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

Final Technical Report

January 1, 2004 – December 31, 2010

Prepared by:

Gary M. Blythe
Conor Braman
Katherine Dombrowski
Tom Machalek

March 2011

Cooperative Agreement No: DE-FC26-04NT41992

URS Corporation
9400 Amberglen Boulevard
Austin, Texas 78729

Prepared for:

Andrew O’Palko

National Energy Technology Laboratory
U.S. Department of Energy
3610 Collins Ferry Road
Morgantown, West Virginia 26507

DISCLAIMER

ABSTRACT

This document is the final technical report for Cooperative Agreement DE-FC26-04NT41992, "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," which was conducted over the time-period January 1, 2004 through December 31, 2010. The objective of this project has been to demonstrate at pilot scale the use of solid catalysts and/or fixed-structure mercury sorbents to promote the removal of total mercury and oxidation of elemental mercury in flue gas from coal combustion, followed by wet flue gas desulfurization (FGD) to remove the oxidized mercury at high efficiency. The project was co-funded by the U.S. DOE National Energy Technology Laboratory (DOE-NETL), EPRI, Great River Energy (GRE), TXU Energy (now called Luminant), Southern Company, Salt River Project (SRP) and Duke Energy. URS Group was the prime contractor.

The mercury control process under development uses fixed-structure sorbents and/or catalysts to promote the removal of total mercury and/or oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone FGD systems. Oxidized mercury not adsorbed is removed in the wet FGD absorbers and leaves with the byproducts from the FGD system.

The project has tested candidate materials at pilot scale and in a commercial form, to provide engineering data for future full-scale designs. Pilot-scale catalytic oxidation tests have been completed for periods of approximately 14 to19 months at three sites, with an additional round of pilot-scale fixed-structure sorbent tests being conducted at one of those sites. Additionally, pilot-scale wet FGD tests have been conducted downstream of mercury oxidation catalysts at a total of four sites. The sites include the two of three sites from this project and two sites where catalytic oxidation pilot testing was conducted as part of a previous DOE-NETL project. Pilot-scale wet FGD tests were also conducted at a fifth site, but with no catalyst or fixed-structure mercury sorbent upstream.

This final report presents and discusses detailed results from all of these efforts, and makes a number of conclusions about what was learned through these efforts.

TABLE OF CONTENTS

Page

LIST OF GRAPHIC MATERIALS

LIST OF TABLES

INTRODUCTION

This document is the Final Technical Report for the project "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," conducted over the time-period January 1, 2004 through December 31, 2010. The objective of this project has been to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion, and the use of a wet flue gas desulfurization (FGD) system downstream to remove the oxidized mercury at high efficiency. Later in the project fixed-structure materials that adsorb was well as oxidize mercury were also investigated. The project was co-funded by the U.S. DOE National Energy Technology Laboratory (DOE-NETL), EPRI, Great River Energy (GRE), TXU Energy (now called Luminant), Southern Company, Salt River Project (SRP) and Duke Energy. URS Group was the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone FGD systems. An alternate configuration tested used fixed-structure materials to adsorb and oxidize mercury in flue gas treated. Oxidized mercury is removed in the wet FGD absorbers with the byproducts from the FGD system. The project has involved testing catalyst (and some fixed-structure adsorbent) materials at pilot scale and in a commercial form, to provide engineering data for future full-scale designs. The pilot-scale oxidation catalyst tests were conducted for 14 months or longer at three sites to provide catalyst life data. Pilot-scale wet FGD tests were conducted at two of the three sites to confirm the ability to scrub catalytically oxidized mercury at high efficiency. The pilot wet FGD system was also used downstream of catalysts that were currently being tested as part of a previous cooperative agreement (DE-FC26-01NT41185), and at a fifth site that did not have an oxidation catalyst in service.

Six utility team members provided project host sites for testing. Luminant hosted pilot catalyst tests and pilot wet FGD tests at their Monticello Station, which fires a Texas lignite/Powder River Basin (PRB) coal blend. Southern Company's Georgia Power Plant Yates, which fires low-sulfur Eastern bituminous coal, hosted both pilot oxidation catalyst and pilot fixed-structure adsorbent tests. Partway through the current project, SRP joined the project to conduct pilot-scale oxidation catalyst tests and pilot wet FGD tests at their Coronado Station, which fires PRB coal.

In addition, GRE provided a test site at their Coal Creek Station, which fires North Dakota lignite, and CPS Energy of San Antonio (CPS) provided a test site at their J.K. Spruce Plant, which fires PRB sub-bituminous coal. Both of these sites hosted mercury oxidation catalyst pilot tests as part of the previous, 41185 project[1], but also hosted pilot FGD tests downstream of the catalysts as part of the current project. Duke Energy hosted pilot wet FGD tests (without a catalyst upstream) at their Marshall Station, which fires low-sulfur Eastern bituminous coal.

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

EXECUTIVE SUMMARY

This project was conducted over a time period of seven years. It was a follow on to pilot-scale mercury oxidation catalyst tests conducted as part of Cooperative Agreement DE-FC26-01NT41185, and a precursor to a full-scale demonstration conducted as part of Cooperative Agreement DE-FC26-06NT42778. The project encompassed pilot-scale testing of mercury oxidation catalysts and/or fixed structure sorbents at three sites; Luminant's Monticello Station, Southern Company's Plant Yates, and SRP's Coronado Station. Also included were pilot-scale wet FGD tests of mercury removal downstream of the oxidation catalysts at four sites: Monticello and Coronado from the current project, and GRE's Coal Creek Station and CPS Energy's Spruce Plant from the previous project.

The objectives of the project were to determine 1). Whether the small-pitched catalyst (typically 64 cells per square inch [cpsi], or 9.9 cells/cm^2) could be operated long term in flue gas downstream of a cold-side ESP without excessive fly ash buildup and corresponding increases in pressure drop; 2). The effective lives of the catalyst materials in flue gas produced by a range of coal types; and 3). How effectively a conventional wet FGD system could remove catalytically oxidized mercury.

Pressure Drop across Oxidation Catalyst Beds

At the completion of the previous, 41185 project, it appeared that a solution had been identified for operating 64 cpsi (9.9 cells/cm^2) catalysts downstream of an ESP – sonic horns operating approximately 10 seconds every half-hour of operation. It was hoped that with sonic energy cleaning in the current project, catalysts at this cell pitch would operate successfully at low pressure drop and with little fly ash buildup over the entire test period of 14 months or longer. This did not prove to be the case, as pressure drop and fly ash buildup issues were encountered at all three long-term catalyst test sites.

However, these results from the project are somewhat inconclusive. For each site there were issues that raised uncertainties as to how effective the sonic horns might have been at controlling fly ash buildup and pressure drop increases. These issues included low inlet flue gas temperatures, unreliable compressed air delivery to the sonic horns, and unscheduled shut downs of the pilot units with no purging of moist flue gas from the catalyst chambers.

Elemental Mercury Oxidation Performance

Pilot-scale mercury oxidation catalyst tests were conducted at three sites over durations of 14 to 19 months. At all three sites, it was determined that high mercury oxidation percentages (>90%) could be achieved with as little as a 9-inch (0.23-m) catalyst depth of the 64 cpsi (9.9 cells/cm^2) catalyst and at a superficial flue gas velocity of 5.5 ft/s (1.7 m/s). This is about the same velocity as flue gas flowing through cold-side ESPs. Both gold- and palladium-based catalysts were shown to be effective in several flue gas matrices, including low-sulfur Eastern bituminous, PRB, and PRB/Texas lignite flue gases. SCR catalysts were shown to be less active for mercury oxidation in this lower-temperature operating regime (about 300^{o}F [150^{o}C]). Regenerated gold and palladium catalysts also proved to be very active in these flue gas matrices, even though they had originally been tested as fresh catalysts in different flue gas types at previous sites.

The intent was to use periodic catalyst activity measurement data from each site to determine a rate correlation of catalyst activity loss versus time in flue gas service, to see if the loss rates would prove to be specific to each flue gas matrix tested. However, because of observed fly ash buildup and pressure drop increases at all three sites, such correlations are not seen as being representative and were not developed and presented in this report. Neither was it seen as worthwhile to use these data to develop process economics.

Laboratory regeneration tests were conducted on gold- and palladium-based catalyst blocks from the pilot unit at Monticello, and the laboratory-regenerated blocks were returned and tested for mercury oxidation activity in the Monticello flue gas. These data were used to develop regression equations that predict the mercury oxidation activity of regenerated catalysts as a function of regeneration temperature and regeneration gas throughput (volumetric flow rate times duration of regeneration). The results show that optimum regeneration occurs with a regeneration gas temperature of approximately 550-650^{o}F (290-340^{o}C), and that regenerated catalyst activity improved with increasing regeneration gas throughput, over the range tested.

Pilot-scale Wet FGD Mercury Capture Co-benefit Tests

Pilot-scale wet FGD tests were conducted at four sites downstream of oxidation catalysts, with the capture of oxidized and elemental mercury being measured across the pilot wet FGD system. Tests were conducted in both limestone forced oxidation and lime reagent, natural oxidation modes. The objective of these tests was to determine whether catalytically oxidized mercury in flue gas could be removed by wet FGD systems at high efficiency, or whether some alternate form of oxidized mercury might be produced that would not be scrubbed.

The pilot wet FGD system was designed with a short absorber vessel, compact enough to be moved between test locations on one semi-trailer. Consequently, there was room for only one stage of mist elimination at the top of the absorber. This proved to be a limitation on the ability to measure co-benefit mercury capture across the pilot scrubber, as carryover of absorber liquor, particularly during mist eliminator washing, produces a high bias in outlet flue gas mercury concentration measurements. With time, workarounds were developed for this problem, but data from the first three tests sites are of questionable accuracy because the workarounds had not yet been developed and implemented.

Regardless of this limitation, the results clearly show that the catalytically oxidized mercury can be removed by wet FGD systems at the same efficiency as mercury oxidized by native effects in the boiler and flue gas path. High oxidized mercury removal efficiencies (≥95%) were measured across the pilot scrubber in several tests. *Total* mercury removal efficiencies as high as 87 to 93% were also measured during several tests. In some cases, much lower total mercury removal efficiencies were measured, though. The limitations on total mercury removal were generally a result of lowered mercury oxidation percentages downstream of the catalyst due to fly ash buildup and/or activity loss, mercury re-emission from the wet scrubber, or both effects. However, these limiting effects can be addressed through optimization of catalyst and FGD design and operating conditions, and do not appear to represent limitations on the effectiveness of low-temperature mercury oxidation catalyst technology for high mercury capture percentages.

Investigation of Fixed-structure Mercury Sorbents/Catalysts

A second round of testing at Plant Yates Unit 1 was focused on fixed-structure materials that have a high capacity for adsorbing mercury and that promote oxidation of the mercury in the flue gas that is not adsorbed. This round of pilot-scale testing was somewhat limited, so few results are presented. The most promising result is that parallel plates of granular carbon inserted in a flue gas stream had a limited capacity for adsorption of mercury, but significant activity for mercury oxidation (~50% oxidation across the parallel plates) after three months of operation. They also operated at very low pressure drop.

EXPERIMENTAL METHODS

The work being conducted as part of this project used three different experimental apparatus types. One is an elemental mercury catalyst oxidation pilot unit (8000 acfm, or 14,600 m^3/h of flue gas treated), the first of which was initially installed and operated at GRE's Coal Creek Station in North Dakota. A second, nearly identical pilot unit was also built and installed and operated at CPS Energy's Spruce Plant. During the course of this project, these two pilot units were relocated and installed at Luminant's Monticello Station and at Southern Company's Plant Yates, respectively. The second is a portable, pilot-scale wet FGD system that was designed and built as part of this project. The pilot wet FGD was used to determine the ability to scrub catalytically oxidized mercury at high efficiency at several sites. The third apparatus is a laboratory-scale device to measure the activity of candidate catalyst materials in synthetic flue gases. Each of these experimental apparatus is described in this section. Also described is the mercury semi-continuous emissions monitor (Hg SCEM), developed with funding from project co-funder EPRI, and used to measure catalyst activity for oxidizing elemental mercury in flue gas.

Oxidation Catalyst Pilot Unit Description

Details of the pilot unit design, construction, catalyst preparation and pilot unit operation have been discussed in a previous Final Report from Cooperative Agreement DE-FC26-01NT41185[1]. Figure 1 shows a simplified piping and instrument diagram (P&ID) for an oxidation catalyst pilot unit. It has provisions to control flow rate and temperature in four separate catalyst chambers, and to measure gas differential pressure and mercury species concentrations across each chamber.

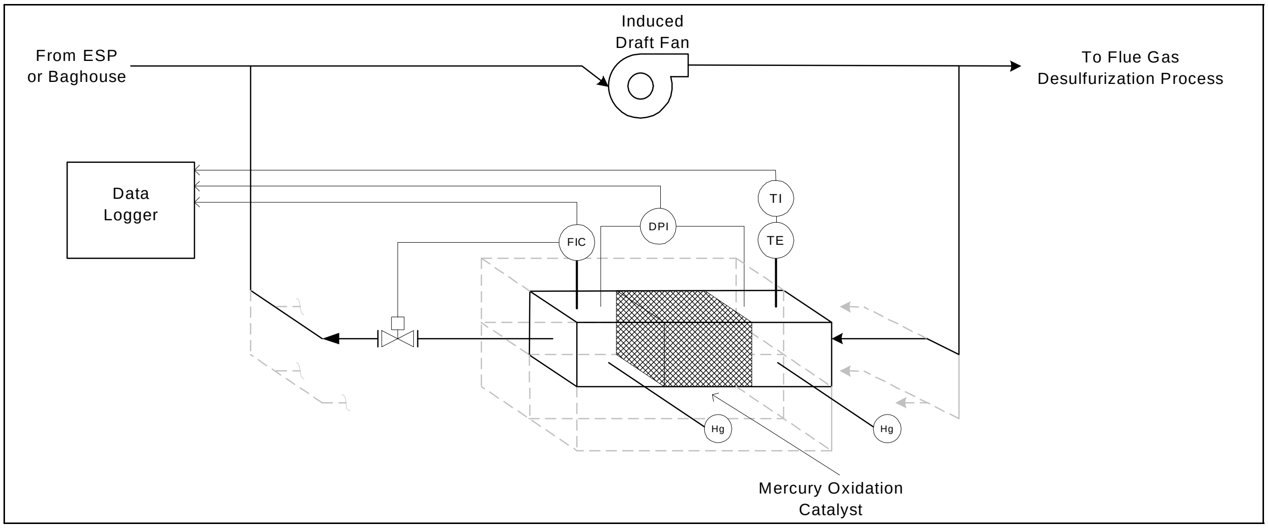


Figure 1. Simplified P&ID for the Catalyst Pilot Unit (one of four catalyst chambers shown)

The pilot unit has four catalyst chambers, each a cube that is nominally one meter in all three dimensions. Each cube has a removable side panel that provides access to the chamber for installing and removing catalysts. The amount of catalyst in each chamber is varied as necessary to achieve desired elemental mercury oxidation performance. For catalysts where the cross-section of the honeycomb installed is less than one meter by one meter, spacers are installed around the catalyst block to fit snugly against the chamber side, top and bottom walls. The spacers center the catalyst block in the chamber and ensure that all of the flue gas flows through the honeycomb and not through the annular space between the honeycomb and chamber walls.

The design flue gas flow rate through each chamber is 2000 acfm (3400 m^3/hr), for a total of nominally 8000 acfm (13,600 m^3/hr) to the skid. The pilot unit inlet gas is pulled from a 5-ft-tall (1.5-m) "scoop" installed through the floor of the host unit's ID fan outlet duct. The "scoop" is a straight piece of pipe cut at a 45^o angle at the end, with the open area facing into the flue gas flow, to result in pulling gas at approximately isokinetic conditions. The 5-ft length is to ensure a representative gas sample is extracted from near the center of the duct rather than along the duct wall. The pilot unit can be isolated from the host unit with wafer-style butterfly dampers at the pilot unit inlet penetration on the ID fan outlet duct and return penetration on the ID fan inlet duct. Each individual catalyst chamber or cube can be isolated by closing the flow control damper on the outlet side and a shop-built manual knife gate valve at the inlet to that chamber. Mercury concentrations and speciation are measured at the pilot unit inlet and at the outlets of each catalyst chamber with the EPRI semi-continuous mercury analyzer, which is described below. During catalyst performance evaluations, the analyzer is cycled between the five measurement locations, and between measuring elemental mercury and total mercury to determine the elemental mercury oxidation across each catalyst. In some testing two analyzers are used to simultaneously measure catalyst inlet and outlet conditions.

Figure 2 shows the completed pilot unit as installed at the first test site in the 41185 project, Coal Creek Station. This photograph was taken before the pilot unit inlet and outlet duct runs were insulated, and before a temporary shed was constructed around the pilot unit to protect it from the weather.

Hg SCEM

The EPRI Hg SCEM is illustrated in Figure 3. The Hg SCEM has been described in detail in a previous publication[2]. The analyzer is based on the amalgamation of elemental mercury with gold, and the cold-vapor atomic absorption of elemental mercury that is subsequently thermally desorbed from the gold. Using an impinger-based, liquid-phase gas conversion system, the analyzer can determine total mercury concentrations by reducing all of the oxidized mercury to the elemental form with stannous chloride upstream of the gold. Alternately, the elemental mercury concentration is measured by using either a tris(hydroxy-methyl)aminomethane (Tris) or potassium chloride (KCl) solution in an impinger to capture oxidized mercury, while allowing elemental mercury to pass through to the gold without being altered. The oxidized fraction of mercury in the flue gas is determined by subtracting the elemental mercury concentration from the total mercury concentration. For these tests, one analyzer was cycled between sampling the catalyst inlet flue gas, catalyst outlet/FGD inlet, and FGD outlet ducts, and between measuring total mercury and elemental mercury at each location.

Figure 2. Pilot Oxidation Catalyst Skid as Installed at Coal Creek Station

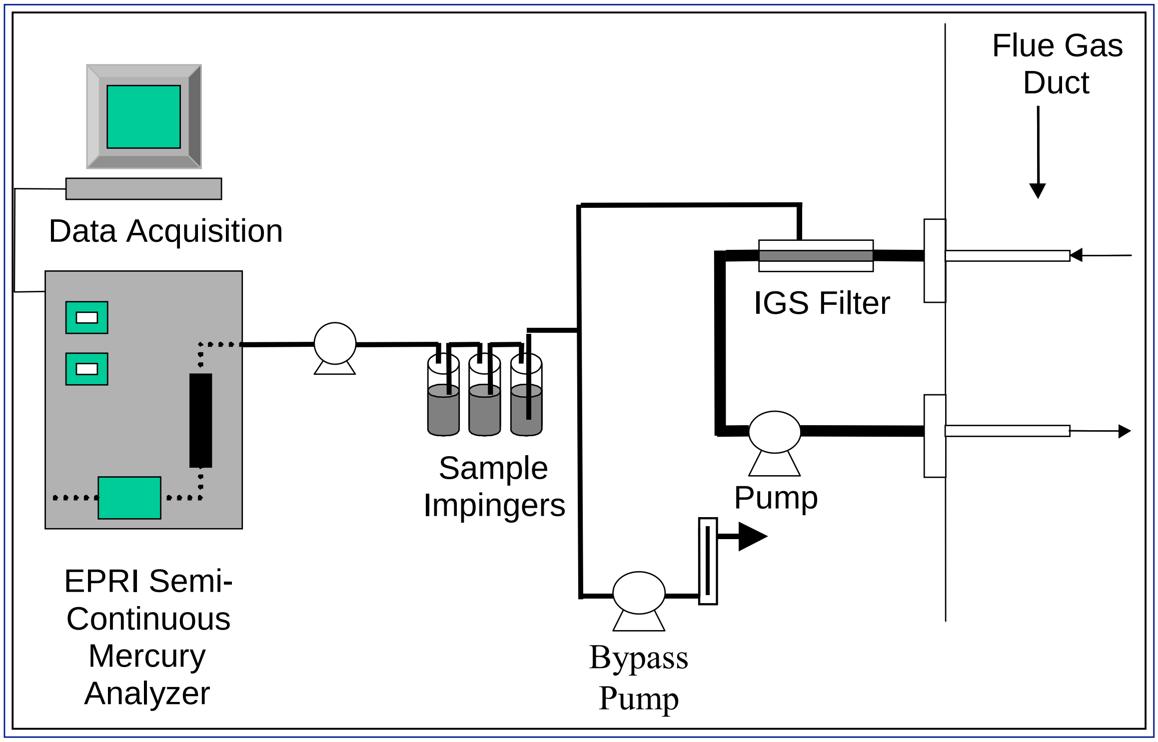


Figure 3. Schematic of EPRI Semi-continuous Mercury Emissions Monitor (Hg SCEM)

An inertial gas separation (IGS) filter is used to extract a particulate-free sample to go to the impingers and then to the gold. In the IGS filter, flue gas flows through the center of the filter element at high velocity and is recycled back to the duct, while a small amount of sample gas is extracted radially through a glass-coated, sintered stainless steel filter tubing wall.

Use of the analyzer on previous projects determined the importance of using only certain materials such as quartz, Teflon®, or Teflon®-lined materials to handle flue gas samples to be analyzed for mercury content. This experience is reflected in the current SCEM design and materials of construction.

Periodically, the analyzer results have been verified by conducting manual flue gas sampling efforts in parallel across each catalyst chamber by the Ontario Hydro (OH) method[3].

Pilot Wet FGD System

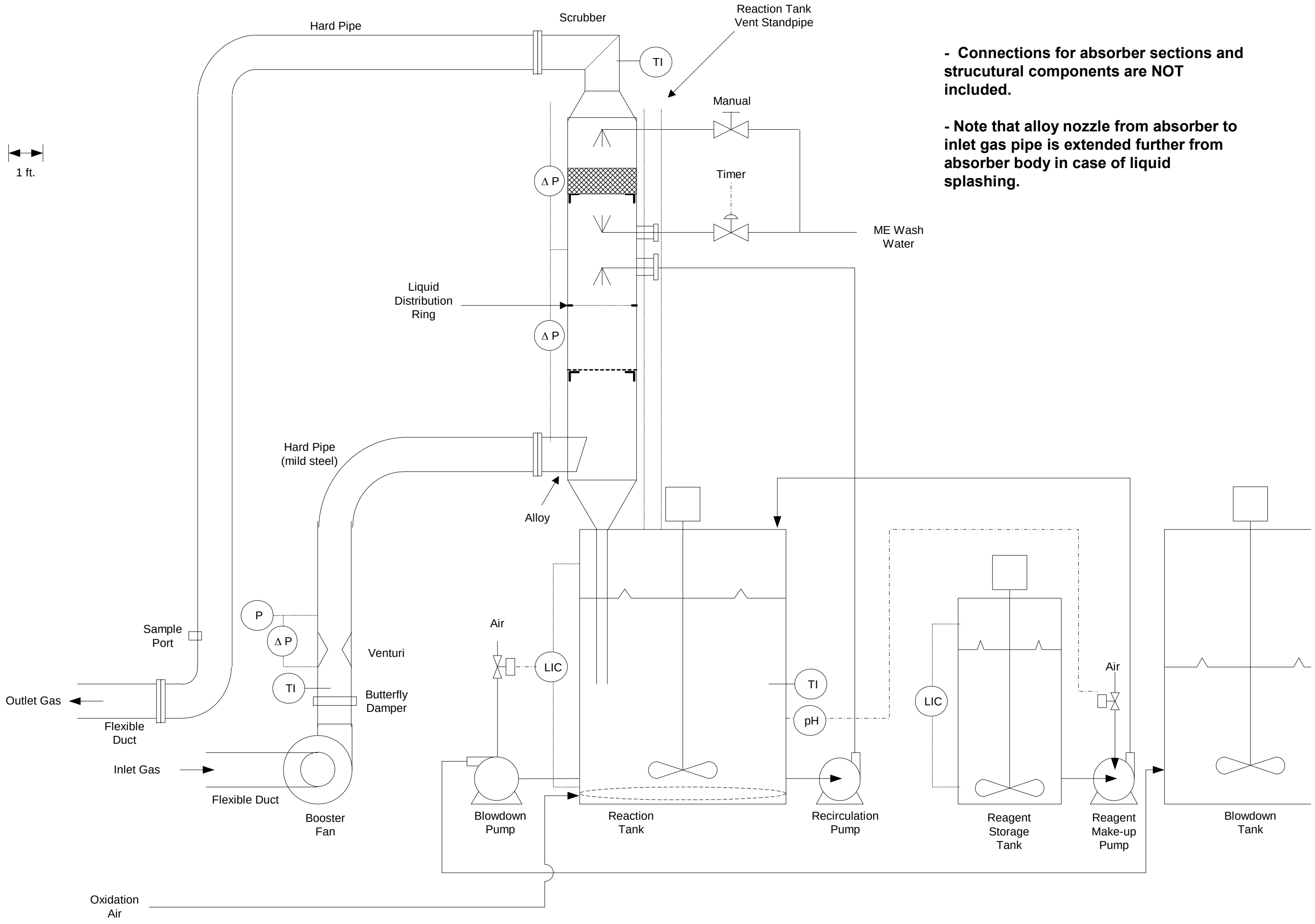
A second experimental apparatus used to support this project is a pilot-scale wet FGD unit that was designed and fabricated as part of the project, to allow the measurement of how effectively catalytically oxidized mercury can be scrubbed. The design basis for the pilot wet FGD system is summarized in Table 1 below. Figure 4 is a simplified piping and instrumentation diagram (P&ID) for the pilot wet FGD system.

Table 1. Pilot-scale Wet FGD Design Basis

Design Feature	**Value**
Gas Conditions:	
Flue Gas flow rate	2000 acfm (3400 m^3/h)
Inlet SO_2 concentration	2000 ppmv max, 1000 ppm or less normal
Inlet temperature	300^{o}F (149^{o}C)
Design SO_2 removal percentage	~95% (varies with inlet SO_2, reagent ratio, LS grind, chloride concentration in slurry liquor)
Scrubber Design Criteria:	
Contactor type	Spray/tray
Flue gas inlet ductwork (including venturi, butterfly control valve)	10-in. (0.25-m)
Booster fan sizing	2000 acfm (3400 m^3/h)at 14-in. H_2O (3.5 kPa) differential
Flue gas inlet duct velocity	60 ft/s (18 m/s)
Flue gas velocity in absorber inlet nozzle	24 ft/s (7.3 m/s)
Flue gas inlet nozzle diameter	16-in. (0.41-m)
Flue gas velocity through absorber	8.4 ft/s (2.6 m/s)
Absorber diameter	24-in. (0.61-m)

Design Feature	**Value**
Tray open area	24%
Tray hole diameter	1.375 in. (3.49 cm)
Recycle slurry rate	200 gpm max (45 m^3/h)
L/G ratio	127 gal/kacf (20 l/Nm^3) max
Slurry nozzle	BETE MP 1625M, 3-in. (7.6 cm), 90° full cone, 10 psig (69 kPa)
Mist eliminator type	Single stage, Koch Otto York, Style VIII-3-1.5
ME wash rate	1.5 gpm/ft^2 (3.7 m^3/h/m^2), each side
ME wash levels	2 (front and back side)
ME nozzle type	90° full cone, 40 psig (276 kPa)
Outlet duct velocity	48 ft/s (15 m/s)
Oxidation air rate, max O/SO_2 ratio	10 at 2000 ppmv inlet SO_2
Tank Sizing:	
Reaction tank dimensions	6-ft diameter x 8-ft high (1.8-m x 2.4-m), covered, baffled, single top entry agitator
Reaction tank solids residence time	18-hr at 2000 ppmv inlet SO_2, 35-hr at 1000 ppmv
Reaction tank liquid holdup, minimum	7.4 minutes
Reagent tank dimensions	3 ft-diameter x 6-ft high (0.9-m x 1.8-m), open top, baffled, single top entry agitator
Reagent tank storage capacity, hrs supply	14-hr at 2000 ppmv inlet SO_2, 27-hr at 1000 ppmv
Blow down tank dimensions	5 ft-diameter x 8-ft high (1.5-m x 2.4-m), open top, baffled, single top entry agitator
Blow down tank storage capacity, hrs of FGD operation	13-hr at 2000 ppmv inlet SO_2, 25-hr at 1000 ppmv
Piping Design:	
Recycle slurry pipe diameter	3-in. (7.6-cm) Schedule 80 CPVC
Recycle slurry pipe velocity, max	9.1 ft/s (2.8 m/s)
All other piping (reagent make-up, slurry blow down, ME wash water)	0.75-in. (1.9-cm) flex hose
Materials of Construction:	
Inlet ductwork, to fan	Flexible duct
Inlet ductwork, fan to absorber inlet nozzle	300-series stainless steel
Absorber vessel, inlet nozzle to outlet nozzle, including tray	AL6XN alloy
Absorber maximum chloride concentration	23,000 ppm (very conservative), 28,000 ppm (conservative)
Recycle slurry nozzle	Cobalt alloy, Stellite #6

Design Feature	**Value**
Mist eliminator	Polysulfone, with FRP nuts and bolts
Absorber outlet duct, to edge of skid	FRP
Outlet ductwork, from edge of skid	Stainless steel lined flexible duct
Reaction tank, reagent tank, blow down tank	Carbon steel lined with vinyl ester
Reaction tank agitator impeller and shaft	254-SMO solid alloy, Pro-Quip
Reagent tank agitator impeller and shaft	Carbon steel, Pro-Quip brand
Blow down tank agitator and shaft	Carbon steel, Pro-Quip brand
Recycle slurry pump	Rubber-lined iron, Weir
Reagent makeup pump, slurry blow down pump	Plastic diaphragm pump (PET), Wilden
Instrumentation:	
Flow rate	Inlet flue gas venturi
Temperature	Inlet flue gas, outlet flue gas, reaction tank slurry
Pressure	Inlet flue gas, recycle slurry, oxidation air
Pressure drop	Gas flow rate venturi, absorber spray/tray section, absorber ME section
Level	Reaction tank, reagent tank, blow down tank
pH	Reaction tank slurry
Mercury concentration	Absorber inlet/outlet sample ports, solenoid valves, heat-traced tubing and IGS filter
Control Strategies:	
Flue gas flow rate	PID controller to control butterfly valve position based on feedback from venturi meter pressure differential
Reaction tank pH	On-off control of air-drive reagent feed pump based on feedback from reaction tank slurry pH meter
Reaction tank, reagent tank, blow down tank	Manual control based on level indication, high and low level alarms
Absorber outlet temperature	Fan trip on high temperature to protect ME
Recycle slurry flow	Manual control based on slurry feed pressure to nozzle, SO_2 removal performance (as measured by gas indicating tubes or CEM); controlled by adjusting “minimum flow” valve controlling slurry bypass from pump discharge back into reaction tank; pump trips on low-low level in reaction tank



- Connections for absorber sections and strucutural components are NOT included.

- Note that alloy nozzle from absorber to inlet gas pipe is extended further from absorber body in case of liquid splashing.

Figure 4. Simplified P&ID for Pilot Wet FGD System

The design and fabrication of the pilot wet FGD unit was completed by mid-2004. Figure 5 shows the completed wet FGD pilot skid as installed at GRE's Coal Creek Station in early July. The oxidation catalyst pilot is shown in the background, to the right of the pilot FGD in the photo, although it is difficult to make out any details of the oxidation catalyst skid because of the plywood structure that was erected around it for weather protection.

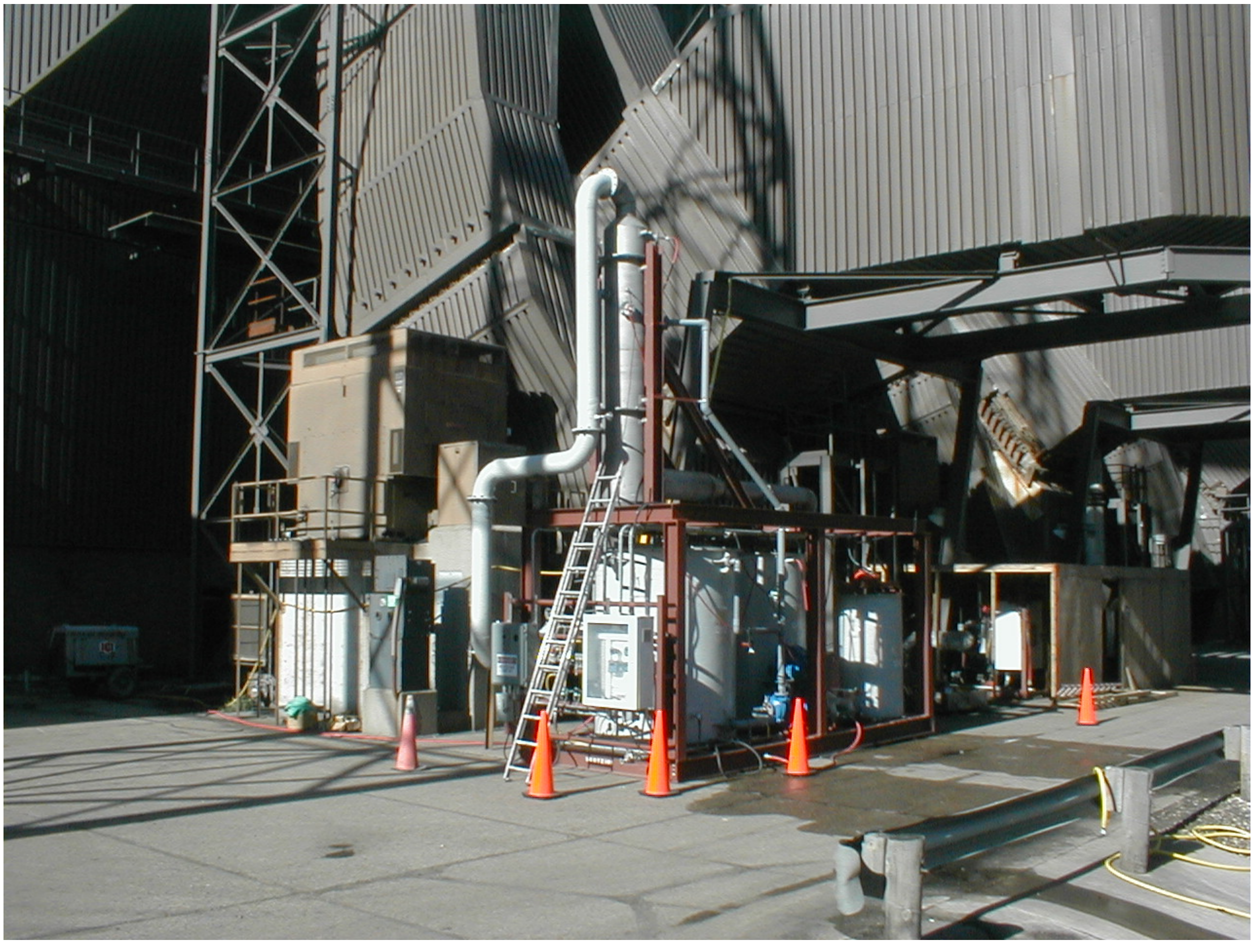


Figure 5. Pilot Wet FGD System Installed at Coal Creek Station

Laboratory-scale Test Unit

The third experimental apparatus is a laboratory-scale test unit that is used to evaluate the activity of candidate catalyst samples under simulated flue gas conditions. In the bench-scale apparatus, a synthetic flue gas is mixed from bottled gases. The synthetic flue gas typically contains nitrogen, oxygen, moisture, CO_2, SO_2, NO_X, and HCl. The proportions of each are adjusted to best match flue gas conditions at the power plant being simulated. The moisture is added by sending a portion of the nitrogen through a saturator that operates at elevated temperature. The gases are mixed to achieve a total gas flow rate of approximately 0.6 to 1.3 L/min (measured at room temperature), then heated to the desired synthetic flue gas temperature, typically in the range of 250^{o}F to 350^{o}F (121^{o}C to 177^{o}C). Elemental mercury is added to the flue gas by passing a small percentage of the dry nitrogen through a permeation tube.

Once mixed, the synthetic flue gas flows through a small catalyst holder, which is heat traced to maintain the target flue gas temperature. In the catalyst holder, catalyst cores of approximately 5/8-in. (1.6-cm) diameter and up to 2-in. (5.1-cm) length are placed for exposure to the synthetic flue gas. Flue gas exiting the catalyst holder is vented to atmosphere through a series of scrubbers to remove acid gases and mercury.

A mercury SCEM, similar to what is described above, is used to monitor the catalyst inlet and outlet flue gas for mercury concentration. At the beginning of a test, flue gas is flowed over the catalyst core and the outlet flue gas mercury concentration is monitored until the catalyst has achieved mercury adsorption equilibrium (i.e., the catalyst outlet total mercury concentration is equal to the inlet total mercury concentration). This may take a day or longer of continuous flue gas exposure to achieve. Once equilibrium has been achieved, the catalyst outlet flue gas is measured for mercury speciation to determine the catalyst oxidation activity. Measurements are made at several flow rates to determine activity as a function of space velocity or area velocity.

Because the catalyst sample cores vary in specific surface area and in mercury oxidation activity, the catalyst core length often has to be adjusted to achieve mercury oxidation percentages in the desired range of approximately 80 to 95+% oxidation across the core. Lower oxidation percentages are below the range of interest, and higher oxidation percentages make it difficult to measure space/area velocity effects. If results from the first series of tests with a catalyst lie outside this desired range, the core length is typically adjusted and the tests are repeated.

RESULTS AND DISCUSSION

This section presents and discusses results from the project. The section is divided into three major subsections. The first discusses laboratory-scale evaluations conducted with synthetic flue gas to screen and select catalysts for evaluation in pilot-scale tests in the actual flue gas, the second subsection presents and discusses results from the pilot-scale catalyst tests, and the third discusses the results of pilot-scale wet FGD tests, most conducted downstream of pilot catalyst modules.

Laboratory Evaluation of Candidate Catalysts

Laboratory evaluations of candidate catalysts were conducted prior to the pilot-scale test programs conducted at the Monticello Station and at Plant Yates. The laboratory testing for each site is discussed in a separate subsection below.

Laboratory Evaluation for Monticello Station

Laboratory evaluation of candidate catalyst materials at simulated Monticello Station Unit 3 conditions began soon after the cooperative agreement was awarded. Table 2 shows the simulation gas species concentrations; Monticello Unit 3 fires a blend of low-sulfur Texas lignite and PRB coal.

Table 2. Target Simulation Gas Composition for Monticello Laboratory Tests

Species	**Concentration**
Hg^0	45-57 μg/Nm^3
SO_2	600 ppmv
HCl	1 ppmv
NO_X	400 ppmv
H_2O	15%
CO_2	12%
O_2	6%
N_2	Balance

Table 3 shows the results of all of the tests conducted. Three catalyst materials were evaluated in the first round of testing: a selective catalytic reduction (SCR) catalyst from Mitsubishi Heavy Industries (MHI); a sample of palladium on alumina (Pd #1) prepared by Johnson Matthey (at the time a new supplier being considered for supply of the catalysts for Monticello), and a sample of a carbon-based (C #6) material remaining from the production run to make a catalyst that was being tested at Coal Creek Station as part of Cooperative Agreement DE-FC26-01NT41185.

Table 3. Laboratory Catalyst Activity Test Results from First Round of Testing

Catalyst, core length	Core Length, in.*	Cell Pitch, cpsi*	No. of Cells in Core	Flow Rate, L/min	Area Velocity, sft/hr*	Hg Concentration, µg/Nm^3		Hg^0 Oxidation, %
						Inlet Total	Outlet Hg^0	
MHI SCR	0.97	47	8	0.61	46	48.9	9.61	80
MHI SCR	0.97	47	8	0.93	70	50.2	6.55	87
MHI SCR	0.97	47	8	1.44	109	45.9	11.8	74
C #6, 2002 production	2.25	77	14	0.61	14	57.0	0.65	99
C #6, 2002 production	2.25	77	14	0.93	22	55.0	5.99	89
C #6, 2002 production	2.25	77	14	1.44	34	53.1	1.31	98
Johnson Matthey Pd #1	1.25	64	13.5	0.61	24	54.6	2.62	95
Johnson Matthey Pd #1	1.25	64	13.5	0.93	36	49.3	3.06	94
Johnson Matthey Pd #1	1.25	64	13.5	1.44	57	44.5	5.68	87
Prototech Pd #1	1.04	64	14	0.61	28	65.4	1.38	98
Prototech Pd #1	1.04	64	14	0.93	42	63.5	8.28	87
Prototech Pd #1	1.04	64	14	1.44	65	65.4	7.36	89
Prototech Au	0.94	64	14	0.61	30	64.4	0.00	100
Prototech Au	0.94	64	14	0.93	46	60.8	0.92	98
Prototech Au	0.94	64	14	1.44	72	63.1	4.14	93
Supplier #2 Pd #1	1.02	64	11	0.61	36	65.8	0.92	99
Supplier #2 Pd #1	1.02	64	11	0.93	54	64.4	5.06	92
Supplier #2 Pd #1	1.02	64	11	1.44	84	63.5	10.13	84
Argillon SCR	1.04	50	8	0.61	43	64.0	5.52	91
Argillon SCR	1.04	50	8	0.93	65	64.0	9.20	86
Argillon SCR	1.04	50	8	1.44	101	65.8	17.03	74
Prototech Pd #1 Repeat	1.02	64	14	0.64	29	100	0.84	99
Prototech Pd #1 Repeat	1.02	64	14	1.00	45	62.2	3.75	94
Prototech Pd #1 Repeat	1.02	64	14	1.41	63	43.3	4.18	90
MHI SCR Repeat	1.04	47	8	0.64	48	78.9	7.94	90
MHI SCR Repeat	1.04	47	8	1.00	76	61.7	8.53	86
MHI SCR Repeat	1.04	47	8	1.41	107	37.4	7.45	80

Note: 1 in. = 2.54 cm; 1 cpsi = 0.155 cells/cm^2; 1 sft/hr = 0.288 Nm/h

Results from this first round of tests are plotted in Figure 6, with elemental mercury oxidation across the catalyst cores on the “Y” axis and the effective catalyst area velocity on the “X” axis (catalyst total geometric surface area divided by flue gas flow rate, in standard ft/hr). All of the results shown are based on the use of “Tris” solutions (rather than KCl solutions) in the Hg analyzer impinger train when measuring elemental mercury concentrations downstream of the catalysts. However, the catalyst outlet gas elemental mercury concentrations were often measured twice, once with KCl and once with Tris impingers, and the results were typically similar. The results show similar activity for all three catalyst types when plotted as a function of area velocity; a single line would appear to reasonably fit the data for all three catalyst types. However, the C #6 sample was tested at relatively low area velocity values, so there is no overlap between the area velocities tested for the C #6 and MHI catalysts.

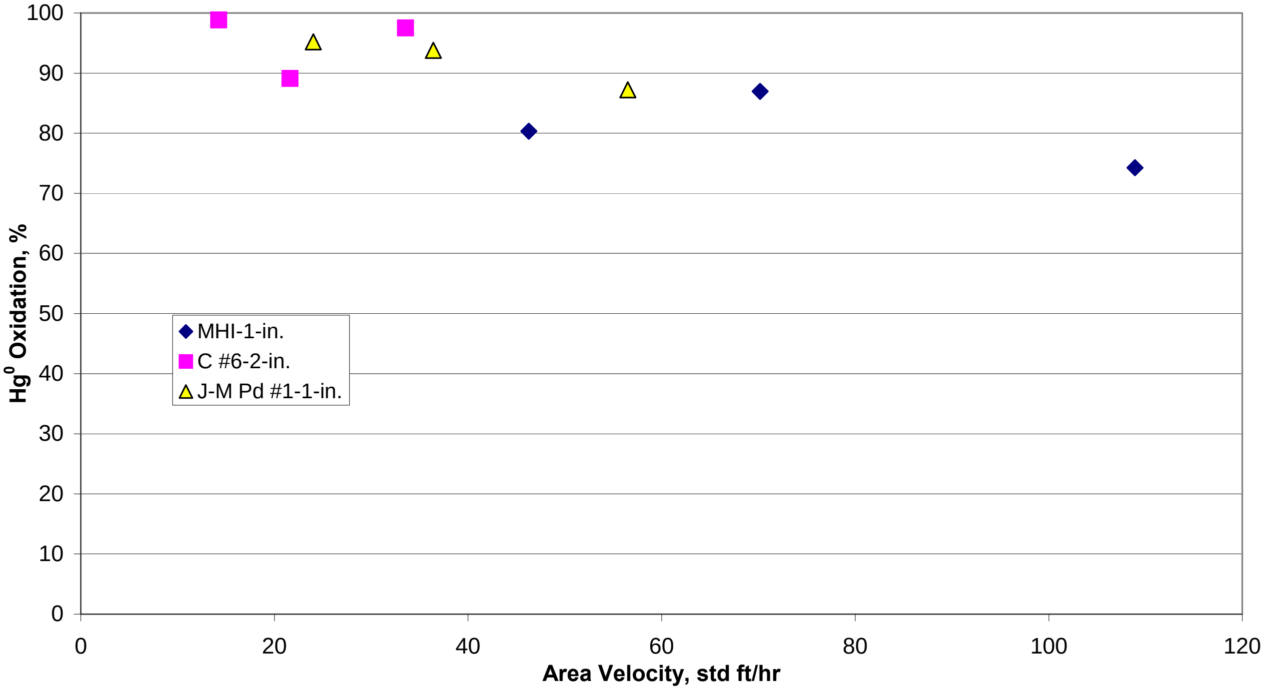


Figure 6. Catalyst Hg^0 Oxidation Activity from the First Round of Tests at Simulated Monticello Plant Gas Conditions

Note: 1 std ft/hr = 0.288 Nm/h

In the next round of testing four candidate catalyst materials were tested. These included two palladium catalysts – one from Sud-Chemie Prototech, who previously supplied the Pd #1 catalyst tested at Coal Creek and Spruce as part of Cooperative Agreement 41185, and one from an alternate supplier that did not want to be identified; gold prepared by Sud-Chemie Prototech; and an SCR catalyst previously supplied by Argillon. Argillon supplied the SCR catalysts tested at Coal Creek and Spruce as part of Cooperative Agreement 41185. Figure 7 shows a plot of these data. Also plotted are data from the first round of testing for the Johnson Matthey Pd #1 core, so the results for all three potential suppliers of Pd #1 can be visually compared.

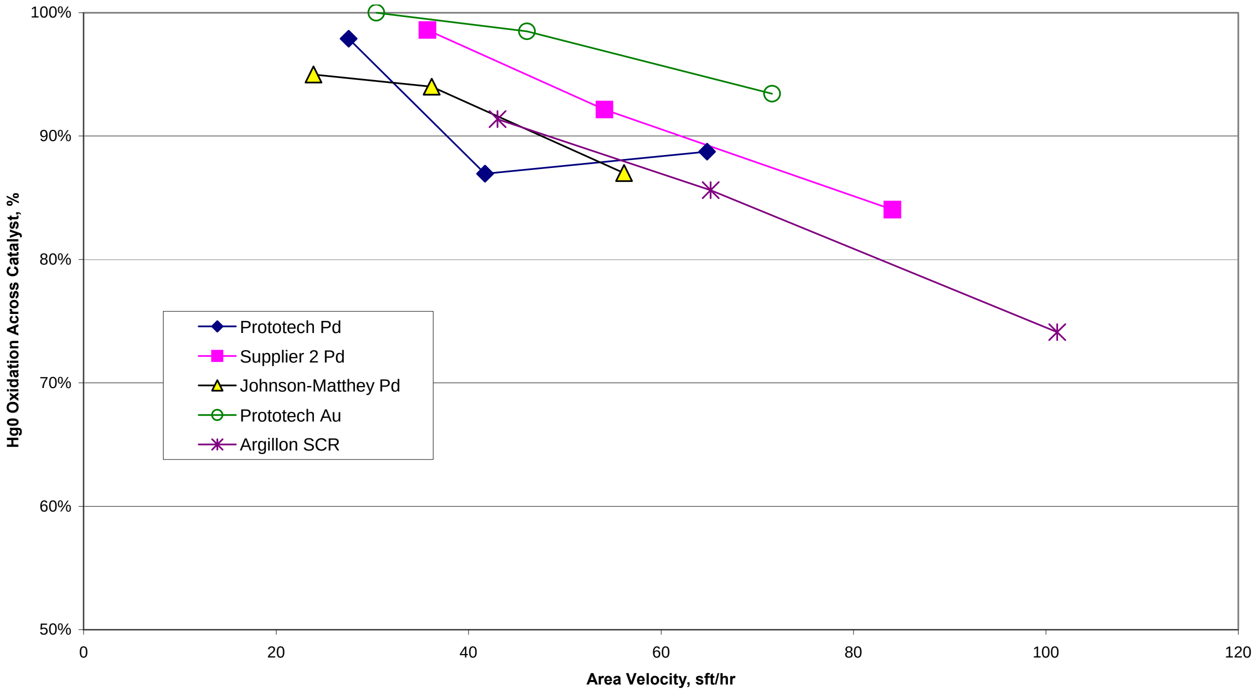


Figure 7. Catalyst Hg^0 Oxidation Activity Results from the Second Round of Tests at Simulated Monticello Plant Gas Conditions

Note: 1 std ft/hr = 0.288 Nm/h

The gold catalyst was the most active of the catalysts tested. The middle data point for the Prototech Pd #1 appears to be an outlier, as the oxidation should gradually drop with increasing area velocity, and the data at the middle area velocity should not show a lower oxidation percentage than the data at the highest area velocity. Of the three potential sources for Pd #1, the material from Supplier #2 was measured to be the most active over the range of area velocity values tested, although not by a wide margin relative to the other suppliers.

Figure 8 shows the data from the first round of catalyst tests with the Argillon SCR catalyst data from the second round of tests added to the plot. This allows the data for the MHI and Argillon SCR catalysts to be directly compared. Based on these data, the MHI catalyst appears to be slightly more active than the Argillon catalyst for elemental mercury oxidation at the two higher area velocity values. The oxidation value for the MHI catalyst at the lowest area velocity value appears to be erroneous, for the same reason as described above for the middle data point for the Prototech Pd #1. That is, the oxidation percentage at the lowest area velocity value should be higher, rather than lower than the value at the middle area velocity value.

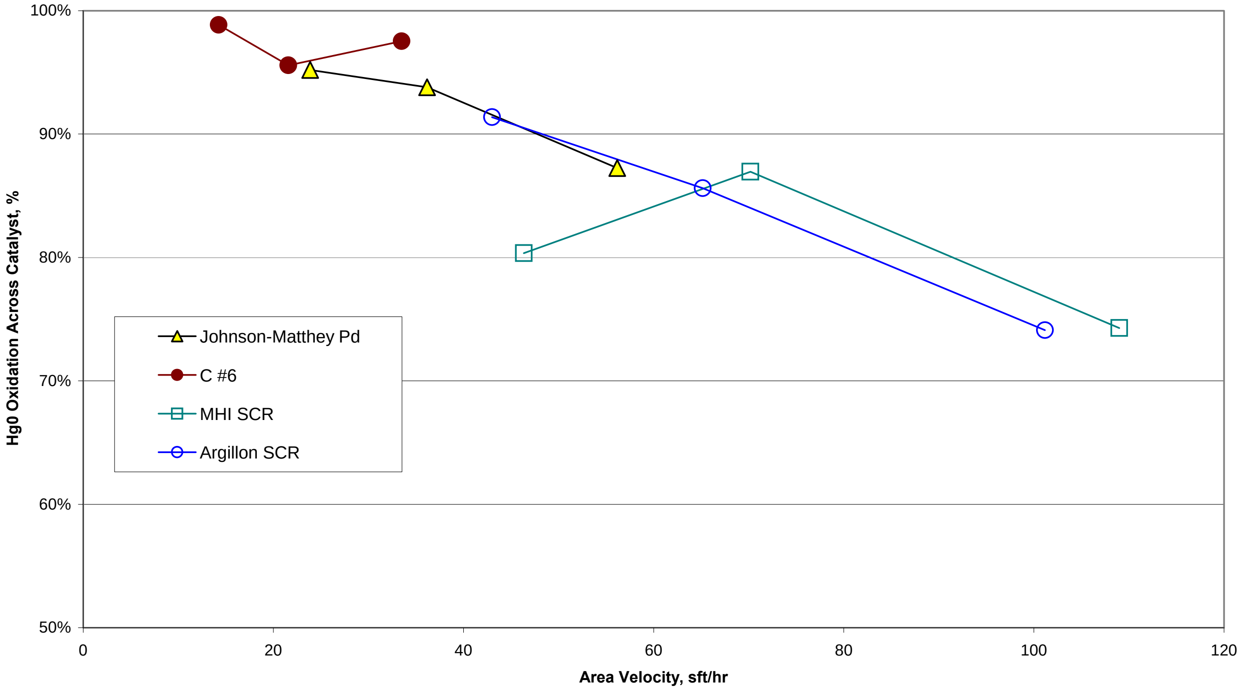


Figure 8. Catalyst Hg^0 Oxidation Activity from the First Round of Tests at Simulated Monticello Plant Gas Conditions with Argillon SCR Catalyst Results Added

Note: 1 std ft/hr = 0.288 Nm/h

Two catalyst materials were repeat-tested because of anomalous results from previous testing: Pd #1 catalyst from Sud-Chemie Prototech, and the SCR catalyst from MHI. Figure 9 shows a plot of the repeated Pd #1 data. Also plotted are data from previous testing for the Prototech, Johnson Matthey, and Supplier #2 Pd #1 cores, so the results for all three potential suppliers of Pd #1 can be visually compared. In the original tests, the middle data point for the Prototech Pd #1 appeared to be an outlier, as the oxidation should gradually drop with increasing area velocity; the data at the middle area velocity should not show a lower oxidation percentage than the data at the highest area velocity. The re-test results show the expected trend of activity decreasing as area velocity increases. With these re-test data, the measured performance of the catalysts from the three potential sources for Pd #1 fell within a relatively narrow band, indicating there was not much difference in activity between the three sources in this synthetic flue gas.

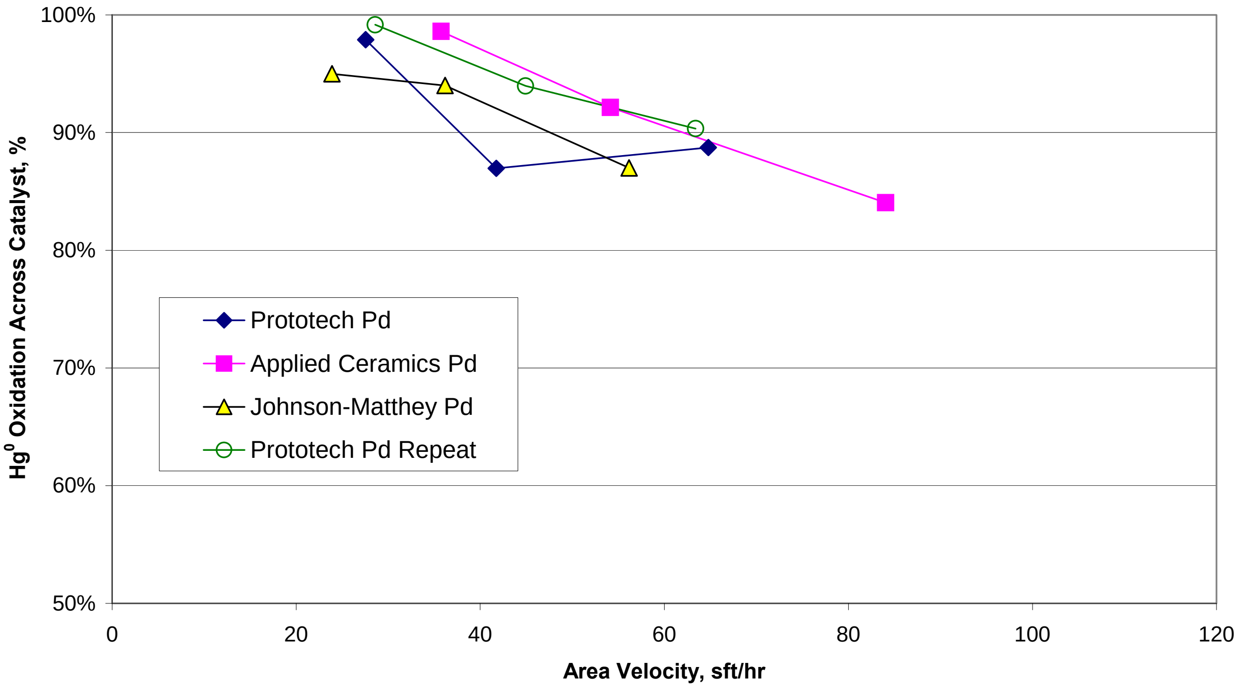


Figure 9. Catalyst Hg^0 Oxidation Activity Results from the Repeat Tests of Prototech Pd Catalyst at Simulated Monticello Plant Gas Conditions

Note: 1 std ft/hr = 0.288 Nm/h

Figure 10 shows the data from the MHI catalyst repeat tests, with the previous MHI and Argillon SCR catalyst data also plotted. In the original MHI catalyst data, the oxidation value at the lowest area velocity value appeared to be erroneous, for the same reason as described above for the middle data point for the Prototech Pd #1. The oxidation percentage at the lowest area velocity value should be higher, rather than lower than the value at the middle area velocity value. In the repeat test the expected trend was seen, with activity steadily decreasing as area velocity increased. The differences in performance between the Argillon and MHI catalysts were seen to be relatively minor, particularly at the lower area velocity.

Based on these results, it appeared that Pd #1 catalysts from any of the three possible suppliers should perform similarly, as should SCR catalyst from either of the two suppliers considered. It was difficult to distinguish between the potential suppliers of these catalyst types based on these data, so the decisions were instead based on other factors including promised catalyst delivery date, and catalyst cost and/or vendor cost sharing. The recommendation was that the other two catalyst chambers should be used to test the Prototech gold and Carbon #6. However, as described later in this section, the actual catalysts tested varied somewhat from this initial recommendation.

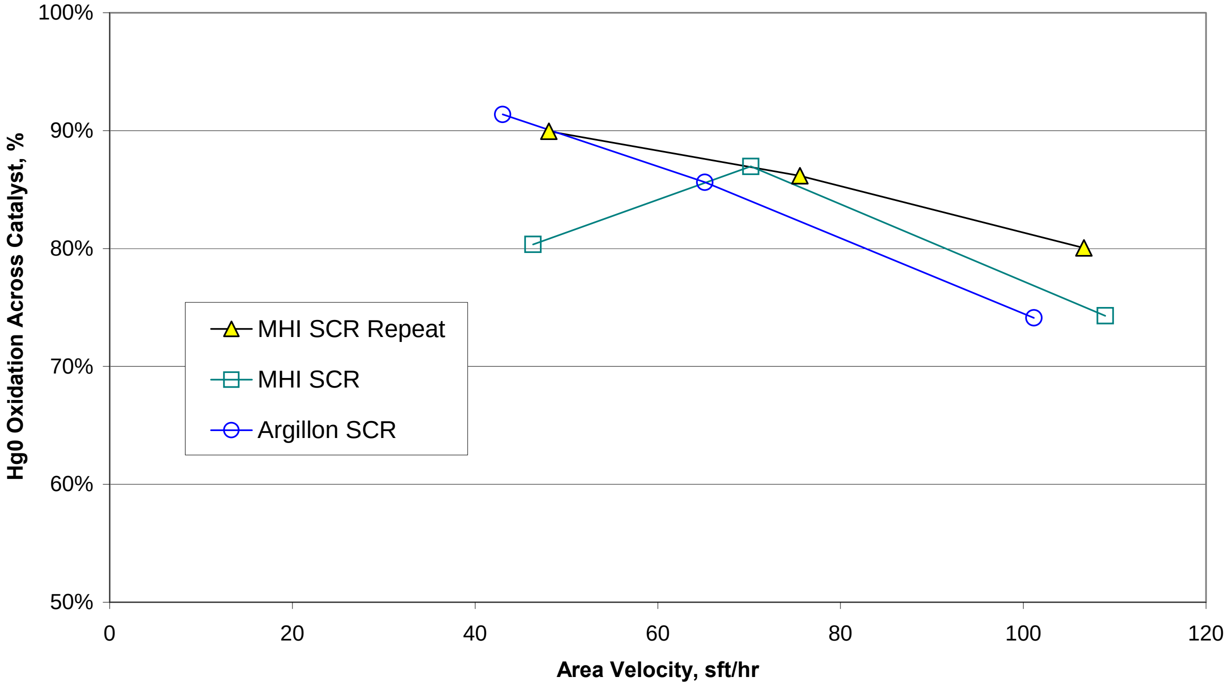


Figure 10. Catalyst Hg^0 Oxidation Activity from the Repeat MHI SCR Catalyst Tests at Simulated Monticello Plant Gas Conditions

Note: 1 std ft/hr = 0.288 Nm/h

Laboratory Evaluation for Plant Yates

Laboratory evaluation was conducted on four candidate catalyst materials at simulated Plant Yates Unit 1 conditions. These included Pd #1 catalyst from Johnson Matthey, gold from Sud-Chemie Prototech, SCR catalyst from MHI/Cormetech, and Carbon #6 from the unidentified supplier. Table 4 shows the laboratory gas species concentrations that were intended to simulate gas conditions at Plant Yates, which fires low-sulfur Eastern bituminous coal.

