projected Area of Most Effective Cleaning Energy for First Catalyst Layer (not to scale)	23
Figure 20. Flue Gas Pressure Drop Across the Catalyst over 17 Months of Operation (note: 1.00 in. H ₂ O equals 0.249 kPa).....	24
Figure 21. Schematic of Mercury Sampling Locations at Fayette Power Plant Unit 3 in May 2008 Measurements	29
Figure 22. Schematic of Mercury Sampling Locations at FPP Unit 3, November 2008.....	44
Figure 23. Schematic of Ontario Hydro Method Measurement Locations, June and September 2009.....	53
Figure 24. Plot of Measured Hg ⁰ Oxidation across Catalyst vs. Time, Through June 2009	56
Figure 25. Plot of Measured Hg ⁰ Oxidation across Catalyst vs. Time	64
Figure 26. Re-emissions across the FPP Unit 3 Absorbers versus Iron in Absorber Slurry.....	71

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LIST OF ACRONYMS AND ABBREVIATIONS

Acfm – actual cubic feet per minute

°C – degrees Celcius

CFD – computational fluid dynamics

Cpsi – cells per square inch, a measure of honeycomb catalyst cell pitch

ESP – electrostatic precipitator; the type of particulate control device used on the host unit

°F – degrees Farenheit

FGD – flue gas desulfurization

FPP – Fayette Power Project, the power plant which hosted this demonstration

Hg – mercury, in an unspecified form

Hg⁰ – elemental or metallic mercury

Hg²⁺ – oxidized mercury, the ionic form of mercury when dissolved in an aqueous environment

Hg^T – total mercury, the sum of elemental, oxidized, and particulate mercury forms in flue gas

ID – induced draft

IGS – inertial gas separator, a flue gas conditioning system that uses a high-velocity flue gas sampling loop and a sintered metal filter to allow sample flow to a mercury SCEM to be particulate free, while minimizing fly ash interactions with the mercury in the sample gas

LCRA – Lower Colorado River Authority, the host utility for this demonstration

LOI – loss on ignition, a measurement parameter used to estimate the amount of unburned carbon in fly ash samples

OH – the Ontario Hydro method, a wet-impinger-based method of measuring speciated mercury concentrations in flue gas

ppb – parts per billion

ppm – parts per million

ppmv – parts per million, flue gas volume basis

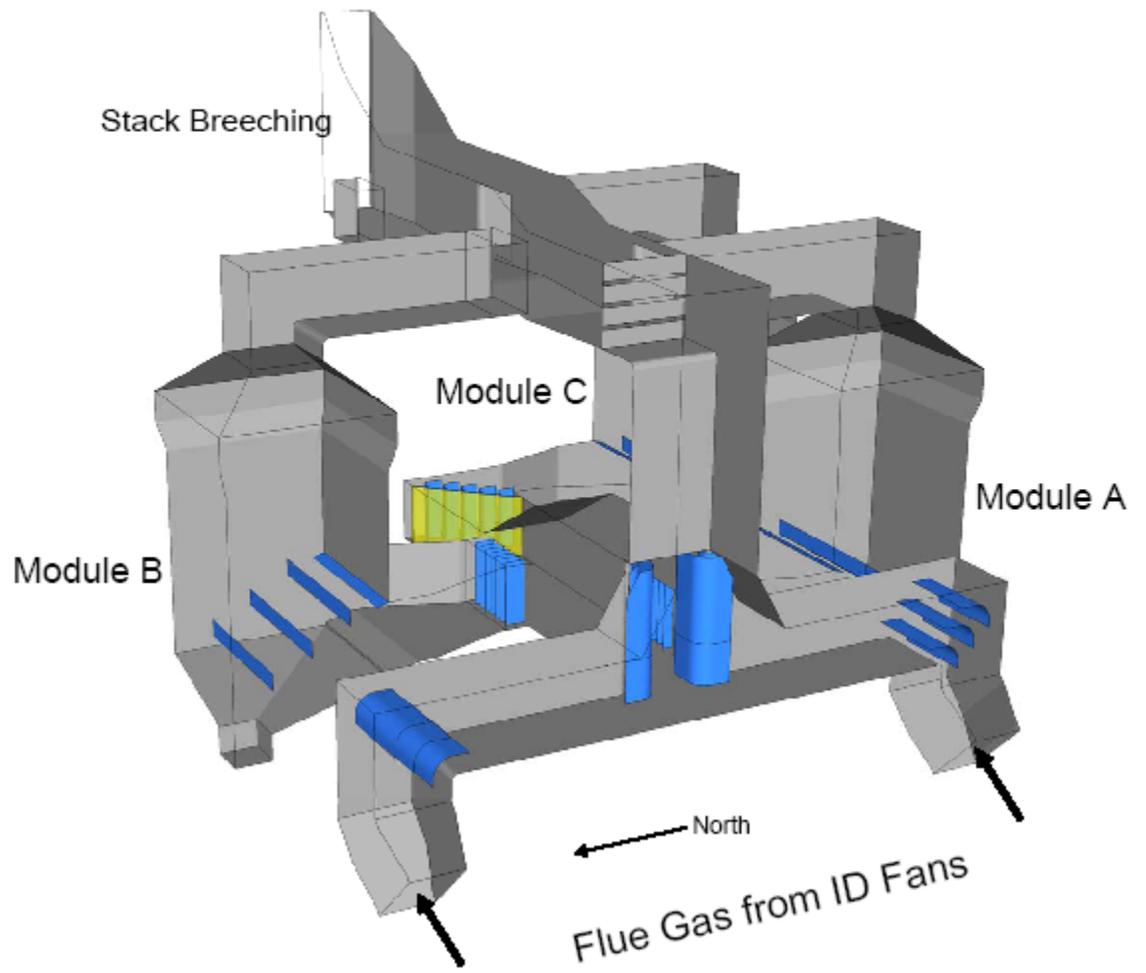
PRB – Powder River Basin, an area of Wyoming and Montana that produces subbituminous Western coal that is fired in much of the Midwest region of the U.S.