Table 4. Target Simulation Gas Composition for Plant Yates Laboratory Tests

Species	**Concentration**
Hg^0	~50 μg/Nm^3
SO_2	600 ppmv
HCl	10 ppmv
NO_X	200 ppmv
H_2O	6%
CO_2	8%
O_2	8%
N_2	Balance

Table 5 shows the results of the laboratory-scale tests conducted. All of the results shown are based on the use of KCl solutions in the Hg analyzer impinger train when measuring elemental mercury concentrations downstream of the catalysts.

Table 5. Laboratory Catalyst Activity Test Results for Simulated Plant Yates Conditions

Catalyst	Core Length, in.*	Cell Pitch, cpsi*	No. of Cells in Core	Flow Rate, L/min	Area Velocity, sft/hr*	Hg Concentration, µg/Nm^3		Hg^0 Oxidation, %
						Outlet Total	Outlet Hg^0	
Johnson Matthey Pd #1	0.55	64	14	0.63	54	50.2	6.59	87
Johnson Matthey Pd #1	0.55	64	14	1.01	86	34.7	6.43	81
Johnson Matthey Pd #1	0.55	64	14	1.40	119	24.8	5.82	77
Prototech Gold	0.50	64	14	0.63	59	55.49	3.44	94
Prototech Gold	0.50	64	14	1.01	94	36.06	4.46	88
Prototech Gold	0.50	64	14	1.40	131	25.72	5.10	80
Prototech Gold	0.99	64	14	0.63	30	58.1	0.28	>99
Prototech Gold	0.99	64	14	1.01	47	35.4	0.84	98
Prototech Gold	0.99	64	14	1.40	66	26.0	1.31	95
MHI SCR	1.00	47	8	0.63	46	51.8	4.49	91
MHI SCR	1.00	47	8	1.01	73	33.4	3.80	89
MHI SCR	1.00	47	8	1.40	102	25.5	5.34	79
C #6	1.02	77	14	0.63	32	55.5**	6.07	89
C #6	1.02	77	14	1.01	52	34.7**	5.44	84
C #6	1.02	77	14	1.40	72	25.0**	5.82	77

*Note: 1 in. = 2.54 cm; 1 cpsi = 0.155 cells/cm^2; 1 sft/hr = 0.288 Nm/h
**Because of observed Hg desorption from this catalyst, values in table are inlet Hg^0 concentrations

Figure 11 shows a plot of these data, which show the gold to be the most active catalyst, followed by the SCR catalyst, the Johnson Matthey Pd #1, and Carbon #6. The gold was tested at two core lengths because initial tests with a 1-in. (2.5-cm) core length produced very high oxidation percentages. Additional tests were conducted with a shorter, 0.5-in. (1.3-cm) core length to get performance data over a wider range of oxidation percentages. The two sets of data show relatively good overlap in terms of percent oxidation versus area velocity. The data summarized in Table 5 and plotted in Figure 11 were used to select and size catalysts for the oxidation catalyst pilot unit at Plant Yates.

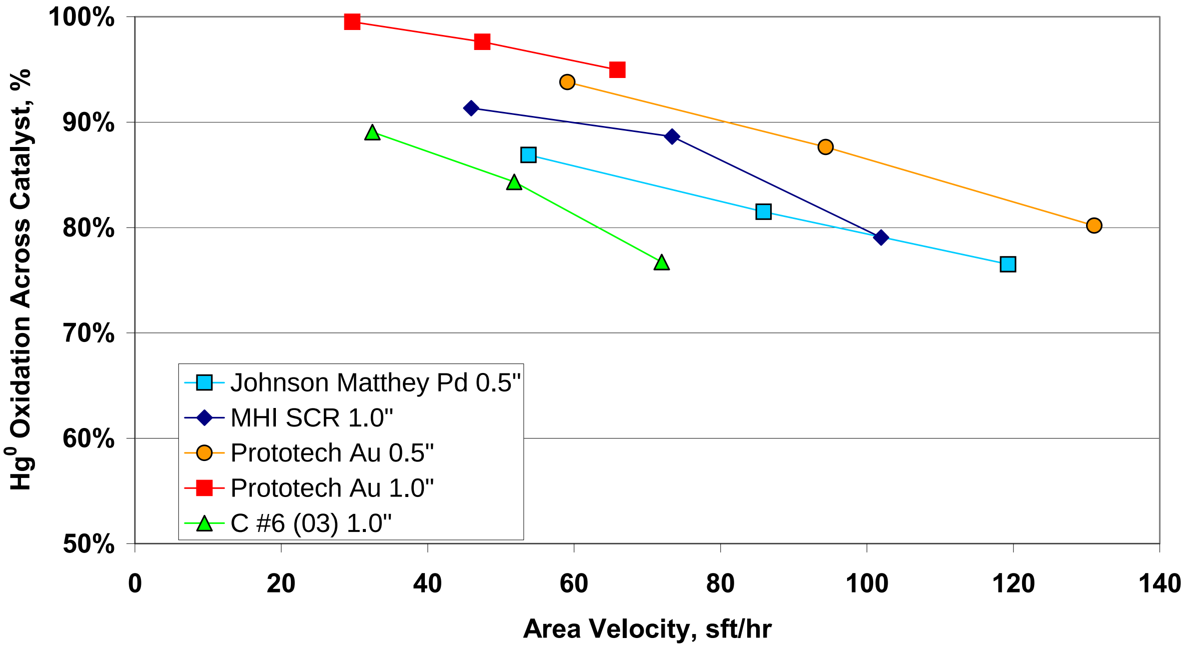


Figure 11. Catalyst Hg^0 Oxidation Activity Results at Simulated Plant Yates Gas Conditions

Note: 1 std ft/hr = 0.288 Nm/h

Catalyst Pilot Unit Operation

Catalyst Pilot Unit Operation at Monticello Station

Unit 3 at Luminant's Monticello Steam Electric Station, which is located near Mount Pleasant, Texas, is a 793-MW unit that fires a blend of Texas lignite and PRB coal. It has a horizontally opposed, pulverized-coal boiler with low NO_X burners. A cold-side electrostatic precipitator (ESP) is used for particulate control and a limestone forced oxidation, open spray tower wet FGD system is used for SO_2 control. The lignite/PRB coal blend contains 0.7 wt% sulfur, 0.14 ppm mercury, and 210 ppm chloride on average. The ESP outlet flue gas typically contains 25-50% oxidized mercury and the balance elemental mercury, with total mercury concentrations of about 20-30 $\mu g/Nm^3$. However, the Texas lignite has roughly four times the mercury content of the PRB on a mass basis, and the percentage of each fuel type fired cannot be closely controlled. Consequently, variations in the percentage of lignite versus PRB fired can greatly influence the flue gas mercury concentration and oxidation percentage.

The catalyst pilot unit used at Coal Creek Station as part of Cooperative Agreement 41185 was shipped to Monticello Station in October 2004. Plant personnel installed the pilot unit adjacent to the 3C ID fan using 20-in. (0.51-m) and 12-in. (0.30-m) pipe runs to connect the pilot unit inlet and outlet, respectively, to penetrations made in the Unit 3 ductwork during a plant outage in the spring of 2004.

Based on laboratory catalyst screening test results presented in the previous subsection, it was decided that the catalysts to be tested at Monticello should include Pd #1 catalyst from any of the three possible suppliers, SCR catalyst from either MHI/Cormetech or Argillon, gold from Sud-Chemie Prototech, and Carbon #6 from an unnamed catalyst manufacturer. For the Pd #1 catalyst, Johnson Matthey was selected as the supplier over the other two candidates based on price and their ability to provide the catalyst in a single, 9-in. (23-cm) length rather than as three, 3-in. (7.6-cm) layers. A single layer was desirable to test because with this little catalyst depth it is possible that future commercial installations of this technology would use only one catalyst layer. For the SCR catalyst, it was decided to test the MHI/Cormetech catalyst for mostly intangible reasons, primarily a desire to broaden the project experience base by working with other catalyst manufacturers.

The gold catalyst was procured by project co-funder TVA and shipped to URS. The Pd #1 and SCR catalysts were procured by URS, and all three were received at Monticello by late November 2004. The three catalysts were installed by plant staff, and the pilot unit was ready for operation by December 1.

The Carbon #6 catalyst was not yet available, so it was decided to leave the regenerated Pd #1 catalyst from the Coal Creek Station pilot tests in place, to provide a measure of the activity of a previously regenerated catalyst in the Monticello flue gas. It was expected to be several months before the Carbon #6 catalyst was available, so the plan was to use this time as an opportunity to compare the activity between fresh and regenerated Pd #1 catalyst over time. The comparison between the two palladium-based catalysts was confounded by the fact that the two versions of Pd #1 were from alternate suppliers and in one versus three layers. Also, the regenerated Pd #1 was previously operated in another flue gas matrix (from North Dakota lignite). Problems were encountered in sourcing a supply of the tire char carbon used to produce pilot quantities of the Carbon #6 catalyst, so the regenerated Pd #1 remained in service over the entire pilot test period. The physical characteristics of the four catalysts installed in the pilot unit and operated over the test duration are summarized in Table 6.

Table 6. Characteristics of Catalysts Installed in Pilot Unit at Monticello

Catalyst	Cross Section, in x in (m x m)	Catalyst Depth	Cell Pitch, mm	Cells per Sq. In., CPSI (cells/cm^2)	Area Velocity, std. ft/hr (Nm/h)
Gold (Sud-Chemie Prototech)	29.5 x 29.5 (0.75 x 0.75)	3 x 3 in. (3 x 7.6 cm)	3.2	64 (9.9)	52 (15)
Pd #1 (Johnson Matthey)	29.5 x 29.5 (0.75 x 0.75)	9 in. (23 cm)	3.2	64 (9.9)	52 (15)
Pd #1 (regenerated from Coal Creek)	29.5 x 29.5 (0.75 x 0.75)	3 x 3 in. (3 x 7.6 cm)	3.2	64 (9.9)	52 (15)
SCR (Cormetech/MHI)	35.4 x 36.2 (0.90 x 0.92)	29.5 in. (75 cm)	3.3	58 (9.0)	38 (11)

Unfortunately, when the plant went to valve in the flue gas to and from the pilot unit, a 12-inch butterfly valve on the return line from the pilot unit to the 3C ID fan was found to have failed closed. After many attempts to force the valve open, it was decided they would have to wait until the next plant outage to remove the valve and either replace it or force it open by direct force on the valve disk rather than just applying force to the valve stem. The pilot unit sat off line through the end of December 2004, but a brief plant outage in early January allowed an opportunity to remove the valve and force it open. The pilot unit was started up on flue gas on January 14, 2005. Results from the pilot unit operation are presented and discussed in the following subsections.

Catalyst Pressure Drop Performance

Figure 12 shows the "full load" pressure drop data for all four catalysts from start up through the first six months of operation. "Full load" was defined as periods where the flue gas flow rate through the highest-flowing catalyst (gold) was at least 1900 acfm. The desired flow rate was 2000 acfm.

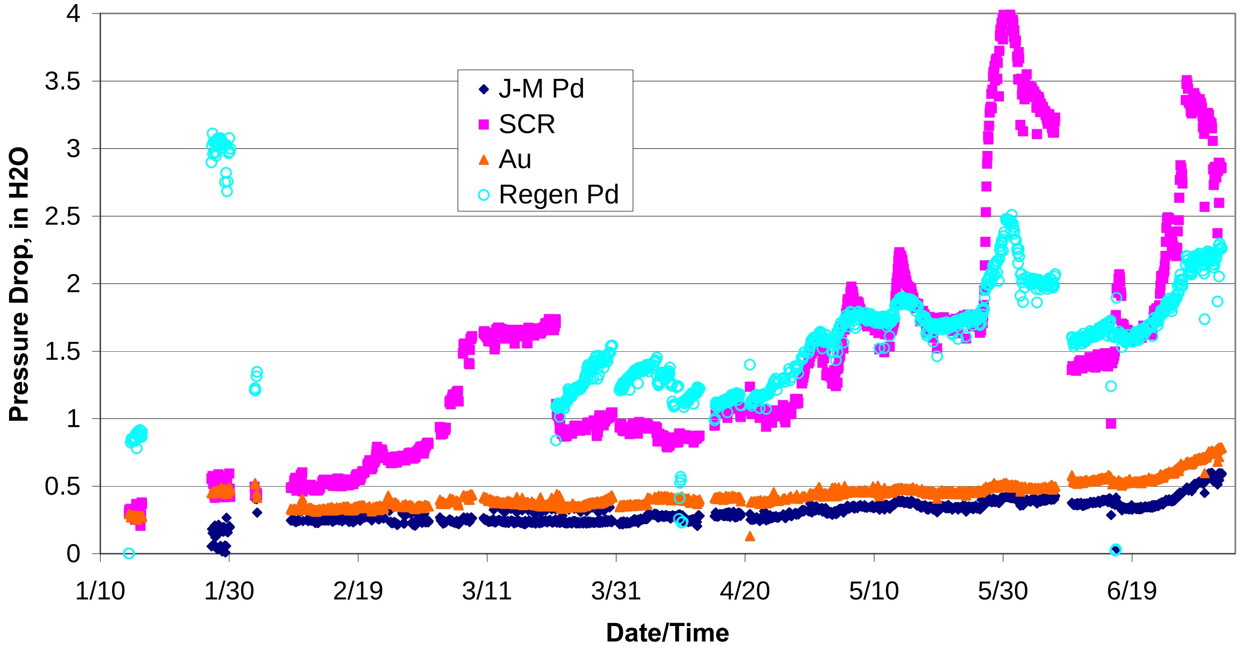


Figure 12. Full-load Catalyst Pressure Drop Data from Monticello Pilot Unit for the First Six Months of Operation (2005)

Note: 1.0 in. H_2O = 0.25 kPa

In previous catalyst testing at Coal Creek, fly ash was observed to build up in the horizontal-gas-flow catalyst cells, resulting in increased catalyst pressure drop and lowered catalyst oxidation performance. Sonic horns were installed there and were generally effective in preventing fly ash buildup[1]. Since Monticello, like Coal Creek, has an ESP for particulate control (the second site tested in Cooperative Agreement 41185, Spruce, has a reverse-gas fabric filter), it was expected that the sonic horns would also be necessary to prevent fly ash buildup at Monticello.

The sonic horns were placed in service on the catalyst pilot unit at the end of January, two weeks after initial startup. However, the sonic horns did not operate properly for the first several months. Because project team members were traveling to the site intermittently, and power plant personnel were not monitoring pilot unit operation, the pilot unit went for weeks at a time with the horns not operating properly. Over the first three months of operation, a failed compressed air pipe nipple was replaced, the horn timer was replaced, the solenoid valves controlling air flow to the horns were replaced, the horns were disassembled and cleaned, and an air pressure regulator was installed to ensure that the optimum air pressure of 70 psig (480 kPa) was supplied to the horns. While these efforts corrected a number of operational issues, it still remained that the solenoid valves controlling air flow to the horns did not turn off properly at the end of their cycle (the horns were intended to sound 30 seconds each every half hour). In the interim, the horns sounded continuously unless an operator intervened to momentarily lower the air pressure to the valves, which allowed them to close. The new solenoid valves were operating within their design air pressure and solenoid voltage range, so project team members continued to work with the valve manufacturer to troubleshoot why they did not cycle properly.

Two other issues impacted the pressure drop data for the oxidation catalysts. One was that the ID fan differential available at Monticello was not as great as at Coal Creek, for which the pilot unit was originally designed. This meant the catalyst pilot only achieved full flue gas flow when Unit 3 was at or near full load. When the unit was at reduced load, the flow rates to the oxidation catalysts also decreased. While this did a good job of simulating the effects of load changes on the oxidation catalysts, it did not allow for extended periods of operation at controlled gas flow rates to observe catalyst pressure drop at simulated full-load gas flow conditions.

The other issue is that the total pressure and differential pressure transducers for the flow meter for one catalyst chamber (Johnson Matthey Pd #1) did not operate properly when the pilot unit was started up. At the end of January 2005, the failed components were exchanged with those from Catalyst 4 (regenerated Pd #1 from Coal Creek) since it was thought to be more important to measure and control the flue gas flow rate through the new catalyst rather than the regenerated one. The total pressure transducer was determined to have failed and was replaced, while the differential pressure transducer appeared only to have lost its calibration and was recalibrated. The failed transducer had a delivery time of six weeks, so it was late March 2005 before the new and recalibrated components were re-installed. In spite of these efforts, the flow rate measurement for the regenerated Pd #1 catalyst remained inaccurate; the recalibrated differential pressure transducer still was not operating properly. Consequently, this catalyst box was operated with the control valve manually set wide open. Spot checks on the flow through this catalyst were made by running “jumper” lines to the transducers for another box, and indicated that the flue gas flow through this catalyst was similar to that across the others (about 1900-2100 acfm [3200-3600 m^3/h] at full unit load).

The data in Figure 12 show that over the first six months, the pressure drop across the Johnson-Matthey Pd #1 and gold catalysts remained low (less than 0.5 in. H_2O (0.12 kPa) for much of the period) while the SCR and regenerated Pd #1 catalysts showed excursions to higher pressure drop. As described above, much of the data for the regenerated Pd #1 are missing for the first two months, while the total pressure and differential pressure instrumentation for the flow meter on that box were removed.

The excursions where the pressure drop across the SCR and regenerated Pd #1 catalysts increased appear to correspond with periods where the sonic horns were not operating because of the issues discussed above. The horns were manually cycled on March 21 during attempted repairs, and as can be seen in Figure 12, this lowered the pressure drop across the SCR catalyst by over 0.7 in. H_2O (0.17 kPa).

It was apparent that properly functioning horns would be required to avoid fly ash buildup in the SCR and regenerated Pd #1 catalysts, while the new Pd #1 and gold catalysts were less sensitive to horn operation. It is likely that the SCR catalyst was more sensitive to horn operation because of its greater catalyst length, and that the regenerated Pd was more sensitive because of residual fly ash remaining on the catalyst surfaces from its 20+ months of service at Coal Creek Station.

In April, one solenoid valve that had been particularly problematic was replaced with a larger valve (¾-in. [1.9 cm] vs. ¼-in. [0.6 cm]) installed upstream of the horn rather than downstream (on the air exhaust from the horn). This change, along with minor wiring and tubing changes, resulted in all four valves cycling properly beginning in late April 2005. The four horns appear to have cycled properly through approximately mid-June.

During the first three months of operation, most of the pressure drop excursions across the SCR and regenerated Pd #1 catalysts appeared to correspond with sonic horn problems, but this did not appear to be the case during the next three months. As an example, there was a sharp increase in pressure drop around May 25, but the sonic horns were observed to be operating properly the next time project team members were on site in mid-June. The pressure drop across these two catalysts appeared to recover briefly following a short outage of the host unit, but increased sharply again in late June. The pressure drop across the gold and Johnson Matthey Pd catalyst also increased at the end of June, for reasons that were not determined.

The pressure drop across all four catalysts increased starting in mid-June, again apparently caused by sonic horn malfunction. Although the air line to the sonic horns had a regulator and filter to control the pressure and to remove impurities from the compressed air, upstream of regulator the air line was rusty on its inner surfaces. During continued horn operation, exfoliated rust particles from the line tended to build up in the regulator inlet, eventually plugging air flow to the regulator. The regulator was found plugged and was cleaned twice during the April to June 2005 time period.

Figure 13 shows the “full load” pressure drop data for all four catalysts from start up through the end of 2005, nearly one year of operation. As noted on the figure, there was a period of about one week where the pilot unit was off line and was being moved by plant personnel. The move was required because of plant construction activity in the vicinity of the pilot unit, but project team members were unaware of this move. The move exacerbated the pressure drop buildup across the catalysts because after the move, the pilot unit was placed back in service but the air to the sonic horns was not turned back on. The pilot unit operated about five days with no air to the sonic horns before this oversight was discovered and corrected.

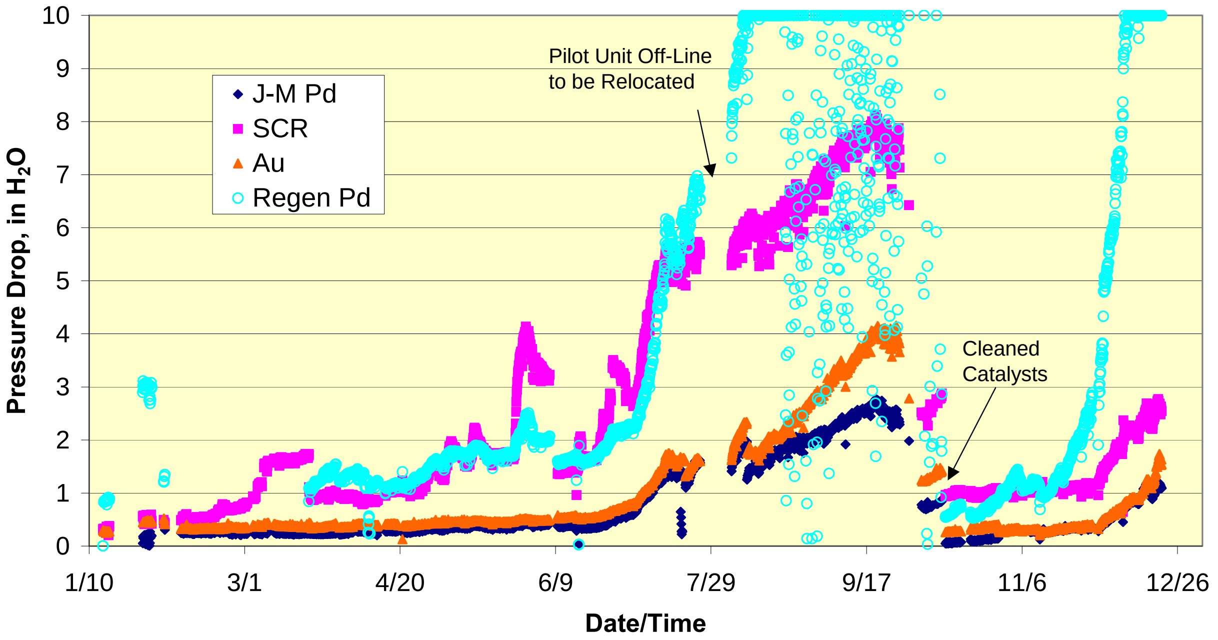


Figure 13. Full-load Catalyst Pressure Drop Data from Monticello Pilot Unit through the End of Calendar Year 2005

Note: 1.0 in. H_2O = 0.25 kPa

The data in Figure 13 show that the pressure drop across all four catalysts increased markedly during this period of operation with the sonic horns not functioning. The pressure drop across the Johnson-Matthey Pd #1 and gold increased to over 2 in. H_2O (0.5 kPa), the pressure drop across the SCR catalyst increased to over 6 in. H_2O (1.5 kPa), and the pressure drop across the regenerated Pd #1 catalyst exceeded 10 in. H_2O (2.5 kPa). After the air flow to the horns was restored, the pressure drop across the catalysts showed a brief recovery, but then showed continuing increases through mid-September 2005. There is no doubt that these pressure drop increases, caused by fly ash buildup in the catalyst flow channels, contributed to the apparent loss in catalyst activity measured during this time period, as discussed later in this section.

In mid-September 2005, the air pressure regulator inlet was again found plugged with rust particles, a likely cause of the preceding gradual increase in pressure drop across all four catalysts. The regulator was cleaned and sonic horn operation was restored. The pressure drop across all four catalysts began to drop. At the end of September, Unit 3 had a short outage, during which the sonic horns continued to operate. The pressure drop across all four catalysts dropped further due to the effects of this short unit outage. As examples, the pressure drop across the SCR catalyst dropped from over 6 in. H_2O (0.5 kPa)on September 30th to less than 3 in. H_2O (0.75 kPa) on October 6th, while the pressure drop across the gold catalyst dropped from about 4 in. H_2O (1 kPa) to 1.5 in. H_2O (0.37 kPa). Such pressure drop recovery during unit outages has been noted in the past, and is apparently due to having the sonic horns and the ID fan operating as the unit comes off line, with no fly ash in the gas (mostly air) flowing through the catalysts.

In early October 2005 it became apparent that although proper sonic horn operation was restored, the fly ash buildup in the catalyst cells would not be removed and the pressure drop across the catalysts would not be restored to clean conditions solely through sonic horn operation. Consequently, the pilot unit was shut down on October 11 and all four chambers were cleaned of fly ash buildup with compressed air and a shop-type vacuum. Considerable fly ash buildup was removed from all four catalysts. Catalyst chamber 1 (Johnson Matthey Pd #1) had a considerable buildup of hardened fly ash on the chamber floor just upstream of the catalyst, which provided evidence of moisture having entered that chamber. While the catalyst chambers were open, the lines to the pressure drop transducers were cleaned out, and the transducers were re-zeroed to improve their accuracy. Plugged, or partially plugged pressure drop tubing connections were found at the inlets to several of the catalyst boxes, and may have contributed to erroneous pressure drop readings. Also, a basket strainer was installed on the air line upstream of the regulator in an effort to prevent future plugging of the regulator.

At startup on October 12, the pressure drop across all four catalysts was markedly reduced. The pressure drop values across the gold and Johnson Matthey Pd #1 were between 0.1 and 0.2 in. H_2O (0.02-0.05 kPa), and the pressure drop across the regenerated Pd #1 from Coal Creek was 0.55 in. H_2O (0.14 kPa). The highest pressure drop was across the SCR catalyst, at 0.9 in. H_2O (0.22 kPa). This is not surprising considering its longer, 29.5-in. (75-cm) catalyst length (the others had only 9 inches [23 cm] of total catalyst length).

In late November, the pressure drop across the regenerated Pd #1 catalyst was observed to increase. URS personnel were on site conducting another project, and observed sonic horn operation on the catalyst pilot unit on November 30th. All four horns appeared to be cycling and sounding properly, and the compressed air pressure to each was at least 70 psig (480 kPa), the desired value, during horn operation. It was decided to continue operation of the pilot unit with no changes and observe the pressure drop values.

On December 2nd, the pressure drop across the four catalysts began to rise; the pressure drop across the regenerated Pd #1 catalyst increased towards 10 in. H_2O (2.5 kPa), the maximum transducer reading. URS personnel were again on site and observed sonic horn operation during the week of December 12th. The solenoid valve for the horn on the gold catalyst chamber was found to not fully close at the end of its cycle, causing that horn to blow continuously. However, even with that horn blowing continuously, the air pressure to the other horns when they operated was observed to be 68 psig (469 kPa), and near the desired pressure of 70 psig (480 kPa). The air pressure regulator setting was increased to produce 70 psig at the horns with two in operation, and the horn on the gold catalyst chamber was left blowing all of the time.

On December 21 flue gas flow to the pilot skid was stopped for then unknown reasons. As a result of holiday and vacation schedules, this unplanned shutdown of the pilot unit was not diagnosed and corrected until early in January 2006. This period is noted by a lack of pressure drop data in Figure 13. The cause was traced to damage to the instrument air line to the pilot unit caused by debris falling from overhead Unit 3 construction, which in turn caused the air-operated flow control valves to fail closed. The line was repaired and the pilot unit came back on line on January 19.

Figure 14 shows the "full load" pressure drop data for all four catalysts from start up through the middle of calendar year 2006. Troubleshooting was conducted in mid-February to diagnose the pressure drop increases observed. This trip showed no outward signs of a problem – the sonic horns were observed to cycle properly, all pressure drop tubing was clear, and the transducers zeroed properly. Because of the construction activity in the vicinity of the pilot unit, it was not possible to shut down and open any of the catalyst chambers to observe the fly ash buildup.

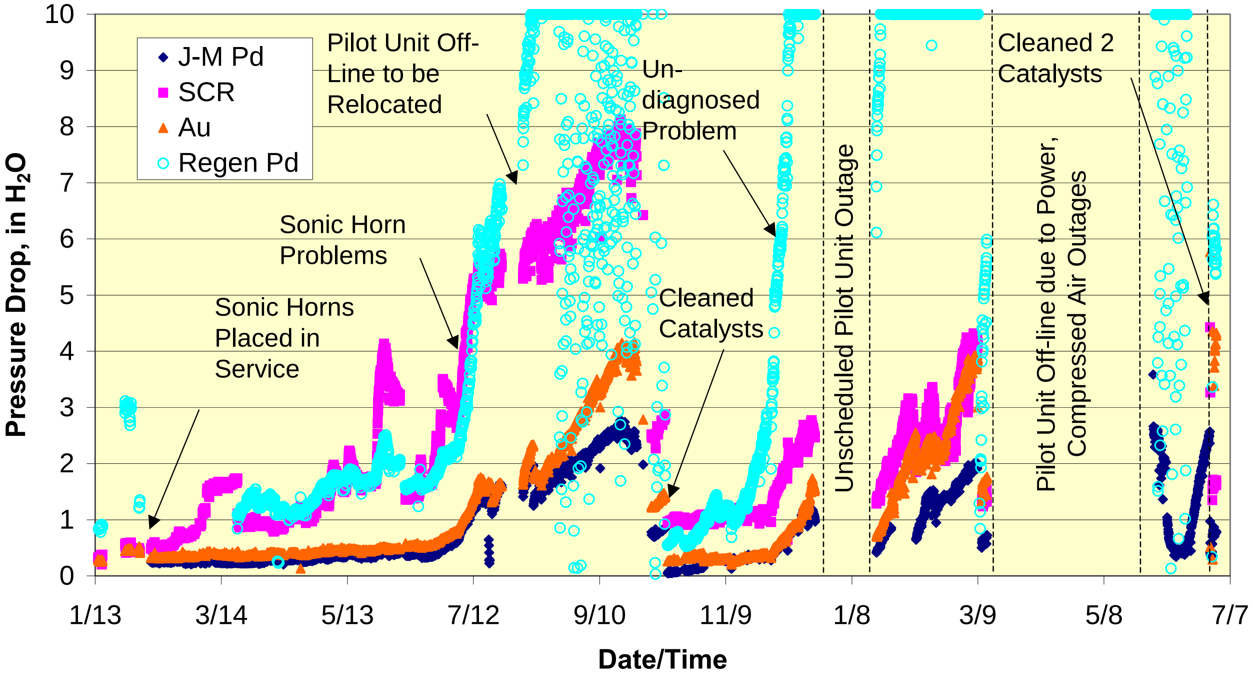


Figure 14. Full-load Catalyst Pressure Drop Data from Monticello Pilot Unit for the first 18 Months of Operation

Note: 1.0 in. H_2O = 0.25 kPa

From mid-February through early March, the pressure drop across the regenerated Pd #1 catalyst remained off scale at greater than 10 in. H_2O (2.5 kPa), while the pressure drop across the other three catalysts remained elevated, in the range of 1.5 to 3 in. H_2O (0.37-0.75 kPa). After March 7, telephone communications with the pilot unit was lost for then unknown reasons, so it was not known if the pressure drop values remained steady or increased further. These data were recovered during a later catalyst activity measurement trip. The data show that on March 9, the pilot unit flue gas flow rate was greatly reduced, possibly due to low unit load. After full flow was restored, late on March 10, the pressure drops across all four catalysts were reduced, with the regenerated Pd #1 catalyst pressure drop ranging from 4 to 6 in. H_2O (1-1.5 kPa) and the pressure drop across the other three ranging from 0.5 in H_2O (0.12 kPa) to less than 2 in. H_2O (0.5 kPa). This "recovery" had been seen before when the sonic horns continued to operate while the flue gas flow rate was greatly reduced.

The pilot unit was brought off line on March 13 while the power to that area was disconnected, related plant construction, and remained off line through May 31. Although power was restored on May 31, the instrument air supply to the pilot unit was inadequate for all four catalyst box flow control valves to operate properly. For this reason, only the Johnson Matthey catalyst saw normal flue gas flow; the other three saw little or no flow.

The low air pressure problem was discovered the last week of June 2006, when project team members were first allowed back on site after construction activities were completed to make catalyst activity measurements. When flow was restored, it was observed that the pressure drop across the regenerated Pd #1 and SCR catalysts was high (>4 in H_2O [>1 kPa]), while the pressure drop across the gold and Johnson Matthey Pd #1 appeared to be normal. It was decided to shut down and manually clean the regenerated Pd #1 and SCR catalysts with compressed air, but not the gold and Johnson Matthey Pd #1. After cleaning those two catalysts and starting back up, the pressure drop across the SCR catalyst was lowered to less than 2 in H_2O (0.5 kPa), but the regenerated Pd #1 remained above 5 in H_2O (1.2 kPa).

However, when the pilot unit was started back up after cleaning the two catalysts and flue gas flow rates were stabilized at 2000 acfm (3400 m^3/h) through each, the pressure drop across the gold catalyst was observed to be higher than thought, at 4 in H_2O (1 kPa) . There was not time during this one-week measurement trip to shut down again and clean the gold catalyst, but a return trip to clean the gold catalyst and JM Pd was conducted several weeks later, on August 10, 2006.

Figure 15 shows the pilot unit pressure drop performance through August 28, 2006, at which time the unit was taken out of service after approximately 19 months of intermittent operation. When the gold and Johnson Matthey Pd #1 catalysts were cleaned on August 10, there was evidence that the catalyst compartments had been exposed to high moisture conditions which led to the formation of a hard, cementitious ash layer at the entrance to the first catalyst layer. The high moisture conditions most likely occurred during previous unplanned pilot unit outages, where hot flue gas was trapped in these compartments because of the loss of air pressure and/or power to the fail-closed compartment-outlet flow-control valves. This cemented ash buildup could not be effectively cleaned from all of the catalyst flow passages and a number remained plugged after the catalyst cleaning. Although the pressure drop through these two catalyst compartments was lowered by the cleaning (to 0.4 in. H_2O [0.1 kPa] across the Johnson Matthey Pd #1 catalyst and 1.2 in. H_2O [0.30 kPa] across the gold), the pressure drop quickly increased. By the time the pilot unit came off line on August 28, the pressure drop across these two catalysts had increased to 3.0 in. H_2O (0.75 kPa) and 4.0 in. H_2O (1.0 kPa), respectively. It is apparent that the presence of cemented ash, particularly at the entrance to the first catalyst layer, exacerbated the rapid buildup of fly ash even with sonic horns in operation.

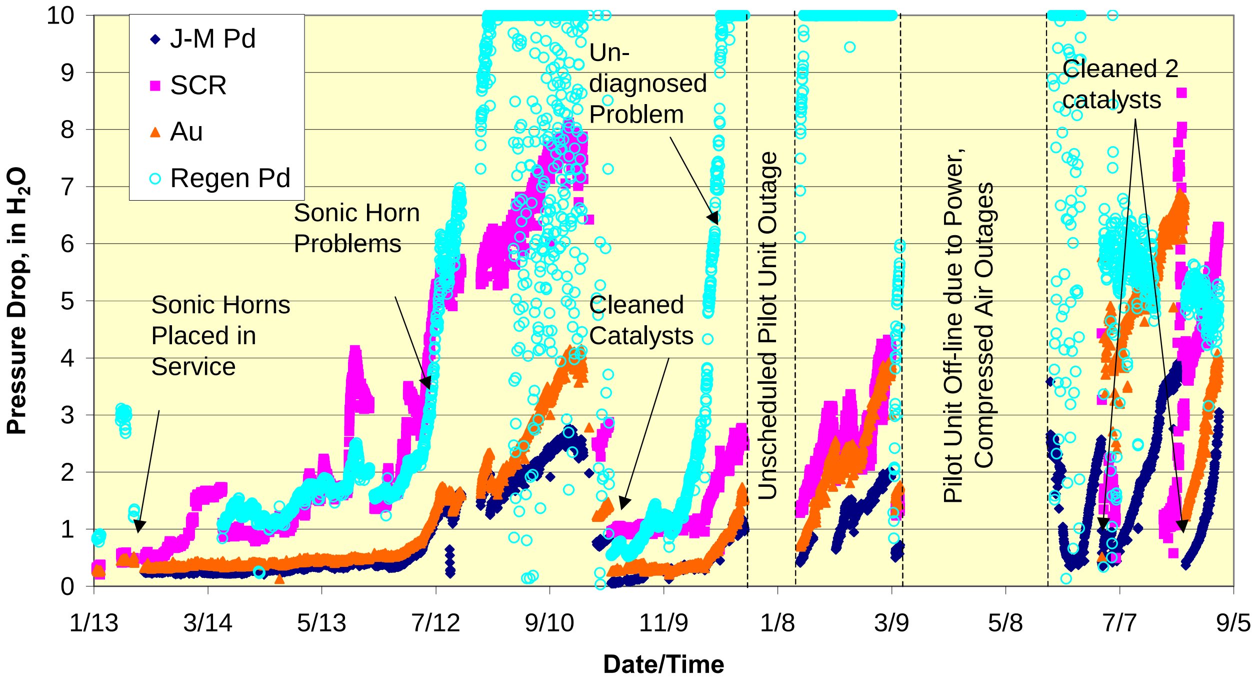


Figure 15. Full-load Catalyst Pressure Drop Data from Monticello Pilot Unit through August 2006

Note: 1.0 in. H_2O = 0.25 kPa

Although the catalyst pressure drop performance was not acceptable over this 19-month test period, the test results were inconclusive. That is, the observed pressure drop increases were generally linked to factors such as sonic horns not cycling properly and unplanned pilot unit outages, where moist flue gas was trapped in the catalyst chambers and allowed to cool. Furthermore, the regenerated Pd #1 had seen nearly 40 months of intermittent operation in two different flue gas matrices, and interaction between the two fly ashes on the catalyst surfaces may have contributed to observed difficulty in cleaning this catalyst with sonic energy. It cannot be determined from these results whether or not with on-site personnel observing and maintaining sonic horn operation as needed on a daily basis, and proper purging of the catalyst on shut down, the observed high pressure drop excursions could have been avoided.

Elemental Mercury Oxidation Activity Performance

The activity of the four catalysts installed in the pilot unit at Monticello Station for oxidizing elemental mercury was measured periodically throughout the 19-months of intermittent operation. The results from each measurement trip are discussed below.

The first measurement trip was conducted the week of January 31, 2005, approximately two weeks after the pilot unit was placed in service. However, an unscheduled unit outage followed by boiler tuning (with widely variable unit load) made it impractical to try to measure catalyst performance that week. Initial activity measurements were delayed until the following week, February 8-10. The results of those measurements are summarized in Table 7.

Table 7. Results of Initial Catalyst Activity Measurements at Monticello, February 8-10, 2005

Sample Location	Hg Concentration, μg/Nm^3 @ 3% O_2*				Total Hg % Oxidation		% Hg Adsorption Across Catalyst*	% Hg Oxidation Across Catalyst
	Catalyst Inlet		Catalyst Outlet**					
	Total Hg	Elemental Hg	Total Hg	Elemental Hg	Catalyst Inlet	Catalyst Outlet**		
Measurements on February 8, 2005								
J-M Pd #1	34.9	16.2	2.4	0.48	53	80	93	***
Measurements on February 9, 2005								
SCR	22.2	9.0	3.0	0.14	59	95	87	***
Gold	22.2	9.0	1.9	0.04	59	98	91	***
Regenerated Pd #1	22.2	9.0	1.8	0.04	59	98	92	***
Measurements on February 10, 2005								
Regenerated Pd #1	22.6	-	3.5	-	-	-	85	-
SCR	22.6	-	1.2	-	-	-	95	-
J-M Pd #1	22.6	-	0.85	-	-	-	96	-
Gold	22.6	-	0.65	-	-	-	97	-

*1 μg/Nm^3 = 0.67 lb Hg/10^{12} Btu heat input
**As explained in the text, Catalyst Outlet location values are suspect due to sampling valve malfunctions
***No oxidation percentage is reported because it is not possible to accurately evaluate catalyst performance with high adsorption of mercury apparent across catalyst

The results showed high apparent levels of mercury adsorption occurring across the catalysts, which meant it was not possible to quantify elemental mercury oxidation across the catalysts. At high adsorption, it is not possible to distinguish whether it is elemental mercury adsorption or oxidation that accounts for the lowered outlet elemental mercury concentrations. However, these high mercury adsorption percentages are suspect. The numbers in the table are all reported after being corrected to a 3%-oxygen (O_2) flue gas basis. The actual oxygen concentrations measured in the sample gas were approximately 7 to 8% at the pilot unit inlet and 11 to 12% at the outlet. While it is possible to correct for air in-leakage into the flue gas and/or sample gas based on measured oxygen concentrations, the accuracy of the corrections become questionable when a large correction of 3 to 4 percentage points must be made.

The next sampling trip was conducted one month later, March 8 and 9. At the beginning of this trip, time was spent investigating the high levels of in-leakage into the flue gas and/or sample gas across the catalyst pilot unit. The problem was traced to new air-operated solenoid valves used to select which catalyst outlet sample is sent to the inertial gas separator (IGS) filter and sample conditioning impingers in the mercury SCEM. The air pressure to the valves was not adequate to allow the sample valves to fully open, meaning a high vacuum level was established in the sample gas. This apparently led to higher-than-normal air in-leakage into the sample gas. When the air supply pressure to the valve operators was increased, the valves fully opened and the measured air in-leakage across the catalyst pilot unit and/or sample delivery system decreased to only a few tenths of a percent of oxygen concentration. After discovering and correcting this issue, it remains impossible to tell with certainty whether the high mercury adsorption levels seen in February were actually occurring, or represented a measurement error due to the sample valves not being fully opened.

The results of measurements made after the sample valve operator air pressure was increased are summarized in Table 8. The results showed the gold catalyst to be the most active, with 93% oxidation seen on March 8 when full measurements (total and elemental mercury) were taken, and 91% on March 9 when only elemental mercury concentrations were measured across the catalyst. The Johnson Matthey Pd #1 was the next most active, with 76% oxidation seen on March 8 but only 66% the following day. The performance of the regenerated Pd #1 was almost identical to the fresh material, with 74% being measured. This lies between the two measurements made for the fresh material. The SCR catalyst was the least active, showing 59% oxidation.

Table 8. Results of Catalyst Activity Measurements at Monticello, March 8-9, 2005

Sample Location	Hg Concentration, $\mu g/Nm^3$ @ 3% O_2*				Total Hg % Oxidation		% Hg Adsorption Across Catalyst	% Hg Oxidation Across Catalyst
	Catalyst Inlet		Catalyst Outlet					
	Total Hg	Elemental Hg	Total Hg	Elemental Hg	Catalyst Inlet	Catalyst Outlet		
Measurements on March 8, 2005								
J-M Pd #1	22.8	10.2	19.1	2.4	55	87	16	76
Gold Outlet	21.3	10.2	19.0	0.7	52	96	11	93
Measurements on March 9, 2005								
J-M Pd #1	-	8.9	-	3.1	-	-	-	66
SCR Outlet	19.0	8.6	17.7	3.5	55	80	6	59
Gold	-	8.9	-	0.8	-	-	-	91
Regenerated Pd #1	18.5	8.9	14.3	2.3	52	84	23	74

*1 $\mu g/Nm^3$ = 0.67 lb Hg/10^{12} Btu heat input

However, the performance of the SCR catalyst and possibly the regenerated Pd #1 may have been adversely affected by fly ash buildup, as indicated by the pressure drop across these two catalyst beds. This issue was discussed in the previous subsection. The average process conditions during the tests on March 8 and 9 are summarized in Table 9.

Table 9. Average Catalyst Conditions During March 2005 Activity Measurements

Catalyst	Flue Gas Flow Rate, acfm (m^3/h)	Catalyst Pressure Drop, in. H_2O (kPa)	Catalyst Temperature, °F (°C) [Location]
J-M Pd #1	1998 (3396)	0.27 (0.067)	283 (139) [outlet]
SCR	1833 (3116)	1.62 (0.404)	282 (139) [outlet]
Gold	2055 (3493)	0.43 (0.107)	293 (145) [outlet]
Regenerated Pd #1	1915 (3255)	1.63 (0.406)	287 (142) [outlet]
Catalyst Pilot Inlet	-	-	301 (149) [inlet]

The results for the SCR catalyst and Johnson Matthey Pd #1 showed lower oxidation percentages than were expected based on previous laboratory catalyst evaluation results. Both were expected to achieve approximately 90% elemental mercury oxidation at the area velocities at which they were being operated. The gold catalyst performance was closest to what was expected (93% versus a laboratory value of >95%). However, these catalysts had been in flue gas service for nearly two months when the field performance values were measured in March, and all were perhaps adversely affected by activity loss and/or fly ash buildup.

Also, in previous catalyst testing at Coal Creek as part of the 41185 cooperative agreement, an Argillon SCR catalyst showed significantly lower initial activity for elemental mercury oxidation than was expected based on laboratory results.[1] Thus, for an SCR-type catalyst there were previous data which showed lower performance in actual flue gas than in simulated flue gas.

The activity of these four catalysts was measured again in early April, coincident with pilot wet FGD tests conducted downstream of each catalyst. However, an unscheduled unit outage delayed the completion of this testing until the week of April 18th. The results of the April 2005 measurements are summarized in Table 10. The pilot wet FGD system was operated for two days downstream of each catalyst, so average elemental mercury oxidation data are shown for two days for each catalyst in the table. The pilot wet FGD mercury removal results are discussed in a separate subsection later in this report.

Since pilot wet FGD tests were also being conducted at the same time these measurements were made, of the two Hg SCEMs used to support these measurements, one was used to monitor the catalyst inlet and outlet locations while the second was used to monitor the FGD outlet. The first monitor was cycled to collect mercury oxidation values and FGD inlet concentration data. This second objective related to pilot wet FGD operation meant that the Hg SCEM cycling between catalyst inlet and outlet sample locations and between quantifying elemental versus total mercury concentrations was not always optimal for determining catalyst performance. Furthermore, because the Monticello Unit 3 boiler fires a blend of PRB and Texas lignite, the total mercury concentration and mercury oxidation at the ESP outlet (catalyst inlet) location can vary significantly with time. Evidence if this variability is seen in the average percent mercury oxidation in the catalyst inlet flue gas which varied significantly, from 31% to 59%. These two effects led to scatter in the comparisons of total mercury and elemental mercury concentrations as shown in the table, which represent arithmetic averages of all valid data points collected during each measurement day.

Table 10. Results of Catalyst Activity Measurements at Monticello, April 2005 (all values represent daily averages)

Sample Location (Sampling Date)	Hg Concentration, μg/Nm^3 @ 3% O_2*				Total Hg % Oxidation		% Hg Adsorption Across Catalyst	% Hg Oxidation Across Catalyst
	Catalyst Inlet		Catalyst Outlet					
	Total Hg	Elemental Hg	Total Hg	Elemental Hg	Catalyst Inlet	Catalyst Outlet		
SCR (4/6)	30.8	21.3	30.6	9.9	31	68	1	54
SCR (4/7)	29.7	15.5	23.1	11.0	48	52	22	29
Regenerated Pd #1 (4/8)	29.2	20.1	22.0	7.8	31	64	25	61
Regenerated Pd #1 (4/9)	32.9	21.5	31.6	5.0	35	84	4	77
J-M Pd #1 (4/10)	30.3	17.1	22.7	7.6	44	67	25	55
J-M Pd #1 (4/18)	28.6	13.4	28.8	7.9	53	73	-1	41
Gold (4/19)	34.3	13.9	30.7	1.22	59	96	11	91
Gold (4/20)	33.3	21.4	31.7	1.50	36	95	5	93

*1 μg/Nm^3 @ 3% O_2 = 0.67 lb Hg/10^{12} Btu heat input

The last two columns in the table, the percentage total mercury adsorption observed across the catalyst and the percentage elemental mercury oxidation across the catalyst, vary significantly from day to day for all but the gold catalyst. It is believed that this variability is due to uncertainty in quantifying the averages shown rather than variations in actual catalyst performance. For the gold catalyst, the relatively low apparent total mercury adsorption shown in the table is most likely due to a more stable lignite/PRB blend percentage during these measurements than on the previous days. The good agreement seen between the daily percent oxidation values seen for the gold is also likely due to a more stable fuel blend, and the fact that the gold was measured to be the most active catalyst (i.e., inlet mercury concentrations have less effect on the calculated oxidation percentage when the actual percentage is greater than 90%).

The results showed the gold catalyst to be the most active, with 91% to 93% oxidation seen on the two measurement days. These values were identical to the percentages measured on two days in early March. The regenerated Pd #1 was the next most active, with 61% to 77% oxidation measured for the two days. The performance of the regenerated Pd #1 was significantly better than that of the fresh material from Johnson Matthey, which showed 41% to 55% oxidation. The SCR catalyst was apparently the least active catalyst, measuring only 29% to 54% elemental mercury oxidation across it.

The difference between the apparent activity of the regenerated Pd #1 and the fresher, Johnson Matthey catalyst may be partially due to the different geometries of the two. The regenerated Pd #1 was installed as three 3-in. (7.6-cm) layers, while the Johnson Matthey Pd #1 was installed as a single 9-in. (23-cm) layer. While the latter is advantageous with respect to ease of installation, particularly for future full-scale installations, it is disadvantageous for mass transfer (diffusion of mercury to the catalyst geometric surface and into the catalyst pores to be oxidized). These catalysts operate with laminar flow within each cell, which is less desirable than turbulent flow for mass transfer. Between each layer, the flow is turbulent because the effective diameter of the flow channel is several hundred times that of an individual cell. The resulting mixing between layers can improve overall mass transfer. URS' laminar flow diffusion model was used to quantify the expected performance difference between three 3-in. (7.6-cm) layers and one 9-in. (23-cm) layer. The model results show that within the range of measured performance for the regenerated Pd #1 catalyst, a change in geometry from three 3-in. (7.6-cm) layers to one 9-in. (23-cm) layer would be expected to lower the oxidation across the catalyst by about 5 percentage points.

The OH method was employed to conduct relative accuracy tests to validate the Hg SCEM results from April 2005. The OH measurements were made by simultaneously sampling the oxidation catalyst pilot unit inlet, catalyst outlet, and wet FGD pilot unit outlet flue gas during the second day of the two-day wet FGD pilot tests conducted downstream of each catalyst. OH measurements were also conducted during baseline (no catalyst) wet FGD pilot tests. OH results related to pilot wet FGD performance are presented later in this section. Table 11 summarizes the results of the relative accuracy tests conducted across the oxidation catalysts.

Table 11. April 2005 OH Relative Accuracy Results for Monticello Pilot (mean and 95% confidence intervals of three runs compared to simultaneous Hg SCEM results)

	Total*	Elemental*	Oxidized*
SCR Catalyst, April 7, 2005:			
Catalyst Inlet – OH, μg/Nm^3*	20.2 ± 4.8	10.9 ± 4.1	9.3 ± 1.1
Catalyst Inlet - SCEM, μg/Nm^3	29.7 ± 2.6	15.5 ± 0.3	14.2 (± 2.3 est.)
Relative Accuracy, % (based on means)	147	142	153
Catalyst Outlet – OH, μg/Nm^3	27.1 ± 1.5	2.4 ± 0.6	24.7 ± 1.0
Catalyst Outlet - SCEM, μg/Nm^3	23.1 ± 3.7	11.0 ± 0.9	12.1 (± 2.8 est.)
Relative Accuracy, % (based on means)	85	460	49
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	78	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	29	-
Regenerated Pd #1, April 9, 2005:			
Catalyst Inlet - OH, μg/Nm^3	17.4 ± 6.3	10.3 ± 6.5	7.1 ± 0.2
Catalyst Inlet - SCEM, μg/Nm^3	32.9 ± 2.1	21.5 ± 2.2	11.4 (± 0.1 est.)
Relative Accuracy, % (based on means)	189	209	160
Catalyst Outlet – OH, μg/Nm^3	23.7 ± 4.0	2.2 ± 0.9	21.5 ± 4.3
Catalyst Outlet - SCEM, μg/Nm^3	31.6 ± 1.7	5.0 ± 0.3	26.6 (± 1.4 est.)
Relative Accuracy, % (based on means)	133	230	124

	Total*	Elemental*	Oxidized*
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	79	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	77	-
Johnson Matthey Pd #1, April 18, 2005:			
Catalyst Inlet – OH, μg/Nm^3	22.2 ± 1.7	16.1 ± 0.9	6.1 ± 0.8
Catalyst Inlet - SCEM, μg/Nm^3	28.6 ± 1.9	13.4 ± 0.6	15.2 (± 1.3 est.)
Relative Accuracy, % (based on means)	129	83	250
Catalyst Outlet – OH, μg/Nm^3	21.1 ± 2.1	2.7 ± 0.3	18.4 ± 1.9
Catalyst Outlet - SCEM, μg/Nm^3	28.8 ± 2.4	7.9 ± 1.9	20.9 (± 0.5 est.)
Relative Accuracy, % (based on means)	136	290	114
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	83	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	41	-
Gold Catalyst, April 20, 2005:			
Catalyst Inlet – OH, μg/Nm^3	30.8 ± 1.7	19.4 ± 0.1	11.4 ± 1.8
Catalyst Inlet - SCEM, μg/Nm^3	33.3 ± 1.7	21.4 ± 2.9	11.9 (± 1.2 est.)
Relative Accuracy, % (based on means)	108	110	104
Catalyst Outlet – OH, μg/Nm^3	29.4 ± 2.8	1.10 ± 0.28	28.3 ± 2.6
Catalyst Outlet - SCEM, μg/Nm^3	31.7 ± 1.9	1.50 ± 0.32	30.2 (± 1.6 est.)
Relative Accuracy, % (based on means)	108	136	107
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	94	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	93	-

*****Note – All concentrations corrected to 3% O_2, dry basis; 1 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

As was reported previously in Table 10, the flue gas total and elemental mercury concentrations varied considerably from day to day, more so in the OH results than in the SCEM results. As measured by the OH method, the catalyst pilot unit inlet total mercury concentrations varied from 17 to 31 μg/Nm^3 (correct to 3% O_2), a factor of nearly two, while the inlet elemental mercury concentrations varied by nearly a factor of two, from 10 to 19 μg/Nm^3.

Because of the observed variability in concentrations, the table shows the mean value for three OH runs as well as the 95% confidence interval about the mean. The magnitude of the 95% confidence interval can be compared to the mean value to provide a measure of the variability of the measurements. The larger the 95% confidence interval relative to the mean value, the more variable were the measurement results. This variability could be due to changes in the actual flue gas concentrations over time, variability within the measurement methods, or both.

Since the Hg SCEM measurements were made with only one analyzer, this meant that four measurements had to be made (catalyst inlet and outlet, total and elemental mercury) while the two OH trains (catalyst inlet and outlet) completed each of three runs. Thus, the Hg SCEM data for each of the four measurements represent a total of one to two hours of data collected during the daily OH run period (approximately 8 hours) while the OH results represent integrated samples collected over three 2-hr runs. With the observed variability in total mercury concentration and speciation in the catalyst inlet flue gas at Monticello, it is possible that much of any disagreement between the OH and SCEM results can be due to differences in averaging time periods for the two methods.

Also shown are 95% confidence interval values for the Hg SCEM data. For the total and elemental mercury concentrations, the mean values were calculated from a number of short-term average measurements (e.g., 10 to 20 measurements of 3- to 4-minute averages) whereas the OH data each represent three 2-hr-average measurements. Oxidized mercury concentrations are measured by the difference between total and elemental mercury with the Hg SCEM, and one SCEM was used to measure both the catalyst inlet and catalyst outlet locations. This meant the oxidized mercury concentrations could only be calculated from averages, not from individual data points. Thus, 95% confidence intervals cannot be calculated directly for oxidized mercury concentrations from the SCEM data. In Table 11, 95% confidence intervals were estimated from the 95% confidence intervals of the total and elemental mercury concentration data used to calculate the mean oxidized mercury concentrations.

Comparing the OH method results to Hg SCEM results, the SCEM values for total mercury at the catalyst inlet were higher than the OH results for all four test days. As mentioned above, at least part of this discrepancy may be due to differences in averaging periods between the two methods. The high 95% confidence intervals for the means, particularly for April 7 (SCR catalyst) and April 9 (regenerated Pd #1 catalyst) indicate that the concentrations were quite variable over those measurement days. On April 18 (Johnson Matthey Pd #1) and April 20 (gold), the 95% confidence intervals were lower, and the relative accuracies between the two methods are better (closer to 100%).

For the catalyst outlet total mercury concentrations, the relative accuracies between the two methods are a somewhat better than at the inlet for April 7 and 9, and similar to those at the inlet for April 18 and 20.

For elemental mercury concentrations, the catalyst inlet results for April 7 (SCR catalyst) and April 9 (regenerated Pd #1 catalyst) again show poorer agreement between the two methods than the results for April 18 (Johnson Matthey Pd #1) and April 20 (gold). This is particularly true for April 9, where the SCEM mean was over twice the mean from the OH measurements, although both means showed high 95% confidence intervals that may have contributed to the discrepancy. At the catalyst outlet, the elemental mercury concentration measurements by the SCEM are significantly higher than were measured by the OH method for all but the April 20 (gold) results, with relative accuracies for the other three catalysts ranging from 230% to 460%. For the SCR catalyst and Johnson Matthey Pd catalyst #1, this discrepancy meant that the OH results showed significantly higher elemental mercury oxidation across those catalysts than the SCEM results. For the regenerated Pd #1 catalyst, the poor relative accuracy also measured for the inlet elemental mercury concentration (209%), as mentioned above, meant the percent oxidation measured across that catalyst by the two methods was similar.

The OH results suggest that the oxidation performance of three of the four catalysts in April 2005 was similar, ranging from 78% to 83% elemental mercury oxidation, with only the gold showing significantly better performance (94%). This is quite a contrast with the SCEM results, which show a marked loss in activity for the SCR and Johnson Matthey Pd #1 catalysts compared to the other two.

Previous results from Coal Creek[1] showed a similar discrepancy between the results by OH and by SCEM for the SCR catalyst tested there, but good agreement between the methods with the Pd #1 catalyst (the regenerated catalyst being tested at Monticello). At Coal Creek it was thought that the OH method results that were biased low (for catalyst outlet elemental concentration) rather than the SCEM results being biased high. However, as discussed later in this report for the wet FGD pilot test results, these Monticello data call into question the SCEM rather than the OH results.

It remains unclear what would cause the elemental mercury concentrations measured by SCEM to be biased high at the catalyst outlet location. It is possible that an oxidized mercury species is formed across the catalysts that captures at a different efficiency in the OH impinger train than in the SCEM train, and that the species formed may vary with catalyst type.

The next time catalyst oxidation performance was measured was June 15-17, 2005. These results are summarized in Table 12.

Table 12. Results of Catalyst Activity Measurements at Monticello, June 2005

	Hg Concentration, $\mu g/Nm^3$ @ 3% O_2*				Total Hg % Oxidation			
	Catalyst Inlet		Catalyst Outlet					
Sample Location	Total Hg	Elemental Hg	Total Hg	Elemental Hg	Catalyst Inlet	Catalyst Outlet	% Hg Adsorption Across Catalyst	% Hg Oxidation Across Catalyst
Measurements on June 16, 2005:								
J-M Pd #1	22.6	10.1	24.6	5.4	56	78	-9	46
SCR	35.8	15.4	34.1	10.6	57	69	5	31
Regen. Pd	35.2	14.7	36.9	5.7	58	84	-5	61
Measurements on June 17, 2005:								
Gold	34.8	12.9	36.2	2.0	63	94	-4	84

*1 $\mu g/Nm^3$ @3% O_2 = 0.67 lb Hg/10^{12} Btu heat input

The measured oxidation across all four catalysts dropped from April to June, indicating a loss of activity with time in service in this flue gas, although this may have been exacerbated by fly ash buildup. The gold dropped from greater than 90% to 84% oxidation, while the SCR catalyst dropped from as high as 54% in April down to 31% in June. The performance of the SCR catalyst and possibly the regenerated Pd #1 may have particularly been affected by fly ash buildup, as indicated by the elevated pressure drop across these two catalyst beds. This issue was discussed above. The Johnson Matthey Pd #1 and gold were apparently relatively clean, as evidenced by the pressure drop values of approximately 0.5 in. H_2O (0.12 kPa) or less for these two catalysts, and were less likely to have been impacted by fly ash buildup.

The catalyst activity data are plotted versus time since startup in Figure 16. The figure is illustrated to show linear trends for activity loss versus time for each of the four catalyst types, extrapolated back to the time they were initially placed in operation. Although there is quite a bit of scatter in the data for all but the gold catalyst, results over the first five months of operation show the expected near-linear decrease in activity versus time.

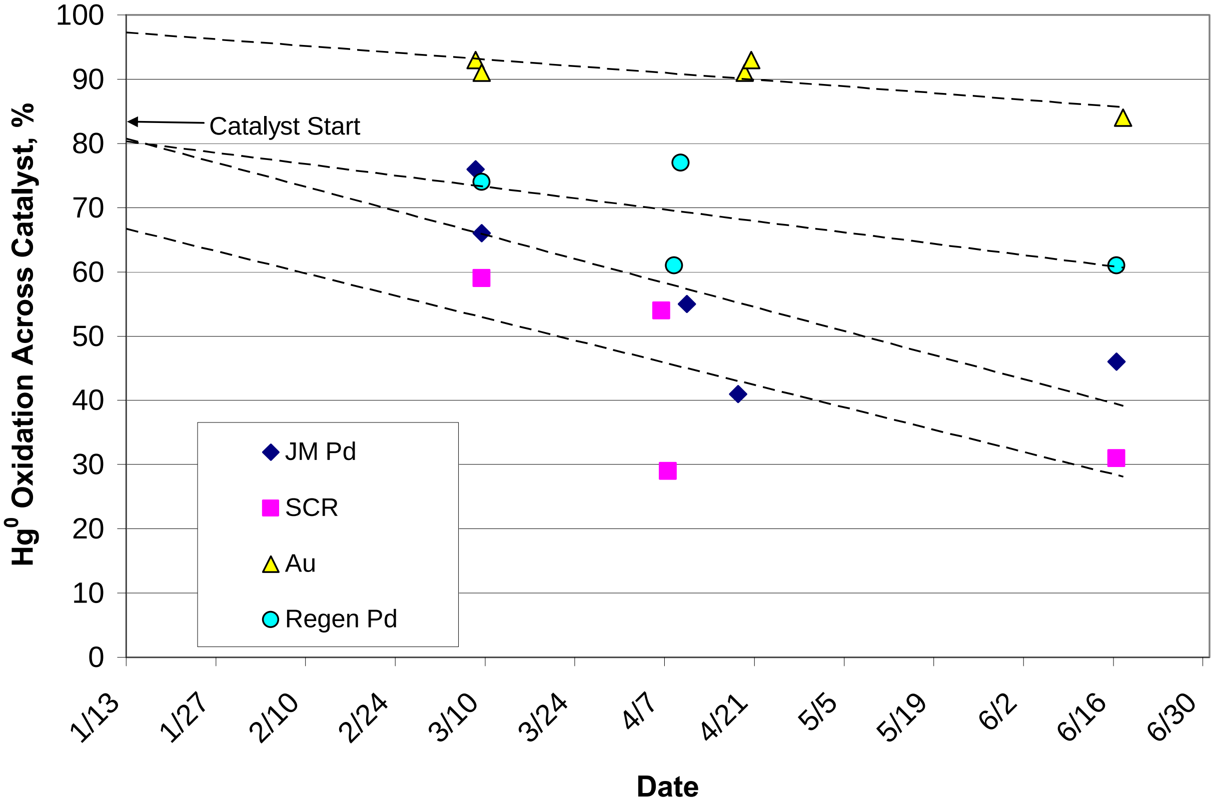


Figure 16. Elemental Mercury Oxidation Activity versus Time for Catalysts at Monticello

The activity of these four catalysts for oxidizing elemental mercury was next measured in mid-July 2005. The results of these measurements are shown in Table 13. Most of the total mercury concentration data were measured on the first day, and elemental mercury concentrations were measured the second. Thus, mercury breakthrough/adsorption data across the catalysts are typically available only for the first measurement day, while mercury oxidation data across the catalysts are typically only available for the second measurement day. The results show a significant decline in mercury oxidation activity across all four catalysts since the June measurements.

Table 13. Results of Catalyst Activity Measurements at Monticello, July 2005 (all values represent daily averages)

Sample Location (Sampling Date)	Hg Concentration, μg/Nm^3 @ 3% O$_2$*				Total Hg % Oxidation		% Hg Adsorption Across Catalyst	% Hg Oxidation Across Catalyst
	Catalyst Inlet		Catalyst Outlet					
	Total Hg	Elemental Hg	Total Hg	Elemental Hg	Catalyst Inlet	Catalyst Outlet		
SCR (7/19)	31.1	-	28.5	-	-	-	8	-
SCR (7/20)	-	5.23	-	5.49	-	-	-	-5
J-M Pd #1 (7/19)	30.9	12.4	29.1	9.24	60	68	6	26
J-M Pd #1 (7/20)	-	5.26	-	5.27	-	-	-	0
Regenerated Pd #1 (7/19)	29.9	-	25.9	-	-	-	13	-
Regenerated Pd #1 (7/20)	-	7.05	-	3.80	-	-	-	46
Gold (7/19)	34.9	-	31.4	-	-	-	10	-
Gold (7/20)	11.0	4.03	-	1.19	63	89	-	70

*1 μg/Nm^3 @ 3% O$_2$ = 0.67 lb Hg/10^{12} Btu heat input

The decline was most evident for the SCR and Johnson Matthey Pd #1 catalysts. These two catalysts were also measured to be the least active, at 26% or less oxidation of elemental mercury. However, it was known that as of mid-July a considerable amount of fly ash had built up in these catalysts due to sonic horn operation issues described earlier in this section. Also, as discussed above there is evidence that the Hg SCEM used to quantify catalyst oxidation performance tended to under-report the performance of the SCR and Johnson-Matthey Pd catalysts compared to OH method results.

The elemental mercury oxidation activity of these four catalysts was measured again in late October 2005, after the catalysts had been manually cleaned of fly ash buildup. The results of these measurements are shown in Table 14. The results show a significant improvement in mercury oxidation activity across all four of the catalysts when compared to the previous measurements. This is most likely because in the previous measurements, fly ash buildup reduced the effective surface area available for mercury oxidation catalysis. This improvement in activity is also illustrated graphically in Figure 17.

Table 14. Results of Catalyst Activity Measurements at Monticello, October 24-25, 2005

Catalyst Type	Catalyst Inlet Total Hg*, µg/Nm^3	Catalyst Inlet Elemental Hg*, µg/Nm^3	Catalyst Inlet Oxidation %	Catalyst Outlet Total Hg*, µg/Nm^3	Catalyst Outlet Elemental Hg*, µg/Nm^3	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst, %	Catalyst Outlet Oxidation, %
J-M Pd #1 (10/24)	15.8	7.29	54	13.6	2.81	14	61	79
SCR (10/25)	19.8	12.7	36	17.0	6.96	14	45	59
Gold (10/25)	18.1	10.3	43	12.4	2.00	31	80	84
Regen. Pd #1 (10/25)	16.3	9.8	40	14.1	1.86	14	81	87

*1 µg/Nm^3 @ 3% O_2 = 0.67 lb Hg/10^{12} Btu heat input

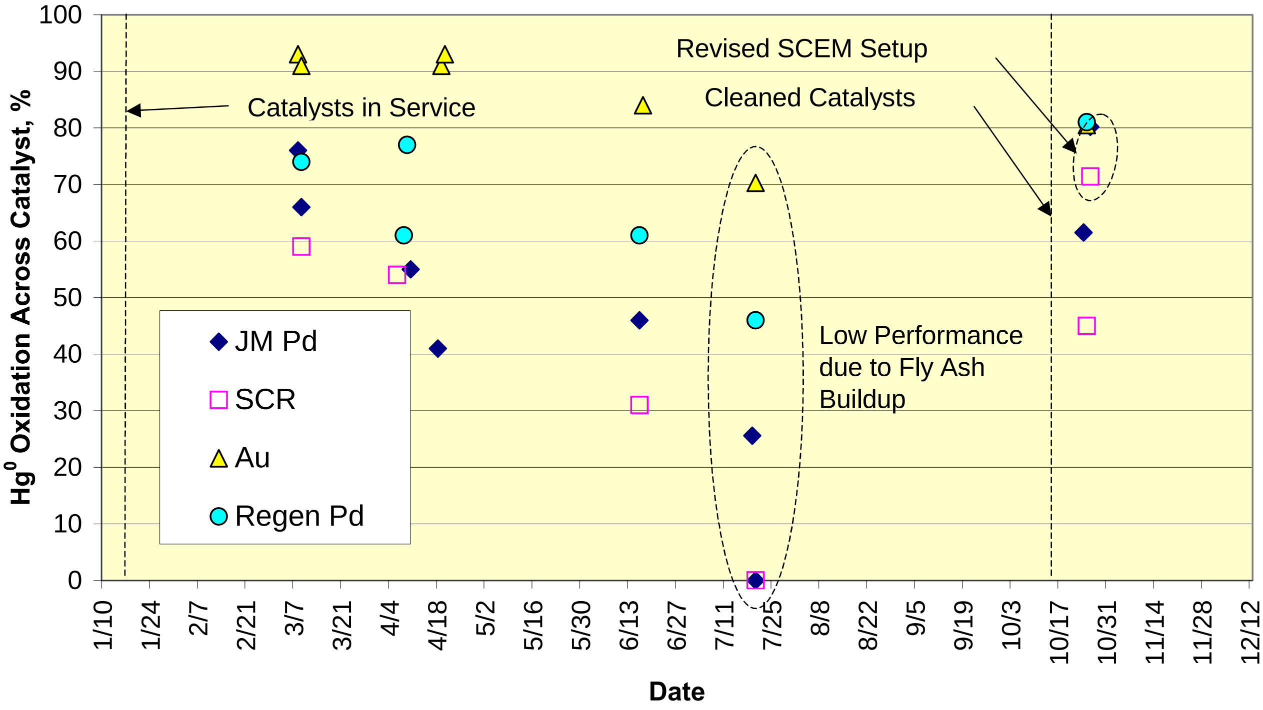


Figure 17. Elemental Mercury Oxidation Activity versus Time for Catalysts at Monticello

The figure shows that the fly ash cleanup appears to have restored much of the activity loss seen over the previous three to six months. Compared to the first activity measurements for these catalysts in March 2005, the Johnson Matthey Pd #1, SCR, and gold catalyst activity values were 10 to 15 percentage points below their original values, while the regenerated Pd was actually measured to be performing better than in March. The latter was possibly due to the fact that the regenerated Pd was not previously cleaned of the fly ash buildup remaining after nearly 21 months of operation at Coal Creek as part of Cooperative Agreement 41185. The physical cleaning in October most likely removed much of the previous fly ash buildup.

The observation that the catalysts retained much of their initial activity after cleaning the fly ash buildup was considered encouraging from two perspectives. One was that if fly ash buildup does occur, it appeared that a simple physical removal of the ash could restore catalyst activity. The second was that the catalyst activity loss rate in this Texas lignite/PRB blend flue gas was lower than appeared in the earlier data, which reflected impacts of fly ash buildup.

Figure 17 includes additional data points for the Johnson Matthey Pd #1 and SCR catalysts, noted with "Revised SCEM Setup," that show greater elemental mercury oxidation performance than was reported above in Table 14. As mentioned above, there was evidence that the Hg SCEM system used to quantify catalyst oxidation performance tended to under-report the performance of the Johnson Matthey Pd #1 and SCR catalysts compared to OH method results. It was suspected that this bias contributed to the lower activity being measured for those two catalyst types. On October 26th, after conducting the routine catalyst activity measurements reported above in Table 14, additional screening tests were conducted downstream of these two catalysts in an attempt to isolate differences between the OH and SCEM measurement trains. One difference between the two methods is how they collect a particulate-free sample. The OH method accomplishes this by pulling the sample gas across a heated (250°F [121°C]) EPA Method 5 filter upstream of the measurement impingers. A potential problem with this filtration method is that in a particulate laden flue gas, the fly ash that collects on the filter during the sampling event could adsorb and/or oxidize the mercury content of the sample gas. In the relatively low particulate loading flue gas downstream of a high-efficiency ESP (such as at the catalyst inlet or outlet locations at Monticello), this potential bias should not be significant, though.

The Hg SCEM used in this project attempts to address this potential bias by using an IGS filter to separate a particulate-free sample gas stream from a larger flow of particulate-laden gas. The particulate-laden gas is drawn through tubing at high velocity with a downstream blower and the sample gas is withdrawn radially, at very low velocity, across a fritted section of the tubing. The concept is that particulate matter in the gas stream will remain with the high-velocity gas stream and not be drawn radially to the frit surface with the small sample gas flow. Thus, the sample gas is not pulled across a layer of collected fly ash, and mercury adsorption or oxidation should be minimized. Again, in the relatively low particulate loading flue gas downstream of a high-efficiency ESP (such as at the catalyst inlet and outlet locations at Monticello), this precaution may not be important.

The IGS filter used on this pilot unit is hard-piped into a sample acquisition system, where stainless steel valves and piping are used to select the sampling location (catalyst inlet, or outlet of any of the four catalyst chambers) and connect that location to the IGS filter inlet. It is possible that, over time, something had built up in this piping or on the IGS filter itself that was reducing oxidized mercury, particularly for the Johnson Matthey Pd #1 and SCR catalysts (although oxidation seems more likely than reduction at these flue gas conditions). These two catalysts were in the lower two boxes in the catalyst pilot unit, and shared a short run of piping that the sample gas from the other three locations did not flow through. It is possible that a problem in this run of piping could affect measurements only for those two catalysts. Also, a clean IGS filter was installed on the pilot unit just before these measurements began. This made biases due to solids buildup on the IGS filter unlikely.

Another difference was in the impinger trains used by the two methods. The OH method uses three KCl impingers in series to collect oxidized mercury, followed by a nitric acid/peroxide impinger and three permanganate/sulfuric acid impingers to collect elemental mercury. These impinger solutions are analyzed for mercury concentration to determine the concentrations of oxidized and elemental mercury in the flue gas sampled. The sampling rate is about 14 L/min, and modified Greenburg-Smith impingers are used.

With the Hg SCEM system, when sampling for elemental mercury concentrations (to determine catalyst activity), two 200 mL "smog bubblers" containing KCl are used to remove the oxidized mercury content of the sample gas, and the sample gas containing all of the remaining mercury is subsequently passed through downstream carbonate buffer and sodium hydroxide bubblers, in which elemental mercury is relatively insoluble, to remove acid gases from the sample gas. The clean sample gas containing only elemental mercury then flows across a gold surface. The mercury adsorbs on the gold and is thermally desorbed, with the amount quantified by cold vapor atomic absorption. The sampling rate is about 1 L/min.

It is possible that the two smog bubblers containing KCl did not quantitatively remove the oxidized mercury, which could cause the remaining oxidized mercury to be measured as elemental mercury and understate catalyst oxidation performance. It is not obvious why this potential bias would affect two catalysts (Johnson Matthey Pd #1 and SCR) and not the other two (gold and regenerated Pd). A possible explanation is that the first two form a different oxidized mercury species than the second two, which is more difficult to collect in a KCl solution. This seems unlikely, though, since one Pd #1 catalyst appeared to be affected and the other did not, and one would assume the two Pd #1 catalysts promote formation of the same oxidized mercury species. Also, it should be noted that in anticipation of oxidized mercury capture in the smog bubblers being an issue, three rather than two KCl smog bubblers in series were used for the measurements reported in Table 14.

To screen for the effects of these possible biases between the methods, additional Hg SCEM tests were conducted for the Johnson Matthey Pd and SCR catalysts on October 26, with changes made to more closely mimic the sample conditioning system in the OH method. The changes included using a heated Method 5 filter instead of the IGS filter to collect the sample gas, and using three KCl "midget impingers" in series to collect oxidized mercury when sampling for elemental mercury concentrations. The midget impingers are more similar in geometry to those used in the OH method than the smog bubblers normally used for the Hg SCEM. Because the two methods sample at much different rates (14 L/min versus 1 L/min) it would not be appropriate to use the much larger Greenburg-Smith impingers in the SCEM method. Also, the heated Method 5 filter drew flue gas from a duct port downstream of the piping to the IGS filter, so this represented a completely different sample delivery system than was normally used with the IGS (i.e., no common piping). Sampling was conducted over a range of flow rates, to see if the sample flow rate significantly changed the measured value. Flow rate sensitivity could particularly indicate an impinger collection efficiency issue.

Results from this testing are summarized in Table 15, and were included in Figure 17 as noted above. The results show that the change to the Method 5 filter setup and three KCl midget impingers resulted in the measurement of higher catalyst performance than was measured the days before with the standard Hg SCEM sample conditioning system (although with three smog bubblers containing KCl). For the Johnson Matthey Pd #1 catalyst the apparent oxidation across the catalyst was 61% with the standard setup and 80% with the revised setup. For the SCR catalyst it was 45% shown in Table 15 versus 71% with the revised setup. The oxidation percentages across the catalysts shown in the table are based on inlet elemental mercury concentrations measured at the Unit 3 ESP outlet (the same gas stream as going to the oxidation catalyst pilot unit) by Hg SCEM as part of another project. Although sampling rate was a variable, the outlet concentration data at the 1.5 L/min flow rate were used for the figure.

Table 15. Results of Hg SCEM Tests Conducted October 2005 to Screen for Sample Conditioning Biases

Catalyst Type	ESP Outlet Elemental Hg, μg/Nm^3	M5 Box and Heated Probe Mercury Measurements, with Mini-impinger Setup*, μg/Nm^3 of Hg^0				Apparent Oxidation Across Catalyst**, %
		0.5 L/min	1.0 L/min	1.5 L/min	1.9 L/min	
J-M Pd #1	10.4	1.8	2.6	2.1	2.1	80
SCR	12.3	3.1	-	3.5	3.4	71

*Three KCl impingers followed by two carbonate buffer impingers and one NaOH impinger
**Based on 1.5 L/min flow rate data

These results suggested there was a bias caused by the IGS filter setup and/or by the impinger train used for the normal Hg SCEM measurements, at least for the Johnson Matthey Pd #1 and SCR catalysts. These results could not be used to elucidate the true cause of the bias, though. There was no clear flow rate effect shown in these results, though, as the variation in results from flow rate to flow rate could be considered as typical temporal variation.

An additional set of measurements was made at the end of the day downstream of the SCR catalyst in an attempt to separate the filter effect from the impinger effect. These measurements were made using the normal IGS filter setup rather than the Method 5 filter setup, but with the three KCl midget impingers rather than the three smog bubbler impingers used to collect the data in Table 14. These data showed 4.7 μg/Nm^3 of Hg^0 (corresponding with 61% oxidation across catalyst) at a sampling rate of 0.5 L/min and 6.1 μg/Nm^3 (50% oxidation) at a sampling rate of 1.0 L/min. These values lie between the values measured for the SCR catalyst with the conventional method and those measured with both the filter and impingers changed, and show a sampling rate effect.

This suggests that there was both a filter and an impinger component to the apparent measurement bias. However, this was a very limited amount of data, so it was difficult to draw any conclusions, particularly given the variability of flue gas mercury concentration and oxidation percentage conditions at Monticello. Ultimately, OH method measurements were used as a benchmark to confirm the activity of these catalysts.

Based on test results shown later in this section for pilot catalyst tests conducted at Coronado Station, a third, more likely possibility for the apparent measurement bias for these two catalysts has been identified: sample gas stratification at the catalyst chamber outlet. This potential bias is explained in detail in the subsection for Coronado Station results.

Because of restricted access to the Monticello oxidation catalyst pilot unit during plant construction in the first half of 2006, the elemental mercury oxidation activity of the four catalysts was not measured again until the last week of June 2006, after the regenerated Pd #1 and SCR catalysts had been manually cleaned of fly ash buildup. The results of these measurements are summarized in Table 16.

Table 16. Results of Catalyst Activity Measurements at Monticello, June 28-30, 2006

Catalyst Type	Catalyst Inlet Total Hg*, μg/Nm^3	Catalyst Inlet Elemental Hg*, μg/Nm^3	Catalyst Inlet Oxidation %	Catalyst Outlet Total Hg*, μg/Nm^3	Catalyst Outlet Elemental Hg*, μg/Nm^3	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst, %	Catalyst Outlet Oxidation, %
JM Pd #1	13.4	6.2	54	14.4	5.5	-7%	11	62
SCR	11.5	6.2	47	17.2	4.2	-45%	33	72
Gold	14.5	6.1	58	14.2	3.9	2%	36	72
Regen. Pd #1	15.1	5.0	67	11.3	2.1	25%	57	81

*1 μg/Nm^3 @ 3% O_2 = 0.67 lb Hg/10^{12} Btu heat input

The results show that all four catalysts had lost a significant amount of activity for elemental mercury oxidation after a total of 13 to 14 months of flue gas exposure. This is illustrated in Figure 18. It was surprising that the regenerated Pd #1 catalyst was measured to be the most active, as the gold catalyst had typically been the most active in previous measurements. However, as mentioned above, the regenerated Pd #1 had just been cleaned of fly ash buildup while the gold was not. The gold was later cleaned of fly ash buildup and activity was measured for the cleaned catalyst, as discussed below.

The elemental mercury oxidation activity of the four catalysts installed in the Monticello oxidation catalyst pilot unit was last measured on August 22 and 23, about two weeks after the gold and Johnson Matthey Pd #1 catalysts had been manually cleaned of fly ash buildup. The results of these measurements are summarized in Table 17.

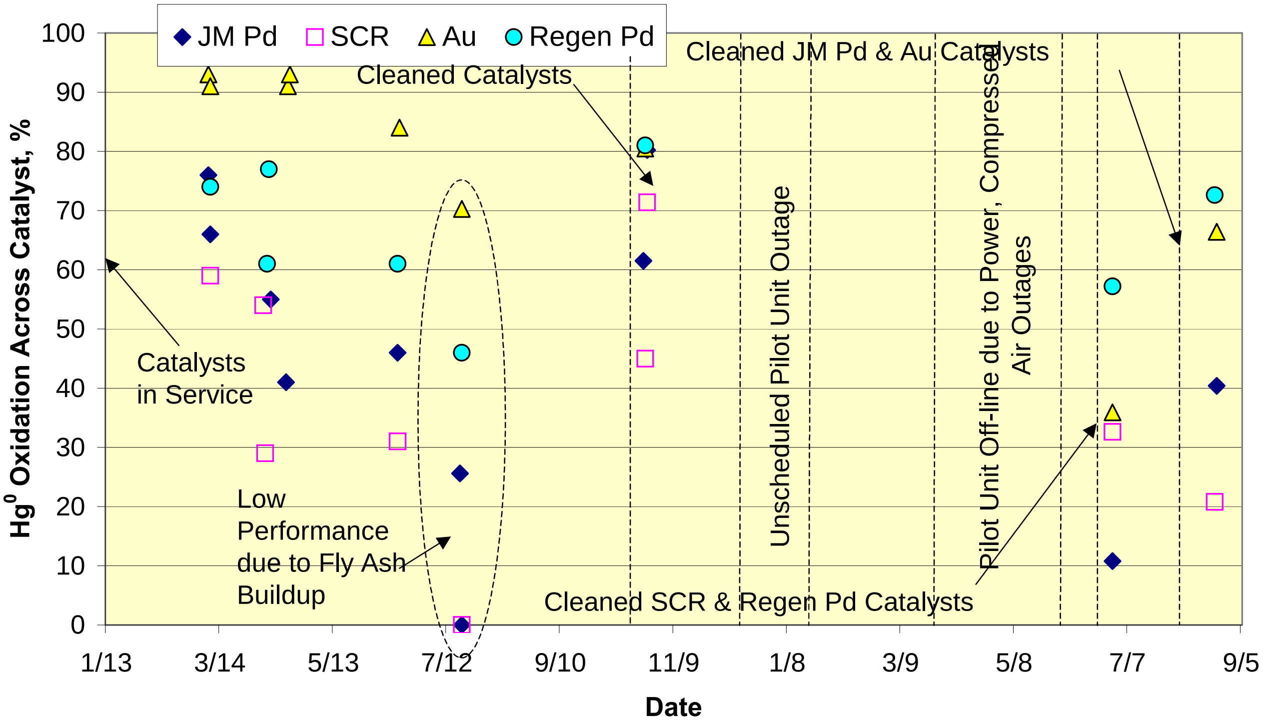


Figure 18. Activity versus Time for the Oxidation Catalysts at Monticello Station over the 19-month Test Period

Table 17. Results of Catalyst Activity Measurements at Monticello, August 22-23, 2006

Catalyst Type	Catalyst Inlet Total Hg*, µg/Nm^3	Catalyst Inlet Elemental Hg*, µg/Nm^3	Catalyst Inlet Oxidation %	Catalyst Outlet Total Hg*, µg/Nm^3	Catalyst Outlet Elemental Hg*, µg/Nm^3	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst, %	Catalyst Outlet Oxidation, %
JM Pd #1	25.2	17.2	32	23.0	10.3	9	40	55
SCR	27.6	17.8	36	27.0	14.5	2	18	46
Gold	25.2	17.2	32	20.4	5.8	19	66	72
Regen. Pd #1	27.6	17.8	36	20.9	5.0	24	72	76

*1 µg/Nm^3 @ 3% O_2 = 0.67 lb Hg/10^{12} Btu heat input

The results for all but the SCR catalyst showed improved activity since the June 2006 measurement trip. However, all four catalysts lost a significant amount of activity for elemental mercury oxidation in a total of 15 to 16 months of flue gas exposure over a 19-month period. This was illustrated above in Figure 18. It remained surprising that the regenerated Pd #1 catalyst was measured to be the most active, as the gold was typically the most active previously and had just been cleaned of fly ash buildup while the regenerated Pd #1 had not been cleaned since June.

It is not known how previous, unscheduled outages of this pilot unit affected catalyst activity. It can only be speculated that several instances of having flue gas flue interrupted for extended periods, without having the opportunity to first purge the catalyst compartments with drier air, adversely affected the catalysts. It is apparent that these unscheduled outages adversely affected the ability to keep the catalysts clean of fly ash buildup, even with the sonic horns in service.

This is evident in the catalyst pressure drop values recorded during the last two catalyst activity measurement trips, which are summarized in Table 18. Also, it is known that a percentage of the first catalyst layer (or single layer for the SCR and Johnson Matthey Pd #1 catalysts) of each catalyst was plugged with the buildup of cemented ash particles. In particular, much of the decrease seen in the Johnson Matthey Pd #1 and SCR catalyst activity may have been due to the effects of fly ash buildup, as shown by the large pressure drop values for those catalysts (~5 in. H_2O [1.2 kPa]). Also, for these single-layer catalysts the entire length of any block flow channel was unavailable for oxidation activity, whereas for the three-layer catalysts there was a possibility for flue gas mixing and redistributing between layers.

Table 18. Catalyst Pressure Drop Values during the Last Two Activity Measurements

Catalyst	Catalyst Pressure Drop, in. H_2O (kPa) June 28-30, 2006	Catalyst Pressure Drop, in. H_2O (kPa) August 22-23, 2006
JM Pd*	0.8 (0.20)	1.5 (0.37)
SCR**	1.7 (0.42)	5.4 (1.3)
Gold*	4.0 (1.0)	3.3 (0.82)
Regenerated Pd**	5.7 (1.4)	4.8 (1.2)

*Cleaned August 10, 2006
**Cleaned June 27-28, 2006

During the August catalyst activity measurement trip, the OH method was used to verify SCEM results for the mercury oxidation performance of each of the four catalysts. The results of these tests are summarized in Table 19.

Table 19. August 2006 OH Method Relative Accuracy Results for Monticello Pilot (mean and 95% confidence interval of three runs compared to simultaneous Hg SCEM results)

	Total Hg*	Elemental Hg*	Oxidized Hg*
Johnson Matthey Pd #1 Catalyst, August 23, 2006:			
Catalyst Inlet – OH, $\mu g/Nm^3$*	25.9 ± 1.1	19.5 ± 2.0	6.4 ± 1.8
Catalyst Inlet – SCEM, $\mu g/Nm^3$	25.2 ± 2.5	17.2 ± 0.3	8.0 ± 2.6
Relative Accuracy, % (based on means)	-3	-12	-25
Catalyst Outlet – OH, $\mu g/Nm^3$	21.3 ± 1.7	12.1 ± 2.3	9.2 ± 0.6
Catalyst Outlet – SCEM, $\mu g/Nm^3$	23.0 ± 0.6	10.3 ± 0.6	12.7 ± 0.7
Relative Accuracy, % (based on means)	+8	-15	+38

	Total Hg*	Elemental Hg*	Oxidized Hg*
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	38	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	40	-
SCR Catalyst, August 22, 2006:			
Catalyst Inlet - OH, µg/Nm^3	31.0 ± 3.2	22.7 ± 1.5	8.3 ± 1.9
Catalyst Inlet - SCEM, µg/Nm^3	27.6 ± 0.5	17.8 ± 1.0	9.9 ± 0.6
Relative Accuracy, % (based on means)	-11	-22	+19
Catalyst Outlet – OH, µg/Nm^3	29.4 ± 3.6	17.3 ± 1.4	12.1 ± 2.3
Catalyst Outlet - SCEM, µg/Nm^3	27.0 ± 1.2	14.5 ± 0.6	12.5 ± 1.6
Relative Accuracy, % (based on means)	-8	-16	+3
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	24	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	18	-
Gold Catalyst, August 23, 2006:			
Catalyst Inlet – OH, µg/Nm^3	25.9 ± 1.1	19.5 ± 2.0	6.4 ± 1.8
Catalyst Inlet – SCEM, µg/Nm^3	25.2 ± 2.5	17.2 ± 0.3	8.0 ± 2.6
Relative Accuracy, % (based on means)	-3	-12	-25
Catalyst Outlet – OH, µg/Nm^3	23.2 ± 1.0	8.0 ± 1.2	15.2 ± 0.7
Catalyst Outlet – SCEM, µg/Nm^3	20.4 ± 1.5	5.8 ± 0.1	14.6 ± 1.4
Relative Accuracy, % (based on means)	-12	-28	-4
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	59	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	66	-
Regenerated Pd #1 Catalyst, August 22, 2006:			
Catalyst Inlet – OH, µg/Nm^3	31.0 ± 3.2	22.7 ± 1.5	8.3 ± 1.9
Catalyst Inlet - SCEM, µg/Nm^3	27.6 ± 0.5	17.8 ± 1.0	9.9 ± 0.6
Relative Accuracy, % (based on means)	-11	-22	+19
Catalyst Outlet – OH, µg/Nm^3	25.3 ± 10.1	7.2 ± 1.7	18.1 ± 8.7
Catalyst Outlet - SCEM, µg/Nm^3	20.9 ± 0.2	5.0 ± 0.2	15.9 ± 0.2
Relative Accuracy, % (based on means)	-17	-30	-12
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	68	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	72	-

*****Note – All concentrations corrected to 3% O_2, dry basis; 1 µg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

On two consecutive days, triplicate OH measurements were made at the catalyst pilot inlet and simultaneously at the outlets of two of the four catalysts. The measurements were made across the SCR and regenerated Pd #1 catalysts on August 22 and across the Johnson Matthey Pd #1 and gold catalysts on August 23.

Because of the observed variability in concentrations, the table shows the mean value for three OH runs as well as the 95% confidence interval about the mean. The magnitude of the 95% confidence interval can be compared to the mean value to provide a measure of the variability of the measurements. A larger 95% confidence interval relative to the mean value means there was more variability in the measurement results. This variability could be due to changes in the actual flue gas concentrations over time, variability within the measurement methods, or both.

The Hg SCEM measurements were made with only one analyzer since the existing sampling port was used at the catalyst pilot unit inlet for the OH measurements. This precluded setting up a second analyzer dedicated to collecting catalyst inlet data during the runs. It also meant that six measurements (catalyst inlet and two catalyst outlets, total and elemental mercury) had to be made with one analyzer while three OH trains (catalyst inlet and the two catalyst outlets) completed each of the triplicate runs. Thus, the Hg SCEM data for each of the six measurements represent a total of less than one-half-hour of data collected at some point during each OH run period, while the OH results represent integrated samples collected over 2-hr runs. With the observed variability in mercury total concentration and speciation in the catalyst inlet flue gas at Monticello, it is possible that much of any disagreement between the OH method and SCEM results can be due to differences in averaging time periods for the two methods.

Also shown are 95% confidence interval values for the Hg SCEM data. For the total and elemental mercury concentrations, the mean values for each OH run period were calculated from a number of short-term average measurements (e.g., 10 or less measurements of 3- to 4-min. averages). A 95% confidence interval was calculated for the mean SCEM value for the three OH runs at each location. Oxidized mercury concentrations are measured by the difference between total and elemental mercury with the Hg SCEM, and one SCEM was used to measure both the catalyst inlet and catalyst outlet locations. This meant the oxidized mercury concentrations could only be calculated from averages, not from individual data points. Thus, the 95% confidence intervals for oxidized mercury concentrations from the SCEM data are of questionable validity.

Comparing the OH method results to Hg SCEM results, the values for total mercury agree very well, with relative accuracies ranging from +8% (SCEM indicates more total mercury than OH method) to –17% (SCEM indicates less total mercury). The elemental mercury and oxidized mercury concentration data showed more relative error, with relative accuracies ranging from –12% to –30% (SCEM indicated less elemental mercury). This is different than in the previous relative accuracy tests conducted in April 2005, where the SCEM measurements tended to show higher elemental mercury concentrations than OH measurements at the outlets of the regenerated Pd #1 and SCR catalysts. In the August 2006 measurements, all of the SCEM elemental mercury measurements showed a negative bias, so the observed percent elemental mercury oxidation percentages agreed reasonably well between the two measurement methods. The observed mean percent oxidation values agreed within 2 to 7 percentage points.

The oxidized mercury concentration relative accuracies varied from –25 to +38%. However, since the SCEM quantifies oxidized mercury concentrations by difference, higher relative accuracy error would be expected.

Overall, the OH results confirm the catalyst activity values measured by the SCEM in August 2006. The results show significant activity loss by all four catalysts in 15 to 16 months of operation, although this loss was likely exacerbated by a number of unscheduled pilot unit outages where moist flue gas was allowed to cool and condense on the catalyst modules.

Flue Gas Characterization Testing

During the oxidation catalyst activity and pilot wet FGD tests conducted during April 2005, extensive flue gas characterization efforts were also made at Monticello. This flue gas characterization included 1). SO_3/sulfuric acid concentrations at the catalyst inlet and outlets; 2). flue gas halogen concentrations at the catalyst pilot inlet; and 3). flue gas trace metals concentrations at the catalyst pilot inlet. Each of these efforts is discussed in a separate subsection below.

Flue Gas SO_3/Sulfuric Acid Concentration Measurements

Measurements were made by the Controlled Condensation System method to determine whether the mercury oxidation catalysts also oxidized a percentage of the flue gas SO_2 to SO_3/sulfuric acid. The tests were conducted by sampling the catalyst pilot unit inlet gas and the outlet gas from two catalysts each on two separate days. The results are summarized in Table 20, and show no evidence of SO_2 oxidation across the catalysts. In fact, it appears that SO_3/sulfuric acid was being adsorbed by the catalysts. The inlet SO_3 concentrations averaged 1 to 2 ppmv (dry basis) while the outlet concentrations were measured at 0.1 to 0.4 ppmv. Adsorption of SO_3/sulfuric acid by the catalyst may contribute to a loss of catalyst activity over time due to the blocking of active catalyst sites.

Flue Gas Halogen Species Concentrations

Sampling was conducted by EPA Method 26a to determine the concentrations of halogen species in the flue gas at the catalyst pilot unit inlet, as halogen species are known to participate in elemental mercury oxidation reactions. The results of these measurements are summarized in Table 21. They show that the Monticello flue gas contained about 2 ppmv of chloride (most likely as HCl) and 6 to 7 ppmv of fluoride (most likely as HF). Small amounts of bromide (0.04 ppm) and iodide (0.15 ppm) were also measured, again most likely as the acids of these halides.

Chlorine (Cl_2) concentrations could not be measured because of chloride contamination of the reagent used for the impinger solutions, which was discovered after the fact when reagent blank samples were analyzed. Concentrations of fluorine (F_2), bromine (Br_2), and iodine (I_2) were all below analytical detection limits, as shown in the table.

Table 20. Summary of Flue Gas Sulfuric Acid Concentration Measurements

Location	**Sample ID**	**Date**	**H_2SO_4, ppmv dry basis**
Catalyst Inlet	Run 1	4/8/2005	3.8
Catalyst Inlet	Run 2	4/8/2005	1.3
Catalyst Inlet	Run 3	4/8/2005	0.6
Catalyst Inlet Average:			1.9
Johnson Matthey Pd #1	Run 1	4/8/2005	0.1
Johnson Matthey Pd #1	Run 2	4/8/2005	0.1
Johnson Matthey Pd #1	Run 3	4/8/2005	0.1
Johnson Matthey Pd #1 Catalyst Outlet Average:			0.1
SCR Catalyst	Run 1	4/8/2005	0.4
SCR Catalyst	Run 2	4/8/2005	0.3
SCR Catalyst	Run 3	4/8/2005	0.4
SCR Catalyst Outlet Average:			0.4
Catalyst Inlet	Run 1	4/19/2005	0.5
Catalyst Inlet	Run 2	4/19/2005	1.2
Catalyst Inlet	Run 3	4/19/2005	1.3
Catalyst Inlet Average:			1.0
Gold Catalyst	Run 1	4/19/2005	0.1
Gold Catalyst	Run 2	4/19/2005	0.1
Gold Catalyst	Run 3	4/19/2005	0.1
Gold Catalyst Outlet Average:			0.1
Regenerated Pd #1	Run 1	4/19/2005	0.1
Regenerated Pd #1	Run 2	4/19/2005	0.1
Regenerated Pd #1	Run 3	4/19/2005	0.1
Regenerated Pd #1 Catalyst Outlet Average:			0.1

Table 21. Results of Flue Gas Halogen Sampling by Method 26a (Catalyst Inlet, 4/5/05)

Sample ID	Sample Start Time	Vol% Water in Sample Gas	Chloride, ppmv	Cl_2, ppb*	Fluoride, ppmv	F_2 ppb	Bromide, ppmv	Br_2, ppb	Iodide, ppmv	I_2, ppb
Run 1	15:18	11.4	1.59	-	5.90	<153	0.04	<36	0.14	<69
Run 2	16:34	12.0	1.70	-	7.18	<154	0.04	<37	0.16	<57
Run 3	17:57	12.1	1.90	-	7.79	<153	0.04	<36	0.16	<69
Average	-	11.8	1.73	-	6.96	<153	0.04	<36	0.15	<65

*Cl_2 concentrations could not be measured because of chloride contamination of the impinger solution reagent

Flue Gas Trace Metals Concentrations

Flue gas metals concentrations were measured by EPA Method 29 at the catalyst pilot unit inlet location. These measurements were made to determine what metals were present in the vapor phase that could potentially be catalyst poisons, although the method also determines particulate-phase metals concentrations. The results of these measurements are summarized in Table 22. The particulate phase results are expressed in the table as an equivalent gas-phase concentration in ppbv (dry basis). The results show that selenium is the metal present in the highest concentration in the vapor phase, followed by copper, arsenic and chromium, in order (mercury concentrations were not quantified by Method 29 in these measurements). Selenium is a suspected mercury oxidation catalyst poison, and arsenic is a known poison for SCR catalysts.

Regenerated Catalyst Activity Testing

After coming off-line on August 28, 2006, the pilot unit was opened up and catalysts were recovered from two of the four compartments for off-site laboratory catalyst regeneration tests. The catalysts recovered included the Johnson Matthey Pd #1 (Catalyst Box 1) and the Sud-Chemie Prototech gold (Catalyst Box 3). These catalysts were taken to URS' Austin, Texas laboratories, where the catalyst "cans" were opened and individual 6-in. by 6-in. catalyst blocks contained in the cans were removed. Individual blocks were thermally regenerated using heated air in the laboratory. Catalyst regeneration variables included air temperature, air flow rate, and heated air flow duration. After regeneration, the individual blocks were re-assembled into the cans and the cans were re-installed in the pilot unit at Monticello Station. A directional sampling probe was used to measure regenerated catalyst activity downstream of individual regenerated blocks, to determine the effectiveness of regeneration conditions on catalyst activity. This testing was conducted late April through early May 2007.

Table 22. Results of Flue Gas Method 29 Measurements (Catalyst Inlet, 4/6/05)

Sample ID	**Units**	**Run 1**	**Run 2**	**Run 3**	**Average**
Sample Start Time		11:35	13:26	15:45	
Moisture in Flue Gas	Volume %	11.4	11.5	11.6	11.5
Gas Phase Results:					
Antimony	ppbv dry	0.002	<0.002	<0.002	<0.002
Arsenic	ppbv dry	0.36	0.41	<0.04	0.27
Barium	ppbv dry	0.06	0.07	0.09	0.07
Beryllium	ppbv dry	ND	ND	ND	ND
Cadmium	ppbv dry	<0.01	<0.00	<0.01	<0.01
Chromium	ppbv dry	0.28	0.20	0.15	0.21
Cobalt	ppbv dry	0.07	<0.01	0.02	0.03
Copper	ppbv dry	2.26	2.56	2.56	2.56
Lead	ppbv dry	<0.01	<0.01	<0.00	<0.01
Nickel	ppbv dry	0.09	0.23	0.04	0.12
Selenium	ppbv dry	22.9	23.9	5.24	17.4
Thallium	ppbv dry	ND	ND	ND	ND
Zinc	ppbv dry	<2.01	<1.86	<1.63	<1.83
Particulate Phase Results:					
Antimony	ppbv dry	0.18	0.11	0.18	0.16
Arsenic	ppbv dry	0.71	0.52	1.71	0.98
Barium	ppbv dry	53.9	35.4	40.8	43.3
Beryllium	ppbv dry	0.07	0.04	0.07	0.06
Cadmium	ppbv dry	0.03	0.05	0.03	0.04
Chromium	ppbv dry	1.74	0.68	8.26	3.56
Cobalt	ppbv dry	0.38	0.23	2.29	0.97
Copper	ppbv dry	1.35	0.89	3.18	1.81
Lead	ppbv dry	0.99	0.58	2.68	1.42
Nickel	ppbv dry	0.14	0.11	0.07	0.10
Selenium	ppbv dry	0.91	1.46	31.5	11.3
Thallium	ppbv dry	ND	ND	ND	ND
Zinc	ppbv dry	1.51	1.23	4.70	2.48

Regeneration Tests

For conducting the thermal regeneration of individual 150 mm by 150 mm blocks, an apparatus was set up to pass heated air over the catalyst as shown in Figure 19. A control valve, venturi and differential pressure gauge were installed upstream of the air heater to measure and control air flow rate, as measured at room temperature. The heater box had a thermocouple with a temperature control panel to measure and control the regeneration temperatures. A Hg SCEM was set up just downstream of the catalyst pieces to measure mercury concentrations of the regeneration air as it left the catalyst piece. The exhaust was then passed through a permanganate-filled impinger to trap the mercury before being released.

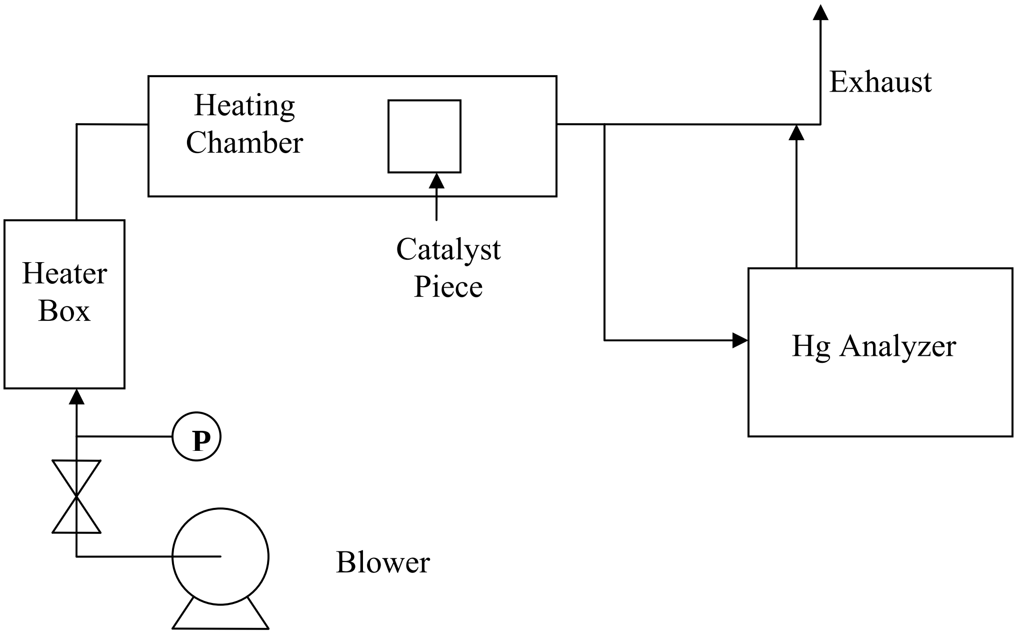


Figure 19. Diagram of Catalyst Regeneration System

Catalyst pieces were regenerated at different conditions by varying air temperature, air flow rate, and duration of regeneration. The heater available was able to generate a maximum air temperature of 800 ºF (427^{o}C). From previous experience with gold amalgamation mercury analyzers, it was known that mercury starts desorbing from gold at approximately 400 ºF. One of the catalysts regenerated was gold based while the other was palladium based. Although the objective of the regeneration was not necessarily to desorb mercury from the catalyst surface, it was believed that since mercury is a relatively volatile metal, the onset of mercury evolution was a good indicator of a minimum temperature where other species might begin to desorb. Therefore the temperature range was set at 450 to 800 ºF (232-427^{o}C) for this series of regeneration experiments.

As described above, regeneration air flow rates were controlled with a valve upstream of the heater box and measured with a venturi flow meter downstream of the valve. The air flow rate was varied between 25 and 52 cfm (42 and 88 m^3/h) at ambient temperature for each individual piece. However, at regeneration temperature conditions, the actual regeneration air flow ranged from approximately 42 to 122 acfm (71-207 m^3/h). For an entire five-by-five (25-piece) catalyst structure as installed in the Monticello pilot unit, this range would correspond with a volumetric flow rate of 1060 to 3060 cfm (1800-5200 m^3/h), or 53% to 153% of the normal flue gas flow through each catalyst chamber during flue gas operation. This regeneration air volumetric flow rate range corresponds with linear face or superficial velocities of 2.9 to 8.4 ft/s (0.88-2.6 m/s) based on the catalyst overall cross-section dimensions, and linear velocities of 3.6 to 10.3 ft/s (1.1-3.1 m/s) through the individual catalyst cells.

The regeneration test duration was set by two approaches, using a prescribed duration or based on the observed desorption of mercury (again, using mercury evolution as an indicator for other species). Using the first approach, several of the pieces were regenerated for set durations of either three hours or overnight. This was done to get a good base of data with similar regeneration times to be able to isolate temperature and flow rate effects on regeneration. Using the second approach, another group of catalysts was allowed to regenerate until the mercury analyzer no longer detected mercury desorbing from the block. For the gold-based catalyst this took from 5 to 12 hours and for the palladium-based catalyst this took up to two full days. Table 23 shows the assigned catalyst piece or block numbers along with their respective regeneration conditions and Table 24 shows their locations once replaced in the catalyst can. These positions were not necessarily the same as when they were removed from service in the Monticello pilot unit. Catalyst block numbers 21 through 25 were left un-regenerated. The same conditions as shown in Table 23 were applied to blocks of the palladium-based catalyst and to both layers of the gold-based catalyst.

The palladium-based catalyst and both layers of the gold-based catalyst were re-assembled into their original catalyst cans as shown in Table 24. In positions 10 and 11, where catalyst pieces had been sent to Johnson Matthey and SCR-Tech to inspect, filler blocks of old catalyst were placed in service just to provide the appropriate gas pressure drop in those positions. The activity of the filler blocks was not measured and reported.

Field results were used to develop correlations for the effects of regeneration air flow rate, temperature, and duration on regenerated catalyst activity. In the field tests, elemental mercury concentration was measured on either side of each catalyst piece (or pairs of pieces in series for the gold-based catalyst) and oxidation was calculated by using the equation below:

$$\%Ox = \frac{Hg_{in}^{0} - Hg_{out}^{0}}{Hg_{in}^{0}} \tag{1}$$

where %Ox is the percent oxidation of elemental mercury across the catalyst, Hg_{in}^{0} is the inlet concentration of elemental mercury, and Hg_{out}^{0} is the outlet concentration of elemental mercury. It is assumed that the total mercury concentration did not change significantly across the catalyst, and thus concentration can be used to accurately calculate elemental mercury oxidation.

Table 23. Master Table of Catalyst Block Number with Experimental Conditions

Block Number	Air Flow Rate, acfm (m^3/h)	Temperature, °F (°C)	Duration, hr
1	25 (42)	650 (343)	*
2	45 (76)	550 (288)	*
3	45 (76)	450 (232)	*
4	45 (76)	650 (343)	*
5	25 (42)	450 (232)	*
6	25 (42)	550 (288)	*
7	35 (59)	650 (343)	*
8	35 (59)	550 (288)	*
9	35 (59)	450 (232)	*
10	Sent to Johnson Matthey to evaluate – not regenerated		
11	Sent to SCR Tech to evaluate – not regenerated		
12	45 (76)	800 (427)	*
13	35 (59)	800 (427)	3.0
14	25 (42)	800 (427)	3.0
15	52 (88)	450 (232)	3.0
16	52 (88)	550 (288)	*
17	52 (88)	650 (343)	3.0
18	52 (88)	800 (427)	3.0
19	25 (42)	550 (288)	3.0
20	25 (42)	650 (343)	3.0

*Varied by catalyst type

Table 24
Positioning of Catalyst Block Numbers as Re-installed in Catalyst Cans (assuming direction of flow is into page)

	Column 1	Column 2	Column 3	Column 4	Column 5
Row 1	13	12	16	14	18
Row 2	7	4	15	1	17
Row 3	8	2	10 (filler)	6	5
Row 4	9	3	11 (filler)	19	20
Row 5	21	22	23	24	25

Field Tests of Regenerated Gold Catalyst

During the field testing of the gold catalyst, only two of the original three layers were used to show regeneration oxidation performance. The first layer was omitted due to the large amount of hard fly ash deposits on the leading edge of that catalyst layer, which was likely limiting that catalysts layer's ability to oxidize mercury. The fly ash collected was also causing significant pressure drop across that catalyst chamber.

Table 25 shows the oxidation results for the regenerated catalyst pieces with the corresponding regeneration conditions. The performance of two layers of catalyst was extrapolated to three layers assuming that each catalyst layer oxidized the same percentage of elemental mercury across it. All subsequent results labeled as elemental mercury oxidation performance are based on extrapolating to three layers of catalyst.

Table 25. Oxidation Results for Regenerated Gold Catalyst

Block ID	Regeneration Conditions			Observed Hg^0 Oxidation across Catalyst, %	Projected Hg^0 Oxidation w/ 3 layers, %	Hg Desorbed During Laboratory Regeneration		
	Flow Rate, acfm@ 75 °F (m^3/h @ 24°C)	Temperature, °F (°C)	Time, hr			Second Layer, µg	Third Layer, µg	Total, µg
1	25 (42)	650 (343)	4.9	45	59	59	242	301
2	45 (76)	550 (288)	5.9	55	70	123	261	384
2 repeat	45 (76)	550 (288)	5.9	28	39	-	-	-
3	45 (76)	450 (232)	13.0	38	51	163	249	412
4	45 (76)	650 (343)	4.8	46	61	39	347	386
4 repeat	45 (76)	650 (343)	4.8	36	49	-	-	-
5	25 (42)	450 (232)	5.6	32	43	99	21	120
6	25 (42)	550 (288)	12.3	40	54	65	17	82
7	35 (59)	650 (343)	5.6	33	45	77	173	250
8	35 (59)	550 (288)	9.8	53	68	71	82	152
9	35 (59)	450 (232)	11.3	54	69	183	79	263
10	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
11	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
12	45 (76)	800 (427)	10.4	53	68	1,086	42	1128
13	35 (59)	800 (427)	3.0	24	34	275	443	718
14	25 (42)	800 (427)	3.0	39	52	357	320	678
15	52 (88)	450 (232)	3.0	41	55	377	4,688	5,064
16	52 (88)	550 (288)	3.0	69	83	359	1,301	1,660

Block ID	Regeneration Conditions			Observed Hg^0 Oxidation across Catalyst, %	Projected Hg^0 Oxidation w/ 3 layers, %	Hg Desorbed During Laboratory Regeneration		
	Flow Rate, acfm@ 75 °F (m^3/h @ 24°C)	Temperature, °F (°C)	Time, hr			Second Layer, µg	Third Layer, µg	Total, µg
17	52 (88)	650 (343)	3.0	25	35	279	582	861
18	52 (88)	800 (427)	3.0	59	73	646	115	761
18 repeat	52 (88)	800 (427)	3.0	10	14	-	-	-
19	25 (42)	550 (288)	3.0	25	35	176	146	322
20	25 (42)	650 (343)	3.0	18	26	190	143	332
20 repeat	25 (42)	650 (343)	3.0	17	25	-	-	-
21	n/a	n/a	n/a	38	51	n/a	n/a	n/a
22	n/a	n/a	n/a	54	69	n/a	n/a	n/a
23	n/a	n/a	n/a	26	36	n/a	n/a	n/a
24	n/a	n/a	n/a	21	30	n/a	n/a	n/a
25	n/a	n/a	n/a	49	64	n/a	n/a	n/a

*n/a – not applicable

The regenerated pieces measured 14% to 83% elemental mercury oxidation when extrapolated to three layers, whereas the un-regenerated pieces ranged from 30 to 69% oxidation. There are a few possible explanations why a regenerated piece might not have performed as well as an un-regenerated piece. First, the pieces came from different locations in the five by five array of catalyst blocks in each layer, and may have seen different levels of activity loss prior to regeneration. For example, the end-of-test mercury oxidation catalyst performance for the gold catalyst installed in the pilot unit at Monticello was 66% oxidation of elemental mercury across the three layers. However, individual pieces could have an oxidation activity that corresponds with much lower than or greater than the 66% average measured. Such a range of activity when the pilot unit was shut down could impact results for both the regenerated and un-regenerated pieces. Also, regeneration at higher than optimum temperatures could have adversely affected the performance of pieces exposed to the highest temperatures.

Even the best regenerated catalyst piece did not perform as well as the fresh gold catalyst, as measured in the Monticello pilot unit in March 2005 (83% versus 91% to 93% for fresh catalyst). It was hoped that optimized regeneration conditions could restore the catalyst to as new activity for mercury oxidation, but this does not appear to have been achieved.

Measurements for several regenerated pieces were repeated during the measurement campaign. The repeat measurements ranged from very good agreement (Block ID 20, 25% versus 26%) to very poor agreement (Block ID 18, 14% versus 73%). The reason for the poor repeat test agreement at some conditions is not apparent, but could be due to factors such as flue gas variations from one test period to the next. It is also possible that the grid installed was not entirely effective at preventing flue gas mixing as it exits each piece, and that the measured performance was sometimes affected by intermixing with flue gas exiting adjacent pieces.

With three different independent variables used during the regeneration process, it became difficult to compare performance data. Therefore it was necessary to either look at individual variables and then compare them to the sets with similar conditions, or find a way to reduce the number of variables through combination.

The range of regeneration air flow rates used was relatively narrow, and flow was always in the laminar regime, well below the transition region to turbulent flow. As Figure 20 illustrates, there was only a small increase in catalyst oxidation performance as the flow rate increased. As such, it was possible to combine both the duration of regeneration and flow rate into a single volumetric throughput variable without losing much information.

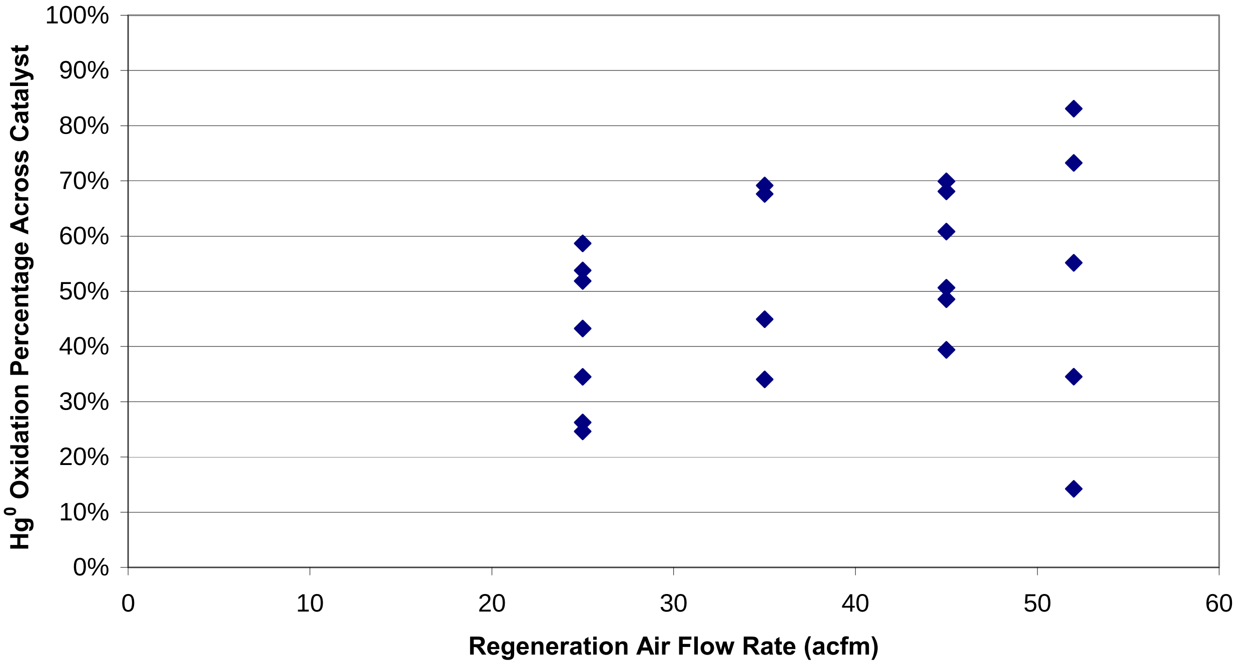


Figure 20. Elemental Mercury Oxidation Percentage across Catalyst as a Function of Regeneration Air Flow Rate, Gold Catalyst

Note: 1.0 acfm = 1.7 m^3/h

Because this reduced the effective number of independent variables to two, the data can be plotted on one three-dimensional graph illustrating how volume throughput and temperature influenced Hg^0 oxidation across the catalyst after regeneration. Figures 21 through 23 display mercury oxidation across the regenerated catalyst as a function of both regeneration air volume throughput and temperature. Oxidation appears to peak at a regeneration temperature near 550 °F (288°C) before decreasing at 650 °F (343°C). The one high oxidation value at 800°F (427°C) is likely an anomaly as most other points at 800 °F (427°C) are lower than those at 550 °F (288°C).

Within the error of the experiment and over the range tested, oxidation also appears to increase with increasing volumetric throughput.