SCEM – semi-continuous emissions monitor, a research-grade mercury analyzer that uses wet-impinger-based gas conditioning and a cold vapor atomic absorption (CVAA) detector to measure speciated mercury concentrations in flue gas

SHE – standard hydrogen electrode, defined as having 0 mV reference electrode potential. During this project actual measurements were made against a silver/silver chloride reference electrode saturated with potassium chloride, 197 mV electrode potential relative to SHE.

APPENDIX A – CFD MODELING RESULTS SUMMARY

Existing Operation



URS

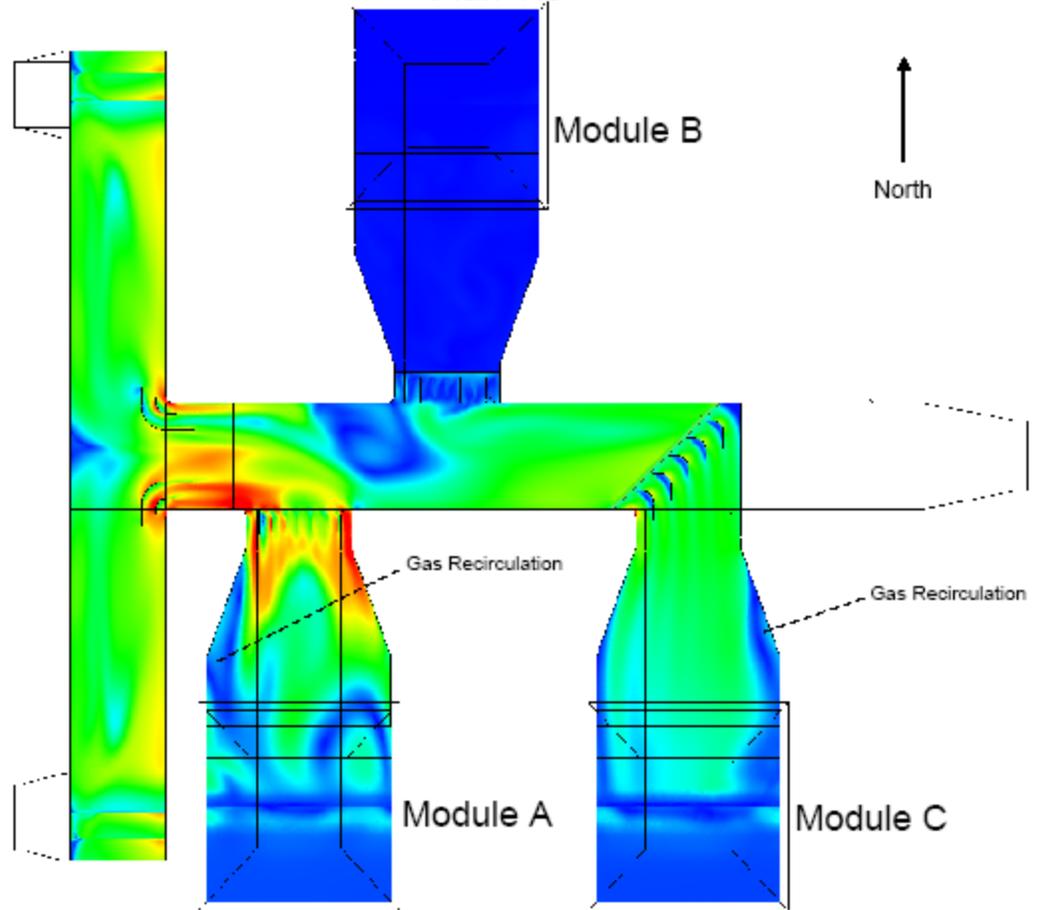
Case 1:
Existing
Operation with
A&C In Service