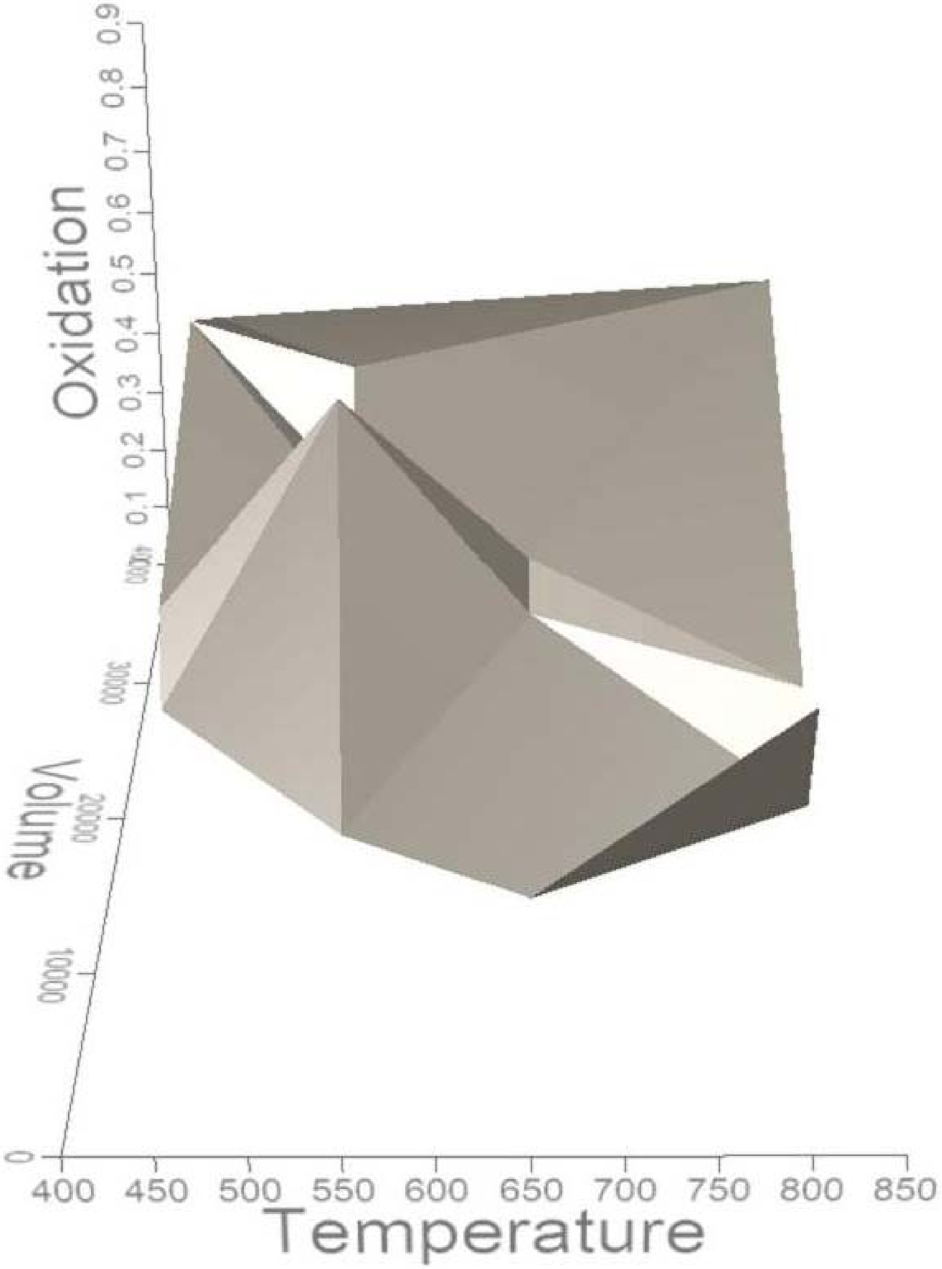


Figure 21. Elemental Mercury Oxidation across Catalyst as a Function of Regeneration Air Temperature and Volumetric Flow, View 1

Note: 1.0 acfm = 1.7 m^3/h; (^oF-32)/1.8 = ^oC

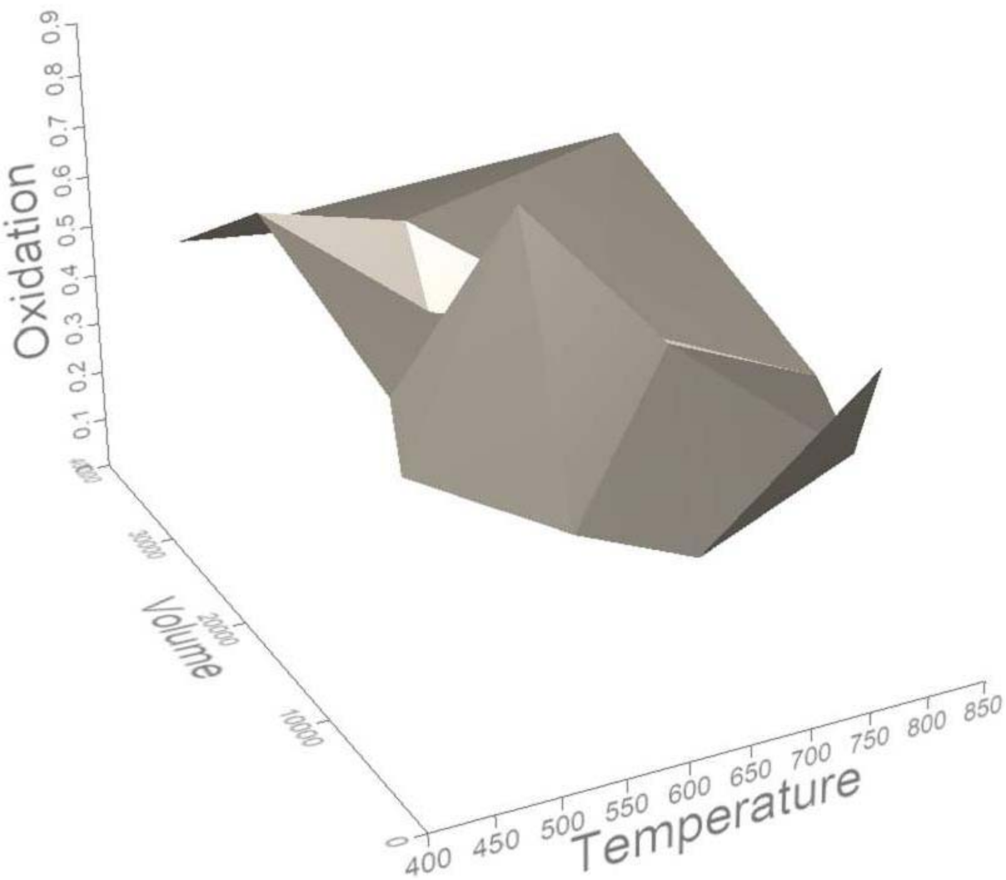


Figure 22. Elemental Mercury Oxidation across Catalyst as a Function of Regeneration Air Temperature and Volumetric Flow, View 2

Note: 1.0 acfm = 1.7 m^3/h; (^oF-32)/1.8 = ^oC

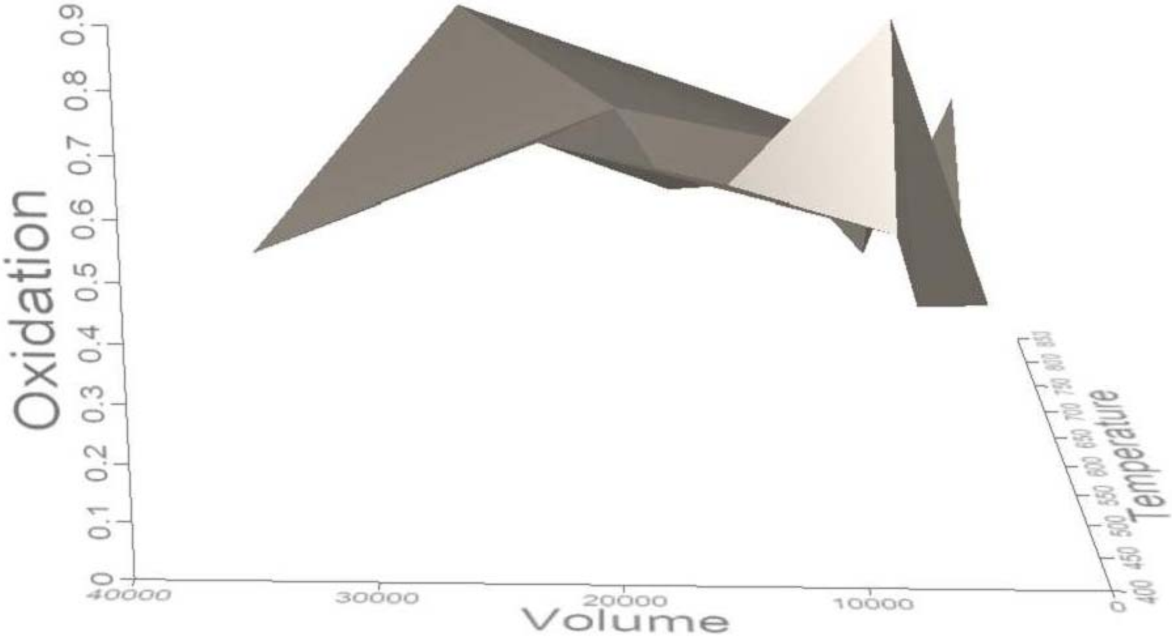


Figure 23. Elemental Mercury Oxidation across Catalyst as a Function of Regeneration Air Temperature and Volumetric Flow, View 3

Note: 1.0 acfm = 1.7 m^3/h; (^oF-32)/1.8 = ^oC

Taking the general trends from these plots, it is possible to mathematically model the relationship between volumetric throughput, temperature, and regenerated catalyst mercury oxidation performance. From the plots it appears that oxidation is a linear function of volumetric throughput and a quadratic function of temperature. Taking this information, dropping data points that appear erroneous, and performing a least squares regression on the data yielded the following equation:

$$\%Ox = 39.04 + 0.001154 * V - 0.000005603 * (T - 981.2)^2 \tag{2}$$

where T is the regeneration air temperature in ^oR and V is the air volume throughput during regeneration, in acf at 75^oF (24^oC). This equation fit the data with an R^2 value of 0.551, which is reasonable given the inherent scatter in the data. Also, the equation achieves a maximum at 521ºF (272^oC), which is close to the observed experimental maximum near 550ºF (288^oC), and predicts 38% elemental mercury oxidation for catalyst not regenerated, which is very close to the mean experiment value of 39%.

When the catalyst pieces were regenerated, total mercury concentrations were measured coming off the pieces in the exhaust stream. Using flow rates and sample times, the amounts of mercury desorbed from the catalysts have been estimated, and were summarized in Table 25 above. These amounts have been plotted against the elemental mercury oxidation performance of the regenerated pieces in Figure 24. There is perhaps a weak trend for higher oxidation performance as more mercury was desorbed from the catalyst during regeneration.

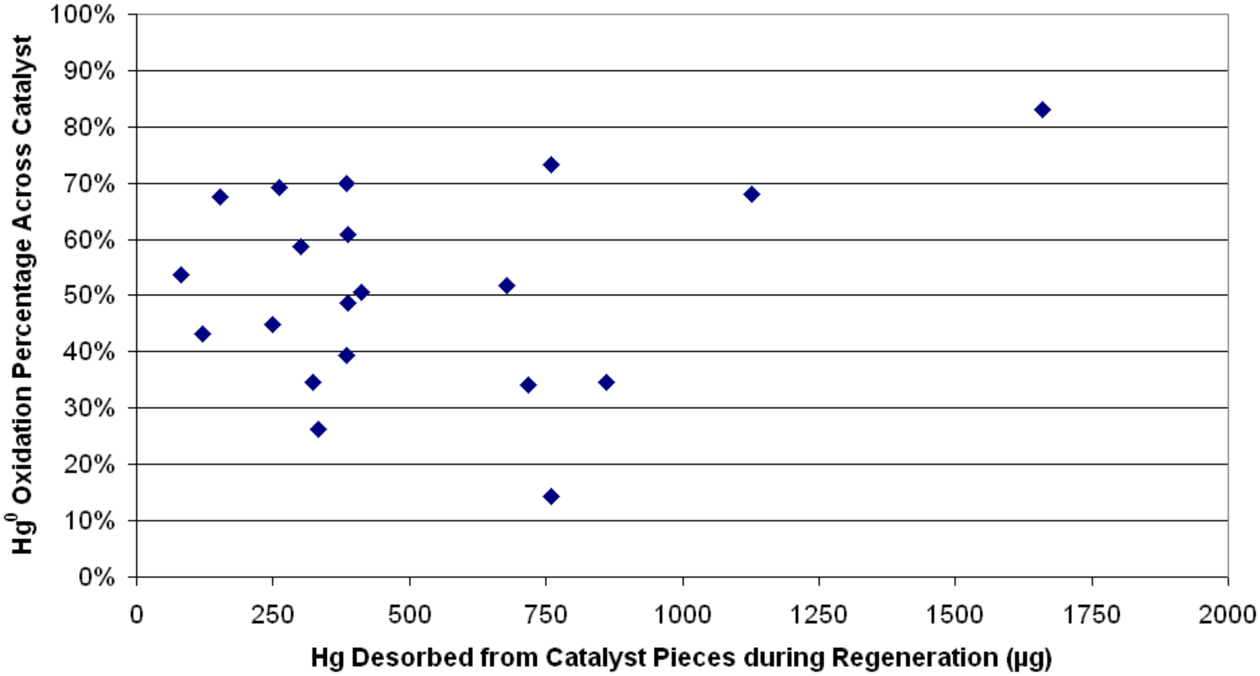


Figure 24. Elemental Mercury Oxidation across Catalyst as a Function of Hg Desorbed During Regeneration

The amount of mercury desorbed has been plotted as a function of the regeneration temperature and volumetric throughput, and the results are shown in Figure 25. The amount of mercury desorbed appears to increase with increasing temperature, with the most dramatic increase occurring at 800°F (427°C). Mercury removed does not appear to change with increasing throughput, indicating that the minimum throughput tested of 4500 ft^3 at 75°F (7650 m^3 at 24oC) was adequate to remove all available mercury.

Field Tests of Regenerated Palladium Catalyst

As with the gold-based catalyst, laboratory regeneration experiments were run with pieces of the palladium-based catalyst altering the regeneration air temperature, flow rate, and duration of regeneration. Table 26 shows the field Hg^0 oxidation results for the regenerated catalyst pieces with their corresponding regeneration conditions.

The regenerated palladium-based catalyst was generally more active for elemental mercury oxidation than the regenerated gold-based catalyst, with oxidation percentages ranging from 41% to 87% being measured. In fact, some of the regenerated pieces were more active than the fresh palladium catalyst as measured in March 2005 (66 to 76% elemental mercury oxidation was measured then).

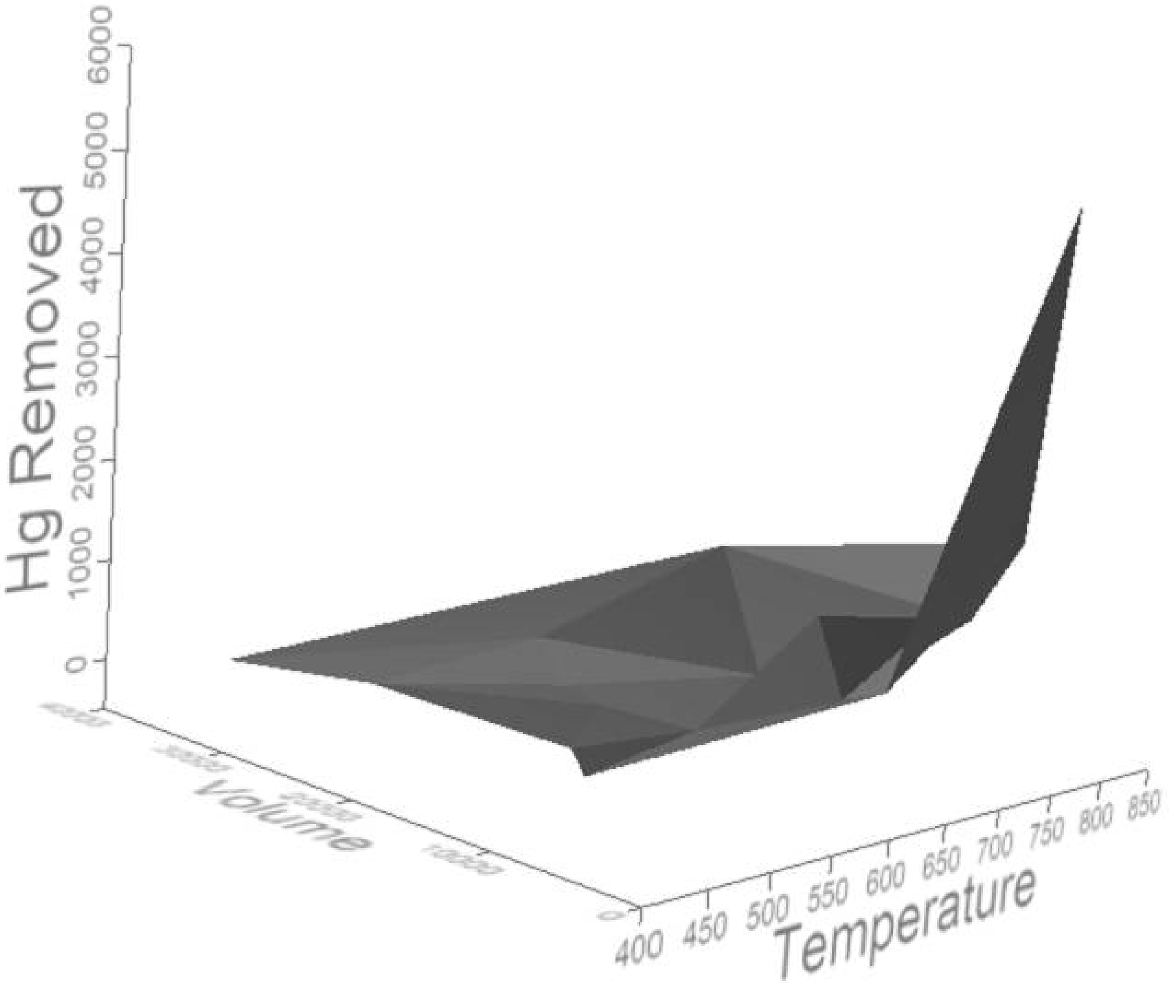


Figure 25. Mercury Desorbed During Regeneration as a Function of Air Temperature and Throughput

Note: 1.0 acfm = 1.7 m^3/h; (^{o}F-32)/1.8 = ^{o}C

Table 26. Oxidation Results for Palladium Catalyst

Block ID	Regeneration Conditions			Hg^0 Oxidation across Catalyst, %	Total Hg Removed During Regeneration µg
	Flow Rate, acfm at 75°F (m^3/h at 24°C)	Temperature, °F (°C)	Time, hr		
1	25 (42)	650 (343)	3.9	86	60
2	45 (76)	550 (288)	7.6	85	897
3	45 (76)	450 (232)	20.9	76	594
4	45 (76)	650 (343)	44.3	87	7,772
5	25 (42)	450 (232)	23.3	51	135
6	25 (42)	550 (288)	21.0	82	370
7	35 (59)	650 (343)	24.5	81	418
8	35 (59)	550 (288)	23.1	78	1,097
9	35 (59)	450 (232)	48.8	63	321
10	n/a	n/a	n/a	n/a	n/a
11	n/a	n/a	n/a	n/a	n/a
12	45 (76)	800 (427)	46.4	79	372
13	35 (59)	800 (427)	22.7	65	418
14	25 (42)	800 (427)	3.0	75	801
15	52 (88)	450 (232)	3.0	61	2,222
16	52 (88)	550 (288)	2.3	41	169
17	52 (88)	650 (343)	3.0	55	1,403
18	52 (88)	800 (427)	3.0	52	1,214
19	25 (42)	550 (288)	3.0	62	580
20	25 (42)	650 (343)	3.0	56	345
21	n/a	n/a	n/a	43	n/a
22	n/a	n/a	n/a	60	n/a
23	n/a	n/a	n/a	Not measured	n/a
24	n/a	n/a	n/a	42	n/a
25	n/a	n/a	n/a	39	n/a

The pieces not regenerated measured 39 to 60% oxidation of elemental mercury, which is reasonably consistent with the end-of-test oxidation percentage of 40% across this catalyst chamber when the Monticello pilot unit was shut down in August 2006. Some minor regeneration of the low-temperature catalysts has been observed in the past when the catalysts are removed from flue gas service, presumably due to minor desorption of poisoning species into the ambient air.

No repeat tests were run during the palladium catalyst field testing due to schedule constraints. The field testing was conducted immediately before the Monticello host unit was scheduled to come off line.

Correlation of Results

As shown in Figure 26 below, there does not appear to be a strong correlation between regeneration air flow rate and post-regeneration Hg^0 oxidation. However, if the data at the highest flow rate were dropped there does appear to be a slight increase in oxidation with increasing flow rate, similar to that of the gold catalyst.

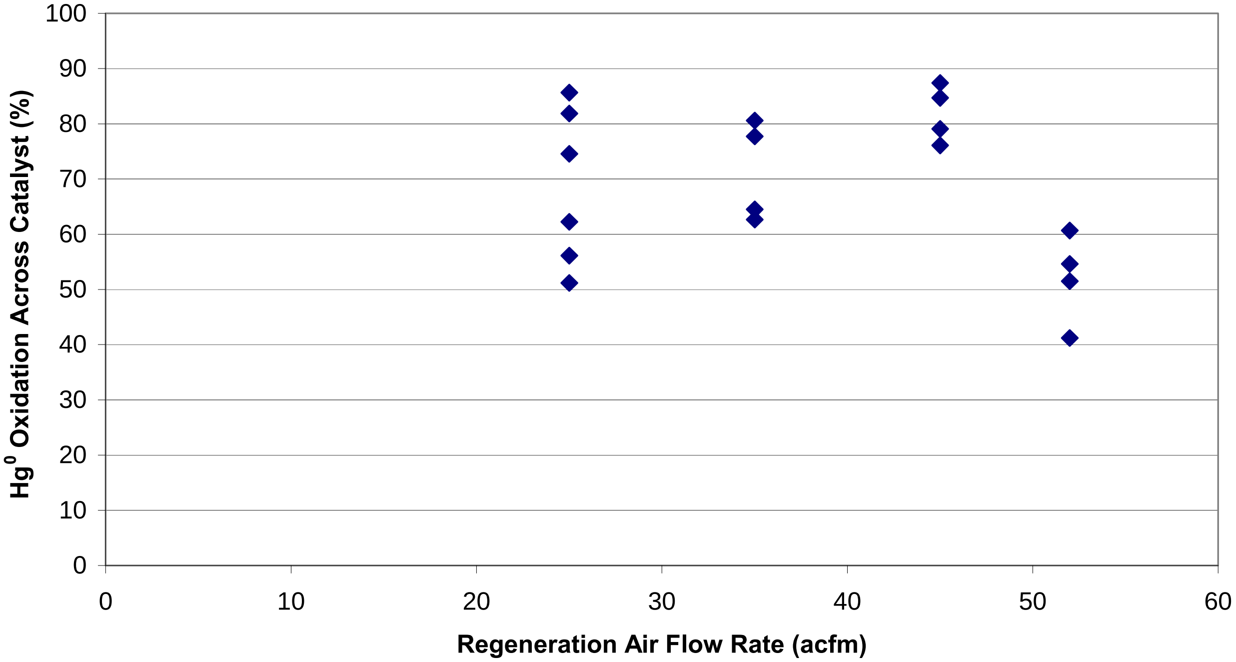


Figure 26. Elemental Mercury Oxidation as a Function of Regeneration Air Flow for Palladium

Note: 1.0 acfm = 1.7 m^3/h

Because of the weak relationship between flow rate and oxidation, as with the gold catalyst the number of independent variables can be reduced to two by combing regeneration air flow rate and regeneration time into a combined volumetric throughput variable. Figures 27 through 29 below demonstrate the relationship between regeneration air temperature, volumetric throughput, and the regenerated catalyst Hg^0 oxidation after being re-installed in the Monticello pilot unit.

Figure 27 primarily depicts the effect of regeneration air temperature on catalyst oxidation; oxidation appears to hit a maximum at nearly 650 ºF (343ºC), slightly higher than the maximum for the gold catalyst near 550 ºF (288ºC). Figures 28 and 29 depict the effect of volumetric throughput on oxidation, with oxidation increasing roughly linearly with increasing volumetric throughput.

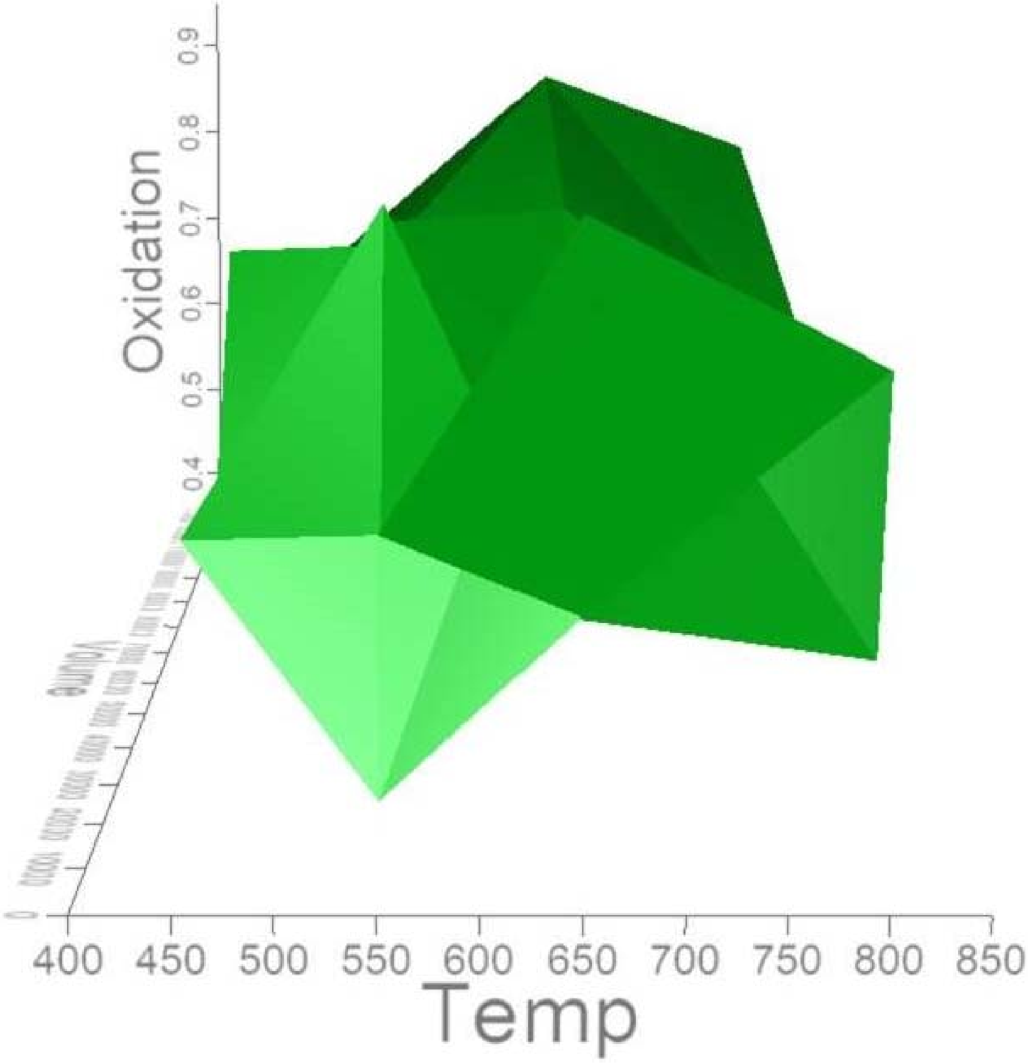


Figure 27. Elemental Mercury Oxidation as a Function of Regeneration Air Temperature and Volume Throughput, View 1

Note: 1.0 acfm = 1.7 m^3/h; (ºF-32)/1.8 = ºC

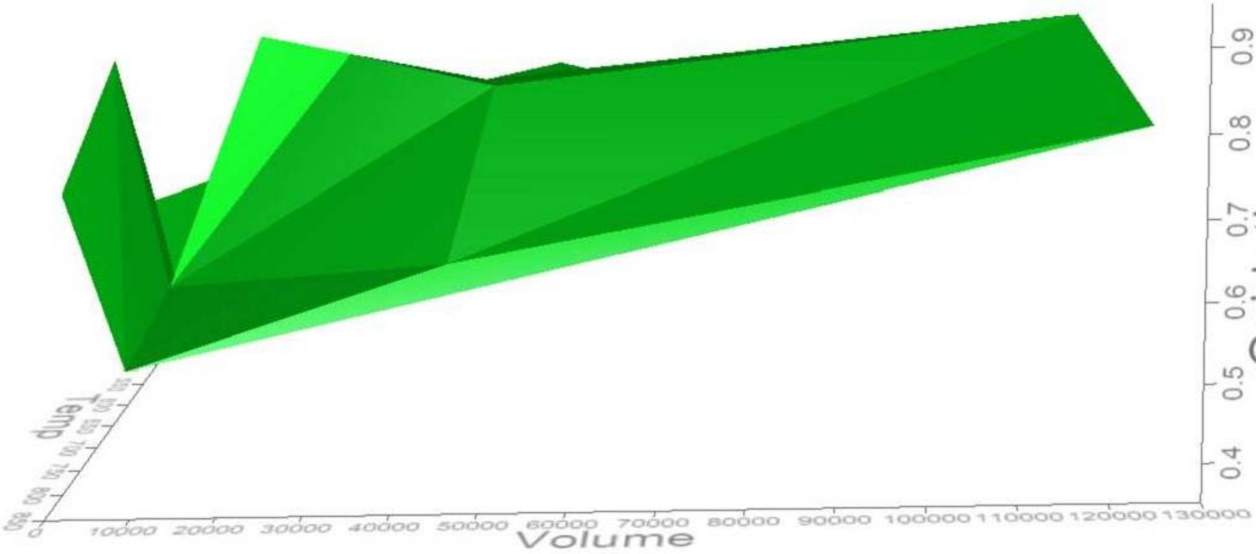


Figure 28. Elemental Mercury Oxidation as a Function of Regeneration Air Temperature and Volume Throughput, View 2

Note: 1.0 acfm = 1.7 m^3/h; (^{o}F-32)/1.8 = ^{o}C

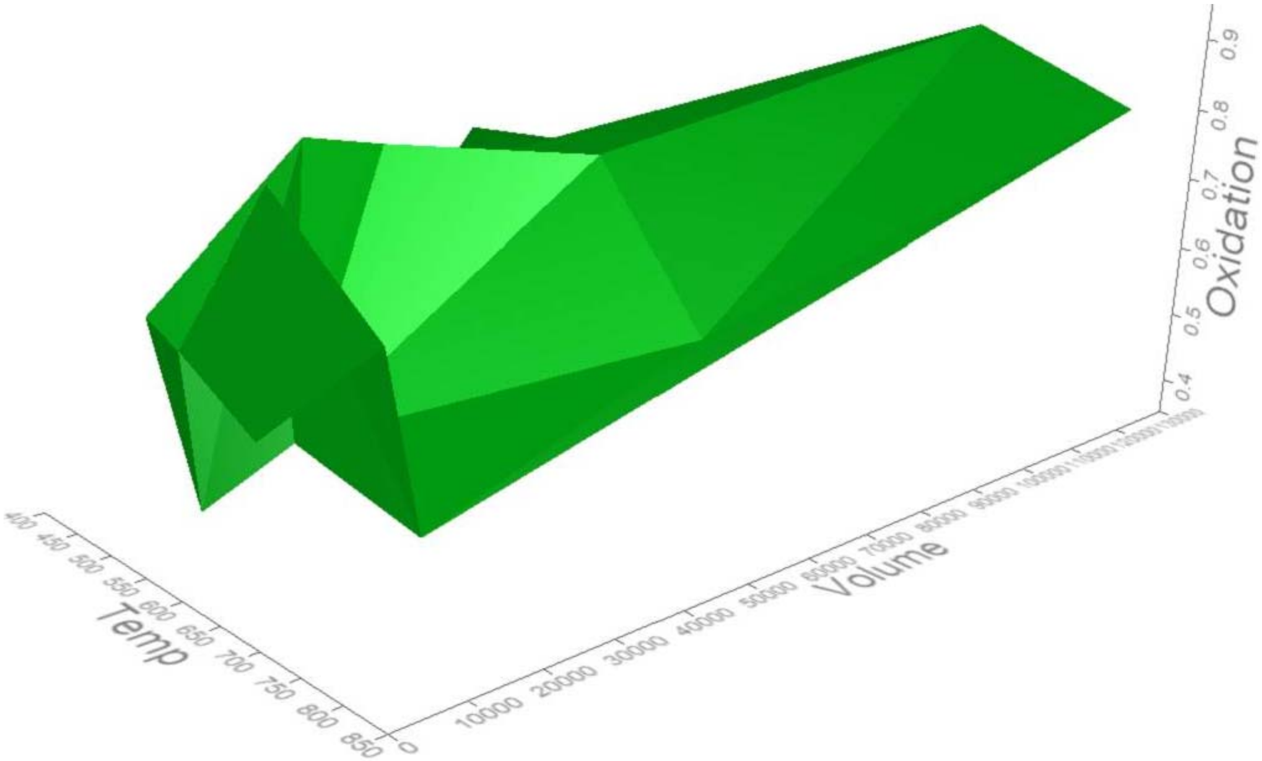


Figure 29. Elemental Mercury Oxidation as a Function of Regeneration Air Temperature and Volume Throughput, View 3

Note: 1.0 acfm = 1.7 m^3/h; (^{o}F-32)/1.8 = ^{o}C

Taking the general trends seen in these plots, it is possible to mathematically model the relationship between regeneration air volumetric throughput, regeneration air temperature, and Hg^0 oxidation across the catalyst after regeneration. From the plots it appears that, like for the gold-based catalyst, oxidation is a linear function of volumetric throughput and a quadratic function of temperature. Taking this information, dropping data points that appear erroneous, and performing a least squares regression on the data yields the following equation:

$$\%Ox = 65.127 + 0.0001727 * V - 0.000123 * (T - 975.3)^2 \tag{3}$$

where T is the regeneration temperature in ^{o}R and V is the volumetric throughput during regeneration, in acf at 75°F (24°C). This equation fits the data with an R^2 value of 0.717, which is quite reasonable given the inherent scatter in the data, and considerably higher than for the gold equation discussed above. The equation achieves a maximum at 515ºF (268°C), which is somewhat lower than the observed experimental maximum at 650ºF (343°C) but nearly identical to the maximum modeled for the gold-based catalyst. The equation calculates 41% elemental mercury oxidation for un-regenerated catalyst, which is virtually identical to the mean of the experimental data.

Comparing the equations developed for the gold and palladium regeneration results, for the gold catalyst the volume throughput of regeneration air has a larger impact (by a factor of nearly seven) than for the palladium catalyst. Temperature had a much smaller effect on the gold catalyst compared to the palladium catalyst, though; the coefficient for the temperature term in the gold equation is about 20 times smaller than the corresponding coefficient for the palladium catalyst.

Using a calculation procedure identical to that described above for the gold-based catalyst, the amount of Hg desorbed during each regeneration test was calculated. This removal was then plotted versus post-regeneration Hg^0 oxidation, as shown in Figure 30. As can be seen in the figure there appears to be a slight increase in the oxidation performance of the regenerated catalyst with increasing mercury desorbed during regeneration.

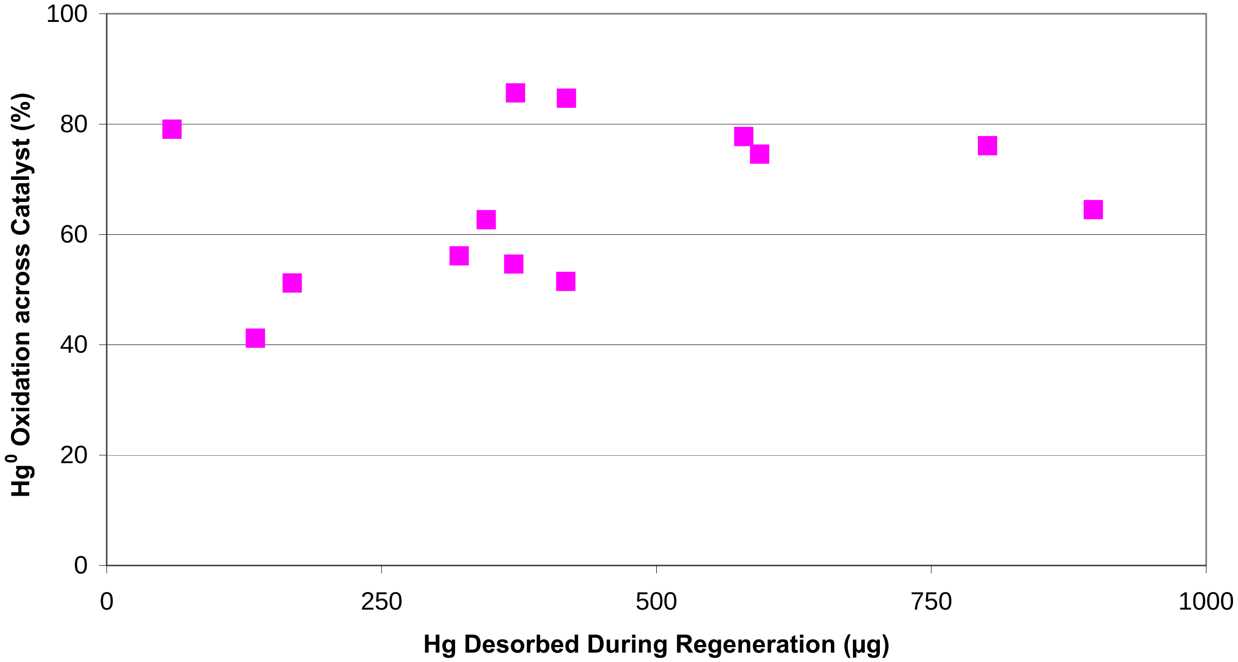


Figure 30. Post-regeneration Elemental Mercury Oxidation across Catalyst as a Function of Hg Desorbed during Regeneration

Figure 31 shows mercury desorbed during regeneration versus regeneration air temperature and volumetric throughput. Mercury desorption increased with increasing air throughput and appeared to reach a maximum at 650ºF (343°C) regeneration air temperature. A similar relationship between these variables and Hg^0 oxidation was also seen for this catalyst, as shown in Figures 27 through 29 above.

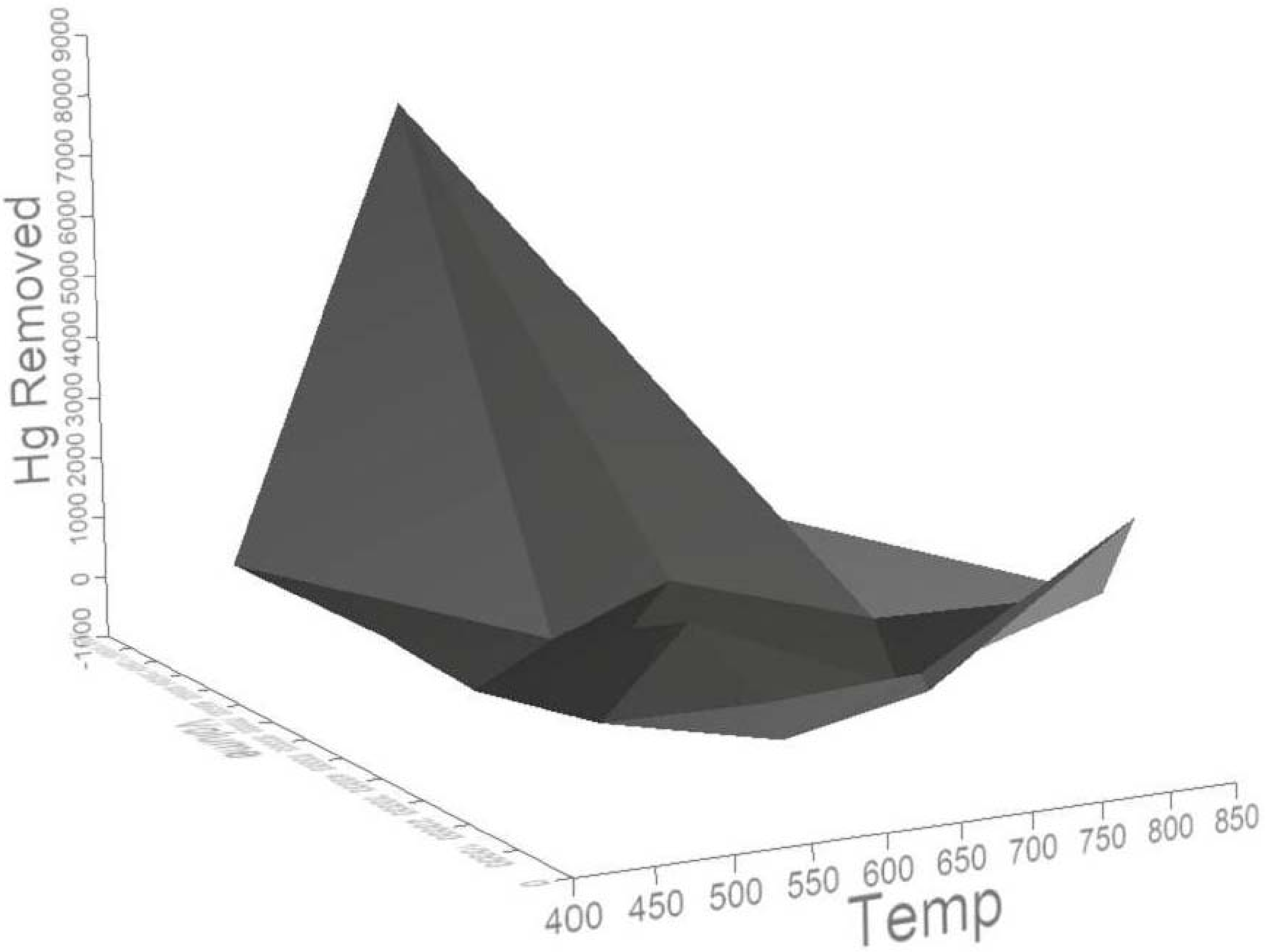


Figure 31. Mercury Desorbed During Regeneration as a Function of Air Temperature and Volume Throughput

Note: 1.0 acfm = 1.7 m^3/h; (^oF-32)/1.8 = ^oC

Method 29 Measurements on Regeneration Air

As mentioned earlier, one objective was to make measurements of what metals desorb from the catalysts when they are thermally regenerated. It is believed that the catalysts lose activity because species other than mercury adsorb from the flue gas onto active catalyst sites and do not readily desorb. The thermal regeneration process is apparently effective because these species desorb due to the reduced adsorption capacity of the catalyst at elevated temperatures. Previous testing during the development of this process showed that for one site, selenium and sulfate were the primary species desorbing upon regeneration[4]. Selenium is a relatively volatile metal present in flue gas in the vapor phase, which may be adsorbing in significant quantities onto the catalyst surface. The sulfate may represent SO_3/H_2SO_4 present in the flue gas which adsorbs onto the catalyst, or may represent SO_2 in the flue gas that gets oxidized at the catalyst surface.

For selected laboratory regeneration runs, a "mini-sampler" was set up to sample the regeneration air as it left the regenerator using the sampling protocols identified in EPA Method

29. Metals are absorbed from the sample gas into nitric acid/peroxide solutions in impinger vessels. The solutions are then recovered, digested and analyzed, also by the Method 29 protocols. An aliquot of the impinger solutions was also analyzed for sulfate content by ion chromatography. The results of this sampling and analysis effort are summarized in Table 27.

Table 27. Results of Method 29 Measurements of Exiting Regeneration Air during Selected Catalyst Regeneration Tests (all results in μg/Nm^3, dry basis unless noted otherwise)

Sample ID	Au Layer 2-12	Pd-12	Au Layer 2-13	Au Layer 2-13	Pd-13	Pd-13
Condition	800°F, 45 acfm (427°C, 76 m^3/h)	800°F, 45 acfm (427°C, 76 m^3/h)	800°F, 35 acfm (427°C, 59 m^3/h)	800°F, 35 acfm (427°C, 59 m^3/h)	800°F, 35 acfm (427°C, 59 m^3/h)	800°F, 35 acfm (427°C, 59 m^3/h)
M29 Run Number	1	1	1	2	1	2
Sample Date	01-Mar-07	02-Mar-07	14-Mar-07	14-Mar-07	15-Mar-07	15-Mar-07
Regenerated Sample Hg^0 Oxidation (%)	68	79	34	-	65	-
As	0.07	<0.03	0.66*	0.40*	0.90*	0.60*
Ba	15.6*	24.2*	14.9*	8.05*	11.1*	7.74*
Be	<0.02	<0.02	0.01	<0.01	<0.01	<0.01
Cd	0.18	<0.02	<0.01	<0.01	<0.01	0.01
Cr	10.6*	11.8*	15.7	8.38	12.3	10.7
Co	23.1*	46.1*	55.1*	37.9*	38.9*	4.16*
Cu	15.8*	19.8*	12.2*	12.2*	4.38*	6.33*
Mn	16.0*	25.1*	12.1*	6.64*	8.97*	7.50*
Ni	11.5*	13.4*	13.9	9.3	13.6	6.75*
Pb	4.03*	3.37*	1.55*	0.92*	0.98*	1.76*
Fe	133*	173*	211*	111*	347*	361*
Se	13.4	56.9	556	89.1	8,110	4,620
Sb	0.32*	0.38*	0.17*	0.13*	0.25*	0.22*
SO_4	2,180	2,970	3,030	476	932,000	84,000
Tl	<0.01	<0.01	<0.00	<0.00	<0.00	<0.00
Zn	50.5*	48.6*	26.7*	14.5*	13.4*	12.1*

*For results noted, field blank concentration value was greater than 20% of measured value in impinger solution

Results are shown for 15 metals and for sulfate. All concentrations in the table are in units of μg/Nm^3 (dry basis at the actual O_2 concentration in the regeneration air). Most of the metals were found to be present at relatively low concentration, other than selenium. Also, there was metals contamination found in field blanks run at the same time as these Method 29 runs, and for most of the metals the concentrations measured were less than five times the concentration in the field blank impingers. Other than selenium and sulfate, only for arsenic, beryllium, cadmium, chromium, and nickel were there quantities in the impingers that were clearly greater than was seen in the field blanks. The concentrations of these metals were much lower than the selenium and sulfate concentrations for any particular measurement run.

For two regeneration tests, two Method 29 runs were made, one early in the regeneration period and one later. In both instances, the concentrations of selenium and sulfate were much higher in the earlier measurement runs, indicating these species mostly desorb early in the regeneration period.

For one regeneration test, for Block 13 of the palladium-based catalyst, huge quantities of selenium and sulfate were measured in the first Method 29 run, and even the second Method 29 run showed higher concentrations of these species than in any of the other runs. It is not apparent why such large quantities were measured to desorb during this test. It may be a function of where this block was originally placed in the Monticello pilot unit and how much of these species adsorbed to this block. Regardless, the field test results for elemental mercury oxidation show that this block, when regenerated, was not the highest performing of the regenerated palladium-based catalyst blocks. Consequently, it does not appear that the amount of these species that desorbs during regeneration controls the activity of the regenerated catalyst.

Catalyst Pilot Unit Operation at Plant Yates

Unit 1 at Plant Yates is rated at nominally 123-MW of generating capacity, although the unit load is typically no greater than 110 MW. It fires low sulfur (~ 1%) Eastern bituminous coal. The coal contains an average of 0.05 ppm of mercury and 220 ppm of chloride. The ESP outlet flue gas typically contains about 60% Hg^{+2} and 40% Hg^0 at a total concentration of 10 $\mu g/Nm^3$ or less. The host unit has a tangentially fired PC boiler and uses a small (design SCA of 173 $ft^2/kacfm$ [9.46 $m^2/10^3$-m^3/h) cold-side ESP with gas conditioning for particulate control, and the CT-121 wet FGD process, which employs a JBR flue gas contactor, for SO_2 control. There is no SCR unit installed on this unit.

The catalyst pilot unit that was previously in service at Spruce Plant as part of Cooperative Agreement 41185 was shipped to Plant Yates at the beginning of September 2005 and station personnel installed it downstream of the ID fan on Unit 1. The unit had an extended outage from October 1 through November 20, so startup was delayed until December 2005.

The unit was shipped with two of the regenerated catalysts from the Spruce Plant testing (gold and SCR) still in place. Two new catalyst charges were ordered from Sud-Chemie Prototech (gold and Pd). The SCR catalyst was intended to be replaced with a second Pd #1 catalyst from an alternate vendor (Johnson Matthey). The manufacture of the Johnson Matthey catalyst was delayed until more information was determined about the activity of their catalyst as installed at Monticello. As discussed above, data from the Monticello tests indicated the Johnson Matthey Pd #1 was less active than the gold or regenerated Sud-Chemie Prototech Pd #1 from Coal Creek. However, also as discussed above, this lower apparent activity might have been the result of a measurement bias rather than a real difference in performance. This discrepancy was never fully resolved and the Johnson Matthey Pd catalyst was not ordered or installed in the pilot unit at Plant Yates. The physical characteristics of the four catalysts tested at Plant Yates are summarized in Table 28.

Table 28. Characteristics of Catalysts Installed in Pilot Unit at Plant Yates

Catalyst Box Number	Catalyst	Cross Section, in. x in. (m x m)	Catalyst Depth, in. (cm)	Cell Pitch, mm	Cells per sq. in. , CPSI (cells/cm^2)	Area Velocity, std. ft/hr (Nm/h)
1	Pd #1 (Sud-Chemie Prototech)	29.5 x 29.5 (0.75 x 0.75)	3 x 3 in. (3 x 7.6 cm)	3.2	64 (9.9)	52 (15)
2	Gold (Sud-Chemie Prototech)	29.5 x 29.5 (0.75 x 0.75)	3 x 3 in. (3 x 7.6 cm)	3.2	64 (9.9)	52 (15)
3	Gold (regenerated from Spruce Plant)	29.5 x 29.5 (0.75 x 0.75)	3 x 3 in. (3 x 7.6 cm)	3.2	64 (9.9)	52 (15)
4	Argillon SCR (regenerated from Spruce Plant)	35.4 x 35.4 (0.90 x 0.90)	29.5 in. (75 cm)	3.7	46 (7.1)	13 (3.7)

After the catalysts were installed early in the week of December 12, the pilot unit was slated for startup on flue gas and collection of initial catalyst activity data. However, the butterfly block valves that were installed on the flue gas piping runs to the catalyst pilot unit when the Unit 1 duct penetrations were made in the spring of 2005 would not open, apparently due to corrosion while exposed to the Unit 1 flue gas. With some difficulty, plant personnel were able to get both valves open by late Friday, December 16, too late to conduct initial catalyst activity measurements. Because of the upcoming Christmas and New Year's holidays, the pilot unit was left in operation, including operation of sonic horns on each compartment, but initial catalyst activity measurements were delayed until January 2006.

Catalyst Pressure Drop Data

The catalyst pilot unit at Plant Yates was equipped with a data logger, but no phone line was available nearby and cellular service in this area of the plant was limited. The approach taken for tracking pilot unit operating data was to download data whenever team personnel were on site for this or other projects.

The catalyst pilot unit pressure drop data from the first year of operation, December 2005 through December 2006, are plotted in Figure 32. In March 2006 there was a noticeable increase in pressure drop across the two regenerated catalysts. Although the cause of this increase is not known, recall that at Monticello the regenerated catalyst from a previous site proved harder to keep clean than catalysts only exposed to flue gas from the Monticello site. It may be that interactions between the fly ashes exacerbate tendencies for fly ash to build up. In particular, there was a significant increase in pressure drop across the regenerated gold catalyst originally tested at Spruce Plant. Of the two regenerated catalysts in service at Plant Yates, the regenerated gold had a smaller pitch (more cells per square inch) than the regenerated SCR catalyst, and thus might have been more likely to experience fly ash buildup issues.

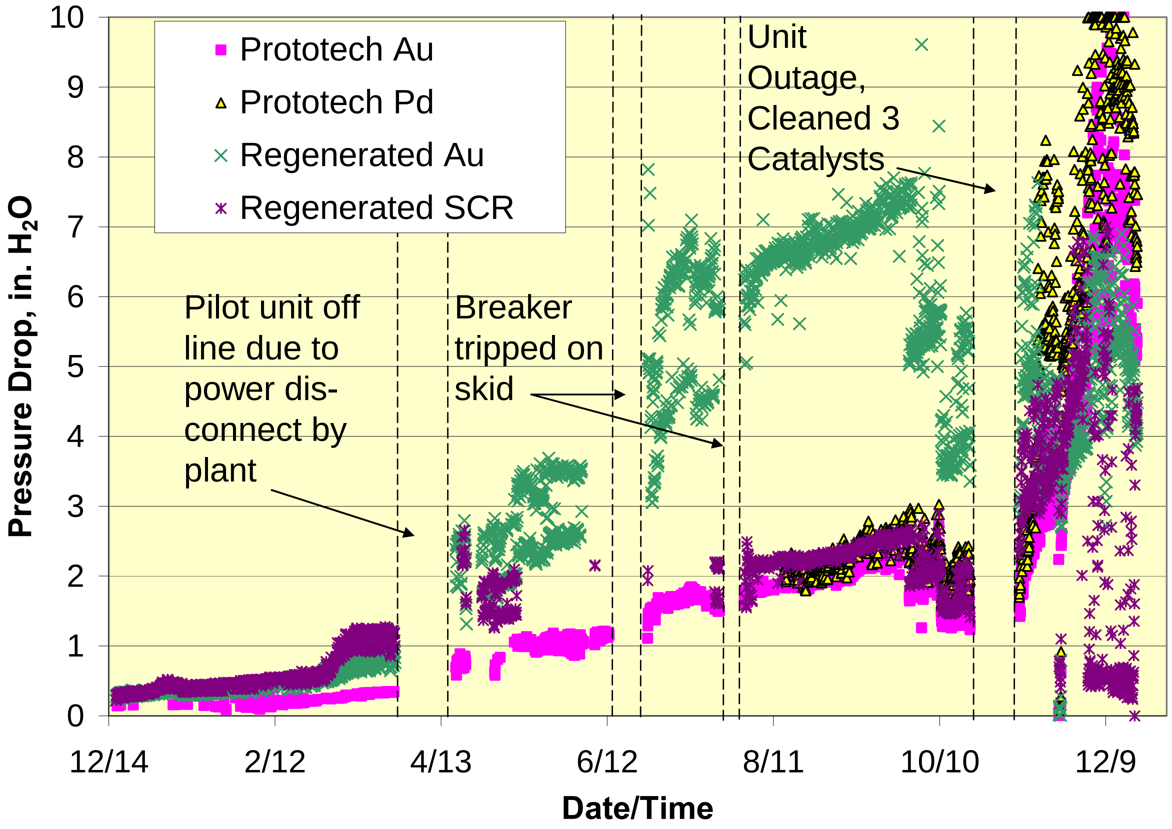


Figure 32. Pressure Drop Data for the Catalyst Pilot Unit at Plant Yates for the First Year of Operation

Note: 1.0 in. H_2O = 0.25 kPa

There were three incidents between April and July 2006 where power was abruptly interrupted to the catalyst pilot unit. As described earlier for the Monticello pilot, when power to one of the pilot units was interrupted the flow control valves (downstream of the catalyst chambers) closed, but the flue gas inlet valve remained open. This allowed flue gas to cool and condense moisture (and sulfuric acid at this site) in the catalyst chamber. These power interruption episodes appear to have adversely affected catalyst pressure drop performance, particularly for the regenerated gold catalyst.

The first interruption was when the host utility temporarily used the power feed to the catalyst pilot unit to instead provide power for other testing on Unit 3. This interruption lasted about three weeks. The second interruption was for about two weeks, and was cause by a ground fault circuit interrupter breaker that tripped in the catalyst pilot unit control panel. The trip occurred when no project team members were on site, and plant personnel did not routinely check pilot unit operation. The breaker was reset once project personnel were back at the site and power loads were redistributed to try to avoid future breaker trips. One more ground fault circuit interrupter trip occurred in late July, and lasted approximately one week before it was discovered and reset.

Pressure drop data are not shown in the figure for the fresh, Prototech Pd #1 catalyst until sometime in August 2006. At startup, the pressure drop transducer for that catalyst enclosure read a value near zero. Initially it was thought that, since all of the catalyst pressure drop values were very low, this merely represented minor zero calibration error for that transducer. However, the other pressure drop values began to increase while this value remained near zero, so it became apparent that there was a significant calibration error or other problem with this transducer. The problem was eventually traced to a bad channel on the data logger, and in August the signal was moved to an unused channel and began reading and logging correctly.

The data show a continued increase in pressure drop across the catalysts in August and September, but decreases in pressure drop over the weeks leading up to a Unit 1 outage in mid-October. This decrease is due to reduced unit load, which correspondingly decreased the flue gas flow rate through the oxidation catalyst pilot unit. Because of the trend for increasing pressure drop over the previous six months, it was decided to clean the catalysts of fly ash buildup before re-starting the pilot unit after the Unit 1 outage. Only three of the four catalysts were cleaned. The fourth catalyst, the regenerated SCR catalyst, was not cleaned because of heavy rainfall and the potential exposure of that compartment to wet conditions if the enclosure had been opened for cleaning.

The other three compartments were cleaned by removing the enclosure side cover and using compressed air to blow fly ash out of the catalyst cells. Water was found standing in the floor of catalyst Box 2 (Prototech gold). The water may have condensed in that box during the Unit 1 outage. Although the water level was below the bottom of the catalyst cans, there was evidence that the leading edge of the first layer had experienced some wetting, which may have led to some cementation reactions. Immediately after the cleaning, the sonic horn operating frequency was increased from 10 seconds every 30 minutes to 10 seconds every 15 minutes to increase the input of sonic cleaning energy.

The data plot in Figure 32 shows little or no decrease in pressure drop across the catalysts when the pilot unit was first put back in service after the outage. However, this is confounded by higher Unit 1 load after the outage, which led to higher flue gas flow rates through the catalyst pilot unit. In spite of this confounding effect, it is clear that the pressure drop across the cleaned catalysts quickly increased to even higher levels than before the cleaning.

Because the data plotted in Figure 32 are confounded by unit load and flue gas flow rate effects, the data for one catalyst (Prototech gold) were "normalized" to a common flue gas flow rate of 1800 acfm (3060 m^3/h) through that compartment (about 90% of the desired flue gas flow rate through each catalyst compartment). The data were normalized by multiplying the actual values by the square of: 1800 divided by the actual flue gas flow rate in acfm. These results are plotted in Figure 33.

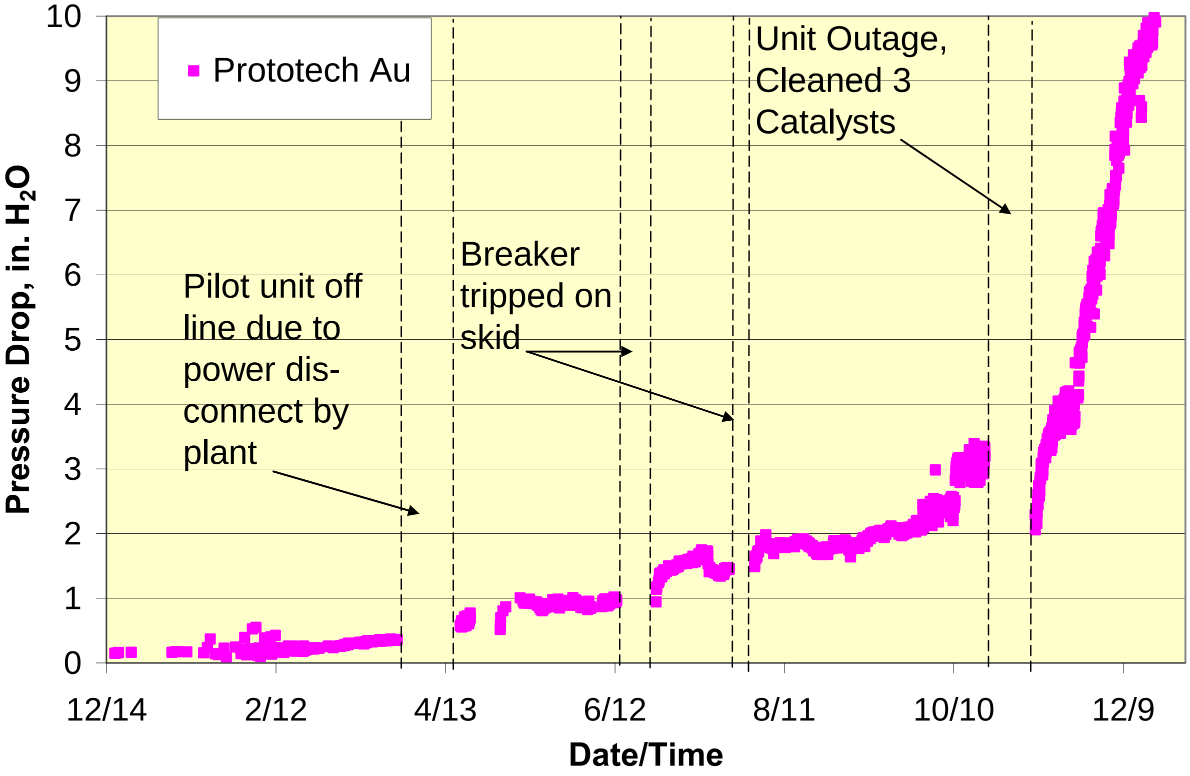


Figure 33. Pressure Drop Data for the Prototech Gold Catalyst at Plant Yates for the First Year of Operation (normalized to a flue gas flow rate of 1800 acfm)

Note: 1.0 in. H_2O = 0.25 kPa

The data in this plot show that the pressure drop across the catalyst was reduced from about 3 in. H_2O (0.75 kPa) to 2 in. H_2O (0.50 kPa) by the cleaning, but increased to nearly 10 in. H_2O (2.5 kPa) by the end of December 2006. The reason for this dramatic increase is not known. It is known that the sonic horns were working properly through most of December, as project team members were working at Plant Yates as part of another project. As mentioned earlier, this catalyst showed some evidence of wetting, which may have exacerbated tendencies for fly ash to collect on the leading edge of the first layer. However, as was shown in Figure 32, the other catalysts saw generally similar pressure drop increases over this time period.

Figure 34 shows pressure drop data through June 2007, which marked the end of testing of these four catalysts. The pilot unit was off line for much of this period because the plant was conducting other testing that was incompatible with oxidation catalyst operation. Because the data plotted in Figure 34 are confounded by unit load and flue gas flow rate effects, the data for the Prototech gold catalyst were again "normalized" to a common flue gas flow rate of 1800 acfm (3060 m^3/h) through that compartment. These results are plotted in Figure 35.

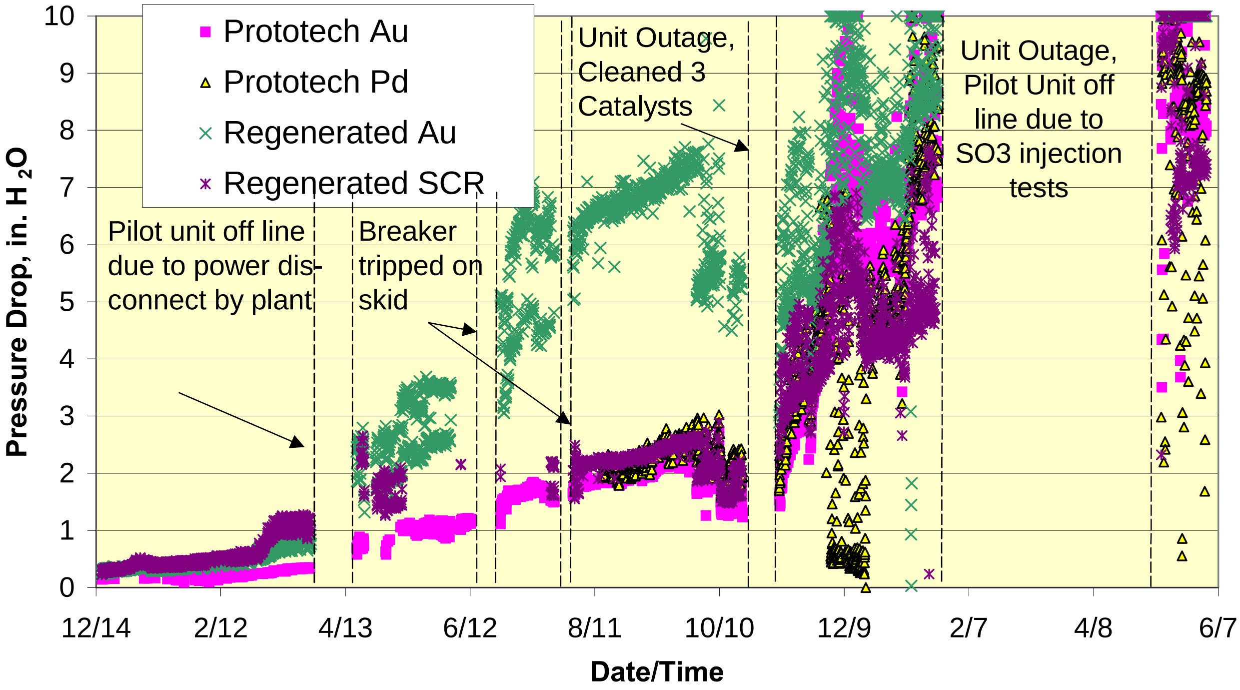


Figure 34. Pressure Drop Data for the Catalyst Pilot Unit at Plant Yates through June 2007

Note: 1.0 in. H_2O = 0.25 kPa

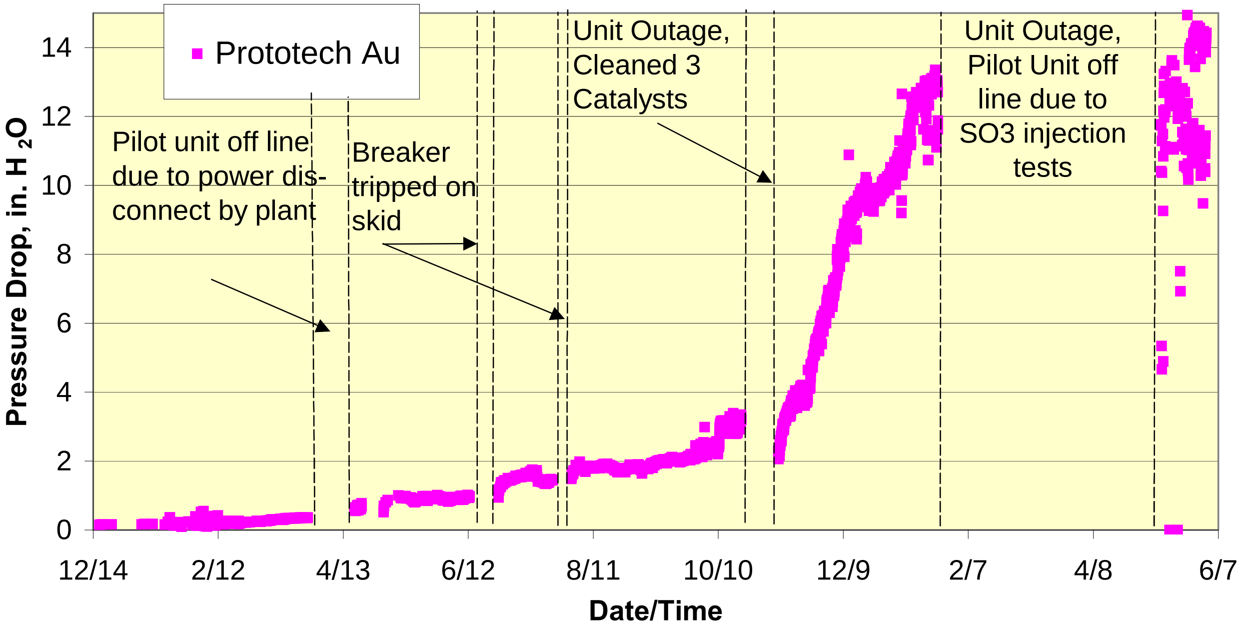


Figure 35. Pressure Drop Data for the Prototech Gold Catalyst at Plant Yates through June 2007 (normalized to a flue gas flow rate of 1800 acfm)

Note: 1.0 in. H_2O = 0.25 kPa

The data plots in Figures 34 and 35 show a continued increase in pressure drop across the catalysts after three catalysts were cleaned late in 2006 until the pilot unit was brought off line for other testing on Unit 1 on January 23, 2007. After the pilot unit was started back up in May 2007, the pressure drop values were similar to those on January 23rd, and quite high. Because of the acute increase in pressure drop, which was not mitigated by off-line cleaning of the catalyst, this pilot catalyst test was curtailed in June 2007.

Elemental Mercury Oxidation Activity Performance

The first catalyst activity measurement trip at Plant Yates was conducted in mid-January 2006, after approximately one month in flue gas service. The results of those measurements are summarized in Table 29.

Table 29. Results of Catalyst Activity Measurements at Plant Yates, January 12-15, 2006

Catalyst Type	Catalyst Inlet Total Hg*, μg/Nm^3	Catalyst Inlet Elemental Hg*, μg/Nm^3	Catalyst Inlet Oxidation %	Catalyst Outlet Total Hg*, μg/Nm^3	Catalyst Outlet Elemental Hg*, μg/Nm^3	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst, %	Catalyst Outlet Oxidation, %
Pd #1 (1/13)	5.04	2.66	47	3.76	0.07	25	97	98
New Gold (1/13)	4.85	3.05	37	5.51	0.07	-13	98	99
Regenerated Gold (1/14)	3.51	2.20	37	4.07	0.06	-16	97	99
Regenerated SCR (1/15)	3.09	0.98	68	2.93	-0.04	5	100	100

*1 μg/Nm^3 @ 3% O_2 = 0.66 lb Hg/10^{12} Btu heat input

The results show that all four catalysts were near adsorption equilibrium, and were achieving very high elemental mercury oxidation percentages. These percentages are higher than had typically been measured at previous pilot testing sites, and may be an effect of the bituminous coal fired at Yates having significantly higher chloride content than the low-rank Western coals fired at all previous sites. Chlorine in coal is primarily converted to HCl in the flue gas; HCl and/or a small amount of Cl_2 in equilibrium with HCl is believed to be a reactant in the heterogeneous oxidation of elemental mercury in flue gas. Although the catalyst inlet flue gas HCl concentration at Plant Yates had not yet been measured as part of this project, previous measurements as part of other projects showed ESP outlet flue gas HCl concentrations in the range of 10 to 20 ppmv. In comparison, the previous mercury oxidation catalyst test sites have had approximately 1-2 ppmv of HCl in the catalyst inlet flue gas. The actual values measured in the flue gas at Plant Yates are presented and discussed later in this section.

A second catalyst activity measurement trip was made to Plant Yates approximately one month later. These results are shown in Table 30. Note that for the regenerated gold, the catalyst outlet elemental mercury concentration was measured one day while the outlet total mercury concentration was measured the following day. Thus, there are two line entries for this catalyst, with the elemental mercury oxidation across the catalyst calculated with one day's data and the mercury adsorption data calculated with the following day's data. The results in the table show slightly lower mercury oxidation percentages across some of the catalysts than the previous month's data. However, all of the percentages were quite high (>90%) and the measured catalyst outlet elemental mercury concentrations were quite low (<0.2 µg/Nm^3).

Table 30. Results of Catalyst Activity Measurements at Plant Yates, February 20-23, 2006

Catalyst Type	Catalyst Inlet Total Hg*, µg/Nm^3	Catalyst Inlet Elemental Hg*, µg/Nm^3	Catalyst Inlet Oxidation %	Catalyst Outlet Total Hg*, µg/Nm^3	Catalyst Outlet Elemental Hg*, µg/Nm^3	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst, %	Catalyst Outlet Oxidation, %
Pd #1 (2/21)	3.98	1.93	52	3.38	0.15	15	92	96
New Gold (2/22)	5.17	2.73	47	4.54	0.04	12	99	99
Regenerated Gold (2/22)	5.17	2.73	47	-	0.11	-	96	-
Regenerated Gold (2/23)	3.95	2.05	48	3.46	-	12	-	-
Regenerated SCR (2/23)	3.95	2.05	48	3.12	0.03	21	99	99

*1 µg/Nm^3 @ 3% O_2 = 0.66 lb Hg/10^{12} Btu heat input

The next catalyst activity measurement trip was in April 2006. The results of those measurements are summarized in Table 31. The results show that all four catalysts were near adsorption equilibrium (±20%), and were achieving elemental mercury oxidation percentages in the range of 68 to 85% across the catalysts. These percentages are lower than were measured in March, and may reflect adverse effects of an unscheduled pilot unit outage earlier in April. Of the four catalysts, the fresh gold catalyst was clearly the most active. This is somewhat different than the previous results, where all four catalysts appeared to be operating at similar activity.

Table 31. Results of Catalyst Activity Measurements at Plant Yates, April, 2006

Catalyst Type	Catalyst Inlet Total Hg*, µg/Nm^3	Catalyst Inlet Elemental Hg*, µg/Nm^3	Catalyst Inlet Oxidation %	Catalyst Outlet Total Hg*, µg/Nm^3	Catalyst Outlet Elemental Hg*, µg/Nm^3	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst,, %	Catalyst Outlet Oxidation, %
Pd #1 (4/19)	8.3	5.8	31	7.8	1.8	6	68	77
New Gold (4/20)	9.9	6.6	34	7.9	0.97	20	85	88
Regenerated Gold (4/20)	9.9	6.6	34	8.1	1.6	19	76	80
Regenerated SCR (4/21)	6.7	6.7	0	7.2	1.8	-8	73	75

*1 µg/Nm^3 @ 3% O_2 = 0.66 lb Hg/10^{12} Btu heat input

A catalyst activity measurement trip was next made to Plant Yates at the end of June 2006. These results are shown in Table 32. As in April, the results show that all four catalysts were near adsorption equilibrium (±20%). The oxidation percentages ranged from 70% for the new gold to 76% for the regenerated gold. This is opposite the results seen in the April trip, where the new gold catalyst was clearly the most active. In the June data the new gold was the least active. However, the range in catalyst performance measured in June was probably within experimental error. That is, all four catalysts appeared to be operating at similar mercury oxidation activity.

Table 32. Results of Catalyst Activity Measurements at Plant Yates, June 2006

Catalyst Type	Catalyst Inlet Total Hg*, $\mu g/Nm^3$	Catalyst Inlet Elemental Hg*, $\mu g/Nm^3$	Catalyst Inlet Oxidation %	Catalyst Outlet Total Hg*, $\mu g/Nm^3$	Catalyst Outlet Elemental Hg*, $\mu g/Nm^3$	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst, %	Catalyst Outlet Oxidation, %
Pd #1 (2/21)	7.0	2.7	38	5.8	0.73	17	73	87
New Gold (2/22)	5.7	2.7	47	4.7	0.79	17	70	83
Regenerated Gold (2/22)	5.4	2.5	47	4.4	0.60	20	76	86
Regenerated SCR (2/23)	5.2	2.2	42	4.2	0.62	20	71	85

*1 $\mu g/Nm^3$ @ 3% O_2 = 0.66 lb Hg/10^{12} Btu heat input

The results from the first four catalyst activity measurement trips are plotted in Figure 36. It is difficult from these data to determine whether the decreases in activity shown in the figure represent a downward trend with general flue gas exposure, or represent "step changes" in activity due to adverse effects from unscheduled pilot unit outages in April and early June.

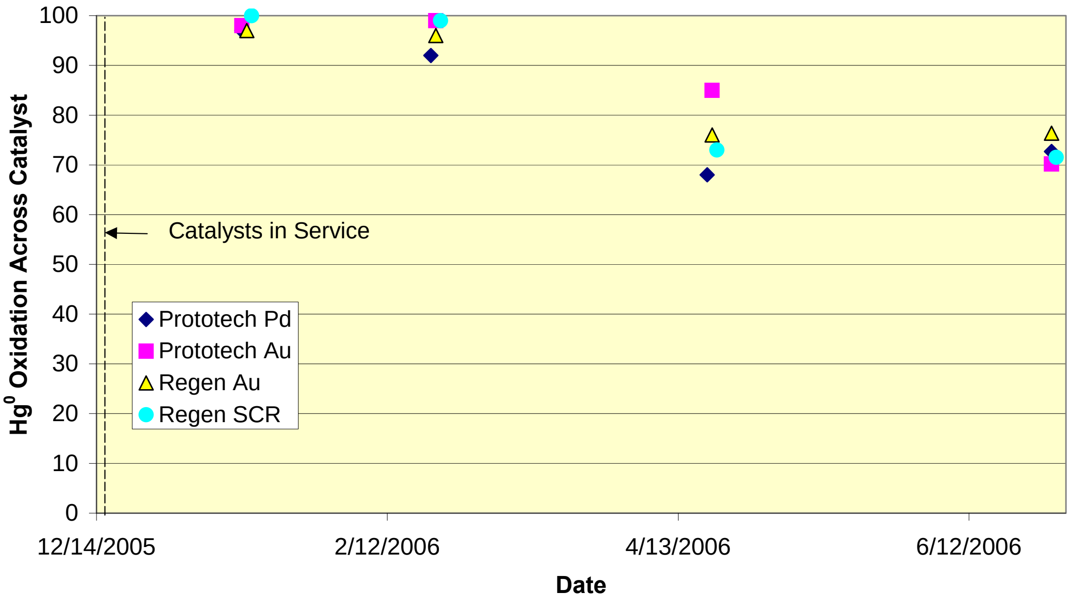


Figure 36. Catalyst Activity versus Time for the Oxidation Catalysts at Plant Yates

A catalyst activity measurement trip was next conducted at Plant Yates at the beginning of August 2006; the results of those measurements are summarized in Table 33. Because OH relative accuracy tests were being conducted simultaneously, and because the greatest measurement concern was on catalyst activity (elemental mercury oxidation across the catalyst), most of the SCEM measurements were focused on catalyst inlet and outlet elemental mercury concentrations, and relatively few catalyst outlet total mercury measurements were made. Thus, there are several blank cells in the table due to a lack of catalyst outlet total mercury concentration data. The one available set of data show that catalyst to be near mercury adsorption equilibrium, and similar results would be expected for the other three catalysts.

Table 33. Results of Catalyst Activity Measurements at Plant Yates, August 2006

Catalyst Type	Catalyst Inlet Total Hg*, µg/Nm^3	Catalyst Inlet Elemental Hg*, µg/Nm^3	Catalyst Inlet Oxidation %	Catalyst Outlet Total Hg*, µg/Nm^3	Catalyst Outlet Elemental Hg*, µg/Nm^3	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst, %	Catalyst Outlet Oxidation, %
Pd #1 (8/02)	9.1	3.7	60	-	2.8	-	25	-
New Gold (8/01)	9.8	1.9	80	-	1.7	-	15	-
Regenerated Au (8/02)	9.1	3.7	60	-	3.0	-	18	
Regenerated SCR (8/01)	9.8	1.9	80	8.4	1.9	14	2	78

*1 µg/Nm^3 @ 3% O_2 = 0.66 lb Hg/10^{12} Btu heat input

During the August catalyst activity measurement trip, the OH method was used to verify SCEM results for the mercury oxidation performance of each of the four catalysts. On two consecutive days, triplicate OH measurements were made at the catalyst pilot inlet and simultaneously at the outlets of two catalysts. The measurements were made across the regenerated SCR and regenerated gold catalysts on August 1 and across the new Pd #1 and gold catalysts on August 2nd. The results of these tests are summarized in Table 34. As previously in this report, because of the observed variability in concentrations, the table shows the mean value for three OH runs as well as the 95% confidence interval about the mean.

Table 34. August 2006 OH Method Relative Accuracy Results for Yates Pilot (mean and 95% confidence interval of three runs compared to simultaneous Hg SCEM results)

	Total Hg*	Elemental Hg*	Oxidized Hg*
Pd #1 Catalyst, August 2, 2006:			
Catalyst Inlet – OH, µg/Nm^3*	12.7 ± 1.9	7.6 ± 2.9	5.1 ± 1.0
Catalyst Inlet – SCEM, µg/Nm^3	9.1 ± 1.0	3.7 ± 1.0	5.4 ± NA
Relative Accuracy, % (based on means)	-28	-52	+7
Catalyst Outlet – OH, µg/Nm^3	12.2 ± 4.1	4.2 ± 3.2	8.0 ± 1.4

	Total Hg*	**Elemental Hg***	**Oxidized Hg***
Catalyst Outlet – SCEM, μg/Nm^3	-	2.8 ± 1.0	-
Relative Accuracy, % (based on means)	-	-34	-
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	45	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	25	-
New Gold Catalyst, August 1, 2006:			
Catalyst Inlet - OH, μg/Nm^3	8.2 ± 0.7	5.7 ± 0.5	2.5 ± 1.0
Catalyst Inlet - SCEM, μg/Nm^3	9.8 ± NA	1.9 ± 0.2	7.9 ± NA
Relative Accuracy, % (based on means)	19	-66	+212
Catalyst Outlet – OH, μg/Nm^3	6.0 ± 1.8	3.0 ± 0.8	3.0 ± 1.1
Catalyst Outlet - SCEM, μg/Nm^3	-	1.7 ± 0.1	-
Relative Accuracy, % (based on means)	-	-44	-
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	48	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	14	-
Regenerated Gold Catalyst, August 2, 2006:			
Catalyst Inlet – OH, μg/Nm^3	12.7 ± 1.9	7.6 ± 2.9	5.1 ± 1.0
Catalyst Inlet – SCEM, μg/Nm^3	9.1 ± 1.0	3.7 ± 1.0	5.4 ± NA
Relative Accuracy, % (based on means)	-28	-52	+7
Catalyst Outlet – OH, μg/Nm^3	12.5 ± 3.6	4.9 ± 2.6	7.5 ± 1.0
Catalyst Outlet – SCEM, μg/Nm^3	-	3.0 ± 0.8	-
Relative Accuracy, % (based on means)	-	-39	-4
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	35	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	18	-
Regenerated SCR Catalyst, August 1, 2006:			
Catalyst Inlet – OH, μg/Nm^3	8.2 ± 0.7	5.7 ± 0.5	2.5 ± 1.0
Catalyst Inlet - SCEM, μg/Nm^3	9.8 ± NA	1.9 ± 0.2	7.9 ± NA
Relative Accuracy, % (based on means)	19	-66	+212
Catalyst Outlet – OH, μg/Nm^3	7.4 ± 1.1	3.2 ± 0.2	4.2 ± 1.3
Catalyst Outlet - SCEM, μg/Nm^3	8.4 ± 0.1	1.9 ± 0.4	6.5 ± NA
Relative Accuracy, % (based on means)	+13	-40	+53
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	45	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	2	-

*****Note – All concentrations corrected to 3% O_2, dry basis; 1 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input
NA – 95% Confidence Interval calculation not applicable

The results do not show good agreement between the two methods, particularly for the measurements of most interest for this project: catalyst inlet and outlet elemental mercury concentrations. The SCEM measurements show lower elemental mercury concentrations at both the catalyst inlet and outlet than the OH results. At the catalyst inlet, the SCEM measurements averaged 66% lower than the OH results on August 1 and 52% lower on August 2nd. At the catalyst outlets, the SCEM results ranged from 34% to 44% lower than the corresponding OH measurements. Also, since the apparent bias for the SCEM was greater at the inlet than the outlet, the SCEM results showed lower catalyst performance than did the OH results.

It is not clear what caused this bias. However, some of the measurements showed a large 95% confidence interval about the mean for three runs. This is an indicator of variability in the results, which could have been introduced by run-to-run changes in flue gas conditions or by sampling or analytical errors in the measurement methods.

For several of the measurements, the large 95% confidence intervals about the means could explain much the observed differences between the two methods. As an example, for the measurements across the regenerated gold catalyst on August 2nd, the OH inlet elemental mercury mean value was 7.6 $\mu g/Nm^3$, but the 95% confidence interval was relatively large at ±2.9 $\mu g/Nm^3$. The corresponding SCEM mean value was 3.7 $\mu g/Nm^3$ with a 95% confidence interval of ±1.0 $\mu g/Nm^3$. The lower end of the OH 95% confidence interval and the upper end of the SCEM 95% confidence interval were equal at 4.7 $\mu g/Nm^3$. Thus, the uncertainty of these measurement means was large enough that it is possible that the true means values for these methods were equal. At the outlet of that catalyst, the 95% confidence intervals for the two methods show even greater overlap.

For other measurements (e.g., regenerated SCR catalyst on August 1st), the 95% confidence intervals for the means of the elemental mercury measurements by the two methods are not as large. In these cases, a clear bias is seen between the two measurement methods for elemental mercury concentration.

With the SCEM elemental mercury concentration measurements all showing a low bias relative to the OH method, the first inclination would be to suspect a systematic error with the SCEM measurements (e.g., calibration error). However, the total mercury concentration measurements do not show a similarly consistent negative bias. At the catalyst inlets, the bias was positive one day and negative the other. For the one catalyst for which outlet total SCEM results are available, the SCEM shows a positive bias compared to the OH results.

The cause of the apparent bias between the two measurement methods, particularly for elemental mercury concentration, remains unknown. However, in spite of this apparent bias, the results show that all four catalysts had lost much of their activity for elemental mercury oxidation since previous measurements. The SCEM data showed oxidation percentages ranging from 2 to 18% for the regenerated catalysts from Spruce and 15 to 25% for the fresh catalysts. The OH measurements did not show activity as low as the SCEM results, but still showed all four catalysts were achieving less than 50% oxidation of the inlet elemental mercury. These percentages were significantly lower than were measured in late June, where the oxidation percentages ranged from 70% for the new gold to 76% for the regenerated gold, and particularly low that initial values of greater than 90% oxidation for all four catalysts. The significant losses measured may further reflect adverse effects of earlier unscheduled pilot unit outages in April (plant disconnected pilot unit power), June and July (tripped ground fault circuit interrupter breaker).

An SCEM catalyst activity measurement trip was also made at the end of September 2006. These results are summarized in Table 35. The percent oxidation values were considerably higher than the August values shown above. However, the relative performance of the four catalysts was the same for both trips, with the new Prototech Pd #1 catalyst being the most active and the regenerated SCR the least active. For the other two catalysts, the new Prototech gold catalyst was slightly less active than the regenerated gold catalyst for both trips.

Table 35. Results of Catalyst Activity Measurements at Plant Yates, September 2006

Catalyst Type	Catalyst Inlet Total Hg*, μg/Nm^3	Catalyst Inlet Elemental Hg*, μg/Nm^3	Catalyst Inlet Oxidation %	Catalyst Outlet Total Hg*, μg/Nm^3	Catalyst Outlet Elemental Hg*, μg/Nm^3	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst, %	Catalyst Outlet Oxidation, %
Pd #1	3.2	1.1	66	2.9	0.24	9	79	92
New Gold	3.2	1.1	66	2.9	0.42	8	61	86
Regenerated Gold	3.2	1.1	66	2.7	0.36	16	67	87
Regenerated SCR	3.2	1.1	66	3.6	0.84	-11	22	76

*1 μg/Nm^3 @ 3% O_2 = 0.66 lb Hg/10^{12} Btu heat input

The coal being fired at the time was apparently quite low in mercury content, and the resulting catalyst inlet elemental mercury concentrations were very low (about 1 μg/Nm^3). This made accurate measurement of catalyst activity difficult, because of the even lower elemental mercury concentrations measured at the catalyst outlet. Consequently, the mercury oxidation percentage results shown in Table 35 for the September trip are considered unreliable.

The next catalyst activity measurement trip was conducted immediately after a catalyst cleaning, in mid-November 2006. The results of those measurements are summarized in Table 36. Mercury adsorption and elemental oxidation were measured on different days for the catalysts, so these results are shown on separate lines in the table. Measurements of mercury adsorption were also made on November 8th, one day after the pilot unit was put back in service. Those results (not included in the table) showed that gold and palladium catalysts were still adsorbing some mercury (26% to 32%). After several days of operation, they were much closer to adsorption equilibrium, as shown in the table (adsorption values of 11% or less).

Table 36. Results of Catalyst Activity Measurements at Plant Yates, November 8-11, 2006

Catalyst Type	Catalyst Inlet Total Hg*, µg/Nm^3	Catalyst Inlet Elemental Hg*, µg/Nm^3	Catalyst Inlet Oxidation %	Catalyst Outlet Total Hg*, µg/Nm^3	Catalyst Outlet Elemental Hg*, µg/Nm^3	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst, %	Catalyst Outlet Oxidation, %
New Pd #1* (11/9)	6.2	1.6	75	-	0.98	-	38	84
New Pd/Al (11/11)	7.8	-	-	7.6	-	3	-	-
New Gold (11/9)	6.2	1.6	75	-	0.67	-	58	89
New Gold (11/11)	7.8	-	-	7.0	-	11	-	-
Regenerated Au (11/10)	5.4	1.1	78	-	0.81	-	26	85
Regenerated Au (11/11)	7.8	-	-	7.8	-	1	-	-
Regenerated SCR (11/10)	5.4	1.1	78	-	0.75	-	32	86
Regenerated SCR (11/9)	6.2	-	-	6.3	-	-2	-	-

*1 µg/Nm^3 @ 3% O_2 = 0.66 lb Hg/10^{12} Btu heat input

The SCEM results for all of the catalyst activity measurement trips through November 2006 are plotted in Figure 37. As can be seen in the figure, the November data show mixed results for the four catalysts as far as changes in elemental mercury oxidation activity since the previous measurements in September. The activity of the Prototech gold catalyst was down only slightly from the September results, while the activities of the Prototech Pd #1 and regenerated gold were down by about 40 percentage points since September. The activity of the regenerated SCR catalyst actually improved by about 10 percentage points compared to the September results.

Only the Prototech gold catalyst results show a consistent trend for oxidation activity versus time (discounting the August 2006 results, which showed unexplainably low performance for all four catalysts). A least squares fit line is shown for the Prototech gold catalyst results without the August 2006 value, and shows a consistent linear decrease in activity over approximately 11 months of catalyst operation in this low-sulfur Eastern bituminous flue gas. While the results for the other three catalysts are not as consistent, they also show a general trend for reduced activity for elemental mercury oxidation versus time in flue gas service.

Because the catalyst pilot unit was out of service during other testing at the plant from January 23 to May 10, 2007, no further activity measurement trips were made until May 2007. OH measurements were made simultaneously. The results from both types of measurements are summarized and compared in Table 37. These data represent the final activity measurements for these four catalysts.

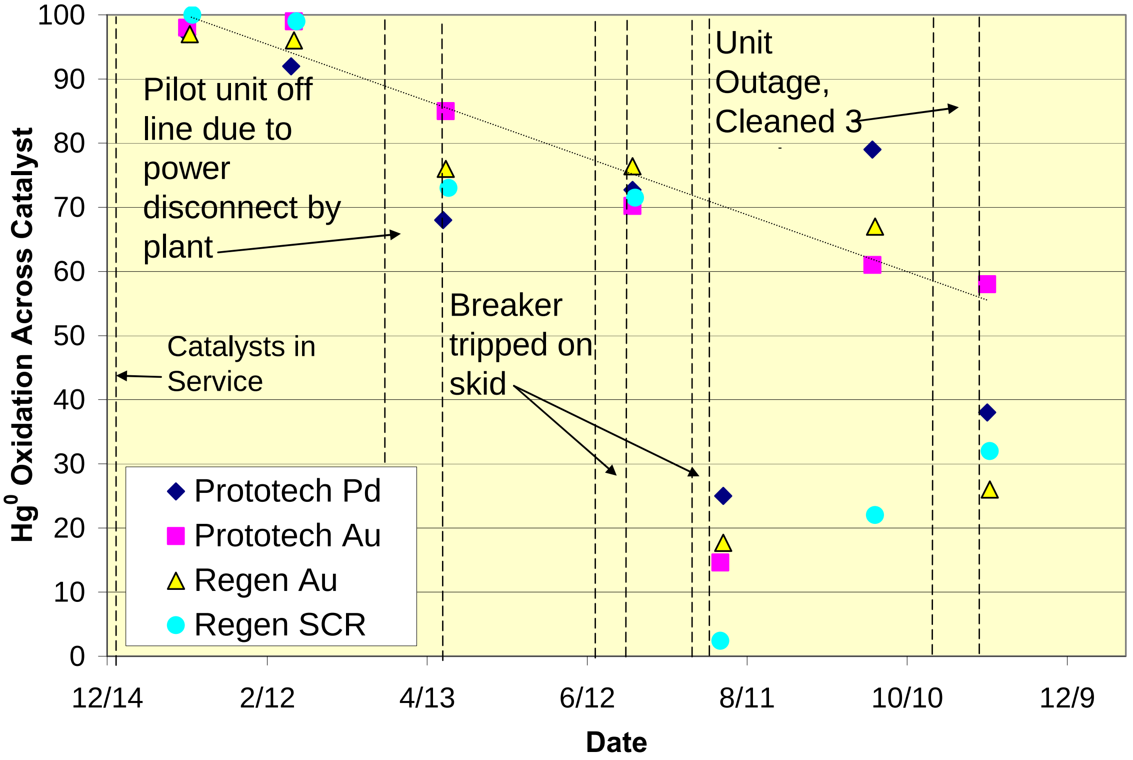


Figure 37. Catalyst Activity versus Time for the Oxidation Catalysts at Plant Yates through November 2006

Table 37. May 2007 OH Method Relative Accuracy Results for Yates Pilot (mean and 95% confidence interval of three runs compared to simultaneous Hg SCEM results)

	Total Hg*	**Elemental Hg***	**Oxidized Hg***
New Pd #1 Catalyst, May 21-22, 2007:			
Catalyst Inlet – OH, µg/Nm^3*	5.5 ± 0.4	2.9 ± 0.4	2.6 ± 0.8
Catalyst Inlet – SCEM, µg/Nm^3	6.6 ± 1.3	1.9 ± 0.1	4.7 ± 1.3
Relative Accuracy, % (based on means)	120	66	180
Catalyst Outlet – OH, µg/Nm^3	7.1 ± 0.3	2.6 ± 0.2	4.5 ± 0.2
Catalyst Outlet – SCEM, µg/Nm^3	5.4 ± 2.3	0.8 ± 0.1	4.6 ± 2.4
Relative Accuracy, % (based on means)	76	31	102
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	9	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	57	-
Measured Flue Gas Flow Rate, acfm	1,180	-	-
New Gold Catalyst, May 23, 2007:			
Catalyst Inlet - OH, µg/Nm^3	10.7 ± 1.8	5.6 ± 0.9	5.1 ± 1.2

	Total Hg*	**Elemental Hg***	**Oxidized Hg***
Catalyst Inlet - SCEM, μg/Nm^3	7.7 ± 0.4	2.0 ± 0.4	5.7 ± 0.4
Relative Accuracy, % (based on means)	72	36	112
Catalyst Outlet – OH, μg/Nm^3	10.3 ± 2.3	4.5 ± 1.2	5.8 ± 1.5
Catalyst Outlet - SCEM, μg/Nm^3	6.6 ± 1.3	1.3 ± 0.1	5.2 ± 1.4
Relative Accuracy, % (based on means)	64	29	90
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	19	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	32	-
Measured Flue Gas Flow Rate, acfm	679	-	-
Regenerated Gold Catalyst, May 21-22, 2007:			
Catalyst Inlet – OH, μg/Nm^3	5.5 ± 0.4	2.9 ± 0.4	2.6 ± 0.8
Catalyst Inlet - SCEM, μg/Nm^3	6.6 ± 1.3	1.9 ± 0.1	4.7 ± 1.3
Relative Accuracy, % (based on means)	120	66	180
Catalyst Outlet – OH, μg/Nm^3	8.8 ± 1.0	2.2 ± 0.2	6.6 ± 1.2
Catalyst Outlet - SCEM, μg/Nm^3	4.8 ± 1.3	0.5 ± 0.4	4.3 ± 1.7
Relative Accuracy, % (based on means)	55	23	65
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	25	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	72	-
Measured Flue Gas Flow Rate, acfm	671	-	-
Regenerated SCR Catalyst, May 23, 2007:			
Catalyst Inlet – OH, μg/Nm^3	10.7 ± 1.8	5.6 ± 0.9	5.1 ± 1.2
Catalyst Inlet - SCEM, μg/Nm^3	7.7 ± 0.4	2.0 ± 0.4	5.7 ± 0.4
Relative Accuracy, % (based on means)	72	36	112
Catalyst Outlet – OH, μg/Nm^3	9.3 ± 1.4	3.8 ± 0.3	5.5 ± 1.2
Catalyst Outlet - SCEM, μg/Nm^3	6.5 ± 1.3	1.3 ± 0.3	5.2 ± 1.0
Relative Accuracy, % (based on means)	70	34	95
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	32	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	34	-
Measured Flue Gas Flow Rate, acfm	1,200	-	-

*****Note – All Hg concentrations corrected to 3% O$_2$, dry basis; 1 μg/Nm^3 Hg at 3% O$_2$ equals 0.67 lb/10^{12} Btu heat input

The results do not show good agreement between the two measurement types, even for total mercury concentrations. The relative accuracy values shown on the table represent the value gas measured by Hg SCEM divided by the value as measured by the OH method. At the catalyst pilot unit inlet, the relative accuracy values for total mercury averaged 120% on the first day (actually the afternoon of May 21 and morning through early afternoon of May 22) and 72% the second day (May 23). While it is desirable that these relatively accuracies be closer to 100%, part of the discrepancy may be due to the measurement periods of the two methods. For each of the three runs, the OH value represents an average concentration over the 2-hr sampling period, whereas the Hg SCEM value represents an average of a number of discrete measurement points collected sometime during that same 2-hr period. The Hg SCEM must cycle between measuring inlet total and elemental mercury concentrations during the 2-hr period, so it may not measure the same average as does the OH method. This is particularly true if the flue gas mercury concentrations vary with time, as they do at Plant Yates Unit 1.

The catalyst inlet elemental mercury concentrations show even poorer relative accuracy between the Hg SCEM and the OH method, with values calculated from the means ranging from 36 to 66%. Since the Hg SCEM measures the oxidized mercury fraction by difference, the relative accuracy of that value is entirely dependent on the relative accuracies of the total and elemental fractions, which as discussed above were not good. The calculated mean relative accuracies for oxidized mercury at the catalyst inlet ranged from 112 to 180 percent.

At the catalyst outlets, the relative accuracies were generally poorer than at the inlet. The effects of cycling by the Hg SCEM on the difference in averaging periods for the two methods are even greater, since one analyzer is cycled between total and elemental mercury fractions for two catalysts during each OH run. Thus, for each catalyst and fraction, there are less than 30 minutes of data collected during the 2-hr period. Relative accuracies for catalyst outlet total mercury concentrations ranged from 55 to 76 percent. For the elemental mercury fraction concentrations the relative accuracies ranged from 23 to 34 percent.

Both the total and elemental mercury concentration measurements by the Hg SCEM appear to be biased low compared to the OH measurements. The bias was more pronounced for the elemental mercury concentrations. This is possibly an impact of the IGS filter used to separate any fly ash from the flue gas sample going to the Hg SCEM. If there is any solids buildup on the surface of the IGS filter, it can lead to oxidation of the mercury in the sample gas, which results in a low bias for the elemental mercury concentration.

Because of this apparent low bias, the Hg SCEM data show considerably higher mercury oxidation performance than do the OH values. For example, the Hg SCEM data showed 72% elemental mercury oxidation across the regenerated gold catalyst while the OH data showed only 25%.

The OH data show that the four catalysts had lost much of their activity, with the Pd #1 catalyst achieving only 9% elemental mercury oxidation across the catalyst and the regenerated SCR catalyst achieving 32%. All four catalysts were also operating at flue gas flow rates well below the desired value of 2,000 acfm. Both of these effects are likely a result of fly ash buildup in the catalysts.

Figure 38 shows the elemental mercury oxidation performance of the four catalysts over the entire test period. For the May 2007 data, OH values rather than Hg SCEM values are shown in the plot. The data in the plot show a continual loss of activity versus time. The rate of loss appears to be relatively linear for the regenerated gold catalyst, but the data show more scatter for the other three catalysts.

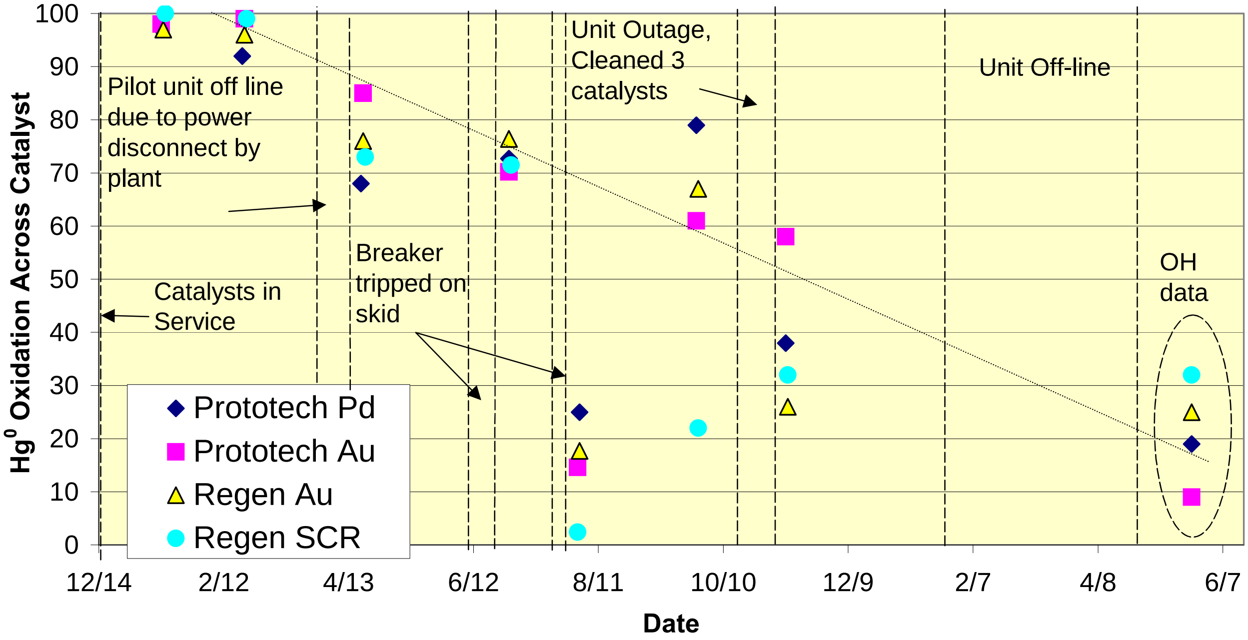


Figure 38. Activity versus Time for Oxidation Catalysts at Plant Yates over the Entire Test Period

While discussing plans for additional testing Plant Yates, the project team noticed that the flue gas temperature at the pilot catalyst skid had been low compared to typical ESP operation. Logger data over operating periods from December 2005 through May 2007 showed the catalyst outlet temperatures to have ranged from approximately 190°F to 260°F (88°C to 127°C). All though as shown below the sulfuric acid concentrations in the flue gas going to the pilot unit were quite low, it is quite likely that during operation at the lower end of this temperature range, the flue gas flowing through the catalyst chambers was below its sulfuric acid dew point, and a small amount of sulfuric acid mist was collected on catalyst surfaces. This in turn would react with fly ash and with catalyst surfaces, contributing to both pressure drop buildup and loss of catalyst activity. A temperature range of 280°F to 300°F (138°C to 149°C) would be more representative of full-scale ESP outlet flue gas conditions on plants that fire bituminous coal. It is very likely that low inlet temperatures in the flue gas flow to this pilot unit contributed to difficulties in maintaining low catalyst pressure drop and to premature loss of catalyst activity. This was undoubtedly exacerbated by several unscheduled pilot unit outages, where moist flue gas was not purged from the catalyst chambers prior to shut down.

Flue Gas Characterization Results

During the week in August 2006 in which OH measurements were made around the pilot unit at Plant Yates, additional flue gas measurements were made, including SO_3/sulfuric acid, halogen gases, and trace metals concentrations. These results are summarized below.

SO_3/Sulfuric Acid

Measurements were made by the Controlled Condensation System method to determine whether the mercury oxidation catalysts also oxidized a percentage of the flue gas SO_2 to SO_3/sulfuric acid. The tests were conducted by sampling the catalyst pilot unit inlet gas and the outlet gas from two catalysts one day, with the outlets of the other two catalysts being sampled the next morning. The results are summarized in Table 38.

Table 38. Summary of Flue Gas Sulfuric Acid Concentration Measurements at Plant Yates

Location	Sample ID	Date	H_2SO_4, ppmv dry basis at 3% O_2
Catalyst Inlet	Run 1	8/3/2006	0.5
	Run 2	8/3/2006	0.4
	Run 3	8/3/2006	0.2
Catalyst Inlet Average:			0.3
Prototech Pd #1 Catalyst	Run 1	8/3/2006	0.5
	Run 2	8/3/2006	0.2
	Run 3	8/3/2006	0.3
Prototech Pd #1 Catalyst Outlet Average:			0.3
Regenerated SCR Catalyst	Run 1	8/4/2006	0.2
	Run 2	8/4/2006	0.2
	Run 3	8/4/2006	0.4
Regenerated SCR Catalyst Outlet Average:			0.2
Prototech Gold Catalyst	Run 1	8/3/2006	0.2
	Run 2	8/3/2006	0.2
	Run 3	8/3/2006	0.8
Prototech Gold Catalyst Outlet Average:			0.4
Regenerated Gold Catalyst	Run 1	8/4/2006	0.2
	Run 2	8/4/2006	0.1
	Run 3	8/4/2006	0.5
Regenerated Gold Catalyst Outlet Average:			0.2

Oxidation of SO_2 to form SO_3/sulfuric acid in the flue gas could lead to issues such as increased duct corrosion and/or increased plume opacity. Adsorption of SO_3/sulfuric acid by the catalyst may contribute to a loss of catalyst activity over time due to the blocking of active catalyst sites. The results show no clear evidence of SO_2 oxidation across the catalysts, or of SO_3/sulfuric acid adsorption by the catalysts. The inlet SO_3 concentrations averaged 0.3 ppmv (dry basis) while the outlet concentrations averaged 0.2 to 0.4 ppmv. These are all extremely low concentrations, and the outlet values are equal to the inlet average within the repeatability of the method.

The flue gas SO_2 concentrations were also measured as part of this effort. The measured concentrations were in the range expected, with 1220 ppmv dry basis at 3% O_2 at the catalyst inlet on August 3rd and 1280 ppmv at the catalyst outlet. On August 4th, the catalyst outlet measurement was 1330 ppmv dry basis at 3% O_2.

Flue Gas Halogen Species Concentrations

Sampling was conducted by EPA Method 26a to determine the concentrations of halogen species in the flue gas at the catalyst pilot unit inlet, as halogen species are known to participate in elemental mercury oxidation reactions. The results of these measurements are summarized in Table 39. They show that the flue gas contains about 25 ppmv dry basis of HCl at the actual flue gas O_2 concentration (35 ppmv dry at 3% O_2), 0.6 ppmv dry basis of Cl_2 (0.8 ppmv dry at 3% O_2) and 9 ppmv dry basis of HF (12 ppmv dry at 3% O_2).

Table 39. Results of Flue Gas Halogen Sampling by Method 26a (Catalyst Inlet, 8/3/06)

Sample ID	Particulate Loading, gr/dscf	Vol% Water in Flue Gas	O_2% in Flue Gas	Chloride, ppmv dry, at measured O_2	Cl_2 ppmv dry, at measured O_2	Fluoride ppmv dry, at measured O_2
Run 1	0.0040	9.2	7.9	23.8	0.5	7.8
Run 2	0.0078	8.4	8.2	26.2	0.6	8.1
Run 3	0.0157	9.0	7.5	25.8	0.6	10.5
Average	0.0091	8.9	7.8	25.2	0.6	8.8

Flue Gas Trace Metals Concentrations

Flue gas metals concentrations were measured by EPA Method 29 at the catalyst pilot unit inlet location. These measurements were made to determine what metals are present in the vapor phase that could potentially be catalyst poisons, although the method also determines particulate-phase metals concentrations. The results of these measurements are summarized in Table 40. The particulate phase results are expressed in the table as an equivalent gas-phase concentration in ppbv (dry basis).

The results show that selenium was the metal present in the highest concentration in the vapor phase, followed by zinc, copper and chromium, in order (mercury concentrations were not quantified by Method 29 in these measurements). Selenium is a suspected mercury oxidation catalyst poison.

Table 40. Results of Pilot Unit Inlet Metals Concentration Measurements by Method 29

Metal	Gas Phase Concentration, ppbv (dry basis at actual flue gas O_2)				Particulate Phase Concentration, expressed as equivalent gas phase concentration in ppbv (dry basis, actual O_2)			
	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average
Antimony	<0.74	<0.73	<0.74	<0.74	0.13	0.37	0.52	0.34
Arsenic	<0.61	<0.59	<0.61	<0.60	7.6	16.0	19.4	14.3
Barium	0.65*	<0.52	<0.53	<0.56	9.5	18.7	24.8	17.7
Beryllium	<0.05	<0.04	<0.04	<0.05	1.8	3.5	4.5	3.3
Cadmium	<0.02	<0.02	<0.02	<0.02	0.08	0.07	0.10	0.09
Chromium	0.21	0.21	<0.18	<0.20	2.9	5.3	13.1	7.1
Cobalt	<0.31	<0.29	<0.30	<0.30	0.9	1.7	2.5	1.7
Copper	0.37*	0.23*	0.17*	0.26*	4.9	7.6	17.9	10.2
Lead	<0.22	<0.21	<0.21	<0.22	0.8	1.7	2.2	1.6
Nickel	0.97	<0.30	<0.30	<0.52	5.5	5.4	101	37
Selenium	10.1	23.3	25.4	19.6	2.7	3.2	4.5	3.5
Thallium	<0.23	<0.22	<0.22	<0.22	0.05	0.12	0.15	0.10
Zinc	2.0	2.0	1.8*	1.9	9.0	15.4	21.4	15.3

*Field blank value was greater than 30% of measured value

Catalyst Pilot Unit Operation at SRP Coronado Station

Unit 2 at Coronado Generating Station is rated at 411-MW of generating capacity, and has a pulverized coal boiler that fires PRB coal. It has a hot-side ESP for particulate control and (at the time) a horizontal, natural oxidation, limestone wet FGD system for SO_2 control. The PRB coal contains 0.2 to 0.4 wt% sulfur, 0.06 to 0.09 ppm of mercury, and less than 100 ppm of chlorine. The flue gas typically contains 10 to 15 $\mu g/Nm^3$ of total mercury, of which greater than 90% is in the elemental form.

A two-chamber catalyst pilot unit was installed at Coronado Station. It was otherwise similar to the four-chamber catalyst pilot units at Monticello and Yates. As shown in Table 41 below, the Coronado testing was focused on gold-based catalyst, but at two superficial gas velocities through the catalyst chambers. One chamber operated at a superficial gas velocity of 5.5-ft/s (1.7-m/s), which is typical of the gold and palladium catalysts in the Monticello and Yates pilot units, while the second chamber operated at a superficial gas velocity of 15-ft/s (4.6-m/s). The objective of this test was to determine whether at this plant, where there is not an existing cold-side ESP enclosure in which catalysts could be installed, adequate oxidation performance could be achieved with a smaller cross-section vessel. Johnson Matthey prepared both gold catalysts for the Coronado pilot unit. Note that the 15-ft/s catalyst chamber has only 72% of the catalyst volume of the 5.5-ft/s chamber, yet treats the same amount of flue gas.

Table 41. Characteristics of Catalysts Installed in Pilot Unit at Coronado Station

Catalyst Type	Source	Cell Pitch, mm	CPSI, cells/ in.^{2} (cells/cm^2)	Catalyst Cross-section, in. x in. (cm x cm)	Catalyst Length	Area Velocity, sft/hr (Nm/h)
Gold-based (Au)	Johnson Matthey	3.2	64 (9.9)	29.5 x 29.5 (75 x 75)	2 x 6 in. (2 x 15 cm)	37 (11)
Gold-based (Au)	Johnson Matthey	3.2	64 (9.9)	17.7 x 17.7 (45 x 45)	4 x 6 in. (4 x 15 cm)	51 (15)

The oxidation catalyst pilot unit at Coronado was started up at the end of March 2006. The activity of these catalysts was not measured as frequently as at Monticello or Yates, so there are fewer results to report.

Catalyst Pressure Drop Data

Figure 39 shows the pressure drop across the two catalyst chambers at Coronado from startup through the end of the test program, over 14 months later. These data were recorded manually, so there are fewer data points than for the other two pilot units. The 15-ft/s catalyst operated at higher pressure drop than the 5.5-ft/s catalyst, as would be expected. Not only was there a velocity effect, but twice the overall catalyst depth in the 15-ft/s catalyst to compensate for the higher velocity so as to achieve high oxidation percentages.

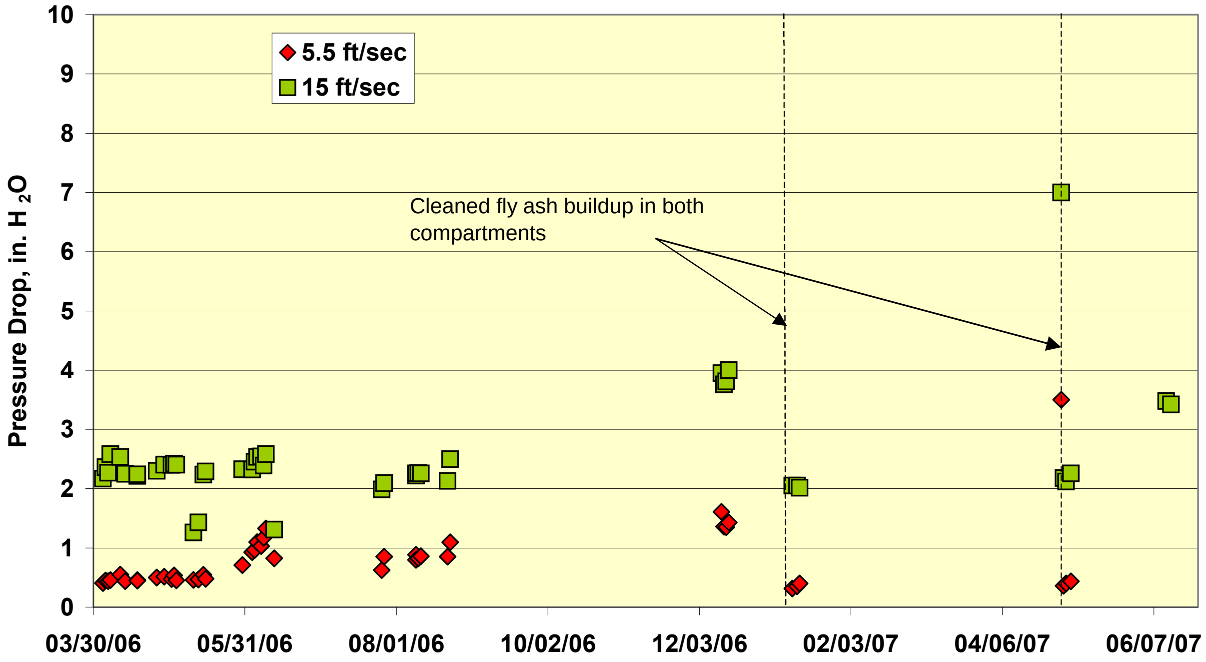


Figure 39. Pressure Drop Data for the Oxidation Catalysts at Coronado

Note: 1.0 in. H_2O = 0.25 kPa

In early June 2006, representing just over two months of operation, the pressure drop across the 5.5-ft/s catalyst increased for unknown reasons, but the next data point showed complete recovery. The sonic horns were working reliably during this period.

Other than that one perturbation, the data show relatively stable pressure drop values for the first five months of operation, then a significant increase in the December 2006 data, after nearly nine months of operation. The sonic horns on the pilot unit continued to work reliably, so it is not clear what caused the increase. The horns were being operated on a relatively infrequent basis, 10 seconds every 30 minutes. Some sonic horn vendors recommend more frequent operation, as often as 10 seconds every 10 minutes. The horn frequency of operation may have needed to be increased to avoid pressure drop build-up with this PRB fly ash.

The catalysts were cleaned of fly ash buildup in January 2007. The fly ash was found to be dry and free flowing, and readily cleaned from the catalyst flow channels with compressed air. As shown in Figure 39, the catalyst pressure drop values returned to essentially fresh catalyst performance.

The catalysts were cleaned of fly ash buildup again in May 2007, and again the fly ash was found to be dry and free flowing, and readily cleaned from the catalyst flow channels with compressed air. As shown in Figure 39, the catalyst pressure drop values returned to essentially fresh catalyst performance after this cleaning as well. After the May cleaning, the sonic horn operating frequency was increased to 10 seconds every 10 minutes. In spite of the increase in cleaning frequency, some increase in pressure drop was noted across the 15-ft/s catalyst over the next month of operation, after which the pilot unit was shut down at the end of the planned test period.

It is not clear why the sonic horns were not effective at preventing fly ash buildup, particularly after the increase in their operating frequency over the last month of operation. However, there is growing evidence from these three sites that, once fly ash buildup in the catalyst flow channels begins, the horns are less effective at removing it.

Elemental Mercury Oxidation Activity Performance

The first catalyst measurement trip conducted at Coronado was in April 2006. Activity data were measured both by SCEM and by the OH method. The measurement results were inconsistent between the two methods, as shown below in Table 42. The results are presented as mercury oxidation at the catalyst outlet, rather than as a percent oxidation of elemental mercury across the catalyst. However, since the mercury in the inlet flue gas was typically 10% or less oxidized, the two percentage values at the catalyst outlet are not markedly different.

Table 42. Hg SCEM and OH Data for Oxidation Catalysts in the Coronado Pilot Unit

	Hg Oxidation at Outlet of 5.5-ft/s Catalyst, % of Total Hg	Hg Oxidation at Outlet of 15-ft/s Catalyst, % of Total Hg
SCEM Result	84	97
OH Result	95	88

The SCEM data showed the 15-ft/s catalyst to be the better performing of the two, while the OH data show the 5.5-ft/s catalyst to be better performing. Possible reasons for this discrepancy are discussed below. Although the OH results showed the 5.5-ft/s catalyst to be the better performing of the two, the 15-ft/s catalyst had only 72% of the catalyst volume of the 5.5-ft/s catalyst. The fact that the performance of the two catalysts was similar illustrates the mass transfer benefits that can be derived from operating at higher velocity through the catalysts.

Wet FGD pilot tests were also conducted downstream of one of the catalysts during this April test period. The intent was to operate the scrubber downstream of the better performing catalyst. Since only SCEM results were available at the time, the decision was made to operate the scrubber downstream of the 15-ft/s catalyst. Based on the OH results, the better choice would have been to conduct these downstream of the 5.5-ft/s catalyst. The wet FGD test results are presented in detail later in this section.

A number of theories were explored as possibilities for the discrepancy in results between the two methods, as follows:

(1) *A calibration bias in either the SCEM or OH measurements.* Because the bias between the oxidation results for the two methods was positive for one catalyst and negative for the other, a calibration bias in one of the methods could not likely be the cause of the discrepancy; such a bias should be consistent for both catalysts. Furthermore, the agreement of the total mercury concentrations between the two methods validates that the calibration of the SCEM and of the cold vapor atomic absorption spectrophotometer used to measure mercury concentrations in the OH impinger catch solutions. The typical tolerance for discrepancies between the SCEM and OH method is ±20%. Of the 18 runs in which either the catalyst inlet or catalyst outlet total mercury concentrations were measured by both OH and SCEM, one OH run was discarded (using Q-test statistics) and four runs were outside the expected ±20% tolerance (with discrepancies of –26%, 23%, 26%, and 49%). The other 13 runs were well within the expected tolerance. On average, the 17 runs (excluding the one discarded) agreed within 5% of the corresponding SCEM results.

(2) A sampling bias in either the SCEM extraction probe or OH sampling probe.
The two catalysts shared the same flue gas extraction setup for the SCEM (only one 12-in. (0.30-m) section of stainless steel pipe was not common between the two catalysts). Because the oxidation bias was positive for one catalyst and negative for the other catalyst, it is difficult to attribute the bias to a shared flue gas extraction probe. Likewise, the same OH probe was used for measuring downstream of both catalysts. It is unlikely that a bias occurred where the probe oxidized mercury for one catalyst and not the other, or where the probe reduced mercury for one catalyst and not the other.

(3) A sampling bias in the chemical conversion/capture system of either method.
As with the flue gas extraction equipment, the chemical conversion and capture systems for both methods were common to both catalysts. And, the two catalysts had the same chemical composition, and should have produced similar mercury species in the flue gas being sampled. Therefore, it is difficult to attribute a bias to the chemical conversion/

capture system that acts in one direction for one catalyst and the other direction for the other catalyst. For the SCEM, the chemical conversion system was subjected to quality control checks in which the ability of the KCl impingers to transmit a known quantity of elemental mercury was measured. The mercury recovery of all these quality control checks was within the acceptance criteria of 80 - 120%.

(4) *A bias attributable to the location from which the flue gas was sampled.*
The OH samples were pulled from a sample port 11-12 ft (3.4-3.7 m) downstream of the catalyst exit, in a section of ductwork with fully turbulent flow. The OH probe was inserted to the midpoint of the 10-in. duct exiting the catalyst. The sample was pulled isokinetically. It was postulated that a well-mixed sample of gas was extracted for OH because of the distance of the ports from the catalyst exit and the fact that the probe was inserted into the middle of the duct. In contrast, the SCEM flue gas extraction ports were located on the tops of the catalyst chamber outlet ducts, just downstream of the outlet transitions and only about a foot downstream of the last catalyst layer in each compartment. The flue gas was in laminar flow at this location. No probe was inserted into the catalyst chamber at the SCEM sample port; therefore, the sampled flue gas likely came from the upper portion of each catalyst chamber. It is possible that the flue gas exiting the catalysts was stratified to some extent at the SCEM sample ports, and thus introduced a bias into one or both measurements. The bias could have gone in either direction at either location.

Based on this evaluation of the April 2006 results, a test plan was devised to compare the two port locations with the SCEM analyzers. A single port was used to extract a sample to make measurements on the catalyst inlet flue gas. The flue gas extraction system consisted of a probe inserted midstream into the catalyst inlet duct followed by an IGS filter. An SCEM analyzer made flue gas measurements at this location.

A diagram and the nomenclature of the catalyst outlet sampling locations used in the August 2006 test program are provided in Figure 40. The flue gas from each catalyst outlet was sampled at two locations. The first location was the built-in IGS filter port described above and used for SCEM measurements in March and April 2006. This sampling system was common between the two catalysts except for two 12-in. (0.30-m) sections of pipe. The second sampling locations were the same ports used for the OH outlet measurements made in April 2006. This time, a flue gas extraction loop was built with an IGS filter at one of these ports and an SCEM was used to make the flue gas mercury measurements. The extraction loop included a probe that was inserted midstream in the outlet duct. The flue gas extraction probe was moved from the outlet of one catalyst to the other as required to sample both catalysts. OH measurements were not made as part of the August 2006 performance verification, during which this test was conducted.