URS

Gas Velocity Magnitude

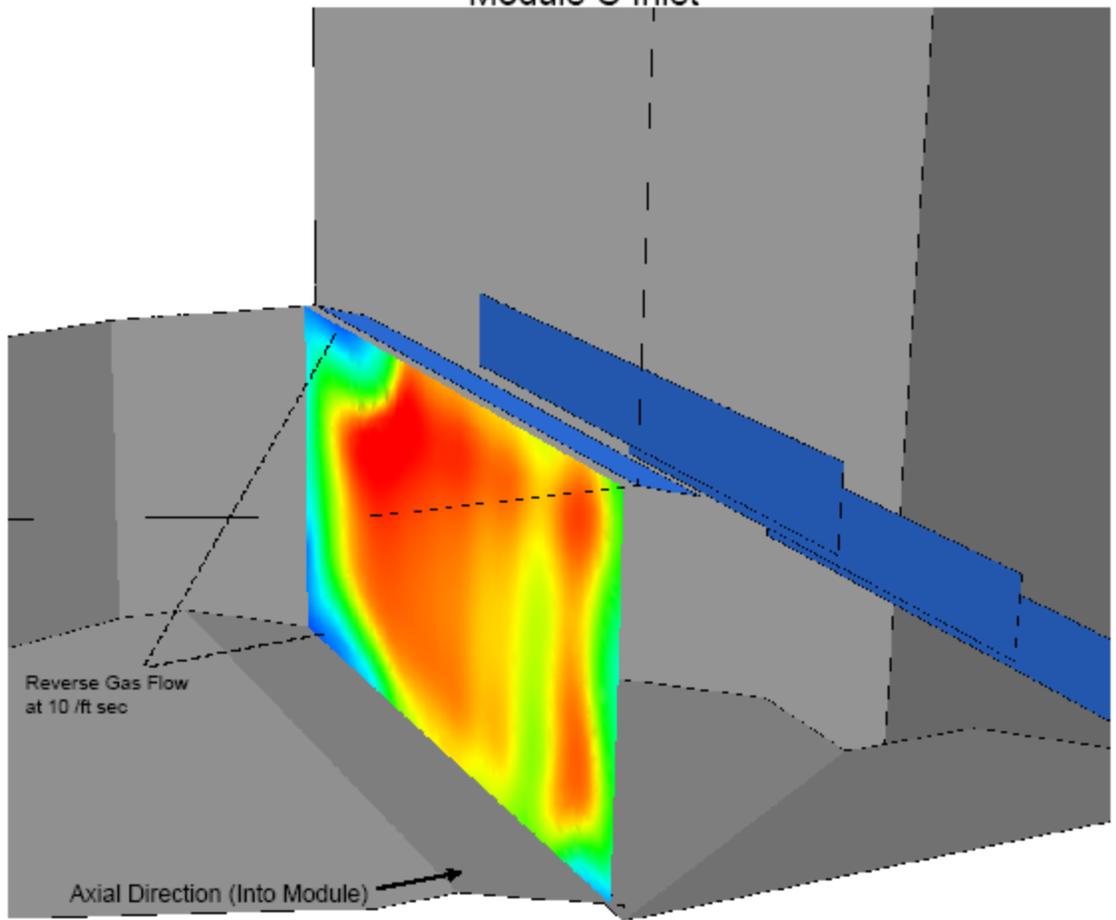
Plan View

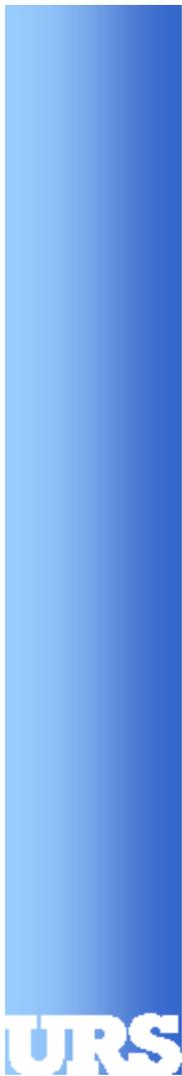


Case 1:
Existing
Operation with
A&C In Service

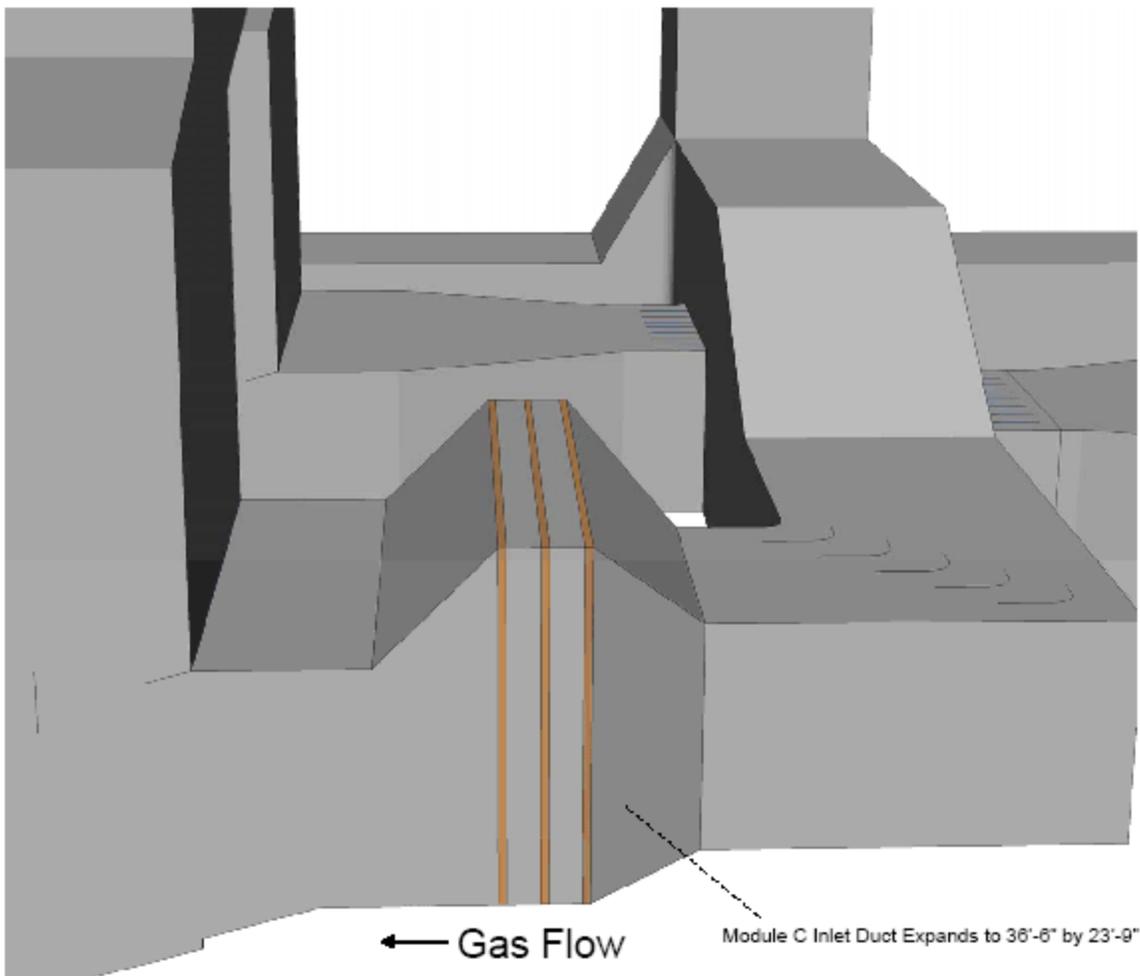