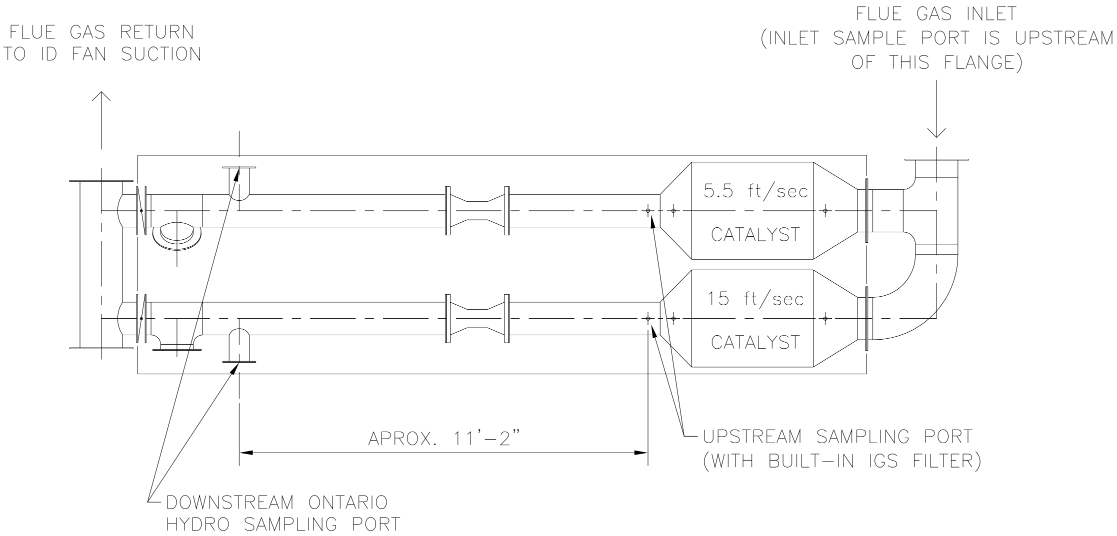


Figure 40. Sampling Port Diagram for Catalyst Units

The catalyst performance metrics calculated from the August SCEM data are summarized in Tables 43 and 44 for the 5.5-ft/s and 15-ft/s catalysts, respectively. These tables show the average total and elemental mercury concentrations measured for the inlet and outlet of each catalyst. From these averaged measurements, the following values were calculated:

- The percent of the total mercury present in the oxidized form at the inlet and outlet of each catalyst,
- The percent of the inlet total mercury adsorbed across the catalyst, and
- The percent of inlet elemental mercury oxidized across the catalyst.

The inlet total mercury concentrations ranged between 8 and 12 μg/Nm^3 when corrected to 3% O_2; however, there were several brief periods where corrected inlet total mercury concentrations were as high as 20 μg/Nm^3. The percent oxidation of mercury at the catalyst inlet varied over the course of the two days of measurements, ranging from 0 to 27% of the total mercury being present as oxidized mercury. However, the percent oxidized mercury was typically less than 10% of the total mercury at the catalyst inlet.

There was significant adsorption of mercury measured across each of the catalysts, ranging between 9 and 41%. The catalysts typically adsorb mercury when the flue gas total mercury concentration increases from previous values, and/or when the flue gas temperature drops from a previously higher value. Conversely, the catalysts have been observed to desorb mercury into the catalyst outlet flue gas when the inlet total mercury concentration drops and/or the inlet flue gas temperature increases. When there is a significant amount of mercury adsorption across a catalyst (greater than approximately 15 to 20%), it becomes difficult to quantify elemental mercury oxidation across that catalyst with accuracy. That is because it is not possible to differentiate between the decrease in elemental mercury concentration across the catalyst due to oxidation versus that caused by adsorption.

Table 43. Mercury Measurement Results for 5.5-ft/s Catalyst

	Catalyst #1 (5.5-ft/s)	
Probe Location	**Downstream port**	**Built in IGS**
Date	8/10/2006	8/10/2006
Time Start - Time End	15:28-17:41	12:30-15:45
Catalyst Inlet Flue Gas:		
Hg^T	12.0	9.6
Hg^0	10.9	10.0
% Oxidation	9%	-4%
Catalyst Outlet Flue Gas:		
Hg^T	6.9	8.6
Hg^0	1.0	1.3
% Oxidation	85%	85%
% Removal of Hg^T Across Catalyst	42%	11%
% Hg^0 Oxidation across Catalyst	90%	87%

Table 44. Mercury Measurement Results for 15-ft/s Catalyst

	Catalyst #2 (15-ft/s)			
Probe Location	**Downstream port**	**Built in IGS**	**Downstream port**	**Built in IGS**
Date	8/9/06	8/9/06	8/10/2006	8/10/2006
Time Start - Time End	15:44-17:34	17:45-19:25	7:52-9:30	9:48-12:16
Catalyst Inlet Flue Gas:				
Hg^T	10.0	12.9	12.71	13.72
Hg^0	10.2	9.4	11.94	10.80
% Oxidation	-2%	27%	6%	21%
Catalyst Outlet Flue Gas:				
Hg^T	9.2	8.8	7.55	9.11
Hg^0	1.6	1.2	1.25	0.48
% Oxidation	83%	87%	83%	95%
% Removal of Hg^T across Catalyst	9%	32%	41%	34%
% Hg^0 Oxidation across Catalyst	84%	87%	90%	96%

In these measurements, there was only a small difference in the measured percentage of the inlet elemental mercury oxidized across the 5.5-ft/s catalyst for the two ports: 87% at the upstream port and 90% at the downstream port.

The results from the upstream port generally agreed with the April 2006 SCEM measurements at the same location, which indicated 85% oxidation of elemental mercury across the catalyst (vs. 87% in August). The consistency of results between the two time periods for the same sampling/measurement method and location indicates no decrease of mercury oxidation performance on the 5.5-ft/s catalyst over this four-month period.

As described above, the April 2006 OH results from the 5.5-ft/s catalyst did not agree well with the SCEM measurements. The OH results indicated 95% oxidation of mercury across the catalyst vs. 85% by SCEM. One theory was that the difference in sampling locations caused the difference between the OH and SCEM results. However, these results from August 2006 show at most a small difference in mercury measurements between the two ports when the same sampling method (SCEM) is used: 90% elemental mercury oxidation across the catalyst when measured at the downstream (OH) port and 87% when measured at the normal, upstream SCEM port. Although this is directionally the same as the bias observed in April 2006 between the OH and SCEM results, the magnitude of the observed difference is much smaller. Also, the measurement at the downstream port may have been biased by the high observed mercury adsorption percentage across the catalyst during that measurement period, which could have introduced a high bias in the observed elemental mercury oxidation percentage across the catalyst. Thus, these results for the 5.5-ft/s catalyst cannot fully explain the difference in mercury oxidation measured by the two methods in April 2006.

In April 2006, the percent elemental mercury oxidation across the 15-ft/s catalyst was not measured, because measurements were not made concurrently at the catalyst inlet while catalyst outlet measurements were made. Only the total percent oxidation of mercury at the catalyst outlet was measured. Because pilot wet FGD tests were being conducted at the same time, the second SCEM and a second OH train were conducting concurrent measurements at the FGD outlet rather than at the catalyst inlet. Thus, it is not possible to compare the measured percent oxidation of inlet elemental mercury across the catalyst between the April and August measurements, and the following discussion compares only the total mercury oxidation values for the catalyst outlet flue gas.

For the 15-ft/s catalyst, the August 2006 measurements made at the upstream, built-in IGS filter port indicated greater total mercury oxidation than at the downstream port (87-95% vs. 83%). This general trend is also directionally consistent with a comparison of the total mercury oxidation measured by SCEM versus OH in April 2006. In April, the SCEM measurements at the built-in IGS filter (upstream port) indicated 95 to 98% of the mercury was oxidized at the catalyst outlet, while the OH measurements at the downstream port indicated 88 to 89% of the total mercury was oxidized at the catalyst outlet.

The catalyst outlet total mercury oxidation percentage results measured on August 10, 2006 were similar to the values measured in April 2006. On August 10, the built-in IGS filter (upstream port) indicated 95% oxidation of mercury at the outlet, while the downstream port indicated 83%

oxidation of mercury at the outlet. This is even greater discrepancy than was seen in the April SCEM versus OH results. However, the oxidation results measured on August 9 at the built-in IGS filter were significantly lower than the measurements made on August 10, showing only 87% oxidation of mercury at the catalyst outlet. The measurements for the downstream port on August 9 repeated the Aug 10 measurements, at 83% total mercury oxidation downstream of the catalyst.

Both days' results indicate higher total mercury oxidation in the sample gas collected at the built-in IGS filter (upstream port) than at the downstream port. While there was some variation in the total mercury oxidation measured at the upstream location on the two days, the measurements were close enough to the April 2006 values to indicate no significant decrease in the mercury oxidation performance of the 15-ft/s catalyst.

However, the total mercury oxidation percentages measured in August 2006 are somewhat confounded with the catalyst inlet mercury oxidation percentages. On both August 9 and August 10, the catalyst inlet total mercury oxidation percentages were significantly higher (27% and 21%, respectively) while sampling the upstream port than while sampling the downstream port (-2% and 6%, respectively).

Measuring the percent decrease in elemental mercury concentration across the catalyst is another measure of catalyst activity that is less impacted by what the inlet oxidation value may be. When comparing the percent oxidation of elemental mercury across the 15-ft/s catalyst as measured at the two locations, a similar trend is seen – higher percent oxidation values are measured at the upstream (built-in IGS filter) location than at the downstream (OH port) location. On August 9, the elemental mercury percent oxidation across the catalyst was measured at 87% at the upstream location and 84% at the downstream location. On August 10, the corresponding values were 96% and 90%.

The August 2006 measurements provided support for one of the postulated theories for the discrepancies between the OH and SCEM measurements conducted in April 2006. Prior to these August 2006 measurements, it had been speculated that the difference in sampling port locations was the reason for the discrepancy. The August 2006 measurements show that for both catalysts the discrepancy between the SCEM measurements made at the two sets of outlet ports correspond directionally with the SCEM versus OH discrepancies measured in April 2006.

Although there is some scatter, the discrepancies seen in August for the 15-ft/s catalyst are similar in magnitude to what was seen in April. These results seem to indicate that the sampling port location may indeed have been the cause of that discrepancy. The August 2006 measurements for the 5.5-ft/s catalyst show less difference in elemental mercury oxidation across the catalyst between the two outlet sample port locations than did the April SCEM versus OH results. However, the direction of the observed bias between the two locations was again consistent.

In summary, the cause of the discrepancies seen in the April 2006 measurements was not conclusively identified in the August measurements. For the 15-ft/s catalyst, there are four days of data from April comparing the OH and SCEM results, and the observed magnitude of the measurement bias appeared to be consistent. The measurements conducted in August 2006 show a bias in the same direction, but not consistently the same magnitude when comparing SCEM results for the two measurement locations for this catalyst. However, the project team concluded that for the 15-ft/s catalyst, the measurement bias observed in April may be introduced predominantly by sample location effects. It was concluded that the OH sampling port was the better location for collecting SCEM data for this catalyst, and appeared to show less optimistic measurements of catalyst mercury oxidation performance than the upstream, built-in IGS filter location.

For the 5.5-ft/s catalyst, there was only one day of comparison data (triplicate runs) between the OH and SCEM results, so the magnitude of the bias was not as well established. Part of the observed bias may have been caused by routine measurement error. As an example, the OH method states that the relative standard deviation for 12 replicate measurements of mercury concentrations less than 3 μg/Nm^3 (such as the catalyst outlet elemental mercury concentration) is less than 34%.[2] Presumably the relative standard deviation for only three measurements could be higher.

The results summarized in Table 43 show that a portion of the observed bias could have been contributed by the sampling location effects investigated in August. Comparison of the elemental mercury oxidation percentage across the 5.5-ft/s catalyst measured by SCEM at the OH port showed somewhat higher oxidation than did the measurement at the upstream, built-in IGS filter port. Thus, it was concluded that the OH sampling port was also the better location for collecting SCEM data for this catalyst, and appeared to show more optimistic measurements of catalyst mercury oxidation performance than the upstream, built-in IGS filter location.

Mercury oxidation performance was next measured across the two catalysts on December 14 and 15, 2006. Based on the August 2006 results comparing sampling location results, as discussed above, the December trip measurements were made only at the downstream ports. The results of these measurements are summarized in Table 45.

Table 45. Results of Catalyst Activity Measurements at Coronado, December 14-15, 2006

Catalyst Type	Catalyst Inlet Total Hg*, μg/Nm^3	Catalyst Inlet Elemental Hg*, μg/Nm^3	Catalyst Inlet Oxidation, %	Catalyst Outlet Total Hg*, μg/Nm^3	Catalyst Outlet Elemental Hg*, (μg/Nm^3	% Hg Adsorption Across Catalyst	Oxidation Across Catalyst, %	Catalyst Outlet Oxidation, %
Au, 5.5 ft/s (12/14)	13.5	13.1	3	13.3	4.6	1	64	65
Au, 15 ft/s (12/15)	14.9	13.5	9	13.4	3.1	10	77	77

*1 μg/Nm^3 @ 3% O_2 = 0.66 lb Hg/10^{12} Btu heat input

These results are compared to previous SCEM results for these catalysts in Figure 41. Because of the observed differences between results measured at the upstream sampling ports compared to the downstream ports, sampling location is shown as a variable in the figure. The previous OH results from April 2006 are also shown. The December 2006 results show a significant drop in catalyst activity for elemental mercury oxidation compared to the August results. This may be an effect of the apparent fly ash buildup in these catalysts, as evidenced by the pressure drop increases shown in Figure 39 above. Consequently, it was decided to go back to the site in early January 2007 to clean out the catalysts of fly ash buildup and re-measure activity.

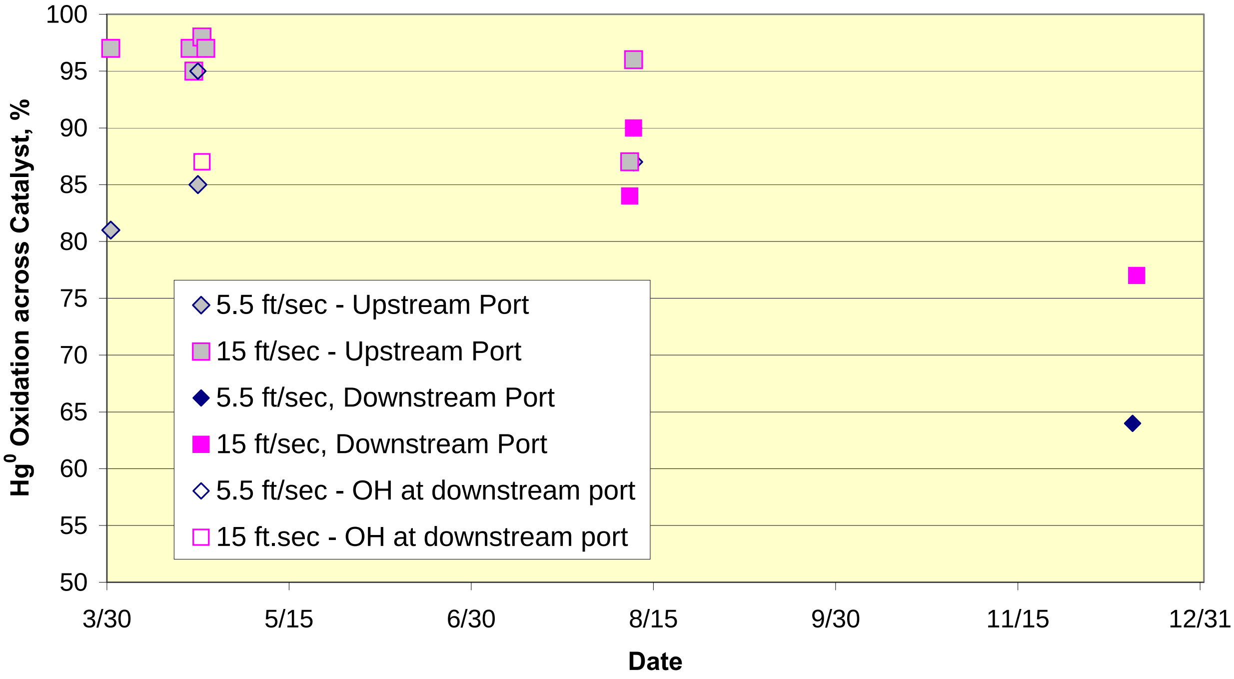


Figure 41. SCEM Results for the Coronado Catalysts Over Time

After catalyst cleaning, mercury concentrations were measured to determine the mercury oxidation and adsorption occurring across each catalyst. The results are summarized in Table 46.

Table 46. Oxidation and Adsorption across Catalyst Units after Cleaning but Prior to Regeneration

Location	Average Total Hg Concentration, μg/dNm^3	Average Elemental Hg Concentration, μg/dNm^3	Total Mercury Adsorption across Catalyst (1/10/2007)	Oxidation of Elemental Mercury across Catalyst (1/10/2007)	Oxidation of Elemental Mercury at Five Months Operation (8/10/06)
Inlet	16.1	14.5	-	-	-
5.5-ft/s Catalyst Outlet	12.5	2.8	22%	81%	90%
15-ft/s Catalyst Outlet	10.4	5.3	35%	63%	87%

The results show a significant decrease in the oxidation occurring across the 15-ft/s catalyst. The 15-ft/s catalyst previously (8/10/06) operated with 87% oxidation of elemental mercury across the unit while now only achieving 63%. The 5.5-ft/s catalyst previously (8/10/06) oxidized 90%

of the inlet elemental mercury, but had dropped to 81%. The next action taken was to thermally regenerate the catalysts.

Catalyst Regeneration

As catalyst is exposed to flue gas, trace metals and other flue gas species adsorb to the surface of the catalyst. This adsorption degrades the mercury oxidation performance of the catalyst. Over time, the oxidation performance of the catalyst decreases to a level unsuitable for its designed use. The catalyst then needs to be replaced or regenerated. Due to the cost of replacing the catalyst, regeneration techniques have been investigated as part of the testing at both Monticello and Coronado.

One method for regeneration is to pass heated air (or flue gas) over the catalyst. The hot air releases the adsorbed species (including mercury) from the catalyst. Previous field tests have shown successful regeneration of catalysts, with a renewal of oxidation capacity[1]. Regeneration procedures were investigated at the completion of the pilot-scale test program at Monticello. Two parameters that were found to affect the time required and success of regeneration are regeneration air flow and air temperature.

In lab regeneration of the Monticello catalysts, as discussed previously, temperatures were varied from 450°F (232°C) to 800°F (427°C) and flow rates were varied from the equivalent of 625 to 1300 acfm (1060 to 2210 m^3/h) for a catalyst the size of the 5.5-ft/s catalyst installed at Coronado. Higher temperatures and flow rates were generally observed to speed the desorption process. However, with a fixed regeneration heater capacity, as the regeneration air flow rate is increased the maximum temperature achievable decreases.

In the lab regenerations, the catalyst outlet mercury concentrations were measured to assess the progress of the regeneration process. Although it is not likely mercury adsorption that adversely affects mercury oxidation performance, the desorption of mercury was used as a surrogate to track the desorption of semi-volatile metals from the catalyst surface. As the catalyst is heated, mercury desorbs from the catalyst and is detected at the catalyst outlet. Lab regenerations were typically run to the point where mercury was no longer detected to be desorbing from the catalyst. With higher temperatures and flow rates, the desorbed mercury comes off in a shorter period of time. In the lab tests, for a detectable amount of mercury to desorb the temperature had to be kept above 400°F (204°C).

A flow rate of 1000 acfm was chosen for the regeneration of the Coronado catalysts. However, the installed heater could not reach the desired temperature of 500°F (260°C) at 1000 acfm (1700 m^3/h) due to a heater element problem. The maximum attainable temperature was 460°F (238°C). The 15-ft/s catalyst was regenerated first, due to its much lower mercury oxidation performance in comparison to the 5.5-ft/s catalyst at that time. The mercury oxidation of both catalysts was measured after this first regeneration. Then the 5.5-ft/s catalyst was regenerated, also at 460°F (238°C) with a flow rate of 1000 acfm (1700 m^3/h). However, during this regeneration, 1000 acfm (1700 m^3/h) also flowed through the 15-ft/s catalyst. Repairs to the heater allowed for both catalyst boxes to attain 460°F (238°C) with the increased flow rate.

Mercury concentrations and speciation were measured the day after regeneration, as shown in Table 47. Inlet total mercury concentration ranged from 12 to 18 µg/Nm^3 while the elemental concentrations ranged from 11 to 15 µg/Nm^3. The oxidation of mercury across the 15-ft/s catalyst greatly increased from the pre-regenerated value of 63% to a post-regenerated value of 91%. The regeneration process returned the oxidation performance of the 15-ft/s catalyst back to the initially high percentage seen when the catalyst was first put into flue gas service. The oxidation across the 5.5-ft/s catalyst remained unchanged (it was not regenerated), but the adsorption of mercury across the catalyst chamber was greatly reduced from 22% to 8%.

Table 47. Catalyst Performance (1/12/07) after First Regeneration of 15-ft/s Catalyst (5.5-ft/s-catalyst was not yet regenerated)

Location	Average Total Hg Concentration, µg/dNm^3	Average Elemental Hg Concentration, µg/dNm^3	Oxidation of Elemental Mercury across Catalyst, %	Adsorption of Mercury across Catalyst, %
Inlet	14.3	11.7	-	-
5.5-ft/s Catalyst Outlet	13.0	2.6	80%	8%
15-ft/s Catalyst Outlet	9.3	1.2	91%	34%

The 5.5-ft/s catalyst was regenerated next. During this regeneration, flow was allowed to pass across both catalysts, extending the regeneration time on the 15-ft/s catalyst. The mercury oxidation performance was measured across both catalysts after overnight regeneration of the 5.5-ft/s catalyst. Table 48 shows the results of the second regeneration.

Table 48. Catalyst Performance (1/13/06) after Second Regeneration Period (flow passing through both catalysts)

Location	Average Total Hg Concentration, µg/dNm^3	Average Elemental Hg Concentration, µg/dNm^3	Oxidation of Elemental Mercury across Catalyst, %	Adsorption of Mercury across Catalyst, %
Inlet	14.3	11.7	-	-
5.5-ft/s Catalyst Outlet	11.1	2.3	80%	22%
15-ft/s Catalyst Outlet	9.2	1.2	91%	34%

Table 49 shows the oxidation results before and after both catalyst regenerations and compares results to oxidation performance measured in August 2006. August 2006 was the fifth month of continuous catalyst operation. The 15-ft/s catalyst did not observe further improvement after undergoing its second regeneration period, suggesting that all desorption of competing species had been completed during the first regeneration period. The oxidation of elemental mercury across the 15-ft/s catalyst remained at 91%.

Table 49. Oxidation of Elemental Mercury across Catalysts before and after Each Regeneration

Location	At Five Months Operation (8/10/06)	Before Regeneration (1/10/06)	After First Regeneration (1/12/06)	After Second Regeneration (1/13/06)
5.5-ft/s Catalyst Outlet	90%	81%	80%*	80%
15-ft/s Catalyst Outlet	87%	63%	91%	91%

*No flow through 5.5-ft/s catalyst during this regeneration, as purpose was to regenerate 15-ft/s catalyst.

The performance of the 5.5-ft/s catalyst did not improve after the attempt to regenerate it. The oxidation of elemental mercury across the 5.5-ft/s catalyst remained approximately 80% after the regeneration process and was not restored to the August 2006 oxidation level of 90%.

Mercury oxidation performance was next measured across the two catalysts on May 4 and May 5, 2007. The May results are summarized in Table 50.

Table 50. Oxidation and Adsorption across Catalyst Units after Cleaning but prior to Failed Regeneration, May 2007

Location	Average Total Hg Concentration, μg/dNm^3	Average Elemental Hg Concentration, μg/dNm^3	Total Mercury Breakthrough across Catalyst, %	Oxidation of Elemental Mercury across Catalyst, %	Total Mercury Oxidation Percentage
May 4, 2007					
Inlet	15.0	13.4	-	-	11
5.5-ft/s Catalyst Outlet	14.9	2.6	100	81	83
15-ft/s Catalyst Outlet	23.4	2.7	156	80	88
May 5, 2007					
Inlet	23.8	15.5	-	-	35
5.5-ft/s Catalyst Outlet	-	-	-	-	-
15-ft/s Catalyst Outlet	15.7	2.8	66	82	82

The results show that both catalysts were achieving about 80 to 82% mercury oxidation of inlet elemental mercury. Attempts were made to thermally regenerate both catalysts overnight the evenings of May 2 and May 3. However, due to heater operating problems, these attempts were not successful. A maximum catalyst inlet temperature of 460°F (238°C) was achieved the evening of May 2, but the heater blew fuses overnight and the flue gas temperature was only 298°F (148°C) the next morning. It is not known how long the catalyst saw inlet flue gas temperatures above 400°F (204°C). The attempt to regenerate the evening of May 3 was also unsuccessful because of equipment issues. It had been desired to attempt to regenerate the catalysts with an inlet flue gas temperature in the range of 500 to 600°F (260 to 316°C).

Figure 42 summarizes catalyst performance data over the 14.5 months of catalyst operation. As discussed above, after several months of operation of the pilot unit it was determined that flue gas samples taken from ports approximately 11 feet (3.4 m) downstream of the catalyst chambers provided more reliable catalyst performance measurements than samples taken from ports immediately downstream of the chambers. Therefore, Figure 42 only shows data collected from the ports further downstream. The data in the figure show that the 5.5-ft/s catalyst initially achieved 95% elemental mercury oxidation, but this decreased to about 80% by the end of the test. For the 15-ft/s catalyst, the initial elemental mercury oxidation was about 87%, while the end of test value was between 70 and 80%. Both catalysts were regenerated in January 2007 and had an attempted, but unsuccessful regeneration in May, and both catalysts had fly ash buildup that may have adversely affected the end-of-test activity measurements.

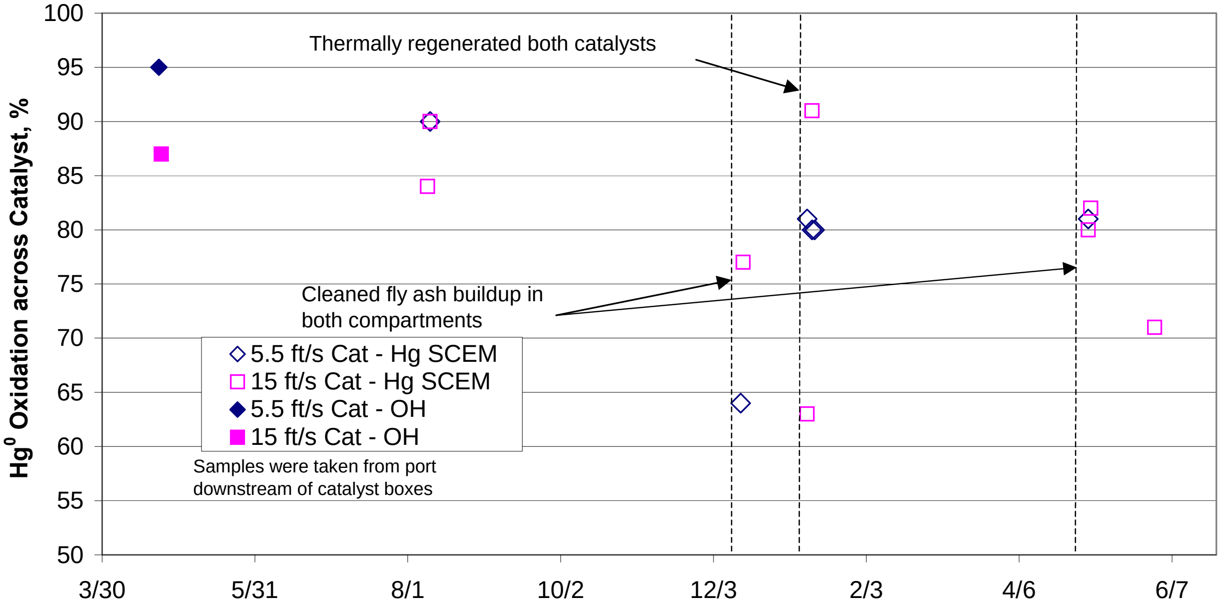


Figure 42. Oxidation Performance for Coronado Pilot Catalysts over Test Duration

Pilot Wet FGD Testing

As described earlier in this report, one objective of this project was to use a pilot-scale wet FGD system designed and built as part of the project to measure the ability to remove mercury in flue gas oxidized across a catalyst. Pilot testing was first conducted at the sites where catalysts were being pilot-tested as part of the 41185 cooperative agreement mentioned elsewhere in this report: Coal Creek Station and Spruce Plant. Pilot wet FGD tests were also planned for the three sites hosting pilot-scale catalyst tests are part of the current project: Monticello Station, Plant Yates, and Coronado Station. Of these, testing was conducted at Monticello and Coronado Stations, but not at Plant Yates. The Plant Yates tests were never conducted because of various conflicts at the site with other test programs, which caused the oxidation catalyst pilot unit to be off line for periods at a time, and the significant pressure drop increases and catalyst losses measured.

Pilot wet FGD tests were also conducted at Duke Energy's Marshall Steam Station, even though no oxidation catalyst pilot tests were conducted there. Those tests were conducted to generate simulated FGD wastewater for pilot-scale wastewater treatment studies for a planned FGD system at that station. In exchange for allowing the DOE-funded pilot FGD system to be used for those tests, the measured mercury removal performance during those tests are reported here as part of this project.

Results for all four of these pilot wet FGD test campaigns are presented and discussed below, in chronological order of when the tests were conducted.

Pilot Wet FGD Tests Downstream of Catalysts at Coal Creek Station

The completed pilot wet FGD skid was shipped from the fabricator in Austin, Texas to Coal Creek Station on July 2, 2004, and the skid was installed and started up the following week. The wet FGD system is sized to treat all of the flue gas exiting a single catalyst compartment. The design basis and a simplified P&ID for the pilot wet FGD system were included in the Experimental Methods section of this project.

Over the following two weeks, the pilot wet FGD system was operated for a series of day shift tests (about 10-12 hours each) downstream of each catalyst compartment, with separate tests being conducted with magnesium-enhanced lime (Mg-lime) and limestone reagents. Mg-lime tests were conducted using the Coal Creek full-scale FGD reagent, while the limestone tests were conducted using dry-ground limestone (90% minus 325 mesh [-44 micrometer in diameter]) that was slurried in plant water in the pilot FGD reagent storage/feed tank. Mg-lime tests were conducted in a natural sulfite oxidation mode, while the limestone reagent tests were conducted in a forced oxidation mode, with FGD liquor sulfite concentrations being controlled below 1 mmol/l (80 mg/l). The FGD reaction tank was not drained between tests. Instead, each test was begun with the FGD slurry remaining from the previous test in the reaction tank. It was felt that this would be better than starting each day with fresh slurry, as the previous days' slurries should have been near steady state with respect to concentrations of chlorides, mercury, and other dissolved species. It was felt that most other potentially important parameters (e.g., pH, sulfite concentration) would reach steady state values soon after startup each day depending on the reagent makeup and pilot unit control parameters.

Wet FGD tests were conducted downstream of what were determined to be the two more active catalysts at Coal Creek, the palladium-based (Pd #1) and carbon-based (C #6) catalysts[1]. Because one catalyst (SBA #5) appeared to be plugged with fly ash buildup and had little mercury oxidation activity, that catalyst was removed, leaving one empty chamber in the pilot unit. This empty chamber provided the opportunity to conduct baseline (no catalyst) tests with both the Mg-lime and limestone reagent chemistries.

FGD outlet mercury concentration and speciation data were measured by SCEM. A single SCEM was used to measure the normal catalyst inlet and catalyst outlet (FGD inlet) locations, and the new FGD outlet location for both total and elemental mercury concentrations. This proved to be a shortcoming in the test design, for two reasons. One is that it proved to be difficult to collect all six data sets in a contemporaneous manner. As an example, many hours typically elapsed between when the catalyst inlet total mercury concentrations were measured (normally the first parameter measured) and when the FGD outlet elemental mercury concentrations were measured (normally the last). Changes in flue gas mercury concentrations over that period could have impacted measured FGD performance.

The second reason this proved to be a shortcoming is that a temporary mercury sampling setup was used at the FGD outlet to connect that location to the normal catalyst pilot sampling system. This temporary system proved to be problematic, such that a number of the test results for mercury capture across the wet FGD are suspect. For several days, scrubber outlet data are questionable or not available because of poor recovery of mercury in QC spikes from the scrubber outlet location. In addition, episodes of gold column contamination in the mercury SCEM invalidated some mercury data.

Because of these issues in measuring FGD outlet mercury concentrations, and because of schedule and budget constraints, high quality data are not available for mercury removal across the pilot FGD system for all of the desired conditions. Table 51 summarizes the reportable results from this effort. For the first five rows of data, the wet FGD outlet data are believed to be biased low due to mercury losses in the temporary sample delivery system from the FGD outlet to the permanent sample delivery system from the oxidation catalyst pilot unit. Evidence of this bias was seen in poor recovery of mercury spikes made into the sample gas immediately upstream of the sample conditioning impingers at the wet FGD outlet location. Evidence of the low bias is also seen in the elemental mercury concentration data from the FGD outlet. For these five tests, apparent elemental mercury removal across the wet FGD system ranged from 36% to 80%, but no removal would be expected. Thus, the low bias was most likely of a similar order of magnitude.

For the final three tests (last three rows of data in the table), the temporary sample delivery system was upgraded with a higher wattage heat-traced sample line, after which the spike recoveries improved to acceptable levels (±10% of 100% recovery). For all three of these tests, the average elemental mercury removal was negative, indicating some mercury re-emissions.

The objective of the wet FGD pilot tests was to determine if the catalytically oxidized mercury could be removed at high efficiency. Mercury removal could be limited by two potential effects. One potential limitation is that a form of oxidized mercury could be produced by the catalyst that is less water-soluble than mercuric chloride, but is still removed by the KCl impinger(s) in the Hg SCEM and OH trains. Such an alternate form would still be measured as oxidized mercury, but may not be scrubbed at high efficiency in a wet FGD system. In such a case, the FGD outlet flue gas would contain significant concentrations of both oxidized and elemental mercury.

Table 51. Summary of Gas Phase Mercury Data from Wet FGD Tests

Catalyst Type	FGD Reagent	Date	Catalyst Inlet Hg, $\mu g/Nm^3$*			Inlet Total Hg Oxidation, %	Catalyst Outlet Hg, $\mu g/Nm^3$			Outlet Total Hg Oxidation, %	Hg^0 Oxidation Across Catalyst, %	Scrubber Outlet Hg, $\mu g/Nm^3$			Hg Removal Across FGD, %		
			Total	Hg^0	Hg^{+2}		Total	Hg^0	Hg^{+2}			Total	Hg^0	Hg^{+2}	Total	Hg^0	Hg^{+2}
Baseline (no catalyst)	Mg-lime	7/11/2004	-	-	-	-	16.5	9.95	6.53	40%	-	6.40**	6.39	0.01	61%	36%	100%
Baseline	Mg-lime	7/12/2004	-	-	-	-	14.5 ***	8.55	5.95	41%	-	4.30	4.04	0.26	70%	53%	96%
Baseline	Mg-lime	7/13/2004	-	-	-	-	14.4	8.48	5.93	41%	-	2.05	1.69	0.35	86%	80%	94%
Carbon #6	Mg-lime	7/14/2004	13.0	6.75	6.29	52%	12.8	4.46	8.33	65%	34%	1.13	0.99	0.14	91%	78%	98%
Carbon #6	Limestone	7/17/2004	18.3	10.4	7.93	57%	17.4	3.64	13.7	79%	65%	2.07	1.79	0.28	88%	51%	98%
Pd #1	Limestone	7/19/2004	18.0	11.9	6.05	66%	17.4	2.71	14.7	84%	77%	3.73	3.76	-0.03	79%	-39%	100%
Pd #1	Mg-lime	7/20/2004	16.9	10.5	6.46	62%	15.9	2.57	13.3	84%	75%	4.98	4.56	0.42	69%	-77%	97%
Carbon #6	Mg-lime	7/21/2004	19.5	10.9	8.55	56%	18.7	3.65	15.1	81%	67%	4.25	4.01	0.24	77%	-10%	98%

*Note: 1.0 $\mu g/Nm^3$ = 0.66 lb Hg/10^{12} Btu heat input

**Values shaded in gray are believed to be biased low due to mercury losses in the sample delivery system for the SCEM

***Estimated value

All eight data sets in Table 51 show that this is not the case. Little oxidized mercury was found in the FGD outlet flue gas from any of the tests, and observed oxidized mercury percentages were all well above 90%. Even for the five tests where the outlet mercury concentrations were biased low, because the oxidized mercury fraction is measured by the difference of the total and elemental mercury concentrations, and both should see the same low bias, it is clear that there was very little oxidized mercury in the outlet gas.

Another limitation on mercury removal by the wet FGD system could be re-emissions, where a portion of the oxidized mercury scrubbed undergoes reduction reactions in the FGD liquor, forming insoluble elemental mercury that is released into the scrubber outlet gas. Because of the low bias in the FGD outlet gas measurements, it is not possible to quantify re-emission across the FGD for the first five tests. Re-emissions are quantified as an increase in elemental mercury concentration measured across the FGD absorber, and for these tests the elemental mercury concentrations were decreased because of an apparent low bias caused by the sample delivery system.

The remaining three test results with good mercury recoveries show evidence of re-emissions, with the FGD outlet flue gas containing 0.4 to 2.0 $\mu g/Nm^3$ higher elemental mercury concentrations than the inlet. It should be noted that upwards of an hour typically elapsed between when the FGD outlet and catalyst outlet elemental mercury concentrations were measured for these tests. The observed re-emissions could in part be due to temporal variations in total and elemental mercury concentrations produced from the boiler.

Also, subsequent wet FGD tests conducted as part of this project have led to an observation that carryover of FGD liquor and/or solids, such as during upper mist eliminator washes, can lead to high biases in measured FGD outlet mercury concentrations. It is possible that after the sample delivery system mercury losses were corrected, the FGD outlet total and elemental mercury concentration data could have been biased high by scrubber carryover. This would tend to overstate observed re-emission levels for the last three tests.

The results of this testing did not provide as much information as was hoped about the ability to scrub catalytically oxidized mercury from flue gas in a conventional wet FGD system. It is quite apparent that there is not a problem of forming oxidized mercury species that are not scrubbed at high efficiency; all of the FGD outlet mercury data show very little oxidized mercury in the FGD outlet flue gas. However, the results are not conclusive about mercury re-emissions when scrubbing the catalytically oxidized mercury. Mercury re-emissions could not be quantified for the first five test results presented. While re-emissions were indicated for the latter three test results, there are potentially confounding effects that may have overstated these re-emissions.

During the tests, FGD slurry samples were collected, preserved, and analyzed off site for routine FGD species concentrations. These results are summarized in Table 52. The results are as expected: the weight percent solids levels in the FGD recirculating slurry were typically in the target range of 10 to 15 wt%, and chlorides were about 1000 to 1200 mg/l (approximately equal to ppm) in the liquor. The Mg-lime tests showed sulfite concentrations in the liquor in the range of 500 to 700 ppm, while the limestone forced oxidation tests showed low sulfite concentrations of 2.7 mg/l or less. The solids analyses showed that the Mg-lime tests produced a mixture of sulfite and sulfate solids, while the limestone forced oxidation tests produced gypsum with a purity of about 95% (dry basis).

Table 52. Analyses of FGD Samples from Pilot Wet FGD Tests at Coal Creek Station

Test Description	**Baseline Mg-Lime**	**Mg-Lime Carbon #6**	**Mg-Lime Carbon #6**	**Limestone Forced Ox. Carbon #6**	**Baseline Limestone Forced Ox.**	**Limestone Forced Ox. Pd #1**	**Mg-Lime Pd #1**	**Mg-Lime Carbon #6**
Date	7/13/04	7/14/04	7/14/04	7/17/04	7/18/04	7/19/04	7/20/04	7/21/04
Time	17:00	16:30	19:30	15:15	17:30	18:30	17:45	15:45
pH	6.6	6.6	6.43	Na*	5.96	5.81	6.49	6.56
Temperature, ^{o}C	55.1	56.1	55	Na	55.1	55.2	na	na
Wt% Solids	10.8	9.9	10.2	12.1	12.5	12.9	15.0	15.9
Slurry Liquor Data:								
Ca^{++}, mg/L	512	500	496	516	512	497	518	511
Mg^{++}, mg/L	2,994	3,045	3,358	3,635	3,479	3,432	3,261	3,391
Cl^{-}, mg/L	1,095	986	1,166	1,138	1,156	1,207	1,160	1,144
$CO_3^{=}$, mg/L	185	187	191	51.6	64.8	97.8	176	179
$SO_3^{=}$, mg/L	500	467	587	2.7	<0.9	2.4	727	643
$SO_4^{=}$, mg/L	16,301	16,349	18,030	18,991	19,058	19,423	17,781	17,108
Hg, μg/L	4.59	2.18	2.56	2.81	2.93	6.14	5.79	3.56
% of Slurry Hg in Liquor Phase	2.1	4.3	3.7	3.4	3.3	1.6	1.7	2.7
Slurry Solids Data:								
Ca, mg/g	258	264	267	221	230	219	222	229
Mg, mg/g	1.2	1.9	1.0	0.7	1.0	0.7	1.0	0.7
SO_3, mg/g	378	369	364	12.0	11.0	10.5	28.2	50.2
SO_4, mg/g	177	197	208	516	515	519	501	480
CO_3, mg/g	8.3	7.5	8.0	7.5	9.0	6.2	6.6	6.0
Inerts, wt%	0.33	0.08	0.12	0.73	0.82	0.85	0.85	0.56
Sulfite Oxidation, %	28%	31%	32%	97%	98%	98%	94%	89%
Gypsum Purity, wt%	-	-	-	94%	94%	95%	-	-
Hg, μg/g	0.61	0.94	0.83	1.17	1.20	0.90	0.85	0.99

*na – value not available

The FGD liquor and solids samples were also analyzed for mercury concentration. These results were used to construct an approximate mercury balance around the wet FGD pilot. It was hoped that the mercury balance results would provide a better indication of overall mercury capture by the wet FGD system. The FGD liquor and solids mercury concentration data are included in Table 52. The mercury balance results are presented and discussed below.

The target SO_2 removal for these tests was 90% across the pilot wet FGD system. The SO_2 concentration results from the CEM used to monitor wet pilot inlet and outlet SO_2 concentrations are shown in Table 53. As shown in the table, the actual daily averages were all near 90%, ranging from 88% to 91%. The SO_2 CEM did not have an oxygen analyzer to measuring the oxygen concentration of the sample gas. The oxygen concentrations shown in Table 53 and used to correct the SO_2 removal data were measured by the Hg SCEM, which was measuring at nominally the same gas locations as was the SO_2 CEM.

Table 53. Daily Average SO_2 Removal Performance across the Pilot Wet FGD System

Date	Inlet SO_2, ppmv (dry)	Outlet SO_2, ppmv (dry)	Inlet O_2, % (dry)	Outlet O_2, % (dry)	SO_2 Removal, %
7/13/2004	718	58	5.6	7.3	91%
7/14/2004	795	64	6.2	6.9	91%
7/15/2004	839	76	5	5.9	90%
7/16/2004	858	84	5	5.7	90%
7/17/2004	874	74	5.1	7.7	90%
7/18/2004	779	75	5.1	7.7	88%
7/19/2004	807	67	5.1	6.9	91%

Lignite sulfur data for this time period were collected from the plant laboratory and used to calculate expected flue gas SO_2 concentrations, using the “F-factor” method described in EPA Method 19. An F-factor of 9860 dscfm/10^6 Btu [1033 $m^3/10^6$ kcal] (at 0% O_2) was used to calculate the predicted flue gas SO_2 concentrations. The data and calculated results are shown in Table 54.

In general, the measured data agreed with the predicted values, with the measured values ranging from 84% to 102% of the predicted values. There was perhaps a small negative bias in the measured results later in the test period. However, a small negative bias in the measured values might be expected for this flue gas, as it is likely that a small percentage of the coal sulfur is captured by the alkaline fly ash and would not be present in the flue gas downstream of the ESP.

Table 54. Lignite Sulfur Data and Expected Flue Gas SO_2 Concentrations versus Measured Concentrations

Date	As-received Moisture Content, wt%	As-received Heat Content, Btu/lb (kcal/kg)	As-received Sulfur Content, wt%	Calculated Flue Gas SO_2 Concentration, ppmv (dry) @3% O_2	Measured Flue Gas SO_2 Concentration, ppmv (dry) @3% O_2	Measured Data, % of Calculated Lignite Data
7/13/04	37.65	6450 (3583)	0.51	822	840	102%
7/14/04	36.99	6446 (3581)	0.59	955	968	101%
7/15/04	37.20	6282 (3490)	0.62	1039	945	91%
7/16/04	36.98	6103 (3390)	0.60	1031	966	94%
7/17/04	36.47	6071 (3373)	0.66	1139	990	87%
7/18/04	36.48	6291 (3495)	0.63	1045	883	84%
7/19/04	36.25	6011 (3339)	0.59	1024	914	89%
7/20/04	36.10	6036 (3353)	0.61	1059	No Data	-
7/21/04	36.14	6095 (3386)	0.60	1025	No Data	-

The plant laboratory data also included mercury concentrations in lignite composite samples. Two composite periods covered the time period during which the pilot wet FGD tests were conducted: July 11-17 and July 18-23. As a check on the Hg SCEM data at the oxidation catalyst unit inlet (or wet FGD pilot unit inlet during baseline FGD tests), the coal composite mercury data were used to calculate an expected flue gas total mercury concentration. These calculated concentrations were then compared to the average Hg SCEM data over the same time period, although the lignite composites each covered a couple of extra days beyond where Hg SCEM data were available. As for the SO_2 calculations described above, the F factor for lignite was used to calculate expected flue gas mercury concentrations from the lignite mercury content. The calculations ignore potential mercury capture on the fly ash collected in the ESP, which, based on previous experience with North Dakota lignite, should be negligible.

The results of these calculations are shown in Table 55. The calculations show very good agreement between the expected and measured calculations, with the measured values accounting for 91% and 99% of the calculated value for the first and second composite periods, respectively.

Table 55. Lignite Mercury Data and Expected Flue Gas Total Mercury Concentrations versus Measured Concentrations

Lignite Composite Date	Lignite Mercury Content, µg/g dry	Lignite Heat Content, Btu/lb dry (kcal/kg)	Calculated Flue Gas Total Mercury, µg/Nm^3@ 3%O$_2$	Measured Flue Gas Total Mercury, µg/Nm^3@ 3%O$_2$	Measured Value, % of Coal Value
July 11-17, 2004	0.112	9964 (5536)	16.8	15.3 (July 13-17)	91%
July 18-23, 2004	0.118	9582 (5323)	18.4	18.1 (July 18-23)	99%

Since the mercury concentrations measured at the pilot unit inlet agreed well with the calculated values based on the composite lignite sample mercury analyses, the lignite data were then used to support cursory mercury balance calculations across the wet FGD pilot unit. A rigorous mercury balance could not be calculated because the quantity of FGD solids produced during pilot FGD operation could not be readily measured. Therefore, the lignite sulfur data were used to calculate an expected FGD byproduct rate, on the basis of pounds of byproduct per 100 lb of coal fired (or g/100 g of coal fired), using observed values for percent SO_2 removal by the FGD system and FGD byproduct chemical composition. This, in turn, was used to calculate a maximum predicted mercury concentration in the FGD byproduct, representing a case where all of the lignite mercury was captured in this amount of FGD byproduct. These maximum mercury concentrations were then compared to the measured FGD byproduct solids mercury concentrations from each test day to calculate an observed mercury capture percentage based on the FGD byproduct solids analyses. The FGD liquor mercury concentrations were also expressed as equivalent solids concentrations, based on the observed wt% solids in the FGD slurry, so the solid and liquid mercury quantities could be summed. Finally, the observed mercury capture percentage based on the FGD byproduct solids and liquor analyses was compared to the mercury removal percentage data measured by Hg SCEM across the wet FGD pilot unit to see how well the data compared. If the two mercury removal percentages agreed well, this would indicate good mercury balance closure, while if they did not it would indicate poor closure.

The results of these calculations are shown in Table 56. Unfortunately, the observed mercury removal percentages based on the FGD byproduct solids analyses did not agree well with the Hg SCEM data. The Hg SCEM data indicated significantly higher removal percentages than did the solids data.

Table 56. Results of Cursory Mercury Balance Calculations across Pilot Wet FGD System

Date	Lignite Sulfur Content, wt% (dry)	Lignite Mercury Content, µg/g (dry)	Calculated FGD Byproduct, lb per 100 lb dry coal	Equivalent Hg Concentration at 100% Hg Removal, µg/g	Measured FGD Byproduct Hg Concentration, µg/g	FGD Liquor Hg Expressed on an Equivalent Solids Basis, µg/g	Apparent % Hg Removal, from FGD Solids and Liquor Analyses	Measured % Hg Removal, by Hg SCEM
7/13/04	0.81	0.112	3.5	3.2	0.61	0.04	20%	86%
7/14/04	0.93	0.112	4.0	2.8	0.89	0.02	33%	91%
7/17/04	1.04	0.112	5.3	2.1	1.17	0.02	56%	88%
7/18/04	0.99	0.118	5.0	2.4	1.20	0.02	51%	No Data
7/19/04	0.92	0.118	4.7	2.5	0.90	0.04	38%	79%
7/20/04	0.96	0.118	4.8	2.4	0.85	0.03	36%	69%
7/21/04	0.94	0.118	4.7	2.5	0.99	0.02	40%	77%

*Values shaded in gray are believed to be biased high due to mercury losses in the sample delivery system for the SCEM

After reviewing these data, there are two possible explanations for why the data appear to be biased, with the solids analyses data showing considerably lower mercury capture percentages than indicated by the Hg SCEM. One is that, as discussed earlier, for the days where the Hg SCEM data are shaded in gray, the Hg SCEM mercury concentration data for the pilot wet FGD outlet location were biased low. This means the observed mercury removal percentage across the pilot FGD based on the Hg SCEM data was biased high.

The second possible explanation comes from a review of how the pilot wet FGD system was designed and operated. First, the pilot wet FGD system was designed to treat flue gas with a range of SO_2 content, including flue gas from high-sulfur coals. The wet FGD reaction tank was sized to provide adequate solids residence time when treating flue gas with as much as 2000 ppmv (wet) of SO_2 in the inlet flue gas, whereas the inlet flue gas at Coal Creek had less than 700 ppmv (wet) of SO_2 content. Consequently, the reaction tank on the pilot unit had approximately three times the required solids residence time, meaning there was a very large inventory of solids in the reaction tank relative to the solids production rate. The solids residence time in the reaction tank at Coal Creek conditions was estimated to have been in the range of 70 to 90 hours.

With the average test day involving approximately 10 hours of FGD operation, it would have taken approximately a week of testing to generate enough FGD byproduct solids to be equivalent to the original solids inventory in the full-scale FGD slurry brought over to initially fill the pilot unit reaction tank. Given that the reaction tank operates like a continuously stirred tank reactor, it would have taken approximately three weeks of operation 10 hours per day to produce solids in the reaction tank that reasonably represented pilot unit operating conditions.

After completing these calculations, it is clear that the FGD solids samples collected could not have been representative of that day's gas-phase mercury capture performance. A review of the FGD byproduct solids analyses showed that the solids mercury content roughly doubled over the time period of July 13 through July 18, showing the expected effects of increased mercury capture across the FGD system once operation downstream of the mercury oxidation catalysts began on July 14. At the same time, the wt% solids levels in the FGD slurry in the pilot reaction tank increased, which tended to reduce the mercury concentrations measured relative to if the solids concentration had been steady.

The mercury concentration of the FGD byproduct dropped on July 19 and remained below 1 µg/g for the final two days' samples. A review of the operating log from this time period shows that for most of the day on July 19, the pilot wet FGD system was operated under baseline (no catalyst upstream) operation, and only switched to treating flue gas from downstream of the Pd #1 catalyst for the last three hours of operation. The Hg SCEM data shown in the table only correspond with the last three hours of operation. At least part of the drop in FGD byproduct mercury concentration seen on July 19 was an effect of approximately seven hours of baseline operation at a low mercury removal percentage.

Pilot Wet FGD Tests at Marshall Station

Four weeks of pilot wet FGD tests were conducted at Duke Energy's Marshall Station, Unit 4, in August 2004. Marshall Station is located in Terrell, North Carolina. Unit 4 is a 648-MW unit with a tangentially-fired pulverized coal boiler equipped with low NO_X burners and that burns low- to medium-sulfur Eastern bituminous coal. At the time the unit had a small cold-side ESP and no SCR or wet FGD system.

Pilot wet FGD operation was generally around the clock from Monday morning through Saturday afternoon each week. The fourth week was an exception, going from Sunday through Thursday. A different coal was fired by Unit 4 each week. An objective of the test was to measure mercury oxidation percentages at the Unit 4 ESP outlet (pilot wet FGD inlet) and to measure the ability of the wet FGD pilot to capture oxidized mercury in the flue gas.

Details of the pilot wet FGD system design were discussed previously in the Experimental Methods section. A trailer-mounted horizontal belt filter was rented by Duke Energy from Compositech of Houston, Texas, and installed adjacent to the pilot wet FGD system. URS operators assisted Duke Energy in operating the belt filter to dewater the FGD blow down slurry once or twice per week, on day shift. Duke Energy collected the recovered FGD liquor and gypsum solids for off-site characterization by others.

FGD inlet and outlet mercury concentrations were measured by Hg SCEM. A single analyzer was cycled between sampling the FGD inlet and FGD outlet ducts, and between measuring total mercury and elemental mercury at each location. IGS filters were installed at the FGD inlet duct and FGD outlet duct and used to extract a particulate-free sample to go to the impingers and then to the gold.

SO_2 removal performance was tracked with a Western Research Model 721 analyzer, which is based on absorption of ultraviolet (UV) light. URS equipment was used to filter, extract, and dry a flue gas sample going to the analyzer, and to log analyzer output data. A single analyzer was intermittently switched between sampling the FGD inlet and outlet flue gas streams.

URS also collected wet FGD slurry and preserved liquor samples, and analyzed those samples off site for routine FGD chemistry and FGD byproduct mercury concentration data.

Results

SO_2 removal results for the pilot FGD system are summarized in Table 57, while corresponding FGD pilot unit process condition data are presented in Table 58. The intent was to maintain 90 to 95% SO_2 removal across the pilot wet FGD. As can be seen from the averages in the table, approximately 90% SO_2 removal was consistently maintained. The operating pH of the pilot FGD was a few tenths of a pH unit lower during the fourth week than during weeks 1 through 3. This was at Duke Energy's request, to operate the pilot FGD at a pH closer to the expected operating pH of a planned full-scale FGD at Marshall. SO_2 removal performance was maintained at the lower pH by sending more slurry flow to the absorber spray nozzle instead of recycling it back to the reaction tank through the minimum flow line.

Samples of the FGD slurry were routinely collected and preserved for off-site analyses using EPRI analytical and physical tests methods established for FGD determinations[5]. Preservation of the FGD slurry liquor included pressure filtration at the point of collection into several pre-weighed solutions, each intended to preserve the integrity of specific FGD cations and anions. This preservation was made to avoid precipitation or dissolution of species from the slurry solids, or other reactions such as oxidation of the liquor species. FGD slurry solids were not preserved in the field, as the relatively small mass of the FGD species that might precipitate from or dissolve into the liquor would not be expected to measurably impact the solids composition. The solids were filtered from the slurry in URS' Process Analytical Laboratory.

The results of chemical analyses of the FGD liquors are shown in Table 59, while the FGD solids analyses are summarized in Table 60. Where available, the pH and temperature of the slurry at the time the sample was taken is shown in the table. Of most interest in Table 59 are the FGD liquor chloride and sulfite concentrations. The chloride concentrations changed somewhat with coal source, with Coals 1 and 2 producing steady-state chloride levels of approximately 4,000 to 5,000 ppm, Coal 3 producing 5,000 to 6,000 ppm, and Coal 4 producing 4,000 to 5,000 ppm. For Coal 3, the chloride levels were controlled to less than steady-state values by blowing down some slurry and making up with fresh water.

Table 57. Daily Average SO_2 Removal Data

Date	**FGD Inlet SO_2, ppmv (dry)**	**FGD Outlet SO_2, ppmv (dry)**	**SO_2 Removal, %**
Coal 1:			
8/10/2004	774	84	89
8/11/2004	757	92	88
8/12/2004	754	72	90
8/13/2004	605	64	89
8/14/2004	737	58	92
Coal 2:			
8/16/2004	571	57	90
8/17/2004	568	65	89
8/18/2004	596	62	90
8/19/2004	579	51	91
8/20/2004	580*	53	91
8/21/2004	580*	58*	90*
Coal 3:			
8/23/2004	580*	61	89
8/24/2004	552	53	90
8/25/2004	557	58	90
8/26/2004	527	54	90
8/27/2004	559	59	89
8/28/2004	590	52	91
Coal 4:			
8/29/2004	675	68	90
8/30/2004	657	59	91
8/31/2004	637	56	91
9/1/2004	641	67	90

*Value estimated due to analyzer malfunction

Table 58. FGD Pilot Unit Process Data Summary

Date	Slurry Pressure to Spray Nozzle, psig (kPa)	Reaction Tank Slurry pH	Reaction Tank Slurry Temperature, °C	FGD Inlet Flue Gas Flow Rate, acfm (m^3/h)
Coal 1:				
8/10/2004	12.7 (87.6)	5.83	49.5	1852 (3148)
8/11/2004	14.5 (100)	5.91	49.7	1795 (3051)
8/12/2004	15.5 (106)	5.92	49.3	1828 (3107)
8/13/2004	15.5 (106)	5.88	49.2	1823 (3099)
8/14/2004	15.7 (108)	5.87	48.1	1799 (3058)
Coal 2:				
8/16/2004	15.9 (110)	5.97	47.9	1764 (2998)
8/17/2004	15.6 (108)	5.97	49.5	1779 (3024)
8/18/2004	15.0 (103)	5.90	50.1	1829 (3109)
8/19/2004	15.1 (104)	6.02	50.6	1831 (3112)
8/20/2004	15.0 (103)	5.81	50.0	1851 (3146)
8/21/2004	15.1 (104)	5.87	49.0	1828 (3107)
Coal 3:				
8/23/2004	15.0 (103)	6.03	48.4	1822 (3097)
8/24/2004	16.0 (110)	5.94	50.4	1812 (3080)
8/25/2004	17.3 (119)	5.94	50.5	1804 (3066)
8/26/2004	17.4 (120)	5.92	50.1	1813 (3082)
8/27/2004	16.7 (115)	5.97	50.8	1833 (3116)
8/28/2004	16.2 (112)	5.95	51.2	1808 (3073)
Coal 4:				
8/29/2004	16.3 (112)	5.56	48.4	1816 (3087)
8/30/2004	16.3 (112)	5.58	50.4	1789 (3041)
8/31/2004	16.3 (112)	5.57	50.7	1787 (3037)
9/1/2004	16.3 (112)	5.53	50.3	1735 (2949)

Table 59. Results of FGD Slurry Sample Liquor Analyses

Date	Time	pH	Temperature, °C	Ca^{++}, mg/L	Mg^{++}, mg/L	Na^{+}, mg/L	Cl^{-}, mg/L	$CO_3^{=}$, mg/L	$SO_3^{=}$, mg/L	$SO_4^{=}$, mg/L
Coal 1:										
8/11/04	12:30	-	-	1,073	-	-	4,803	-	-	-
8/12/04	11:15	5.85	-	1,330	733	2,982	6,762	91	19.3	2,498
8/13/04	12:10	-	-	1,347	555	1,678	4,792	66	9.4	1,861
8/14/04	10:35	-	-	1,428	412	1,041	3,575	98	1.3	1,641
Coal 2:										
8/16/04	14:50	5.83	48.7	1,089	-	-	1,657	-	-	-
8/17/04	15:28	6	49.6	1,561	-	-	2,872	-	-	-
8/18/04	15:35	5.85	50.6	2,331	-	-	4,535	-	-	-
8/19/04	15:30	5.79	51	2,482	472	482	4,635	123	0	1,568
8/20/04	15:10	5.94	50.4	2,368	420	352	4,209	93	0	1,570
8/21/04	11:10	5.9	49.5	2,180	381	232	3,687	87	0	1,527
Coal 3:										
8/23/04	14:15	-	-	-	-	-	3,801	-	-	-
8/24/04	14:30	-	-	-	-	-	4,303	-	-	-
8/25/04		-	-	2,473	683	147	4,774	77	0	1,239
8/26/04	14:50	-	-	2,798	874	145	6,245	70	0	1,213
8/27/04	9:30	-	-	2,924	826	114	5,684	79	0	1,250
8/28/04	11:00	-	-	2,793	664	83	5,435	50	0	1,130
Coal 4:										
8/29/04	11:00	-	-	-	-	-	4,695	-	-	-
8/30/04	15:40	-	-	2,391	598	57	4,540	44	0	1,203

Table 60. Results of FGD Slurry Sample Solids Analyses

Date	Time	Inerts, wt%	Solids, wt%	Ca, mg/g	Mg, mg/g	SO_3, mg/g	SO_4, mg/g	CO_3, mg/g	Oxidation, %	Gypsum, wt%
Coal 1:										
8/11/2004	12:30	-	7.5	-	-	-	-	-	-	-
8/12/2004	11:15	2.2	16.8	229	1.1	0.0	507	14.6	100.0	90.8
8/13/2004	12:10	1.0	15.3	229	0.9	0.0	519	10.7	100.0	92.9
8/14/2004	10:35	1.9	13.6	229	0.9	0.0	522	12.0	100.0	93.5
Coal 2:										
8/16/2004	14:50	-	7.0	-	-	-	-	-	-	-
8/17/2004	15:28	-	11.6	-	-	-	-	-	-	-
8/18/2004	15:35	-	15.4	-	-	-	-	-	-	-
8/19/2004	15:30	2.5	16.7	226	0.6	0.0	530	8.9	100.0	95.0
8/20/2004	15:10	2.4	15.5	229	0.7	0.0	513	9.5	100.0	92.0
8/21/2004	11:10	2.6	13.3	226	1.9	0.0	502	13.9	100.0	89.9
Coal 3:										
8/23/2004	14:15	-	12.9	-	-	-	-	-	-	-
8/24/2004	14:30	-	13.1	-	-	-	-	-	-	-
8/25/2004	-	2.4	15.6	225	4.4	0.0	496	29.6	100.0	88.9
8/26/2004	14:50	2.5	17.7	225	3.8	0.0	496	24.8	100.0	88.8
8/27/2004	9:30	2.5	17.4	226	3.8	0.0	499	22.3	100.0	89.5
8/28/2004	11:00	3.2	15.3	229	3.1	0.0	505	21.2	100.0	90.4
Coal 4:										
8/30/2004	15:40	3.8	17.6	221	1.9	0.0	504	14.8	100.0	90.3

The FGD liquor sulfite analyses results in Table 59 showed measurable levels in the first week on Coal 1, and all non-detectable levels for Coals 2 through 4. The higher values for Coal 1 are a result of low air pressure to the pilot wet FGD skid during the first week of operation. After the air supply was moved to another source in the plant, the oxidation air supply was adequate to ensure complete FGD liquor sulfite oxidation. Even the highest value for Coal 1, 19.3 mg/L, would be considered acceptable for most FGD systems that produce wallboard-grade gypsum, though (40 mg/L or lower is typically acceptable).