Axial Component of Gas Velocity Module C Inlet





Module C Inlet Duct Modifications

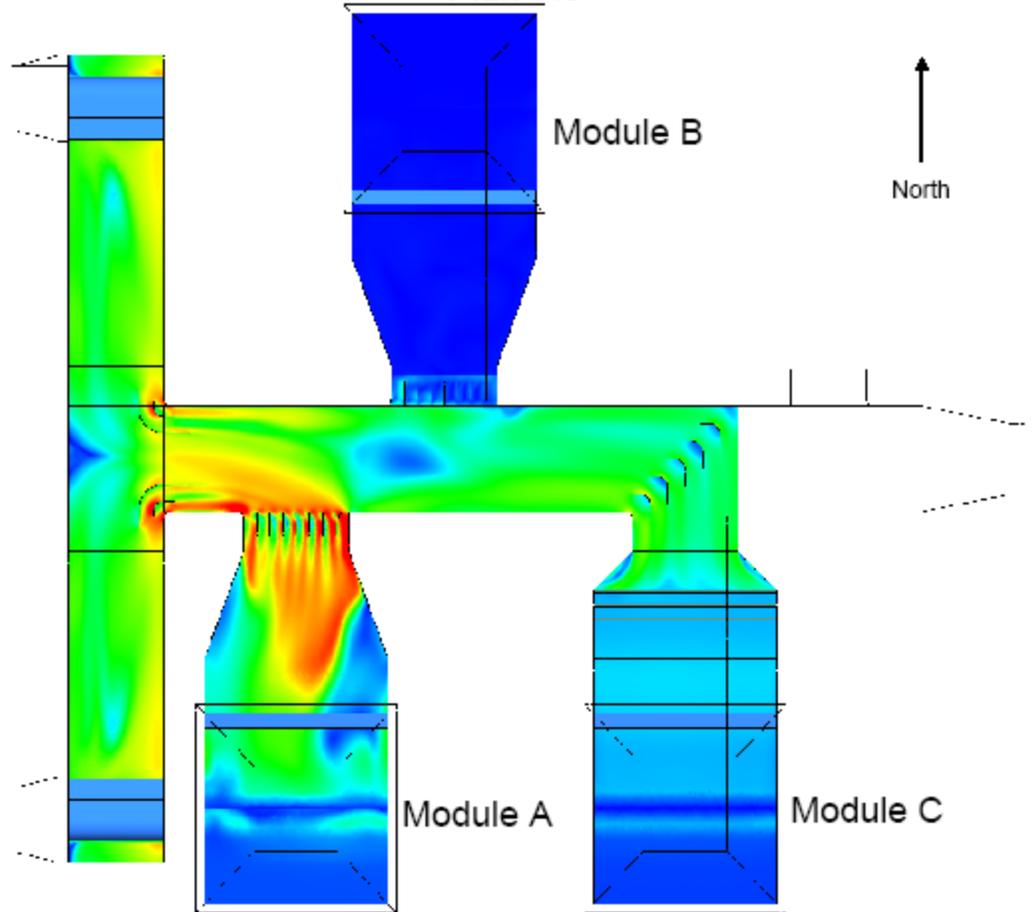


Case 9:
Oxidation
Catalyst,
Perf Plate
Removed,
A&C In Service



URS

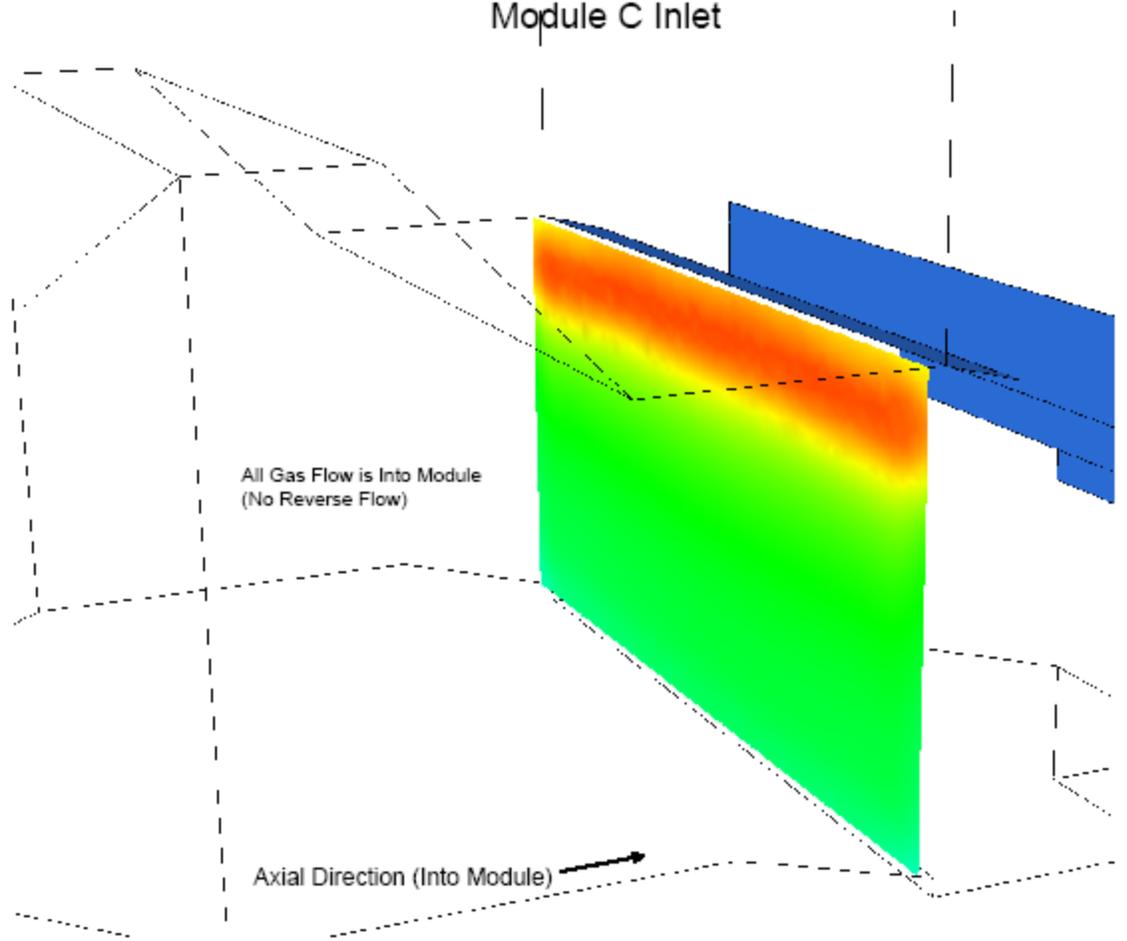
Gas Velocity Magnitude Plan View



Case 9:
Oxidation
Catalyst,
Perf Plate
Removed,
A&C In Service



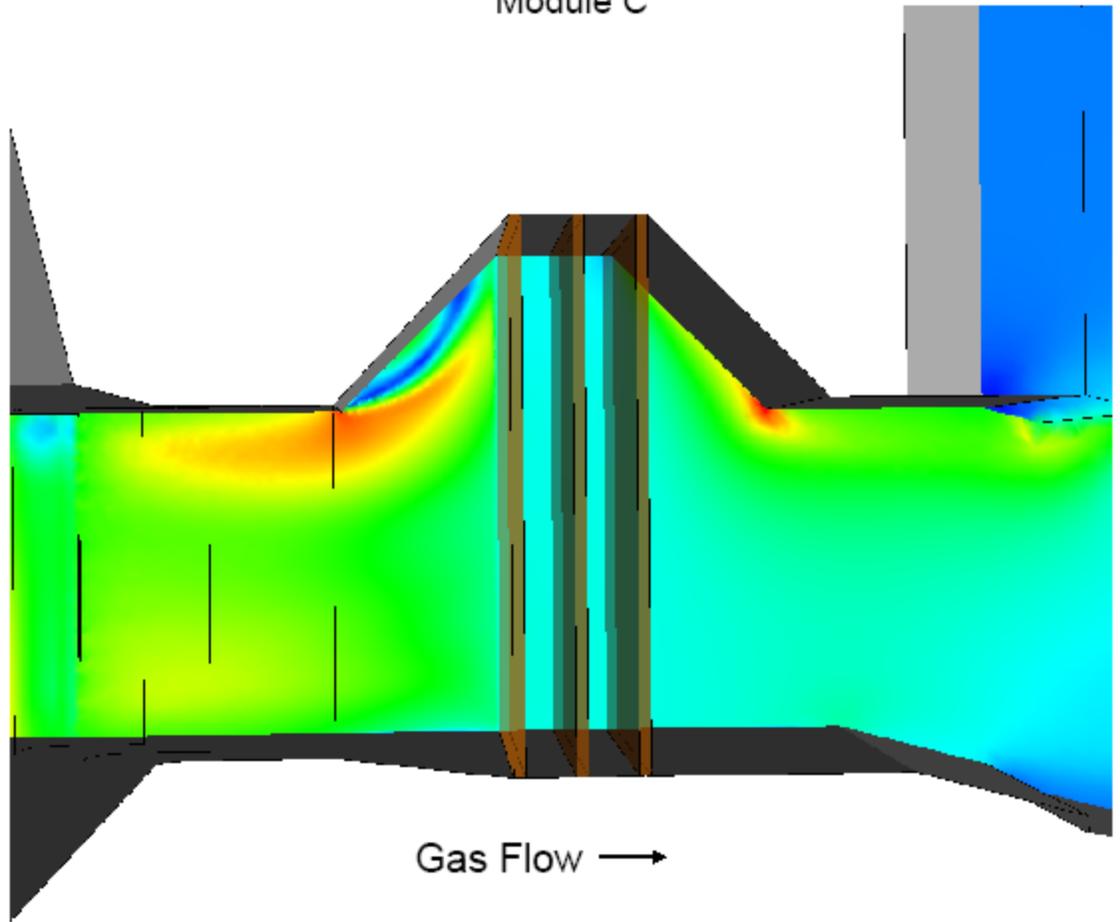
Axial Component of Gas Velocity Module C Inlet