The FGD solids analyses in Table 60 all show 100% sulfite oxidation in the solid phase. Calculated gypsum purity values range from 88.8 to 95.0%, limited primarily by acid insoluble species (fly ash entering with the flue gas and insoluble minerals entering with the limestone), unreactive dolomite ($CaCO_3 \bullet MgCO_3$) from the limestone (evidence of which is seen in the magnesium content of the byproduct solids) and excess limestone in the byproduct. Excess limestone levels were most likely elevated by the relatively coarse particle size of the preground, bagged limestone supply, which was reportedly sized at 80% minus 325 mesh [-44 micrometers]. Most FGD systems that produce wallboard grade gypsum grind their limestone to a finer 90 to 95% minus 325 mesh.

Table 61 summarizes the results of gas phase mercury measurements made across the pilot wet FGD system, all by Hg SCEM. The FGD outlet mercury data are discussed in the following paragraphs.

Recall that one analyzer was used to measure the FGD inlet and outlet flue gas streams, and to measure elemental and total mercury concentrations in each stream. The mercury analyzer was only operated during day shift, and typically it took most of the shift to complete all four of these measurements. The daily averages shown in the table might include FGD inlet values measured in the morning and outlet values measured in the afternoon. Thus, variations in flue gas conditions over the course of the day could impact the calculated mercury oxidation and removal percentages. For this reason, it is probably best to look at the weekly average data for each coal rather than the daily averages.

A second point is that the FGD outlet mercury concentration data do not appear as expected for a limestone forced oxidation system. With this FGD chemistry, one would expect to see virtually no removal of elemental mercury, since elemental mercury is relatively insoluble in aqueous solutions, and a high percentage removal of soluble, oxidized mercury. Some FGD chemistries can be prone to mercury “re-emissions”, wherein a portion of the oxidized mercury removed in the absorber is reduced by reaction with sulfite ion. Re-emissions are characterized by an increase in flue gas elemental mercury concentration across the FGD absorber, but typically a high observed removal percentage of oxidized mercury across the absorber.

The data in Table 61 show almost no evidence of re-emissions, but instead show significant percentage removal of elemental mercury on some days. However, for Coals 2, 3 and 4 the weekly data average little or no elemental mercury percent removal. It is believed that this apparent elemental mercury removal on some days is a measurement anomaly, possibly caused by an observed buildup of fine black particles on the surfaces of the IGS filter in the analyzer sampling train for the FGD outlet location. It is assumed that these black particles were fine fly ash particles that contained unburned carbon. The particles may have been oxidizing elemental mercury as the sample gas flowed across the sintered metal surface of the IGS filter, thus lowering the concentration of elemental mercury in the FGD outlet sample gas. As the test program progressed, the IGS filter was repeatedly cleaned to limit biases caused by this fine particle buildup, but it is believed that data from a number of days of measurements were, in fact, biased.

The data in Table 61 also show lower than expected removal percentages for oxidized mercury. One would expect to see greater than 90% apparent capture of oxidized mercury across the wet scrubber, while the data averaged only 49% to 69% over the four weeks. There are two possible explanations for these lower-than-expected removal percentages. One is oxidation of elemental mercury in the IGS filter, as described above, which would have the effect of increasing apparent elemental mercury removal at the expense of the observed oxidized mercury removal.

Table 61. Mercury Removal Data (all mercury concentration data shown on a dry basis at 3% O_2)

Coal Fired in Unit 4	Date	Start Time	End Time	Inlet Hg, µg/Nm^3		Inlet % Oxidized Hg	Outlet Hg, µg/Nm^3		Outlet Hg, lb/10^{12} Btu	Total Hg Removal, %	Elemental Hg Removal, %	Hg^0 Re-emission, % of inlet Hg^{2+}	Oxidized Hg Removal, %
				Total	Elem.		Total	Elem.					
Coal 1	8/11/2004	9:50	16:16	8.79	3.47	61%	3.41	1.34	2.26	61%	61%	-40	61%
	8/12/2004	9:50	14:24	5.65	1.69	70%	3.14	1.26	2.08	44%	25%	-11	53%
	8/13/2004	8:42	15:51	2.40	0.90	62%	1.25	0.90	0.83	48%	0%	0	77%
	Average:			5.62	2.02	64%	2.60	1.17	1.73	54%	42%	-24	60%
Coal 2	8/17/2004	9:22	17:03	7.99	1.65	79%	3.32	1.45	2.20	58%	12%	-3	71%
	8/18/2004	9:49	16:44	3.25	0.59	82%	*	*	*	*	*	*	*
	8/19/2004	10:16	17:41	6.53	0.67	90%	2.43	0.52	1.61	63%	23%	-3	67%
	8/20/2004	11:30	15:48	3.93	0.46	88%	0.85	0.44	0.56	78%	4%	-1	88%
	Average:			5.43	0.84	84%	2.20	0.80	1.46	59%	5%	-1	69%
Coal 3	8/24/2004	8:56	17:10	2.58	0.17	93%	0.83	0.20	0.55	68%	-18%	1	74%
	8/25/2004	10:02	15:18	3.64	0.60	83%	2.58	0.64	1.71	29%	-6%	1	36%
	8/26/2004	9:11	16:02	2.17	0.31	86%	0.75	0.26	0.50	65%	18%	-3	73%
	8/27/2004	8:47	15:45	1.95	0.29	85%	1.51	0.40	1.00	22%	-40%	7	33%
	8/28/2004	8:50	13:20	2.21	0.28	87%	1.61	0.19	1.07	27%	30%	-5	27%
	Average:			2.51	0.33	87%	1.46	0.34	0.97	42%	-2%	0	49%
Coal 4	8/29/2004	9:30	14:24	2.97	0.64	78%	1.30	0.34	0.86	56%	48%	-13	59%
	8/30/2004	9:44	18:34	2.45	0.37	85%	1.32	0.26	0.88	46%	30%	-5	49%
	8/31/2004	9:00	16:00	2.57	0.42	84%	1.34	0.56	0.89	48%	-32%	7	63%
	9/1/2004	9:30	16:30	2.19	0.46	79%	1.31	0.66	0.87	40%	-43%	12	62%
	Average:			2.55	0.47	81%	1.32	0.45	0.88	48%	5%	-1	58%

*Not reported due to data quality issues

Another possible effect is that a small amount of FGD liquor and/or solids was carried over from the FGD absorber mist eliminator and drawn through the IGS filter with the sample gas. This liquor and/or solids would contain mercury, which would be released into the sample gas when heated to approximately 450 to 500°F in the IGS filter. Evidence of such carryover and measurement bias has been seen in subsequent testing with this pilot unit, particularly when the back side of the single-stage mist eliminator is washed. In later test programs the protocol was changed to stop flue gas flow to the outlet Hg SCEM when the pilot wet FGD mist eliminator was washed.

Notwithstanding these measurement issues, the results in Table 61 show FGD inlet total mercury concentrations averaging between 5 and 6 μg/dNm^3 for Coals 1 and 2, and between 2 and 3 μg/dNm^3 for Coals 3 and 4. The inlet mercury speciation showed 60 to 70% oxidized mercury for Coal 1 and between 80 and 90% oxidized mercury for Coals 2 through 4.

The weekly average FGD mercury removal percentages measured were lower than expected, and ranged from 42% to 59%. However, these values were likely biased low by measurement issues related to mist eliminator washing as described above. In spite of these potential biases, the FGD outlet total mercury emissions averaged below 2.0 lb/10^{12} Btu heat input for each of the four coals.

A number of FGD slurry samples were analyzed for mercury concentration. The samples analyzed were "grab" samples of the FGD recirculating slurry. Liquor samples were filtered from the slurry as they were collected and preserved in a nitric acid solution. Solid samples were filtered from the slurry later, in the URS Process Analytical Laboratory. At the time it was expected that, as for the major FGD species analytes, most of the mercury in the FGD system would be found with the solids, and that precipitation, adsorption, or desorption between the solids and liquor would have a negligible impact on measured solids mercury concentrations. Since these tests were conducted in 2004, it has been determined that mercury can range from being found mostly in the FGD slurry solids to mostly in the slurry liquor, so the approach taken for these tests would not now be considered good practice. Instead, the solids and liquor samples should be separated by filtration and preserved in the field, soon after collecting the slurry sample. However, the results of these analyses, as summarized in Table 62, show that for these tests most of the mercury was found in the solids and a lesser percentage in the liquor. This means there were likely only minor errors associated with waiting until days later to filter the solids from these slurry samples; the expected bias would be a slight over-reporting of the percent of mercury in the slurry solids for the samples where the FGD liquor mercury concentrations were above detection limits.

The FGD solids mercury concentrations ranged from about 0.3 to 0.8 μg/g (ppm) while the liquor concentrations ranged from less than 1 to 22 μg/L (~ppb). The reason for the variation in liquor concentrations (although all relatively low in concentration) is not obvious. For some coals the concentrations varied from non-detectable to the high end of the range during the week, or vice versa, while for Coal 2 the liquor mercury concentrations remained at the higher end of the range all week.

Table 62. Results of FGD, Coal and Ash Mercury Analyses, and Other Coal Analysis Results

Date	FGD Solids Hg, µg/g	FGD Solids, Wt. fraction	FGD Liquor Hg, µg/L	% of Hg in Slurry Solids	Coal Hg, µg/g	Fly Ash Hg, µg/g	Coal Ash, Wt. %	Coal S, Wt. %	Coal HHV, Btu/lb (kcal/kg)
Coal 1:									
8/12/2004	0.751	0.168	<0.7	>99.5	0.102*	0.42	10.56	0.84	12,475 (6,931)
8/13/2004	0.767	0.153	<0.8	>99.4	0.04	0.15	10.56	0.84	12,475 (6,931)
8/14/2004	0.454	0.136	15.3	82.4	0.10	0.61	10.56	0.84	12,475 (6,931)
Coal 2:									
8/19/2004	0.350	0.167	22.4	75.8	0.12	0.46	12.65	0.72	12,032 (6,684)
8/20/2004	0.380	0.155	21.4	76.5	0.08	0.27	12.66	0.75	12,071 (6,706)
8/21/2004	0.393	0.133	20.2	74.9	0.10	0.57	12.66	0.75	12,071 (6,706)
Coal 3:									
8/25/2004	0.347	0.156	15.5	80.5	0.06	0.42	9.94	0.76	12,678 (7,043)
8/26/2004	0.345	0.177	Not analyzed	-	0.06	0.30	9.33	0.75	12,409 (6,894)
8/27/2004	0.321	0.174	11.6	85.4	0.06	0.38	10.15	1.02	12,668 (7,038)
8/28/2004	0.507	0.153	<0.9	>99.0	0.06	0.46	9.59	0.89	12,721 (7,067)
Coal 4:									
8/30/2004	0.537	0.176	<0.8	>99.3	0.07	0.55	13.84	0.88	12,341 (6,856)

*Results from a URS analysis of this coal sample are shown and were used in the material balance calculations; the third party value of 0.17 µg/g appeared to be erroneous.

Also shown in Table 62 are coal and fly ash sample mercury concentrations, and coal sulfur, ash, and heat content as measured by a third party Duke Energy contractor. The data in Table 62, along with flue gas mercury concentration data from Table 61 and SO_2 removal data from Table 57 were used to calculate a mercury balance around Unit 4 and the wet FGD pilot unit. It was not possible to conduct a rigorous mass balance, and several parameters had to be estimated.

For example, the percentage of the coal ash that ends up as fly ash rather than bottom ash or economizer ash was estimated at 80%, and the amount of flue gas generated relative to the coal fired was estimated from an EPA “F” factor of 9780 dscf at 0% excess air per million Btu of heat input (1025 $m^3/10^6$ kcal). FGD solids generation rates were estimated from the coal sulfur and the observed SO_2 removal across the pilot FGD system. Also, it had to be assumed that the coal, ash, FGD solids, and FGD liquor samples collected and analyzed were representative of conditions at a common time on the date shown.

The latter is probably the biggest assumption that had to be made in making these mercury balance calculations. In particular, it is known to be difficult to collect representative fly ash samples from ESP hoppers, given potential side-to-side and field-to-field stratification of the solids collected. Such stratification is particularly possible for fly ash mercury content, and was seen in previous testing by URS at Marshall Station. Also, because of the long residence time in the FGD reaction tank, the FGD slurry solids samples represented an average composition over a much longer period (in some cases, several days) than the day shift during which the samples and flue gas data were collected.

The results of these mercury balance calculations are summarized in Table 63. The mercury balance is expressed in terms of μg of mercury per kg of coal fired. These units were chosen out of convenience, because they result in mercury mass values between 1 and 100 for most of the table entries.

Table 63. Mercury Balance Calculation Summary

Date	Hg in Coal, μg/1000g of coal	Hg Recovery, μg/kg of coal				Calculated Hg Recovery, %	Apparent Removal of Coal Hg, %	
		Hg in Fly Ash	Hg in FGD Solids	Hg in FGD Liquor	Hg in Flue Gas		Based on Hg in Fly Ash, FGD Byproducts	Based on FGD Outlet Flue Gas
Coal 1:								
8/12/2004	102	36	32	<0.1	26.0	92	66	75
8/13/2004	40	13	33	<0.2	10.4	139	113	74
8/14/2004	100	52	20	4.2	12.4	88	76	88
Average	*81*	*33*	*28*	*2*	*16*	*98*	*78*	*80*
Coal 2:								
8/19/2004	120	47	13	4.2	19.4	69	53	84
8/20/2004	80	27	15	4.5	6.8	67	58	91
8/21/2004	100	58	15	5.0	12.0	90	78	88
Average	*100*	*44*	*14*	*5*	*13*	*75*	*63*	*87*
Coal 3:								
8/25/2004	60	33	14	3.3	21.7	120	84	64
8/26/2004	60	22	13	-	6.2	70	59	90
8/27/2004	60	31	17	2.8	12.7	105	84	79
8/28/2004	60	35	23	<0.2	13.6	121	98	77
Average	*60*	*30*	*17*	*2*	*14*	*105*	*82*	*77*
Coal 4:								
8/30/2004	70	61	24	<0.2	10.8	137	122	85

The individual mercury recovery percentages in Table 63 range from 70% to 139%. For the coals where multiple balances were conducted, the average mercury balance closures improved to 98% for Coal 1, 75% for Coal 2, and 105% for Coal 3. An average closure is probably a better indicator of data quality than individual days' data, for reasons described previously (e.g., representativeness of grab samples, FGD solids residence time in the reaction tank, and using one mercury SCEM to collect all of the flue gas data). Particularly for Coals 1 and 3, the average closures near 100% provide some confidence in the ability to account for the mercury coming in with the coal.

Also shown in the table are apparent total capture percentages of the coal mercury with the fly ash and wet FGD system. One percentage is based on the calculated recovery of mercury in the fly ash, FGD gypsum and FGD blow down liquor, while the other is calculated by difference based on the amount of mercury measured to be leaving with the flue gas. In theory the two methods should provide equivalent results for coal mercury capture. For Coals 1 and 3, where the mercury balance closures were near 100% on average, the average coal mercury capture percentages were around 80% by both methods, indicating good agreement between the calculation methods. For Coals 2 and 4, where the overall mercury balance closures were not as close to 100%, there is a wider range in the apparent removal percentages by the two methods.

Pilot Wet FGD Tests Downstream of Catalysts at Spruce Plant

The pilot wet FGD skid was shipped to Spruce plant in September 2004, and the skid was installed and started up in October. Spruce Plant fires PRB coal and has a reverse gas fabric filter for particulate control followed by a limestone natural oxidation wet FGD system.

Over the last two weeks in October and continuing into the first week of November 2004, the pilot wet FGD system was operated for a series of day-shift tests (about 10-12 hours each) downstream of each catalyst compartment, with separate tests being conducted with lime and limestone reagents. Both reagent types are used in wet FGD systems installed on plants that fire PRB coal. One baseline (no catalyst upstream) limestone test was also conducted.

Lime reagent tests were conducted using dry high-calcium hydrated lime powder slurried in plant water in the pilot wet FGD reagent tank, while the limestone tests were conducted using the Spruce full-scale wet FGD reagent. Lime reagent tests were conducted in a natural sulfite oxidation mode, while the limestone reagent tests were conducted in a forced oxidation mode, with FGD liquor sulfite concentrations being controlled below 1 mmol/l (80 mg/l).

For each reagent type, the FGD reaction tank was not drained between tests. Instead, each test was begun with the FGD slurry remaining from the previous test in the reaction tank. It was felt that this would be better than starting each day with fresh slurry, as the previous days’ slurry should have been near steady state with respect to concentrations of chlorides, mercury, and other dissolved species. Most other potentially important parameters (e.g., pH, sulfite concentration) would reach steady state values soon after startup each day, and would depend on the reagent makeup and pilot unit control parameters. However, the reagent tank inventory was changed when making the transition from lime to limestone reagent. For both reagent types, the pilot wet FGD reaction tank was originally charged with recycle slurry from one of the Spruce full-scale wet FGD module reaction tanks (limestone natural oxidation) to begin with realistic background concentrations of chlorides, other halogens, and trace elements that enter the FGD system over time with the flue gas and reagent.

Wet FGD tests were conducted downstream of all four catalysts tested at Spruce, including palladium-based (Pd #1), carbon-based (C #6), gold, and SCR catalysts. The baseline (no catalyst) test was conducted by withdrawing flue gas from the 20-in. inlet duct to the oxidation catalyst pilot unit through a 10-in. (0.25-m) port installed by Spruce Plant personnel.

Two Hg SCEMs were used to measure flue gas mercury concentration and speciation data for the catalyst inlet, catalyst outlet (FGD inlet), and FGD outlet locations. The arrangement of the analyzers was different for the lime and limestone reagent tests, as described below.

For the lime reagent tests, it was desired to also measure oxidation catalyst performance. Because of catalyst pilot unit inlet flue gas mercury concentration and speciation variability at Spruce, it was best to measure the inlet and outlet flue gas across each catalyst with separate analyzers, so mercury concentrations could be measured at both locations simultaneously. Analyzers at each location were simultaneously switched between measuring total and elemental mercury concentrations. Therefore, for the lime reagent tests, each morning one analyzer was used to monitor the catalyst pilot inlet flue gas while the second analyzer was used to monitor the outlet flue gas from the catalyst being tested. In the afternoon, the inlet monitor was moved to the FGD outlet location, so the two monitors were then measuring the catalyst outlet/FGD inlet and FGD outlet locations. This allowed the catalyst performance to be measured with two analyzers simultaneously in the mornings, during the time the wet FGD system was started up and brought to steady operating conditions, and the pilot wet FGD mercury control performance to be measured with two analyzers during the afternoon.

During the limestone reagent tests, OH method relative accuracy tests were also conducted. When a dedicated Hg SCEM was used to monitor the oxidation catalyst pilot inlet flue gas at Spruce, an IGS filter sample extraction system was installed on a 4-in. port on the pilot unit inlet duct. However, this port was also used for sample collection when OH measurements were conducted. Therefore, for the limestone tests it was not possible to install a dedicated Hg SCEM to measure oxidation pilot unit inlet flue gas mercury concentrations and still be able to conduct the OH measurements for that location. Instead, an existing, hard-piped sampling manifold and solenoid valve arrangement was used to alternate between sampling the oxidation catalyst pilot inlet and the outlet of the catalyst being tested, which was also the wet FGD pilot inlet flue gas. The sample selected was routed through a single IGS filter to a single Hg SCEM. This single Hg SCEM was alternated between sampling the catalyst pilot unit inlet and catalyst outlet flue gases, and between measuring total and elemental mercury concentrations in each stream. The second Hg SCEM was dedicated to sampling the wet FGD outlet flue gas. Table 64 summarizes the mercury concentration results from this effort.

Table 64. Summary of Hg SCEM Data from Wet FGD Tests at Spruce Plant

Catalyst Type	FGD Reagent	Date	Catalyst Inlet Hg, μg/Nm^3			Inlet Total Hg Oxida-tion, %	Catalyst Outlet Hg, μg/Nm^3			Outlet Total Hg Oxida-tion, %	Hg^0 Oxida-tion Across Catalyst, %	Scrubber Outlet Hg, μg/Nm^3			Hg Removal Across FGD, %			Hg^0 Re-emission % of inlet Hg^{2+}
			Total	Hg^0	Hg^{+2}		Total	Hg^0	Hg^{+2}			Total	Hg^0	Hg^{+2}	Total	Hg^0	Hg^{+2}	
Baseline (no catalyst)	Limestone	11/3/204	8.5	0.6	7.9	93	-	-	-	-	-	5.3	3.8	1.5	38	-509	81	41
Pd #1	Limestone	10/27/04	6.0	0.9	5.1	85	6.0	0.5	5.5	91	39	2.8	1.4	1.4	54	-161	75	16
C#6	Limestone	10/29/04	8.4	0.7	7.7	91	6.3	1.1	5.2	83	-51	1.5	1.1	0.3	77	-3	93	0
Au	Limestone	10/26/04	8.9	2.7	6.2	70	10.9	1.0	10.0	91	64	2.5	2.1	0.4	77	-116	96	11
SCR	Limestone	10/28/04	7.2	0.4	6.8	95	7.7	0.6	7.1	93	-58	2.9	2.1	0.8	62	-259	88	21
Pd #1 (a.m.)	Lime	10/19/04	10.7	2.7	8.0	75	12.1	0.6	11.5	95	76	-	-	-	-	-	-	-
C#6 (a.m.)	Lime	10/21/04	13.8	3.4	10.4	75	10.4	0.7	9.7	94	80	-	-	-	-	-	-	-
Au (a.m.)	Lime	10/20/04	9.7	3.9	5.8	60	10.0	0.3	9.7	97	92	-	-	-	-	-	-	-
SCR (a.m.)	Lime	10/22/04	8.1	1.6	6.5	80	9.1	1.0	8.1	89	41	-	-	-	-	-	-	-
Pd #1 (p.m.)	Lime	10/19/04	-	-	-	-	7.5	0.4	7.1	95	-	3.3	1.1	2.2	56	-197	69	10
C#6 (p.m.)	Lime	10/21/04	-	-	-	-	11.7	0.5	11.2	96	-	8.9	7.1	1.8	24	-1319	84	59
Au (p.m.)	Lime	10/20/04	-	-	-	-	8.1	0.4	7.7	96	-	2.8	0.4	2.4	65	0	68	0
SCR (p.m.)	Lime	10/22/04	-	-	-	-	9.3	0.6	8.7	93	-	6.1	6.1	0	35	-880	100	63

Note: 1.0 μg/Nm^3 = 0.66 lb Hg/10^{12} Btu heat input

*NA – value not measured because of IGS filter heater failure

Note that for the lime reagent tests, the analyzer configuration made it necessary to report the catalyst oxidation results (catalyst inlet and outlet) measured in the morning separately from the wet FGD results (catalyst outlet and FGD outlet) measured in the afternoon. The flue gas mercury total and elemental mercury concentrations vary so rapidly over time at Spruce Plant that the catalyst performance numbers from the morning could not be assumed to apply during the afternoon measurements. As an example, on October 19, the average catalyst outlet total mercury concentration was measured at 12.1 μg/Nm^3 in the morning, and only 7.5 μg/Nm^3 in the afternoon.

The objective of the wet FGD pilot tests was to determine if the catalytically oxidized mercury could be removed at high efficiency. As described earlier in this report, mercury removal could be limited by two potential effects. One is that a form of oxidized mercury could be produced by the catalyst that is less water-soluble than mercuric chloride, but is still removed by the KCl impinger in the Hg SCEM train. Such an alternate form would still be measured as oxidized mercury, but may not be scrubbed at high efficiency in a wet FGD system and the FGD outlet flue gas would contain significant concentrations of oxidized as well as elemental mercury. Another limitation could be re-emissions, where a portion of the oxidized mercury scrubbed undergoes reduction reactions in the FGD liquor, forming insoluble elemental mercury that is released into the scrubber outlet gas. Re-emissions would result in an increase in elemental mercury concentration measured across the FGD absorber.

Before discussing the wet FGD mercury removal results in Table 64, the mercury oxidation percentage levels in the flue gas at Spruce bear discussion. Spruce Plant fires PRB coal, which, for most power plants, produces a flue gas with predominantly elemental rather than oxidized mercury. However, Spruce has a reverse gas fabric filter that operates at a low air-to-cloth ratio (~1.5 ft/min) for particulate control, and this fabric filter has been measured to oxidize most of the elemental mercury in the flue gas. The fabric filter outlet flue gas, which is the oxidation catalyst pilot inlet flue gas, typically contains 60 to 95% oxidized mercury, and therefore only 5 to 40% elemental mercury. Fabric filter outlet elemental mercury concentrations range from less than 1 μg/Nm^3 to nearly 4 μg/Nm^3.

Also, as mentioned above, the total mercury concentrations and mercury speciation in the fabric filter outlet gas have been observed to fluctuate significantly from hour to hour and day to day. This fluctuation makes it difficult to measure oxidation catalyst performance, particularly when the elemental mercury concentrations at the catalyst inlet are 1 μg/Nm^3 or less. When catalyst inlet elemental mercury concentrations are less than 1 μg/Nm^3, this challenges the ability to even measure catalyst performance using existing Hg SCEM technology. Some of the data in Table 64 show negative mercury oxidation across the catalysts. This is believed to be a measurement anomaly reflecting the difficulties described above. Measurement of pilot FGD mercury capture performance is similarly difficult at such low mercury concentrations.

Furthermore, when the catalyst pilot unit mercury is already highly oxidized, as it was on several of the test days represented in Table 64, it is difficult to say whether the downstream pilot wet FGD tests truly represent capture of catalytically oxidized mercury. Only for four of the nine test days (October 19-21, and October 26) was there enough elemental mercury in the catalyst inlet flue gas to result in a significant fraction of catalytically oxidized mercury in the wet FGD pilot inlet gas. For the other days the mercury was oxidized at high efficiency across the fabric filter instead, and there was little, if any, contribution from the catalysts.

Notwithstanding these caveats, three of the four limestone FGD tests and two of the four lime FGD tests showed relatively high percentage removal of oxidized mercury across the pilot absorber, with removal percentages ranging from 84 to 100%. The baseline (no catalyst) performance for oxidized mercury removal averaged 81%, so for these five tests conducted downstream of mercury catalysts, the percentage capture of oxidized mercury was greater than at baseline. While the baseline oxidized mercury removal percentage measured for the pilot wet FGD system was lower than expected (it should be greater than 90%), it was similar to that measured for the full-scale wet FGD system at Spruce Unit 1 in January 2004 (84%).

Of the remaining three tests, a lower removal of 75% was measured during the first limestone FGD test, with Pd #1 catalyst. However, the amount of catalyst outlet/FGD pilot inlet mercury concentration data was limited because of a failure of an IGS filter in the sampling train. The limited amount of data may have skewed these results (see the OH results below). Two lime reagent tests showed lower oxidized mercury removal percentages of 68 to 69%. It is not clear why the removal percentages were lower for these two tests. It is possible that the biases introduced by mist eliminator washing on the pilot unit, as discussed with the Marshall results, lowered the percentage oxidized mercury removal percentages for these tests.

The data were reviewed to see whether or not this lower oxidized mercury removal could be a catalyst-specific effect. One catalyst that showed lower downstream oxidized mercury removal in the lime reagent test, gold, showed very high removal (96%) in the limestone reagent test. The other lime reagent test with a lower oxidized mercury removal percentage was downstream of the Pd #1 catalyst, but in this case the corresponding data for the limestone reagent test also showed a relatively low oxidized mercury removal percentage. However, as noted above, this result may be erroneous because of IGS filter problems.

The data were also reviewed to see whether the lower oxidized mercury removal percentages corresponded with the four days when there were appreciable fractions of mercury oxidized across the pilot unit catalysts. The two lime tests with lower oxidized mercury removal percentages were conducted on October 19th and 20th, days when there were higher elemental mercury concentrations at the catalyst inlet (at least in the morning, when those measurements were made). However, on the other two days where there were higher elemental mercury concentrations at the oxidation catalyst inlet, the downstream oxidized mercury removal percentages across the wet FGD were relatively high (84% on October 21st and 96% on October 26th).

Six of the eight catalyst tests showed evidence of mercury re-emissions, as did the baseline (no catalyst) test. The two tests that did not were the limestone reagent test conducted downstream of the C #6 catalyst and the lime reagent test conducted downstream of the gold catalyst. Both of these tests showed essentially no elemental mercury removal, an expected result when there are no re-emissions, and therefore do not indicate any measurement anomalies.

Three tests showed relatively low re-emissions levels of ~1 μg/Nm^3 or less. These were the two tests conducted downstream of the Pd #1 catalyst (lime and limestone reagent), and the test conducted downstream of the gold catalyst with limestone reagent. Given the potential variability associated with measuring low mercury concentrations in flue gas, these are not considered to be significant re-emissions levels. The observed, small re-emission percentages could be within the uncertainty of the measurements.

Three catalyst tests (one limestone and two lime reagent tests) and the baseline (no catalyst) limestone forced oxidation test showed significant re-emissions across the pilot wet FGD system. The three catalyst tests showing significant re-emissions levels were conducted downstream the C #6 catalyst (lime reagent) and SCR catalyst (lime and limestone reagent). Re-emissions are thought to occur primarily due to reactions between sulfite and oxidized mercury absorbed in the FGD liquor, but are believed to be influenced by a number of factors such as pH, chloride concentrations in the liquor, etc.

It should be noted that the full-scale wet FGD system at Spruce is a limestone, natural oxidation system with measurable liquid-phase sulfite concentrations. In gas characterization tests conducted at Spruce in January 2004, some re-emissions were noted across the full-scale wet FGD system (a 78% increase in elemental mercury concentration across the absorber).[4]

Also, it was while these pilot wet FGD tests were being conducted that it was first observed that carryover of liquor and/or solids during upper mist eliminator washes can lead to high biases in measured FGD outlet mercury concentrations. It is possible that, for some of these tests, the FGD outlet total and/or elemental mercury concentration data were biased high by scrubber carryover. As mentioned above, such biases could account for lower than expected oxidized mercury removal percentages, and/or a high bias in measured elemental mercury re-emissions levels.

For the limestone reagent tests conducted downstream of the four catalysts, OH method relative accuracy tests were also conducted. The results of these OH measurements are compared to the Hg SCEM results in Table 65. In general, the OH results show agreement with the Hg SCEM results with respect to mercury control performance across the pilot wet FGD system. The OH results show high removal percentages of oxidized mercury downstream of all four catalyst types (90 to 96% removal) with limestone reagent, whereas a limited amount of Hg SCEM data show a lower percentage of 75% for one of the limestone tests, downstream of the Pd #1 catalyst.

The OH mean results for re-emission levels are similar to the Hg SCEM results, showing no re-emissions when operating downstream of the C #6 catalyst, low levels of re-emissions (0 to ~1 μg/Nm^3) when operating downstream of the palladium and gold catalysts, and a slightly higher re-emissions level of 1.5 μg/Nm^3 when operating downstream of the SCR catalyst. When expressed as a percentage of the FGD inlet oxidized mercury concentration, the re-emission levels are zero downstream of the C#6 catalyst, low for the gold catalyst (~10%), but more significant for both the Pd#1 and SCR catalysts (~20%).

Table 65. October 2004 OH Relative Accuracy Results for Spruce Pilot (mean and 95% confidence interval of three runs, compared to Hg SCEM results from same time period)

	Total Hg	Elemental Hg	Oxidized Hg
Pd #1, October 26, 2004:			
Catalyst Outlet - OH, µg/Nm^3	5.7 ± 3.7	0.5 ± 0.2	5.2 ± 3.5
Catalyst Outlet - SCEM, µg/Nm^3	6.0 ± 2.2	0.5 ± 0.5	5.5 ± 1.7
Relative Accuracy, % (based on means)	7	17	6
FGD Outlet - OH, µg/Nm^3	2.0 ± 1.0	1.7 ± 0.8	0.3 ± 0.4
FGD Outlet - SCEM, µg/Nm^3	2.8 ± 0.6	1.4 ± 0.6	1.4 ± 0.1
Relative Accuracy, % (based on means)	41	-17	407
Observed Hg Removal Across Wet FGD, % by OH	65	-264	95
Observed Hg Removal Across Wet FGD, % by SCEM	54	-161	75
Hg^0 Re-emission, % of inlet Hg^{2+}, by OH	-	23	-
Hg^0 Re-emission, % of inlet Hg^{2+}, by SCEM	-	16	-
C #6, October 28, 2004:			
Catalyst Outlet - OH, µg/Nm^3	10.4 ± 0.4	0.4 ± 0.4	10.0 ± 0.2
Catalyst Outlet - SCEM, µg/Nm^3	6.3 ± 0.0	1.1 ± 0.3	5.2 ± 0.3
Relative Accuracy, % (based on means)	-40	170	-48
FGD Outlet - OH, µg/Nm^3	0.8 ± 0.2	0.4 ± 0.2	0.4 ± 0.1
FGD Outlet - SCEM, µg/Nm^3	1.5 ± 0.3	1.1 ± 0.5	0.3 ± 0.2
Relative Accuracy, % (based on means)	90	179	-25
Observed Hg Removal Across Wet FGD, % by OH	93	0	96
Observed Hg Removal Across Wet FGD, % by SCEM	77	-3	95
Hg^0 Re-emission, % of inlet Hg^{2+}, by OH	-	0	-
Hg^0 Re-emission, % of inlet Hg^{2+}, by SCEM	-	0	-
Gold, October 27, 2004:			
Catalyst Outlet - OH, µg/Nm^3	10.3 ± 3.1	0.4 ± 0.3	10.0 ± 2.8
Catalyst Outlet - SCEM, µg/Nm^3	10.9 ± 0.8	1.0 ± 0.4	10.0 ± 0.4
Relative Accuracy, % (based on means)	6	162	0
FGD Outlet - OH, µg/Nm^3	2.3 ± 0.7	1.3 ± 1.2	1.0 ± 0.5
FGD Outlet - SCEM, µg/Nm^3	2.5 ± 0.8	2.1 ± 0.7	0.4 ± 0.2
Relative Accuracy, % (based on means)	10	59	-56
Observed Hg Removal Across Wet FGD, % by OH	78	-255	90
Observed Hg Removal Across Wet FGD, % by SCEM	77	-116	96
Hg^0 Re-emission, % of inlet Hg^{2+}, by OH	-	9	-

	Total Hg	**Elemental Hg**	**Oxidized Hg**
Hg^0 Re-emission, % of inlet Hg^{2+}, by SCEM	-	11	-
SCR Catalyst, October 29, 2004:			
Catalyst Outlet - OH, μg/Nm^3	7.9 ± 2.4	0.2 ± 0.1	7.7 ± 2.4
Catalyst Outlet - SCEM, μg/Nm^3	7.7 ± 1.5	0.6 ± 0.2	6.9 ± 2.7
Relative Accuracy, % (based on means)	-2	248	-11
FGD Outlet - OH, μg/Nm^3	2.4 ± 0.9	1.7 ± 0.6	0.7 ± 0.4
FGD Outlet - SCEM, μg/Nm^3	2.9 ± 1.0	2.1 ± 0.6	0.8 ± 0.6
Relative Accuracy, % (based on means)	24	25	21
Observed Hg Removal Across Wet FGD, % by OH	70	-900	91
Observed Hg Removal Across Wet FGD, % by SCEM	62	-259	88
Hg^0 Re-emission, % of inlet Hg^{2+}, by OH	-	19	-
Hg^0 Re-emission, % of inlet Hg^{2+}, by SCEM	-	21	-

Note – All concentrations corrected to 3% O_2, dry basis; 1 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

In some cases the calculated relative accuracies between the two measurements show high percentage errors, particularly for measurements at low concentrations (~1 μg/Nm^3 or less). However, the run-to-run variability in making these measurements was, in some cases, quite large. Table 65 shows 95% confidence intervals about the mean values for the mercury concentrations, which is a measure of run-to-run variability. The OH means and 95% confidence intervals are for three runs, while the Hg SCEM values are based on average results for each of two to three OH run periods. In some cases Hg SCEM results were not available for one of three OH run periods because of the IGS filter heater failure mentioned above.

When the 95% confidence intervals of the means are considered, it is clear that much of the observed difference in the mean values by the two methods may be due to run-to-run variability. That is, in most cases the 95% confidence intervals of the mean values by the two methods overlap. The only clear bias between the two methods is seen in the results for the catalyst outlet/FGD inlet on October 28 (C #6 catalyst), where the OH method showed a total mercury concentration of 10.4 μg/Nm^3 while the Hg SCEM showed only 6.3 μg/Nm^3. Since the Hg SCEM measures the oxidized mercury concentration by difference, the apparent bias carries over to that oxidized mercury concentration value as well.

Samples of the FGD liquors and solids were collected during these pilot wet FGD tests, and were being analyzed for typical FGD species and mercury concentrations. These chemical analysis results are reported in Tables 66 and 67 below.

Table 66. Summary of FGD Liquor Analyses from Pilot Wet FGD Tests at Spruce Plant

Date	Catalyst	Ca^{++}, mg/L	Mg^{++}, mg/L	Na^{+}, mg/L	Cl^{-}, mg/L	$CO_3^{=}$, mg/L	$SO_3^{=}$, mg/L	$SO_4^{=}$, mg/L	Hg, µg/L
Lime Reagent Tests:									
10/20/04	Gold	742	1,717	5,078	7,247	240	0	7,167	NA*
10/21/04	C #6	755	1,326	4,117	5,763	149	0	6,085	NA
10/22/04	SCR	746	1,460	4,146	5,990	197	0	5,890	14.4
Limestone Reagent Tests:									
10/26/04	Gold	747	2,868	8,306	11,644	63	4	11,153	33.0
10/27/04	Pd #1	730	2,645	7,224	10,442	44	3	10,326	NA
10/29/04	C #6	754	2,366	6,854	9,813	38	3	9,276	9.2

*NA – no analysis

Table 67. Summary of FGD Solids Analyses from Pilot Wet FGD Tests at Spruce Plant

Date	Catalyst	Inerts, wt% of total solids	Solids, wt% in slurry	Ca, mg/ g	Mg, mg/ g	SO_3, mg/ g	SO_4, mg/ g	CO_3, mg/ g	Hg, µg/ g	Sulfite Oxida-tion, %	Reagent Utiliza-tion, %
Lime Reagent Tests:											
10/20/04	Gold	2.44	6.35	217	0	0	518	2	NA*	100	99
10/21/04	C #6	2.07	6.85	224	0	0	522	2	NA	100	97
10/22/04	SCR	1.94	7.11	221	0	0	518	2	1.55	100	97
Limestone Reagent Tests:											
10/26/04	Gold	3.26	6.83	224	0	0	509	7	3.32	100	94
10/27/04	Pd #1	2.49	9.06	221	0	0	517	2	NA	100	97
10/29/04	C #6	2.92	6.67	218	0	0	510	7	2.45	100	97

*NA – no analysis

The results show that there was not much difference between the lime and limestone test chemistries, except that concentrations of highly soluble species (e.g., Mg, Na and Cl) and sulfate were higher during the limestone tests. This indicates that liquor concentrations cycled higher during the limestone tests. However, this may have just been a function of how concentrated or dilute the full-scale absorber liquor was running at the time absorber recycle slurry was brought over to fill the pilot FGD system reaction tank. The pilot FGD reaction tank was filled at the beginning of the lime tests and again at the beginning of the limestone tests.

Both the lime natural oxidation and the limestone forced oxidation test results showed complete sulfite oxidation, which is common under low-sulfur-coal FGD conditions. Also, the observed reagent utilization was high for both reagent types, ranging from 94 to 97% for the limestone tests and 97 to 99% for the lime tests.

The liquor and solids mercury analysis results were used to calculate the percentage of mercury in the slurry in the solids versus that in the liquid phase. In all three sample sets, the mercury was predominantly in the solid phase (88 to 95%). Because these tests were generally only one day in duration each, the relatively long solids residence time in the reaction tank, and because the reaction tank slurry was not changed from day to day, it was not possible to use these analytical data along with gas-phase data to calculate a mercury balance around the pilot unit.

Pilot Wet FGD Tests Downstream of Catalysts at Monticello Station

In April 2005, the pilot wet FGD system was operated at Monticello Station for two days each downstream of the four catalysts. A baseline test (no catalyst upstream of the FGD system) was also conducted. The results of these tests are summarized in Table 68.

Table 68. Results of Pilot Wet FGD Tests Conducted Downstream of Oxidation Catalysts at Monticello Station, April 2005

Sample Location (Sampling Date)	Hg Concentration, μg/Nm^3 @ 3% O_2*				Total Hg % Oxidation @ Catalyst Outlet	Total Hg Removal Across Wet FGD, %	Hg^0 Removal Across Wet FGD, %	Hg^{+2} Removal Across Wet FGD, %	Hg^0 Re-emission % of inlet Hg^{2+}
	Catalyst Outlet/FGD Inlet**		Wet FGD Outlet						
	Total Hg	Hg^0	Total Hg	Hg^0					
Baseline [no catalyst] (4/5)	22.4	13.9	12.1	9.9	38	46	29	74	-47
SCR (4/6)	30.6	9.9	8.1	8.9	68	74	10	104	-5
SCR (4/7)	23.1	11.0	6.4	4.5	52	72	59	85	-54
Regenerated Pd #1 (4/8)	22.0	7.8	4.2	2.5	64	81	69	88	-37
Regenerated Pd #1 (4/9)	31.6	5.0	8.6	3.4	84	73	31	81	-6
J-M Pd #1 (4/10)	22.7	7.6	11.4	3.9	67	50	48	51	-25
J-M Pd #1 (4/18)	28.8	7.9	4.6	2.4	73	84	70	89	-26
Gold (4/19)	30.7	1.22	5.2	3.1	96	83	-150	93	6
Gold (4/20)	31.7	1.50	7.7	2.1	95	76**	-43	81**	2

*1 μg/Nm^3 @3% O_2 = 0.67 lb Hg/10^{12} Btu heat input

**Value is believed to be biased low by FGD recycle pump cavitation

There are several things to note in the data presented in the table. One is that, as in some of the previous pilot-scale wet FGD results from other sites, for a number of these tests significant elemental mercury removal percentages are seen (29 to 70%). This would not typically be expected, as elemental mercury is not very water soluble and would not be expected to be removed at a significant percentage in an aqueous-based wet absorber. In some instances, this appears to be a result of a measurement bias in the FGD outlet speciation. For example, in the baseline (no catalyst upstream) test, the elemental mercury removal percentage was measured at 29% while the oxidized mercury removal was measured at 74%. One would expect oxidized mercury to be removed at 90% or higher percentages in an efficient wet FGD absorber (SO_2 removal performance was maintained at 90% or greater across the absorber). These data suggest that elemental mercury was being oxidized in the sample delivery system for the FGD outlet SCEM, biasing the outlet elemental mercury concentration low and the outlet oxidized mercury concentration (total minus elemental) high.

However, the FGD outlet total mercury concentration data suggest that some elemental mercury was being removed, or that the FGD inlet mercury oxidation percentage was biased low. If only oxidized mercury were removed by the wet FGD, the total mercury removal percentage measured should be no greater than the mercury oxidation percentage at the FGD inlet. For the baseline test, the FGD inlet mercury oxidation percentage was 38%, while the total mercury removal across the wet FGD absorber was higher at 46%. Four other days' data show the same effect, where the FGD total mercury removal percentage was greater than the FGD inlet mercury oxidation (April 6th and 7th, SCR catalyst; April 8th, regenerated Pd #1 catalyst; and April 18th, Johnson Matthey Pd #1 catalyst). The remaining four days' data show the expected trend, where the total mercury removal percentage across the FGD was lower than the FGD inlet oxidation percentage. This suggests less than 100% removal of the oxidized mercury in the FGD inlet flue gas and little or no removal of elemental mercury.

OH method measurements were made in concert with these tests (for the second test day downstream of each catalyst) to provide a measure of Hg SCEM relative accuracy. The results of the OH measurements are compared to the Hg SCEM results in Table 69. Also included in the table are results from a baseline test conducted with the wet FGD pilot unit, where flue gas from the catalyst pilot unit inlet rather than the outlet from one of the catalyst modules was treated.

The baseline results in Table 69 show good agreement between the OH and Hg SCEM measurements for the FGD inlet, with relative accuracies ranging from 85% for the elemental mercury concentrations to 99% for oxidized mercury concentrations. However, at the FGD outlet, the relative accuracies do not show good agreement.

The baseline test total mercury concentrations measured at the FGD outlet show a relative accuracy of 76% when comparing the SCEM result to the OH result. However, the 95% confidence intervals about the mean for both methods are high, suggesting that variability in the measured concentrations during the day may have contributed to the apparent bias between the two methods.

Table 69. April 2005 OH Relative Accuracy Results for Monticello FGD Pilot (mean and 95% confidence interval of three runs compared to simultaneous Hg SCEM results)

	Total Hg	Elemental Hg	Oxidized Hg
Baseline (no catalyst upstream), April 5, 2005:			
FGD Inlet - OH, μg/Nm^3	24.9 ± 1.8	16.3 ± 1.5	8.6 ± 0.9
FGD Inlet - SCEM, μg/Nm^3	22.4 ± 0.7	13.9 ± 0.6	8.5 (± 0.1 est.)
Relative Accuracy, % (based on means)	90	85	99
FGD Outlet - OH, μg/Nm^3	16.0 ± 3.9	15.5 ± 4.0	0.48 ± 0.17
FGD Outlet - SCEM, μg/Nm^3	12.1 ± 0.9	9.9 ± 0.4	2.2 (± 0.5 est.)
Relative Accuracy, % (based on means)	76	64	460
Observed Hg Removal Across Wet FGD, % by OH	36	5	94
Observed Hg Removal Across Wet FGD, % by SCEM	46	29	74
SCR Catalyst, April 7, 2005:			
FGD Inlet/Catalyst Outlet - OH, μg/Nm^3	27.1 ± 1.5	2.4 ± 0.6	24.7 ± 1.0
FGD Inlet/Catalyst Outlet - SCEM, μg/Nm^3	23.1 ± 3.7	11.0 ± 0.9	12.1 (± 2.9 est.)
Relative Accuracy, % (based on means)	85	460	49
FGD Outlet - OH, μg/Nm^3	3.6 ± 1.7	2.1 ± 1.7	1.50 ± 0.03
FGD Outlet - SCEM, μg/Nm^3	6.4 ± 0.6	4.5 ± 0.3	1.86 (± 0.3 est.)
Relative Accuracy, % (based on means)	180	210	124
Observed Hg Removal Across Wet FGD, % by OH	87	14	94
Observed Hg Removal Across Wet FGD, % by SCEM	72	59	85
Regenerated Pd, April 9, 2005:			
FGD Inlet/Catalyst Outlet - OH, μg/Nm^3	23.7 ± 4.0	2.2 ± 0.9	21.5 ± 4.3
FGD Inlet/Catalyst Outlet - SCEM, μg/Nm^3	31.6 ± 1.7	5.0 ± 0.3	26.6 (± 1.4 est.)
Relative Accuracy, % (based on means)	130	230	124
FGD Outlet - OH, μg/Nm^3	7.9 ± 1.1	6.2 ± 0.9	1.71 ± 1.02
FGD Outlet - SCEM, μg/Nm^3	8.6 ± 2.2	3.4 ± 0.3	5.2 (± 1.9 est.)
Relative Accuracy, % (based on means)	110	55	300
Observed Hg Removal Across Wet FGD, % by OH	67	-187	92
Observed Hg Removal Across Wet FGD, % by SCEM	73	31	81
J-M Pd, April 18, 2005:			
FGD Inlet/Catalyst Outlet - OH, μg/Nm^3	21.1 ± 2.1	2.7 ± 0.3	18.4 ± 1.9
FGD Inlet/Catalyst Outlet - SCEM, μg/Nm^3	28.8 ± 2.4	7.9 ± 1.9	20.9 (± 0.5 est.)
Relative Accuracy, % (based on means)	136	290	114
FGD Outlet - OH, μg/Nm^3	4.4 ± 0.4	3.9 ± 0.4	0.55 ± 0.05

	Total Hg	Elemental Hg	Oxidized Hg
FGD Outlet - SCEM, µg/Nm^3	4.6 ± 0.3	2.4 ± 0.3	2.2 (± 0.1 est.)
Relative Accuracy, % (based on means)	105	62	400
Observed Hg Removal Across Wet FGD, % by OH	79	-44	97
Observed Hg Removal Across Wet FGD, % by SCEM	84	70	89
Gold, April 20, 2005:			
FGD Inlet/Catalyst Outlet - OH, µg/Nm^3	29.4 ± 2.8	1.10 ± 0.28	28.3 ± 2.6
FGD Inlet/Catalyst Outlet - SCEM, µg/Nm^3	31.7 ± 1.9	1.50 ± 0.40	30.2 (± 1.5 est.)
Relative Accuracy, % (based on means)	108	136	107
FGD Outlet - OH, µg/Nm^3	7.0 ± 1.0	3.2 ± 0.4	3.8 ± 0.7
FGD Outlet - SCEM, µg/Nm^3	7.7 ± 1.0	2.1 ± 0.4	5.6 (± 0.6 est.)
Relative Accuracy, % (based on means)	110	66	150
Observed Hg Removal Across Wet FGD, % by OH	76	-189	87
Observed Hg Removal Across Wet FGD, % by SCEM	76	-43	81

Note – All concentrations corrected to 3% O_2, dry basis; 1 µg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

The mercury speciation data for the FGD outlet clearly show a bias between the two method results; the OH method results show more elemental mercury and less oxidized mercury than the Hg SCEM results. The OH results better match expectations for the performance of the pilot wet FGD system operating in limestone forced oxidation mode: relatively high oxidized mercury removal (94%) and little elemental mercury removal (5%). The SCEM results (74% oxidized mercury removal and 29% elemental mercury removal) show evidence of elemental mercury oxidation in the sample collection train, as the oxidized mercury removal appears to be biased low while the elemental mercury removal appears to be biased high.

For the mercury oxidation catalyst outlet FGD test results, the FGD inlet (catalyst outlet) total mercury concentration results agree reasonably well between the two methods. For the wet FGD outlet total mercury measurements, the results for the regenerated Pd, Johnson Matthey Pd, and gold catalysts show good agreement between the two methods, with relative accuracies ranging from 105 to 110%. However, for the SCR catalyst, the Hg SCEM results show much more total mercury at the FGD outlet than the OH results (a relative accuracy of 180%). The 95% confidence intervals about the means for the two measurement methods suggest that at least part of this discrepancy can be attributed to variability in the actual flue gas concentrations during the measurement period, though.

Note that the OH results are internally consistent for the SCR catalyst outlet FGD test. That is, they show a low FGD inlet elemental mercury concentration (2.4 µg/Nm^3) and a correspondingly low outlet total mercury concentration (3.6 µg/Nm^3). The expectation is that the wet FGD system would remove oxidized mercury at a high percentage, and achieve little or no elemental mercury removal. This would make the outlet total mercury concentration slightly higher than the inlet elemental mercury concentration, as seen in the OH results.

The Hg SCEM results for the SCR catalyst test are not as consistent by this comparison. Both the FGD inlet elemental mercury concentration and the FGD outlet total mercury concentration are higher than the corresponding OH concentrations. However, the FGD outlet total mercury by Hg SCEM is significantly lower than the inlet elemental mercury concentration (6.4 vs. 11 $\mu g/Nm^3$). This would require significant elemental mercury capture to achieve; 59% is shown in the table for the SCEM results. This high percentage elemental mercury capture is unlikely, which brings the SCEM results into question.

For all catalyst types, the comparison between the OH and Hg SCEM results for elemental mercury concentrations also shows poor agreement. The FGD outlet results show relative accuracy percentages ranging from 55% (less elemental mercury reported by the Hg SCEM) to 210% (more elemental mercury reported by the Hg SCEM). The OH results showed elemental mercury re-emissions for three of the four catalyst outlet tests, with only a small percentage elemental mercury capture for the fourth catalyst (SCR, at 14% capture). In contrast, the Hg SCEM data showed re-emissions only from the gold catalyst test, and elemental removal percentages ranging from 31 to 70% for the other three catalyst tests.

The FGD outlet oxidized mercury concentration relative accuracy percentages ranged from 107% to 400%, indicating that the Hg SCEM always showed more oxidized mercury than did the OH results. Furthermore, the OH data showed higher percentage capture of oxidized mercury than did the Hg SCEM data. The oxidized mercury removal percentages ranged from 87% to 97% by the OH method, which is within the expected range (note that the 87% value is known to be biased low by FGD recycle pump cavitation), while the Hg SCEM data showed lower-than-expected percentages of 81 to 89%.

These results all provide further evidence that the sampling system for the Hg SCEM was oxidizing some elemental mercury. The apparent bias was least for the gold catalyst, which because of its high oxidation activity produced the least amount of elemental mercury in the FGD inlet flue gas.

In summary, the wet FGD data suggest that the OH results provide the more accurate measure of catalyst and downstream wet FGD mercury performance for the SCR and Johnson Matthey Pd #1 catalysts. The two methods agree reasonably well for evaluating the regenerated Pd #1 and gold catalysts and their downstream wet FGD mercury capture.

For the SCR catalyst, the OH results show the FGD total mercury capture percentage is a few percentage points lower than the FGD inlet total mercury oxidation, as would be expected if the wet FGD system is removing oxidized mercury at a high percentage and little or no elemental mercury. In contrast, the Hg SCEM results for the SCR catalyst show considerably higher percentage mercury capture in the wet FGD system than would be expected based on the measured inlet total mercury oxidation. The same effect is seen for the Johnson Matthey Pd #1 catalyst: the OH results show an FGD total mercury removal percentage somewhat less than the inlet total mercury oxidation percentage, while the SCEM results show greater total mercury capture than the inlet speciation would lead one to expect. For the other two catalysts, this comparison shows the expected trend of somewhat lower total mercury capture than the inlet total mercury oxidation percentage for both measurement types. These comparisons are summarized in Table 70.

Table 70. Summary of Comparison of OH and SCEM Results for Oxidation Catalyst Performance and Downstream Wet FGD Mercury Capture for April Monticello Results

Catalyst	Measurement Method	Hg^0 Oxidation Across Catalyst, %	Total Hg Oxidation at FGD Inlet, %	Total Hg Capture Across Wet FGD, %
SCR	OH	78	91	87
	SCEM	29	52	72
Regenerated Pd	OH	79	91	67
	SCEM	77	84	73
Johnson Matthey Pd	OH	83	87	79
	SCEM	41	73	84
Gold	OH	94	96	76
	SCEM	93	95	76

Another thing to note about these SCEM results is that the mercury capture by the wet FGD system downstream of the gold catalyst was clearly limited by re-emissions. Evidence of re-emissions is seen when the FGD outlet elemental mercury concentrations are larger than the inlet elemental mercury concentrations. These wet FGD pilot tests were conducted in forced oxidation mode, and the sulfite concentrations were generally below detectable levels. Furthermore, the oxidation/reduction potential (ORP) was measured during the latter tests, and showed an ORP of greater than 600 mV, which is indicative of highly oxidizing conditions that might be expected to minimize re-emissions. However, URS has subsequently conducted measurements on other wet FGD systems and found re-emissions from other limestone forced oxidation FGD systems that operate with a combination of high ORP and relatively low chloride concentrations in the FGD slurry liquor, as did this gold catalyst test[6].

It should also be noted in the second day of the gold catalyst test that the oxidized mercury removal was most likely biased low for much of the measurement day by cavitation of the absorber recycle pump, which significantly lowered the liquid-to-gas ratio (L/G). This cavitation was an inadvertent effect of a decision to maintain the absorber reaction tank at a minimum level during this test, which was run overnight in an attempt to approach steady state in the reaction tank slurry (the other tests were run approximately 10 hours per day, during daylight hours only). While attempting to maintain a minimum level, net evaporation of water from the absorber in excess of liquid makeup lowered the absorber reaction tank level to the point where the recycle pump suction was no longer flooded, leading to cavitation. It was several hours into the daytime operation on the second day, during which time the SCEM data were collected, before this problem was corrected by adding service water to raise the slurry level in the tank.

Notwithstanding these issues, it was apparent that having the oxidation catalysts upstream increased the pilot wet FGD mercury capture percentage from 46% up to 84% for seven of the eight days of operation downstream of catalysts. The gold catalyst was clearly the most active for elemental mercury oxidation, yet the mercury removal percentage for the gold catalyst test days was no higher than was measured for one day each with the regenerated Pd #1 and Johnson Matthey Pd #1. It might be possible to use scrubber additives (e.g., Evonik's TMT-15 or Nalco's 8034) to prevent elemental mercury re-emissions and improve the overall mercury capture with the gold catalyst upstream of the wet FGD absorber, or to optimize scrubber operation to minimize re-emissions.

During the wet FGD pilot tests, samples were collected and preserved of the FGD recycle liquor and recycle slurry solids. The samples were analyzed for typical FGD species and for mercury concentration. Also, coal and fly ash samples were collected; coal samples were analyzed for mercury, chloride, fluoride, bromide and iodide concentrations, and fly ash samples were analyzed for mercury content and loss on ignition (LOI). These analysis results are reported in Tables 71 through 76 below.

The results of the routine FGD sample analyses in Tables 71 and 72 show expected trends. The FGD liquor from all tests was highly oxidized, with no measurable sulfite ion content. Chloride ion concentrations were relatively low, ranging from approximately 1000 to 2000 ppm. The sample from the second day of the gold catalyst FGD test, which was run around the clock for greater than 30 hours, indicate that the reaction tank liquor became somewhat more concentrated in dissolved salts than the full-scale scrubber, with the sulfate, chloride, and magnesium ion concentrations being higher for this sample than in any of the other pilot-scale or the full-scale module samples. The solids samples from all of the catalyst pilot tests and in the full-scale module sample contained greater than 95% gypsum (calcium sulfate dihydrate) and indicated a high limestone utilization of 98% or greater.