Case 9:
Oxidation
Catalyst,
Perf Plate
Removed,
A&C In Service



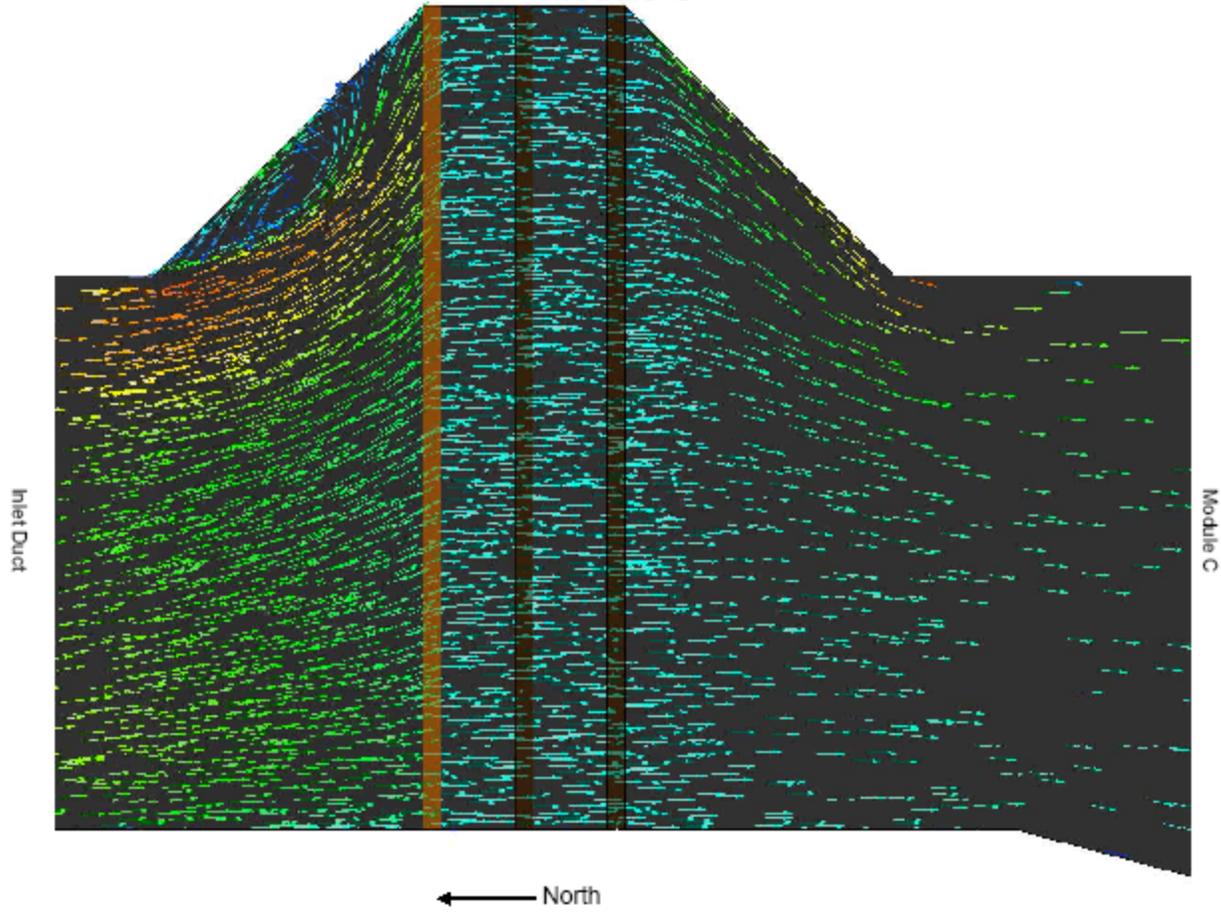
Gas Velocity Magnitude Module C



Case 9:
Oxidation
Catalyst,
Perf Plate
Removed,
A&C In Service



Gas Velocity Vectors Module C

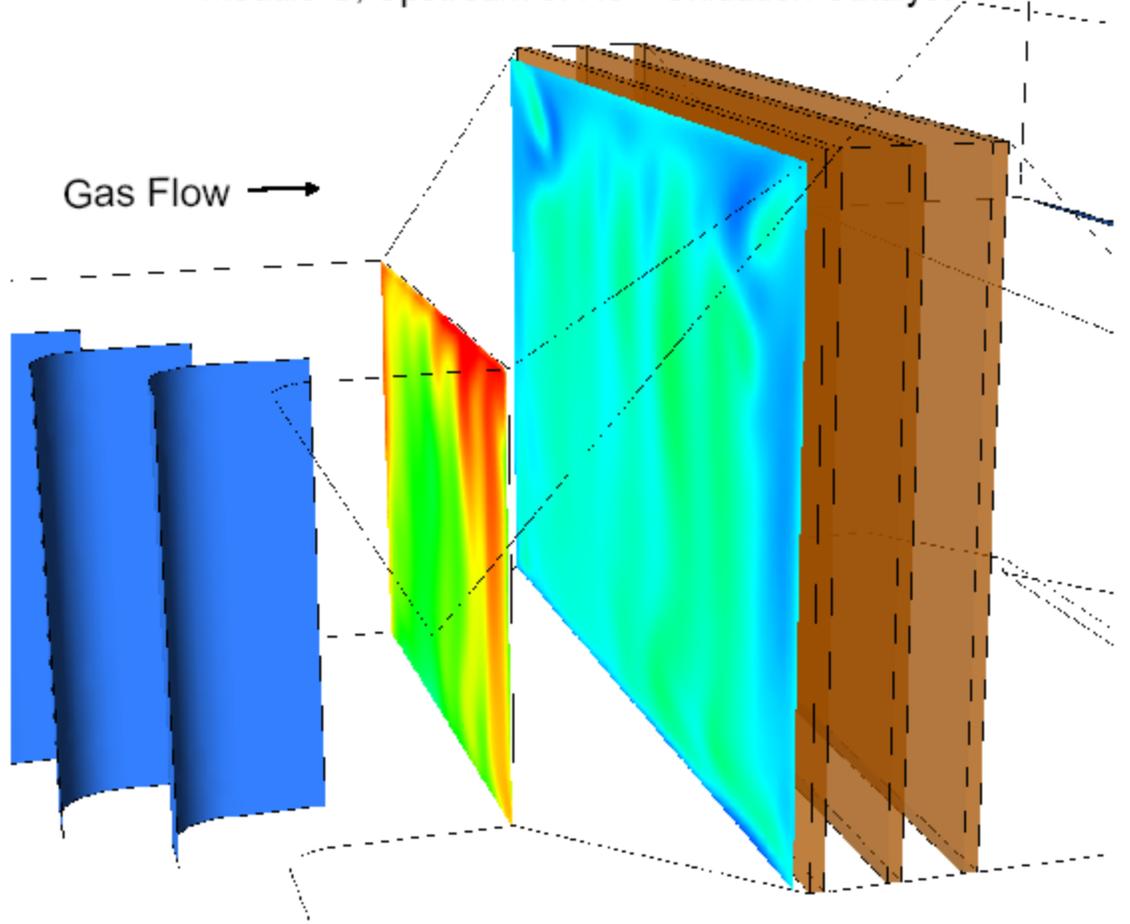


Case 9:
Oxidation
Catalyst,
Perf Plate
Removed,
A&C In Service



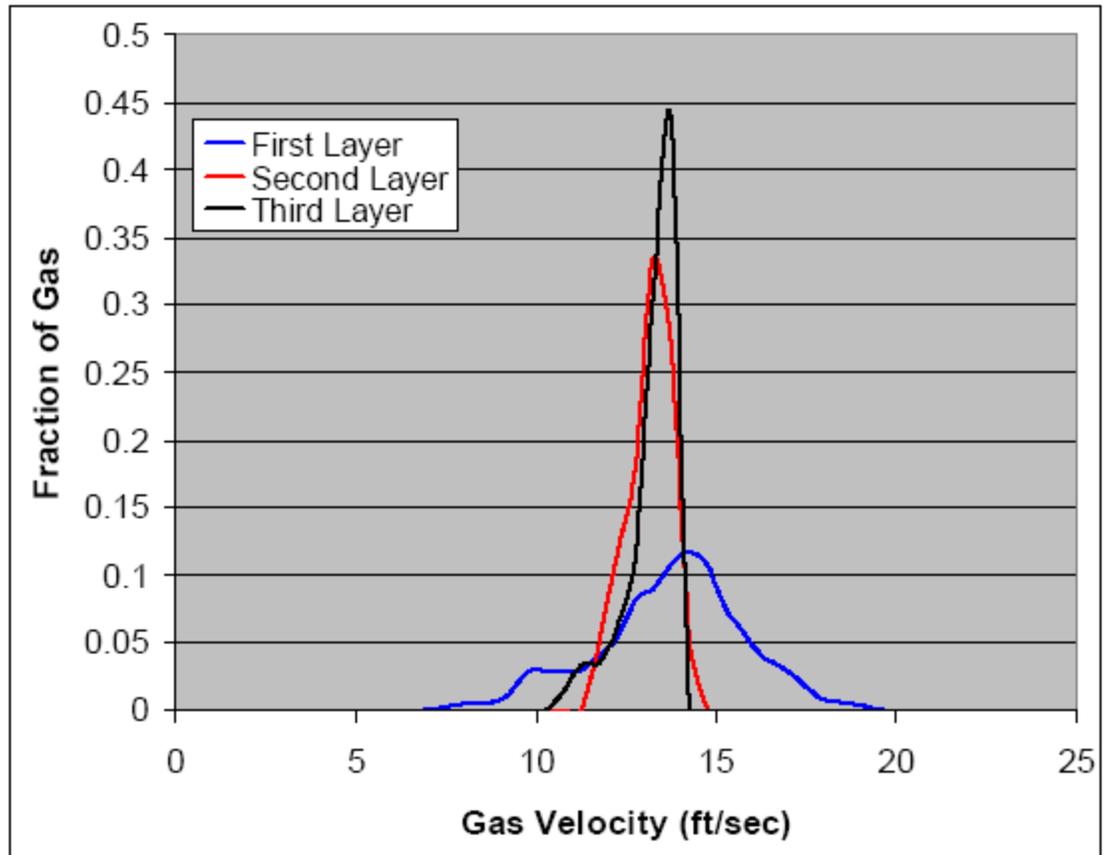
URS

Gas Velocity Magnitude Module C, Upstream of New Oxidation Catalyst



Case 9:
Oxidation
Catalyst,
Perf Plate
Removed,
A&C In Service

Gas Velocity Distribution Upstream of Each Catalyst Layer



URS

APPENDIX B – OH INDIVIDUAL RUN RESULTS FROM THE FOUR MEASUREMENT PERIODS

Results from First Measurement Period, May 2008

Location	South ID Fan Outlet/Module A Inlet				Module A Outlet			
Run Number	2*	3*	4*	Average	2*	3*	4*	Average
Date	13-May-08	14-May-08			13-May-08	14-May-08		
Start Time	15:31	10:42	14:50		15:34	10:42	14:49	
Particulate Mercury	<0.03	<0.03	<0.03	-	0.16	0.18	0.41	0.25
Oxidized Mercury	6.18	7.93	7.17	7.09	0.28	0.35	0.44	0.36
Elemental Mercury	7.29	6.52	8.18	7.33	7.45	11.7	7.62	8.93
Total - Gas phase mercury only	13.5	14.5	15.4	14.4	7.73	12.1	8.06	9.29
Total Mercury (gas + particulate)	13.5	14.5	15.4	14.4	7.89	12.3	8.47	9.54

*Run 1 on May 13 was aborted; in the report these runs have been relabeled as Runs 1-3 rather than 2-4

Location	South ID Fan Outlet/Catalyst Inlet				Catalyst Outlet				Module C Outlet			
Run Number	1	2	3	Average	1	2	3	Average	1	2	3	Average
Date	16-May-08				16-May-08				16-May-08			
Start Time	8:48	12:29	15:45		8:49	12:31	15:46		8:47	12:28	15:44	
Particulate Mercury	<0.03	<0.07	<0.08	-	0.1	<0.13	<0.16	-	0.24	0.17	0.2	0.20
Oxidized Mercury	5.89	5.91	3.20	5.00	10.2	11.2	14.0	11.8	0.23	0.34	0.32	0.30
Elemental Mercury	8.81	9.34	9.56	9.24	1.76	2.57	1.14	1.82	3.22	2.05	2	2.42
Total - Gas phase mercury only	14.7	15.3	12.8	14.2	11.9	13.8	15.2	13.6	3.45	2.39	2.33	2.72
Total Mercury (gas + particulate)	14.7	15.3	12.8	14.2	12.0	13.8	15.2	13.7	3.68	2.56	2.53	2.92

Results from Second Measurement Period, November 2008

Location	ID Fan Outlet				Module A Outlet			
Run Number	1	2	3	Average	1	2	3	Average
Date	19-Nov-08	20-Nov-08			19-Nov-08	20-Nov-08		
Start Time	12:40	9:48	15:05	Average	12:40	9:47	15:05	Average
Particulate Mercury	<0.07	<0.04	<0.02	-	<0.06	<0.06	<0.04	-
Oxidized Mercury	3.96	5.19	6	5.05	<0.14	<0.15	0.16	0.16
Elemental Mercury	4.76	4.75	4.3	4.60	6.23	6.05	5.7	5.99
Total - Gas phase mercury only	8.72	9.95	10.3	9.66	6.23	6.05	5.86	6.05
Total Mercury (gas + particulate)	8.72	9.95	10.3	9.66	6.23	6.05	5.86	6.05

Location	Catalyst Inlet/ID Fan Outlet				Catalyst Outlet				Module C Outlet			
Run Number	1	2	3	Average	1	2	3	Average	1	2	3	Average
Date	19-Nov-08	20-Nov-08			19-Nov-08	20-Nov-08			19-Nov-08	20-Nov-08		
Start Time	12:40	9:48	15:05	Average	12:40	9:48	15:05	Average	12:40	9:47	15:05	Average
Particulate Mercury	<0.07	<0.04	<0.02	-	<0.05	<0.05	<0.03	-	0.19	<0.05	<0.05	0.19
Oxidized Mercury	3.96	5.19	6	5.05	8.95	9.24	8.66	8.95	0.23	<0.17	0.35	0.29
Elemental Mercury	4.76	4.75	4.3	4.60	1.04	0.94	1.16	1.05	4.45	4.83	4.84	4.71
Total - Gas phase mercury only	8.72	9.95	10.3	9.66	9.99	10.2	9.82	10.0	4.68	4.83	5.19	4.90
Total Mercury (gas + particulate)	8.72	9.95	10.3	9.66	9.99	10.2	9.82	10.0	4.86	4.83	5.19	4.96

Results from Third Measurement Period, June 2009

Location	ID Fan Outlet/Module A Inlet				Module A Outlet			
	2*	3*	4*	Average	2*	3*	4*	Average
Run Number	2-Jun-09	3-Jun-09			2-Jun-09	3-Jun-09		
Date	14:35	7:50	11:45	Average	14:35	7:50	11:45	Average
Particulate Mercury	<0.06	0.17	0.11	0.14	<0.04	0.03	0.05	0.04
Oxidized Mercury	4.58	4.69	5.23	4.83	<0.15	<0.13	<0.13	-
Elemental Mercury	4.61	7.43	6.21	6.08	4.71	7.81	5.95	6.16
Total - Gas phase mercury only	9.19	12.1	11.4	10.9	4.71	7.81	5.95	6.16
Total Mercury (gas + particulate)	9.19	12.3	11.5	11.0	4.71	7.85	6.00	6.19

*Run 1 on June 2 was not reported due to an impinger recovery error

Location	Catalyst Inlet/ID Fan Outlet				Catalyst Outlet				Module C Outlet			
	2*	3*	4*	Average	2*	3*	4*	Average	2*	3*	4*	Average
Run Number	2-Jun-09	3-Jun-09			2-Jun-09	3-Jun-09			2-Jun-09	3-Jun-09		
Date	14:35	7:50	11:45	Average	14:35	7:50	11:45	Average	14:35	7:50	11:45	Average
Particulate Mercury	<0.06	0.17	0.11	0.14	<0.04	<0.06	<0.07	-	0.28	0.08	<0.07	0.18
Oxidized Mercury	4.58	4.69	5.23	4.83	5.86	8.86	9.52	8.08	<0.16	<0.16	<0.17	-
Elemental Mercury	4.61	7.43	6.21	6.08	2.14	3.28	3.26	2.89	2.81	3.7	2.86	3.12
Total - Gas phase mercury only	9.19	12.1	11.4	10.9	8.00	12.1	12.8	11.0	2.81	3.70	2.86	3.12
Total Mercury (gas + particulate)	9.19	12.3	11.5	11.0	8.00	12.1	12.8	11.0	3.08	3.78	2.86	3.24

*Run 1 on June 2 was not reported due to an impinger recovery error

Results from Fourth Measurement Period, September 2009

Location	ID Fan Outlet/Module A Inlet				Module A Outlet			
Run Number	1	2	3	Average	1	2	3	Average
Date	9-Sep-09		10-Sep-09		9-Sep-09		10-Sep-09	
Start Time	10:40	18:05	8:25	Average	10:40	18:05	8:25	Average
Particulate Mercury	<0.06	<0.05	<0.03	-	0.05	<0.04	<0.04	0.05
Oxidized Mercury	7.87	8.98	6.47	7.77	<0.30	<0.27	<0.26	-
Elemental Mercury	6.13	5.91	7.36	6.47	6.57	6.92	7.55	7.01
Total - Gas phase mercury only	14.0	14.9	13.8	14.2	6.57	6.92	7.55	7.01
Total Mercury (gas + particulate)	14.0	14.9	13.8	14.2	6.62	6.92	7.55	7.03

Location	Catalyst Inlet/ID Fan Outlet				Catalyst Outlet				Module C Outlet			
Run Number	1	2	3	Average	1	2	3	Average	1	2	3	Average
Date	9-Sep-09		10-Sep-09		9-Sep-09		10-Sep-09		9-Sep-09		10-Sep-09	
Start Time	10:40	18:05	8:25	Average	10:40	18:05	8:25	Average	10:40	18:05	8:25	Average
Particulate Mercury	<0.06	<0.05	<0.03	-	<0.05	<0.06	<0.07	-	<0.07	0.6	<0.05	-
Oxidized Mercury	7.87	8.98	6.47	7.77	8.96	12.6	9.94	10.5	<0.49	<0.41	<0.39	-
Elemental Mercury	6.13	5.91	7.36	6.47	2.52	2.43	3.46	2.80	7.69	8.95	9.56	8.73
Total - Gas phase mercury only	14.0	14.9	13.8	14.2	11.5	15.0	13.4	13.3	7.69	8.95	9.56	8.73
Total Mercury (gas + particulate)	14.0	14.9	13.8	14.2	11.5	15.0	13.4	13.3	7.69	9.55	9.56	8.93