Table 71. Monticello FGD Liquor Major Species Analysis Results (mg/L)

Sample ID	SO_3	SO_4	Cl^-	Mg	Ca	Na	CO_3
Baseline [no catalyst] (4/5)	0	4,651	1,355	934	685	698	1.06
SCR (4/6)	0	5,035	1,440	1,092	640	773	1.27
SCR (4/7)	0	4,956	1,458	1,107	662	787	1.48
Regenerated Pd #1 (4/8)	0	4,489	1,178	898	650	652	1.06
Regenerated Pd #1 (4/9)	0	4,415	1,198	902	625	657	1.03
J-M Pd #1 (4/10)	0	4,484	1,205	889	640	650	1.04
J-M Pd #1 (4/18)	0	3,010	633	475	633	333	0.86
Gold (4/19)	0	3,240	729	547	613	404	0.83
Gold (4/20)	0	7,033	2,296	1,727	621	715	1.57
Full-scale Module 3C (4/20)	0	4,903	1,441	1,027	627	1,226	0.74

Table 72. Monticello FGD Slurry Solids Major Species Analysis Results

Sample ID	Slurry Wt% Solids	Solids Wt% Inerts	Solids Analysis, mg/g				
			Ca	Mg	SO_4	SO_3	CO_3
Baseline [no catalyst] (4/5)	7.41	1.53	227	0	540	0	4
SCR (4/6)	8.88	1.50	227	0	540	0	3
SCR (4/7)	10.24	1.52	231	0	538	0	2
Regenerated Pd #1 (4/8)	7.96	1.45	234	0	536	0	4
Regenerated Pd #1 (4/9)	9.06	1.53	227	0	546	0	2
J-M Pd #1 (4/10)	17.07	1.02	229	0	547	0	2
J-M Pd #1 (4/18)	5.33	0.84	233	0	535	0	7
Gold (4/19)	5.67	0.84	229	0	538	0	4
Gold (4/20)	10.58	1.99	230	0	540	0	1
Full-scale Module 3C (4/20)	7.99	0.97	234	0	549	0	7

Table 73. Monticello FGD Liquor Mercury Analysis Results

Sample ID	Measured Hg Concentration Range, µg/L	No. of Analyses
Baseline (4/5/05 17:00)	69-316	2
SCR Catalyst (4/7/05 09:30)	92-160	2
Regenerated Pd (4/9/05)	148-274	5
J-M Pd (4/18/05 16:55)	155-264	2
Gold (4/20/05)	151-474	2
Full-scale Module 3C (4/20/05)	162-468	3

Table 74. Monticello FGD Slurry Solids Mercury Analysis Results

Sample	Hg Concentration, µg/g
Baseline (4/5/05 17:00)	0.99
SCR Catalyst (4/7/05 09:30)	1.30
Regenerated Pd (4/9/05)	1.22
J-M Pd (4/18/05 16:55)	1.17
Gold (4/20/05)	4.96
Full-scale Module 3C (4/20/05)	0.44

Table 75. Monticello Unit 3 Coal Analysis Results

Sample ID	Hg, µg/g	Cl, mg/kg	F, mg/kg	Br, mg/kg	I, mg/kg
Unit 3 Lignite 3/8/05 12:40	0.399	95.1	73.5	<12	<25
Unit 3 PRB 3/8/05 14:20	0.093	26.3	42.6	<23	<27
Unit 3 Lignite 3/9/05 09:15	0.386	63.6	74.3	<12	<25
Unit 3 PRB 3/9/05 12:20	0.108	27.3	45.4	<25	<25
Unit 3 Lignite 4/5/2005 16:20	0.328	50.9	55.7	<12	<25
Unit 3 PRB 4/5/2005 16:00	0.107	16.7	39.7		
Unit 3 Lignite 4/6/2005 16:30	0.300	82.7	57.0	<12	<25
Unit 3 PRB 4/6/2005 15:15	0.113	19.4	40.3		
Unit 3 Lignite 4/7/2005 8:30	0.122	16.6	50.6	<13	<24
Unit 3 PRB 4/7/2005 10:05	0.099	10.3	39.3		
Unit 3 Lignite 4/8/2005 13:09	0.314	42.4	55.2	<5	
Unit 3 PRB 4/8/2005 11:41	0.133	20.9	40.3		
Unit 3 Lignite 4/9/2005 11:30	0.245	25.1	46.6	<12	<24
Unit 3 PRB 4/9/2005 11:38	0.244	15.5	41.9		
Unit 3 Lignite 4/18/2005 12:30	0.312	42.1	46.6	<12	<25
Unit 3 PRB 4/18/2005 11:30	0.092	29.0	56.8	<24	<26
Unit 3 Lignite 4/19/2005 8:00	0.329	54.0	56.8	<13	<24
Unit 3 PRB 4/19/2005 10:30	0.126	30.0	48.9	<25	<25
Unit 3 Lignite 4/20/2005 16:30	0.269	63.5	56.5	<13	<25
Unit 3 PRB 4/20/2005 16:00	0.083	20.7	44.5	<24	<26

Table 76. Monticello Unit 3 Fly Ash Sample Analysis Results

Sample	LOI, wt%	Hg, µg/g
Unit 3 B5 3/8/05	-	0.13
Unit 3 B5 3/9/05	-	0.13
Unit 3 B-6 4/5/05 15:15	0.10	0.10
Unit 3 B-2 4/6/05 15:15	0.25	0.11
Unit 3 4/7/05	0.45	0.16
Unit 3 B-5 4/9/05 16:10	0.27	0.10
Unit 3 4B 4/18/05 11:15	0.42	0.14
Unit 3 1st Field Hopper B6 4/20/05 15:50	0.42	0.13
Unit 3 2nd Field Hopper B17 4/20/05 15:52	0.34	0.21

The liquid-phase sample mercury concentration analyses proved to be difficult to conduct, even when using the method of standard additions to attempt to compensate for interferences within the sample matrix. There is apparently an interfering species in the FGD liquor from Monticello Unit 3 that prevents the accurate quantification of mercury concentrations. The samples were analyzed on several occasions at differing sample dilution levels, with different results for virtually every analysis. Because of these difficulties, the liquid-phase mercury concentrations cannot be reported with certainty. However, it is clear that the liquid-phase concentrations are relatively high, ranging from 92 to 470 µg/L for the catalyst test samples. These high liquor mercury concentrations are likely a result of operating at high oxidation-reduction potential (ORP) conditions during these tests, although ORP was not measured.

The solid phase results were a bit surprising at first glance. The gypsum mercury concentration was about 1 µg/g for the baseline pilot FGD test, and only increased to about 1.2-1.3 µg/g for the first three catalyst tests. The mercury concentration increased markedly for the sample from the gold catalyst test, to nearly 5 µg/g. This is probably due to the fact that the gold catalyst test was run continuously for greater than 30 hours, whereas the other three catalyst tests were only run during day shift on two consecutive days (except for the J-M Pd catalyst test, which was split between two non-consecutive days due to a boiler outage). Thus, the gold catalyst test results probably better reflect steady-state operation with enhanced mercury capture downstream of the catalyst than the other three, shorter-term catalyst test results.

The FGD liquor and solids sample analysis results were used to calculate the percentages of the mercury in the FGD slurry found in the liquor versus the solid phase. These results are summarized in Table 77. They show that a high percentage of the mercury captured in the wet FGD system was found in the liquor, particularly if the high end of the range of liquor mercury concentrations measured was accurate, with 45 to 92% found in the liquor. These values represent some of the higher percentages of mercury found in the FGD slurry liquid phase that URS has measured in FGD systems on U.S. coal-fired power plants.

Table 77. Summary of Mercury Partitioning Between the Liquor and Solids in FGD Slurry Samples from the April Monticello Tests

Sample	Slurry Wt% Solids	Liquor Hg Conc. Range, µg/L	Solids Hg Conc., µg/g	Hg in Liquor Based on Low Conc., µg/kg slurry	Hg in Liquor Based on High Conc., µg/kg slurry	Hg in Solids, µg/kg slurry	% of Hg in Liquor Based on Low Conc.	% of Hg in Liquor Based on High Conc.
Baseline [no catalyst] (4/5)	7.41	69-316	0.99	64	293	73	47%	80%
SCR (4/7)	10.24	92-160	1.3	83	144	133	38%	52%
Regenerated Pd #1 (4/9)	9.06	148-274	1.22	135	249	111	55%	69%
J-M Pd #1 (4/18)	5.33	155-264	1.17	147	250	62	70%	80%
Gold (4/20)	10.58	151-474	4.96	135	424	525	20%	45%
Full-scale Module 3C (4/20)	7.99	162-468	0.44	149	431	35	81%	92%

The data in Table 77 were used to calculate the apparent mercury capture in the pilot wet FGD per gram of gypsum byproduct for the longer-term gold wet FGD test, taking into account the measured mercury in the gypsum (4.96 µg/g) and the corresponding mercury in the FGD liquor. It was not seen as being worthwhile to do these calculations for the other tests, as they were not run for long enough periods to approach steady state with respect to mercury concentration in the gypsum byproduct.

The calculations for the gold catalyst test showed that the mercury in the FGD slurry sample represented 6.2 to 9.0 µg of mercury per gram of byproduct gypsum, based on the low and high measured concentrations of mercury in the FGD liquor, respectively. The gas phase data for SO_2 capture and for mercury capture across the pilot wet FGD absorber were also used to calculate an expected amount of mercury captured per gram of byproduct gypsum formed. The gas phase SO_2 capture data averaged approximately 300 ppmv at the FGD inlet and 30 ppmv or less at the outlet (90+% SO_2 capture). These calculations show an expected amount of 7.2 µg of mercury captured per gram of gypsum byproduct.

Thus, the value calculated from gas-phase data is bracketed by the FGD slurry sample analysis results, using the low and high measured liquor mercury concentrations. Within the limitations imposed by the inability to accurately measure the FGD liquor mercury concentrations, these calculations show good mercury balance closure for the gold catalysts longer-term (30+ hour) wet FGD pilot test, somewhere between 86% and 125%.

Table 75 summarizes coal sample analyses for mercury and halogen species concentrations. Each day, both the PRB and lignite fired were sampled and analyzed individually. It was not possible to collect a representative sample of the blend actually fired each day, nor was it possible to accurately track what blend percentage was being fired at any given time. The results show that the lignite had considerably higher mercury concentration than the PRB coal, with 0.30 µg/g average mercury content for the lignite versus 0.11 µg/g for the PRB. Also, the PRB has a higher heat content than the lignite (not shown in the table), so the differences in mercury content would be even greater if expressed on the basis of mass per Btu heat input. It is apparent from the large difference in mercury concentration between the two fuels why the flue gas mercury concentration can vary significantly during the day, since the percentage of each fired at any one time is not specifically controlled.

The lignite also tended to average more chloride (54 ppm) and fluoride (57 ppm) content than the PRB (22 and 44 ppm, respectively). Both fuels tended to have more fluoride than chloride content, which is not unusual for low-rank western coals. Neither had measurable bromide or iodide concentrations.

Table 76 summarizes the results of loss on ignition (LOI) and mercury concentration analyses of ash samples collected from a first-row ESP hopper on Unit 3 during these tests. The results are as expected: little LOI in the samples (0.3 wt% average) and correspondingly little adsorbed mercury (0.13 ppm average).

Comparison of Pilot- and Full-scale Wet FGD Mercury Capture Performance

OH measurements were also made on the outlet flue gas from the full-scale wet FGD system on Monticello Unit 3, from module 3C. Results are summarized in Table 78. There were no corresponding Hg SCEM measurements made there, so there are no relative accuracy data for this location. Also, OH measurements were not made at the full-scale wet FGD inlet, although there were flue gas mercury concentrations measurements made by SCEM at the oxidation catalyst pilot unit inlet that day. Since the oxidation catalyst pilot unit pulls flue gas from the 3C induced draft fan exhaust, the oxidation catalyst pilot unit SCEM results should reasonably represent the module 3C full-scale wet absorber inlet flue gas on that day. The table also shows OH results from the pilot wet FGD system under baseline (no catalyst) operation the day before.

Table 78. Results of OH Measurements at Monticello Full-scale Module 3C Wet FGD Absorber Outlet Compared to Pilot Wet FGD Results

Sample Location (Sampling Date)	Hg Concentration, μg/Nm^3 @ 3% O$_2$*, mean and 95% confidence interval of mean						Hg Removal Across Wet FGD, %			Hg^0 Re-emission % of inlet Hg^{2+}
	Catalyst Inlet/FGD Inlet			Wet FGD Outlet						
	Total Hg	Hg^0	Hg^{+2}	Total Hg	Hg^0	Hg^{+2}	Total Hg	Hg^0	Hg^{+2}	
Wet FGD Pilot Baseline [no catalyst] (4/5)	24.9 ± 1.8	16.3 ± 1.6	8.6 ± 0.9	16.0 ± 3.9	15.5 ± 4.1	0.48 ± 0.17	36	5	94	-9
Full-scale Module 3C (4/6)	30.8 ± 3.8**	21.3 ± 1.3**	9.5 (± 2.5 est.)**	27.9 ± 3.5	27.6 ± 3.5	0.25 ± 0.03	9	-30	97	66

*1 μg/Nm^3 at 3% O$_2$ equals 0.67 lb/10^{12} Btu heat input

**Measured by Hg SCEM; all other values in table are by the OH method

The results show that both the pilot- and full-scale wet FGD systems achieved a high percentage removal of oxidized mercury from the flue gas. For elemental mercury capture, the pilot wet FGD absorber showed a low percentage removal, while the full-scale wet FGD absorber showed significant levels of elemental mercury re-emissions. This results in the calculated overall mercury removal percentage being higher for the pilot wet FGD than for the full-scale absorber. The inlet mercury oxidation percentages were similar for the two days (35% on April 5, when the pilot data were collected, and 31% on April 6), so the percentage mercury capture across the two FGD absorbers would have otherwise been expected to be similar.

However, the full-scale wet FGD removal percentages are calculated from measurements by two different methods, and do not necessarily represent average concentrations over the same time period. Given the observed variability in the measured mean concentrations (as indicated by the relatively high 95% confidence intervals about the mean values), it is possible that the full-scale wet FGD re-emissions levels are overstated and the overall mercury removal percentage is understated.

Pilot Wet FGD Tests Downstream of Catalysts at Coronado Station

In April 2006, shortly after the oxidation catalyst pilot unit was brought on line, pilot wet FGD tests were conducted on flue gas treated by the 15-ft/s (4.6-m/s) catalyst. The decision to use the 15-ft/s catalyst was based on the SCEM data available at the time of testing. In light of the subsequent OH data which were discussed earlier in this section, the 5.5-ft/s (1.7 m/s) catalyst was apparently more active and should have been tested instead. Despite this fact, the data gathered with the 15-ft/s catalyst can be used to estimate the mercury removal and re-emissions that would have occurred had the 5.5-ft/s catalyst been tested.

Four separate conditions were tested with the 15-ft/s catalyst and the pilot wet FGD system:

- Natural oxidation, pH 5.4, high dibasic acid (DBA) concentration,
- Natural oxidation, pH 5.4, high DBA concentration, TMT-15 addition at 40 ml/ton coal,
- Forced oxidation, pH 5.8, low DBA concentration, and
- Forced oxidation, pH 5.8, low DBA concentration, TMT-15 addition at 40 ml/ton coal.

Each condition was tested on a separate day. Results are discussed below.

Pilot Wet FGD Operating Data

For the first two scrubber test days, the scrubber was operated to mimic the existing Unit 2 full-scale scrubber, which was currently using DBA, a mixture of adipic, glutaric and succinic acids that serve as a weak organic acid buffer to enhance SO_2 removal performance. The pH of the reaction tank was controlled to approximately 5.4. On the first test day, the weight percent solids of the slurry in the pilot reaction tank was 17%, which is higher than expected for the slurry in the full-scale scrubber. The most likely explanation is that the initial charge of slurry for the pilot reaction tank was pulled from a quiescent zone in the full-scale scrubber where solids had settled. The weight percent solids decreased to 10.7% on the second test day after diluting the pilot reaction tank with water. The liquor sulfite concentration was 3.2 mM (256 ppm) on the first test day and 0.8 mM (64 ppm) on the second test day. Particularly for the first day, this sulfite concentration was higher than expected based on observations from the full-scale wet FGD system, where essentially no sulfite was measured. The DBA concentration was 38 meq/L (approximately 2800 ppm as adipic acid) on the first test day and dropped to 20 meq/L (~1500 ppm) on the second test day due to the dilution of the reaction tank described above and DBA degradation and co-precipitation losses.

The last two days of scrubber testing were intended to mimic possible future scrubber operation (forced oxidation, no DBA). The pH of the reaction tank was controlled to 5.8 and the reaction tank slurry was diluted in an effort to achieve a low DBA concentration. This caused the slurry weight percent solids to be low (5%) because solids do not build up quickly in the relatively large pilot reaction tank (which was sized for treating flue gas from higher-sulfur coal). Dilution of the pilot scrubber reaction tank decreased the DBA concentration for these test days to 6-7 meq/L (~400 to 500 ppm).

The SO_2 removal by the pilot wet FGD averaged 94% for the first three test days. The SO_2 removal decreased to 85% on the fourth and final test day because of an operational problem with the slurry recycle pump that decreased the slurry recycle rate.

Table 79 summarizes the results from daily samples of the scrubber liquor and solids that were collected and analyzed. The concentrations of the highly soluble species (Cl, Na, Mg) decreased significantly from Day 1 through Day 3, due to the dilution of the reaction tank slurry described above. The liquor mercury concentration results show the expected effect of Evonik's TMT-15 mercury re-emission additive, greatly reduced liquid-phase mercury concentrations, when comparing Day 3 and Day 4 results, but not when comparing Days 1 and 2. The reason why no effect was seen comparing Day 2 to Day 1 results is not known at this time. The FGD solids data show that the solids from the first day had a low mercury concentration of 0.39 µg/g, and increased steadily to 2.90 µg/g by Day 4. This is likely a residence time effect, but may also be influenced by TMT addition. On Day 1, the solids in the pilot scrubber reaction tank were mostly solids from the full-scale scrubber slurry used to charge the tank at the beginning of the tests. By Day 4, after several days of operation and frequent blow down of portions of the tank's inventory, it is likely that the solids became more representative of treating flue gas with mostly oxidized mercury content.

Evaluation of Mercury Removal across Pilot Scrubber

Flue gas mercury measurements were made with both the OH and Hg SCEM methods at the FGD outlet. As described previously with the oxidation catalyst test results, post-test analysis of the OH and SCEM data indicates that the OH data were more reliable at the catalyst outlet (FGD inlet). In contrast, the SCEM data appear to be more reliable at the FGD outlet, as explained below.

By the time these tests were conducted in 2006, past experience with mercury sampling at scrubber outlet locations (both pilot- and full-scale) had shown that scrubber carryover can be pulled into the Hg SCEM's IGS extraction probe. As the slurry is heated in the extraction probe, mercury from the liquid carryover is volatilized and then detected as vapor-phase mercury in the sample gas. With the pilot FGD this phenomenon is most obvious when the mist eliminator is washed. The Hg SCEM shows an immediate large increase in mercury concentration, which then takes almost an hour to clear. During this test program, the mist eliminator was not washed during the 2-hr OH runs. It was washed only between runs, and the Hg SCEM total mercury data were monitored for a return to normal concentrations before the next OH run was begun.

Even when the mist eliminator wash had not just occurred, there was a smaller, but still significant amount of slurry carryover. At the pilot FGD outlet sampling location, the extraction scheme for the Hg SCEM was set up with two extraction loops in series and with lower operating temperatures to minimize scrubber carryover being pulled into the Hg SCEM analyzer. In contrast, the OH probe was not modified but was implemented according to the method, so scrubber carryover could have been pulled into the probe and collected on the filter. The OH filter is heated to 250^{o}F, causing the carryover liquor to evaporate and mercury in the scrubber carryover to volatilize and be captured in the impinger catch.

Table 79. Results of Daily Pilot FGD Solid and Liquor Analyses

Date	**4/20/2006**	**4/21/2006**	**4/23/2006**	**4/24/2006**
Time	**17:50**	**17:15**	**17:15**	**17:15**
pH	5.63	5.18	5.77	5.77
Temperature	45.8	46.2	41.7	43.3
Solid Results:				
Hg, µg/g	0.39	0.96	1.35	2.90
Ca, mg/g	219	218	224	222
Mg, mg/g	0.8	0.9	0.6	0.5
SO_3, mg/g	<0.6	<0.7	<0.6	<0.7
SO_4, mg/g	522	519	494	525
CO_3, mg/g	3	<0.7	36	4
Acid Insoluble Inerts, wt%	5.64	5.48	4.74	4.46
Slurry Solids, wt%	8.8	6.6	4.4	3.9
Sulfite Oxidation, %	100.0	100.0	100.0	100.0
Limestone Utilization, %	99.0	99.5	90.1	98.5
Analytical Closures:				
Weight, %	-0.4	-1.2	-1.3	-0.7
Molar, %	0.2	0.7	-1.0	0.3
Acceptable, %	7.0	7.0	6.7	7.0
Liquid Results:				
Hg, µg/L	10.7	12.1	42.6	1.7
Ca^{++}, mg/L	638	577	613	862
Mg^{++}, mg/L	4,280	2,289	892	1,025
Na^{+}, mg/L	17,654	9,514	3,058	3,656
Cl^{-}, mg/L	14,222	7,434	2,406	1,895
$SO_3^{=}$, mg/L	255	65	<2	<2
$SO_4^{=}$, mg/L	36,540	18,045	7,688	6,326
Charge Imbalance:				
Calculated, %	-0.6	3.7	1.9	21.5
Acceptable, %	5.2	5.1	5.0	4.9

In the data collected from this test program, the total mercury concentrations measured by OH at the FGD outlet were higher than the Hg SCEM measurements. The Hg SCEM total mercury measurements for the first three test conditions were on average 42% lower than the OH measurements, and the elemental mercury concentrations were on average 44% lower. The exception is the fourth test condition, in which the liquid-to-gas recycle rate was lower than the previous three tests due to an operational problem with the slurry recycle pump. With the low liquid-to-gas recycle rate, the amount of slurry carryover was reduced, and the positive bias on the OH results was lowered. In this case, the total mercury concentrations agreed within 20% and the elemental mercury concentrations agreed within 5%. Therefore, to evaluate re-emissions from the scrubber, the authors believe it is most prudent to compare the OH measurements at the catalyst outlet with the SCEM measurements at the FGD outlet as shown in Table 80.

Table 80. Pilot Scrubber Results Presented with Inlet OH and Outlet SCEM Data

Date	**4/20/2006**	**4/21/2006**	**4/23/2006**	**4/24/2006**
Catalyst	15-ft/s	15-ft/s	15-ft/s	15-ft/s
Oxidation Mode	Natural	Natural	Forced	Forced
TMT Dosage, ml/ton coal	0	40	0	40
DBA Concentration, meq/L	38.1	19.5	7.3	5.7
Wt% Solids in Recycle Slurry	17.3	10.7	4.7	4.9
SO_2 removal, %	93%	94%	95%	85%*
pH	5.4	5.3	5.8	5.8
Sulfite in Liquor, mM, as measured by IC	3.2	0.8	<0.02	<0.02
Slurry Pump Pressure, psig	13	14	13	8
FGD Inlet Flue Gas Flow Rate, acfm	1746	1430	1327	1195
Catalyst Outlet/FGD Inlet Flue Gas, μg/Nm^3:				
Hg^T (OH)	9.5±1.7	9.5±0.4	12.1±1.4	13.2±1.8
Hg^0 (OH, by difference)	1.1±0.2	1.1±0.3	1.4±0.2	1.7±0.4
Hg^{2+} (OH)	8.4±1.9	8.4±0.6	10.7±1.7	11.5±2.2
FGD Outlet Flue Gas (μg/Nm^3):				
Hg^T (SCEM)	1.8±0.9	1.2±0.1	2.1±0.4	2.7±0.1
Hg^0 (SCEM)	1.4±0.5	1.0±0.0	1.8±0.6	1.5±0.2
Hg^{+2}(SCEM, by difference)	0.4±1.4	0.2±0.1	0.3±1.0	1.2±0.3
Calculated Efficiencies:				
% Oxidation at Catalyst Outlet	88%	89%	88%	88%
% Removal of Hg^T across FGD	81%	87%	83%	79%
% Removal of Hg^{+2} across FGD	96%	97%	97%	89%*
Hg^0 Re-emissions, % of inlet Hg^{+2}	4%	-1%	3%	-1%

*SO_2 and Hg^{+2} removal efficiencies were adversely affected by a recycle slurry pump problem on the final test day

These data show that the pilot wet FGD scrubber was effective at removing oxidized mercury (greater than 96% capture for the first three test days). The oxidized mercury capture decreased to 89% on the fourth test day because of operational problems with the slurry recycle pump.

Likewise, the SO_2 removal for this fourth test day was 85%, much lower than the 94% average SO_2 removal from the first three test days when the slurry recycle pump was operating correctly.

However, note that even during the first three tests, when the recycle pump was operating normally, the SO_2 and Hg^{+2} removal efficiencies were lower than can be achieved by a high-efficiency wet FGD absorber. The pilot wet FGD absorber was originally designed to be as short as possible, to make it more mobile. This compromises the amount of surface area available for mass transfer compared to a full-scale module. Because Hg^{+2} is highly soluble in wet FGD liquor, there is essentially no "back pressure" on Hg removal like there is for SO_2 removal, and Hg^{+2} should be removed at or near an absorber's upper mass transfer limit. A high-efficiency SO_2 absorber should be capable of 98% or greater removal at the mass transfer upper limit, compared to the values of 96 to 97% measured for the pilot absorber.

The data in Table 80 also show that the mercury re-emissions were fairly low for both the natural and forced oxidation operation modes. With no TMT addition, the re-emissions were small (0.3 $\mu g/Nm^3$), representing less than 5% of the inlet oxidized mercury. With TMT addition at a rate of 40 ml/ton coal, there were no re-emissions in either the natural or forced oxidation modes. That is, the elemental mercury concentration at the catalyst outlet (as measured by OH) was equal to the elemental mercury concentration at the scrubber outlet (as measured by Hg SCEM). Re-emissions would be overstated if using the Hg SCEM data at the 15-ft/s catalyst outlet, because the oxidized mercury concentration at this location was apparently biased high (as discussed previously in this report).

Baseline (no catalyst) mercury removal was not measured with the wet FGD pilot unit. However, based on the typical mercury oxidation percentage measured upstream of the oxidation catalyst pilot unit (less than 10%), the mercury removal across the wet FGD system would also be estimated at less than 10%.

Second Round of Wet FGD Testing

Testing was performed across the 15-ft/s catalyst and pilot wet FGD system at the end of May 2007. The results are shown in Table 81. The Hg SCEM results showed that the catalyst inlet oxidation was 27% and the catalyst outlet oxidation was 75%, corresponding with 71% oxidation of the inlet elemental mercury across the catalyst. This was down from 82% measured on May 4th, which may be due to fly ash buildup (see the catalyst pressure drop plot presented earlier in this report). Mercury adsorption across the catalyst varied from an average of 4 to 17% throughout the test period, which indicates near equilibrium operation. The mercury removal across the pilot scrubber was only 28% in spite of the inlet mercury oxidation percentage being 75%.

Table 81. Results of Wet FGD Pilot Unit Operation Downstream of 15-ft/s Catalyst at Coronado, May 2007

Test Date	Catalyst Inlet, µg Hg/Nm^3		Catalyst Inlet Oxidation, %	Catalyst Outlet, µg Hg/Nm^3		Catalyst Outlet Hg Oxidation, %	Pilot Scrubber Outlet, µg Hg/Nm^3		Mercury Removal across Wet FGD, % of catalyst outlet	Mercury Re-emissions, % of FGD Inlet Hg^{+2}	
	Total Hg	Hg^0		Total Hg	Hg^0		Total Hg	Hg^0		Measured	Estimated
May 31, 2007	14.8	10.8	27	12.3	3.1	75	8.8	4.4	28	14	91

The measured FGD outlet total mercury concentration was considerably higher than the outlet elemental mercury concentration, which indicates a high oxidized mercury concentration at the scrubber outlet (4.4 µg/Nm^3). At face value this suggests poor oxidized mercury removal across the wet scrubber, with a calculated removal percentage value of only 52% based on the measured scrubber outlet total and elemental mercury concentrations. An oxidized mercury removal percentage of 95% was expected. Normally, only mechanical problems that adversely affect mass transfer in the FGD absorber would lower the oxidized mercury removal percentage. However, no adverse effect on mass transfer was observed during this period. SO_2 removal across the wet scrubber was measured at 95% during this test. The low apparent oxidized mercury removal percentage is more likely a measurement artifact, such as a result of elemental mercury being oxidized on the surface of the IGS filter used to filter particulate matter from the sample gas before it goes to the Hg SCEM.

It is more likely that the wet scrubber overall mercury removal was limited by mercury re-emissions. An increase in elemental mercury concentration across the wet scrubber is evidence of re-emissions. In this case the measured outlet elemental mercury concentration was only 1.3 µg/Nm^3 higher than the inlet elemental mercury concentration, which indicates that only 14% of the FGD inlet oxidized mercury was reduced and re-emitted as elemental mercury. However, it is more likely that a measurement artifact, as mentioned above, biased the scrubber outlet elemental mercury concentration low and under-reported the effects of re-emission. Based on this observation, an "estimated" re-emission level was calculated, by assuming that the actual oxidized mercury removal across the wet scrubber was 95% (equal to the SO_2 removal percentage), rather than the observed value of 52%. As shown in the table, the estimated re-emission level indicates that 91% of the FGD inlet oxidized mercury was reduced and re-emitted, which is a very high re-emission percentage.

This is a much different result than was seen in previous testing with this pilot scrubber when operating in the limestone forced oxidation mode downstream of the oxidation catalyst in April 2006. In those test results, the pilot wet FGD system achieved 83% total mercury capture with the scrubber flue gas inlet mercury being 88% oxidized. The re-emissions level measured in the April 2006 test represented only 3% of the inlet oxidized mercury. The reason for the difference in results between these two tests is not obvious.

However, both of these scrubber tests were run starting with slurry from the Coronado Generating Station Unit 2 full-scale FGD blow down as the initial makeup to the pilot FGD reaction tank. Between April 2006 and May 2007, the mode of operation of the full-scale wet FGD system changed, from lower pH operation with adipic acid as a performance additive, to higher pH operation with no performance additive. The change in chemistry in the slurry used as the initial makeup to the pilot FGD reaction tank may have impacted tendencies for mercury re-emissions.

The pilot FGD chemistry during the two tests is compared in Table 82. There are some variations in FGD liquid phase concentrations between the April 2006 and May 2007 tests, with the April 2006 liquor typically being more dilute in soluble species. This was intentional, as the dilution was intended to reduce the effects of adipic acid in the liquor on scrubber performance. The most notable difference between the two test periods is in the amount of mercury present in the FGD liquor. In May 2007, the mercury concentration in the liquor was much higher than in April 2006, while the FGD solid mercury concentration was lower. Since mercury must be in the liquid phase to undergo re-emission reactions, higher liquor mercury concentrations would increase tendencies for re-emissions. The reason why the liquor mercury concentration was considerably higher in May 2007 remains unclear. Based on URS experience sampling other wet FGD systems, it is possibly a result of operating at higher ORP values in the slurry liquor in May 2007. However, ORP values were not measured during these tests.

Additional Testing of Fixed-structure Mercury Adsorbents/Catalysts at Plant Yates

Corning Fixed-structure Sorbents

In December 2008, URS personnel returned to Plant Yates to remove the oxidation catalysts from the previous (December 2005 to May 2007) pilot testing, make general repairs to the pilot skid, and begin a structural stability test of a fixed structure adsorbent/catalyst (honeycomb) sample provided by Corning, Inc. While on site, the gold catalysts and the newer Pd #1 catalysts were removed from chambers 1 and 2 along with the support structures that had been installed. Repairs were made to the skid including freeing the flow control butterfly valves, calibrating the flow and pressure instruments, and checking operation of the sonic horns.

While planning for additional testing Plant Yates, the project team noticed that the flue gas temperature at the pilot catalyst skid was low compared to typical ESP operation. Logger data over the time period December 2005 through May 2007 were reviewed and showed the catalyst outlet temperatures to range from approximately 190°F (88°C) to 260°F (127°C). A temperature range of 280°F (138°C) to 300°F (149°C) would be more desirable, to avoid sulfuric acid condensation and deposition, and would provide more representative results for full-scale ESP outlet flue gas conditions. EPRI, a project co-funder, agreed to purchase a duct heater to be installed upstream of the pilot system. A Chromalox electric heater and silicon-control-rectifier (SCR) controller were purchased and were delivered to the plant to be installed in the spring of 2009. A housing for this heater was also fabricated and shipped to Plant Yates.

Table 82. Comparison of FGD Samples Analyses from May 2007 versus April 2006

Date	**5/31/07**	**4/23/2006**
Time	14:00	17:15
pH	5.92	5.77
Temperature	47.3	41.7
Solid Results:		
Hg, µg/g	0.343	1.35
Ca, mg/g	237	224
Mg, mg/g	0	0.6
SO_3, mg/g	0	<0.6
SO_4, mg/g	550	494
CO_3, mg/g	2	36
Acid Insoluble Inerts, wt%	1.15	4.74
Slurry Solids, wt%	8.74	4.4
Sulfite Oxidation, %	100.0	100.0
Limestone Utilization, %	99.3	90.1
Liquid Results:		
Hg, µg/L	155.5	42.6
% of Slurry Hg in Liquor	21.0	6.6
Ca^{++}, mg/L	587	613
Mg^{++}, mg/L	2,105	892
Na^{+}, mg/L	5,960	3,058
Cl^{-}, mg/L	6,379	2,406
Br^{-}, mg/L	132	Not analyzed
$CO_3^{=}$, mg/L	74	Not analyzed
$SO_3^{=}$, mg/L	0	<2
$SO_4^{=}$, mg/L	13,188	7,688

The Corning structural stability test was intended to determine if the fixed-structure substrates would be able to withstand forces from fly ash buildup, sonic cleaning energy, etc., while maintaining acceptable pressure drop performance. The substrates consisted of seven banks of honeycombs with pitch sizes ranging from 100 cpsi (15.5 cells/cm^2) to 64 cpsi (9.9 cells/cm^2). These were arranged with the larger openings (fewer cpsi) on the flue gas inlet side of the bank of honeycombs, and the smaller openings (higher cpsi) towards the outlet. The inactive structural integrity honeycombs were to eventually to be replaced by long-term adsorption-test honeycombs prepared at a cell pitch selected based on the structural integrity test results.

Once repairs to the pilot unit were complete, the test samples of the Corning honeycomb were loaded into chamber 1. The system was sealed, flue gas was started through the Corning honeycombs at approximately 2000 acfm (3400 m^3/h), and the sonic horns were set to sound 15 seconds every 10 minutes. The Corning structural integrity test samples continued to run through February 2009. The temperature, pressure drop, and flue gas flow were continually logged until the test was concluded, at which time the inlet flue gas damper was closed and installation of the flue gas heater began. Figure 43 is a plot of the pressure drop over the duration of the test.

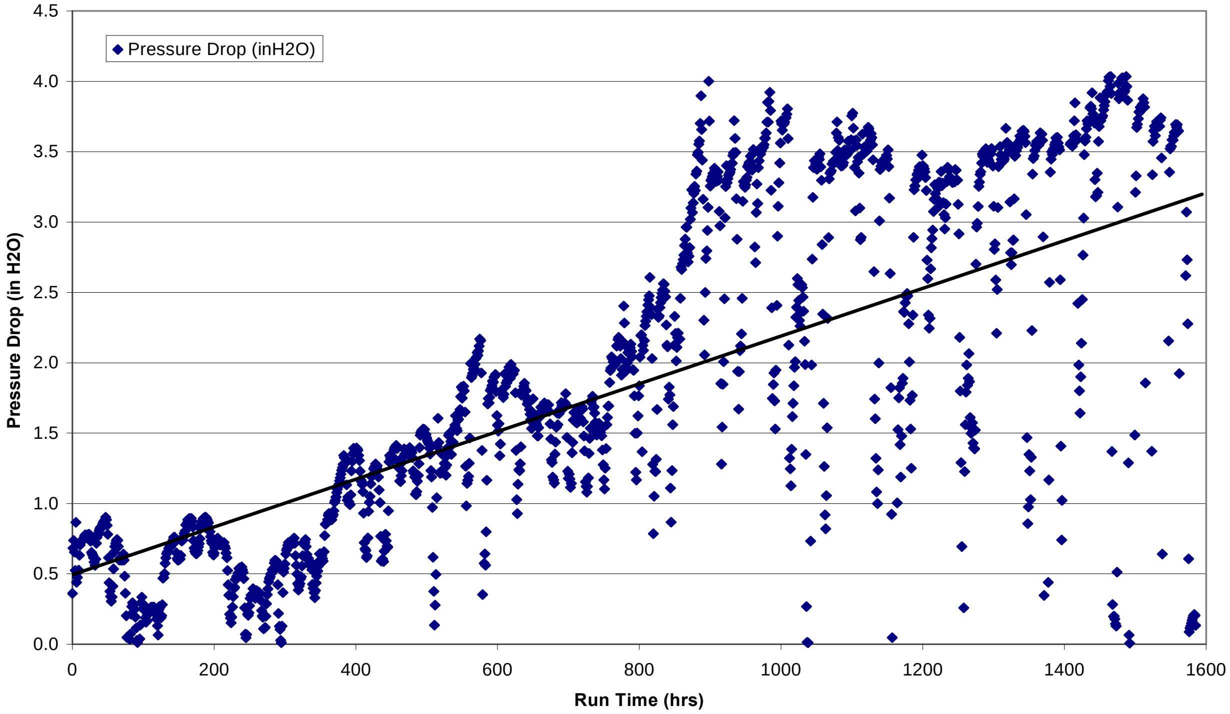


Figure 43. **Pressure Drop across the Corning Honeycombs at Plant Yates**

Note: 1.0 in. H_2O = 0.25 kPa

The pressure drop across the entire bank of honeycombs started at approximately 0.5 in. H_2O (0.12 kPa) and rose to approximately 3.5 in. H_2O (8.7 kPa) over 67 days. As with the previous catalyst tests at Plant Yates, much of this plugging could be attributed to fly ash that is not captured in the relatively small ESP on Plant Yates Unit 1. The flue gas temperature was also relatively low at this location (~200°F [93°C]), as the duct heater had not yet been installed. This would cause acid gases to condense and moisture to absorb on the fly ash and test structure surfaces, thus making them more sticky and prone to plugging. Figure 44 is a plot of the flue gas temperature and flue gas flow rate over the duration of the test.

The average flue gas flow rate over the duration of the test was approximately 2000 acfm (3400 m^3/h); however, there was some scatter in the data, especially towards the end of the test. Low flue gas temperatures and a significant fly ash loading might have also contributed to some of this scatter by condensing water and partially plugging some of the pressure drop and flow instrumentation lines. The planned addition of a flue gas heater was expected to prevent much of this condensation and plugging in future tests.

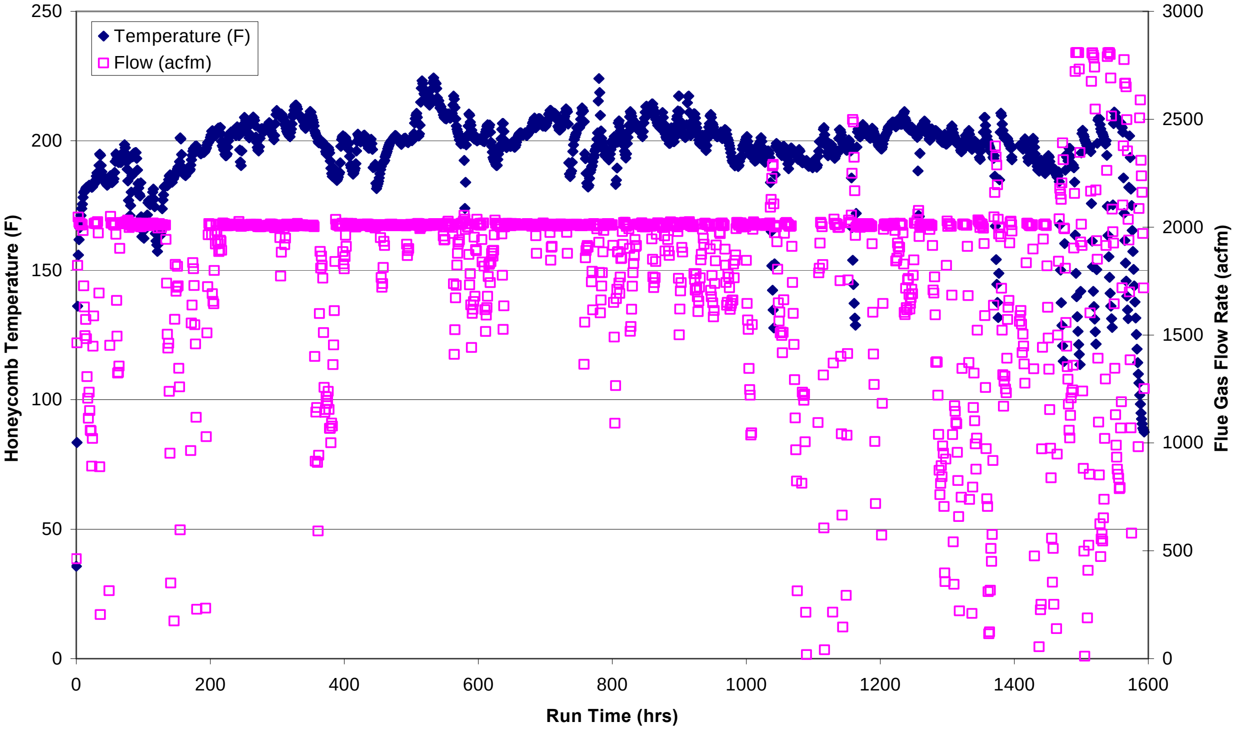


Figure 44. Flue Gas Temperature and Flow Rate for the Corning Honeycomb Test

Note: 1.0 in. H_2O = 0.25 kPa

In April 2009 the structural integrity test honeycombs were replaced with three banks of new honeycomb material that had the same effective length as the previous test, but were configured in two banks of 9-in. (23-cm) long substrates and one bank of 3-in. (7.6-cm) substrates. Flue gas was started to the system with the new upstream duct heater maintaining the flue gas temperature between 280°F (137°C) and 300°F (149°C). A plot of the pressure drop as a function of test duration appears in Figure 45.

After 1800 hours of operation the pressure drop across these honeycombs remained relatively stable at approximately 0.4 in. H_2O, with instantaneous values ranging from 0.2 to 0.6 in. H_2O. During the month of July 2009, between 1800 hours and 2300 hours of operation, the pilot system was taken off line and put back in service several times for installation of mercury oxidation catalysts/sorbents in other chambers. After the system was brought back on line in August 2009, the pressure drop across the honeycombs increased to approximately 0.8 inches of water and continued to rise. Even though the pilot unit was isolated from flow during the startup and shut down periods, some moisture may have condensed in the honeycombs that would cause plugging and contribute to the pressure drop rise.

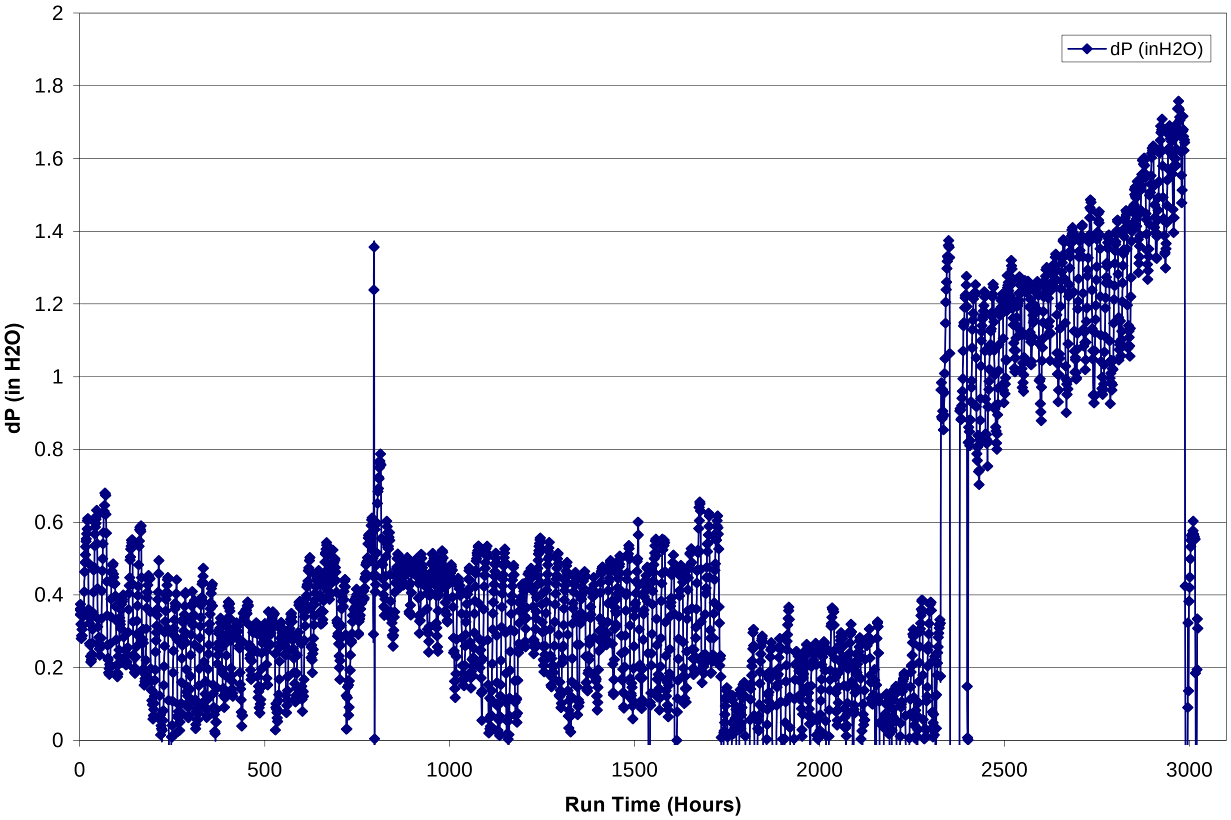


Figure 45. Pressure Drop across Corning Honeycomb Samples

The honeycombs were removed from the chamber in August 2009, after nearly 3000 hours of operation. The face of each honeycomb bank appeared to be between 50% and 75% obstructed. The blockage appeared to be mainly concentrated near the center of each honeycomb with the periphery mostly open. There was also some material on the trailing edges of the honeycombs; however, almost all blocking of the cells appeared to occur within ¼-in. (0.6-cm) of the front face.

After these tests were completed, Corning, Inc. decided to take another path in the development of their fixed-structure, long-term mercury adsorbents. Consequently, no additional tests of these materials were conducted at Plant Yates as part of this project.

Parallel Plate Fixed Mercury Sorbents/Catalysts

In June 2009, URS personnel traveled to Plant Yates to perform baseline mercury measurements across the pilot skid with the new duct heater in service, as well as to install and measure the performance of two sets of mercury fixed sorbents/catalysts. The baseline mercury measurements showed no effect of the new duct heater on the removal of mercury or oxidation of elemental mercury from the inlet to the outlet of the empty pilot skid. The baseline measurements were made over the course of 24 hours, and the inlet and outlet measurements agreed within ± 5-10%.

Following the baseline measurements, two sorbents/catalysts were installed in separate chambers of the pilot unit. These two sorbents/catalysts included plates of chemically treated activated carbon granules that were placed parallel to the gas flow, and sheets of activated carbon fiber cloth (ACF) that were also placed parallel with the gas flow. The parallel configuration was designed to allow flue gas to contact the material while maintaining a low pressure drop. Table 83 contains a summary of the key design characteristics of these two systems.

Table 83. Summary of Design Parameters for Parallel Plate Sorbents/Catalysts

Material	Plate Dimensions	Plate Spacing, in. (cm)	Number of Plates	Flue Gas Flow Rate, acfm (m^3/h)	Flue Gas Velocity, ft/s (m/s)	Theoretical Removal / Oxidation, %
Norit Darco Hg-LH 4x8 Granules	36 in (L) x 34 in (H), 1.5 in (D) [0.91 m x 0.86 m x 3.8 cm]	0.5 (1.3)	17	850 (1440)	5.0 (1.5)	70
Activated Carbon Fiber	36 in (L) x 12 in (H) [0.91 m x 0.30 m]	0.25 (0.64)	40	250 (420)	5.0 (1.5)	85

Carbon Granule Plates

Mercury measurements across the granulated carbon plates showed consistently high mercury oxidation over the initial period of operation. Figure 46 is a plot of the mercury adsorption and oxidation as a function of run time for the carbon granule test. Even though the mercury adsorption of the carbon degraded throughout this period, the mercury oxidation across the parallel plates remained steady between approximately 78% and 93%. The pressure drop across this parallel plate configuration was also steady and very low throughout the test, averaging approximately 0.1 in. H_2O (0.025 kPa).

Mercury measurements across the carbon granule plates conducted a month later showed diminished elemental mercury oxidation across the plates. While during the first 180 hours of operation the elemental mercury oxidation across the plates was consistently greater than 80%, after 910 hours of operation the mercury oxidation was reduced to approximately 55%. Figure 47 shows a plot of the mercury oxidation as a function of run time for the carbon granule test between 890 and 970 hours of total operation. The mercury adsorption across the plates in the parallel configuration was negligible.

Since the oxidation performance was greatly diminished and adsorption was negligible in the parallel plate configuration, after approximately 915 hours in service three of the plates were turned perpendicular to the gas flow. This created a fixed bed with a depth of approximately 4.5 inches through which the flue gas flowed. The mercury adsorption rate increased to approximately 60% in this configuration; however, the mercury oxidation remained steady between 55%-65%, as shown in Figure 47.

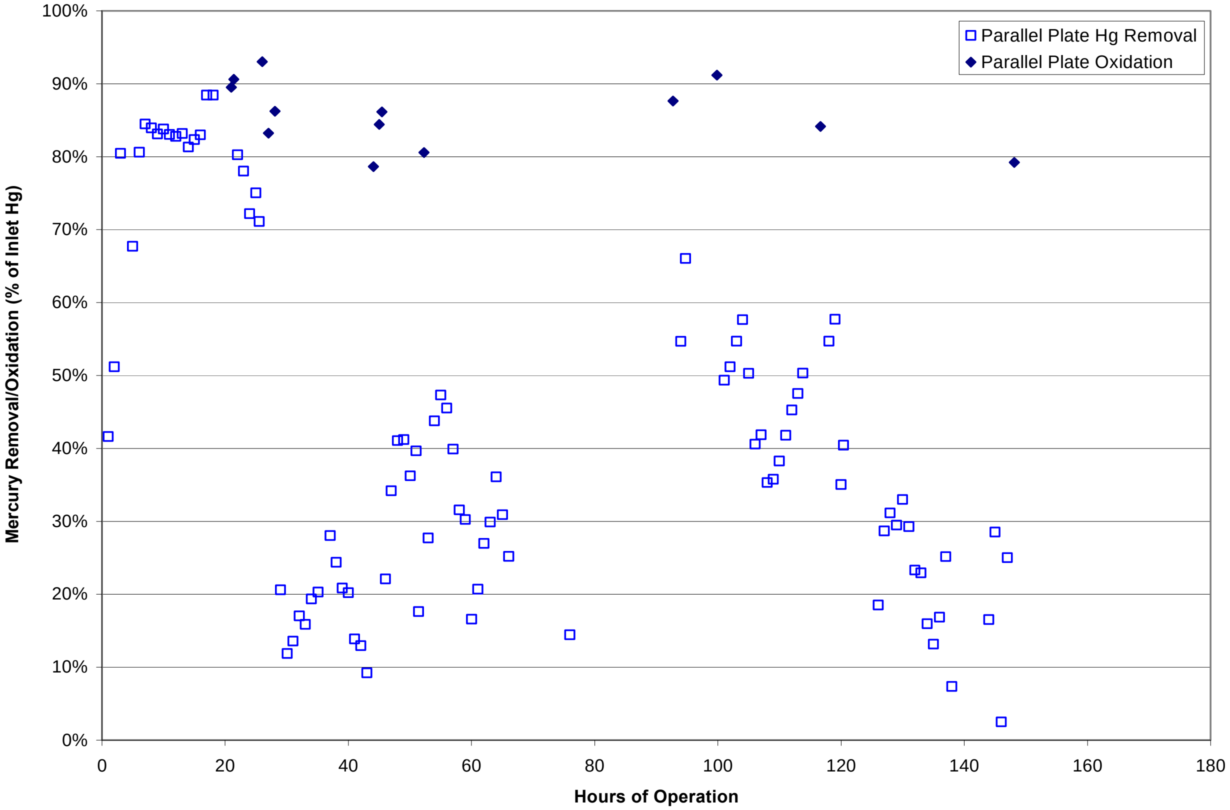


Figure 46. Mercury Oxidation and Adsorption across Parallel Plates with Granulated Carbon

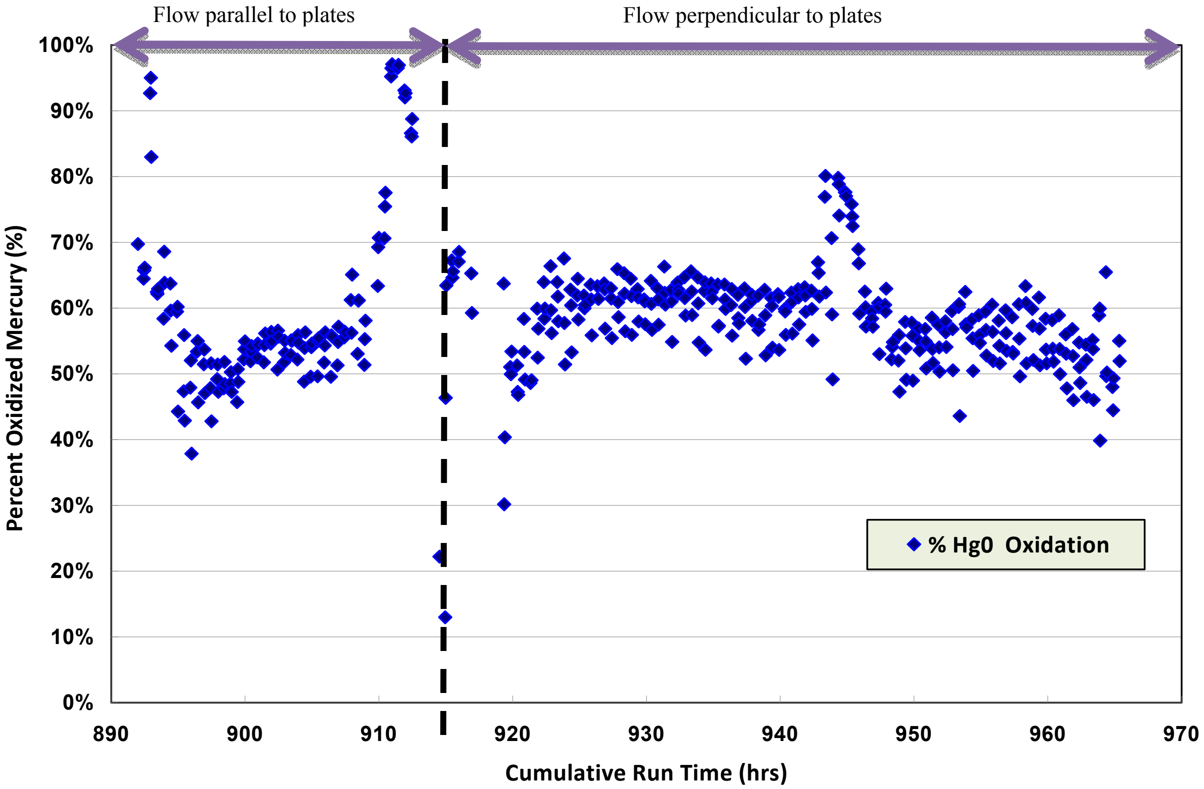


Figure 47. Mercury Oxidation across Parallel and Perpendicular Plates with Granulated Carbon

Activated Carbon Fiber Cloth Plates

A plot of the initial mercury oxidation and adsorption performance of the ACF cloth appears in Figure 48. The adsorption and oxidation percentages measured with the parallel cloth plates were not as high as were measured with the carbon granules. The mercury adsorption began relatively low, with the highest measurement showing 39% removal, and degraded to nearly 0% after 50 hours of operation. The oxidation of the inlet elemental mercury varied between 35% and 27% across the plates, and showed a decreasing percentage versus time. Previous lab testing of this material showed high levels of adsorption and oxidation across these plates, so these results were surprising and somewhat disappointing.

After 970 hours of operation, minimal mercury oxidation between 0%-5% and approximately 0% adsorption were measured. A sample of the cloth that was previously extracted from the pilot system was tested in the URS Austin laboratory for mercury capacity. The capacity of the used cloth was approximately 400 μg/g, whereas a new sample of the cloth tested under the same conditions had a capacity greater than 4000 μg/g. This indicates that the cloth was deactivated by some component in the flue gas such as SO_3 or fly ash, in spite of the duct heater maintaining the flue gas temperature above its acid dew point.

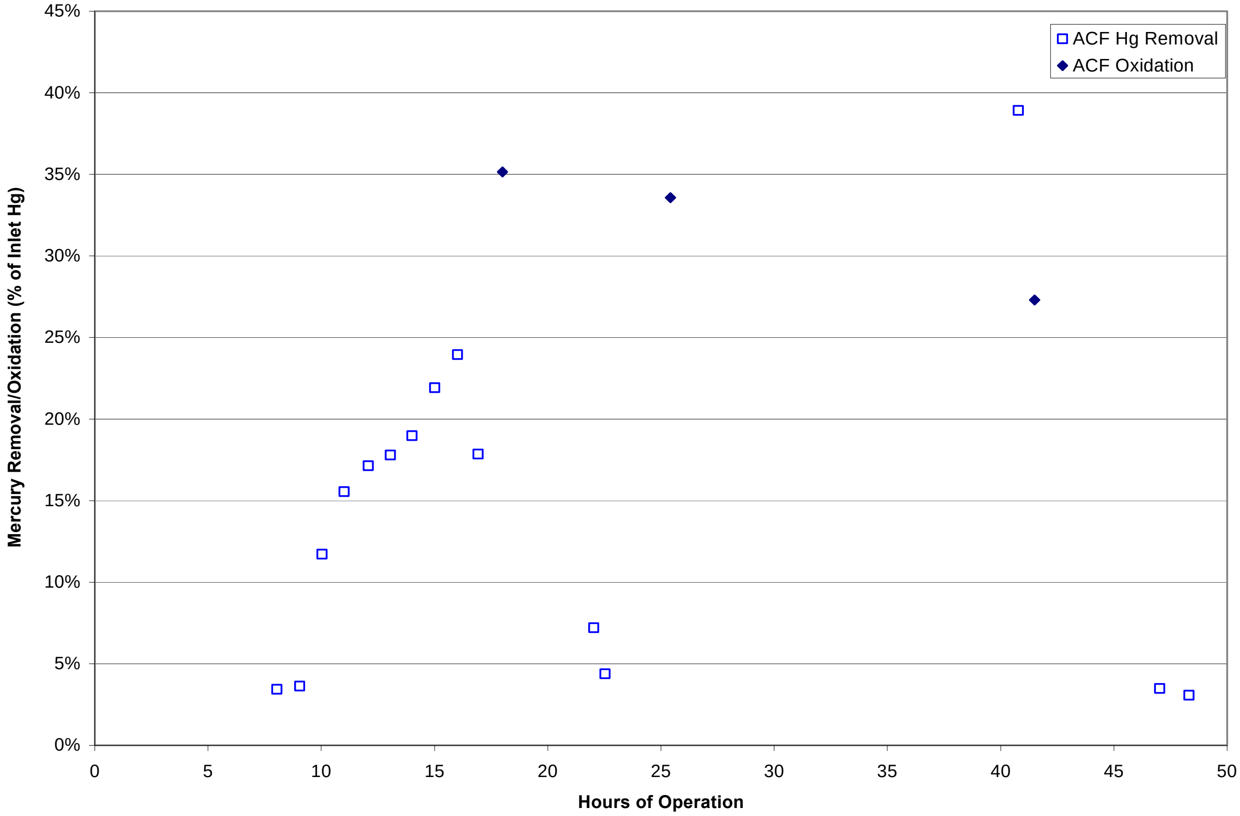


Figure 48. Mercury Oxidation and Adsorption across ACF Reactor

Conclusion of Testing at Plant Yates

In April 2010, while attempting to start flow through the system after a pilot unit outage, it was discovered that the inlet valve to the pilot was partially frozen or blocked. The valve would only open approximately 5-10 degrees, which only allowed a flue gas flow of approximately 200-300 acfm. The valve is located at an elevation approximately 25 feet above grade and is not accessible via walkway, and is normally operated from the ground level by a chain operator attached to a gearbox situated on top of the valve. Because the chain operator could be used to partially open the valve, it was thought that the valve wafer was partially blocked by the buildup of fly ash in the duct or on the valve sealing surfaces, and might be cleared by applying more leverage to the gearbox shaft. In the first attempt to do this, a mechanic in a man-lift used a long pipe wrench to operate the valve, but because of the position of the lift he was not able to get close enough to the valve to apply appropriate force. In the second attempt, a scaffold was erected around the valve so there was a platform to work from. When force was applied to the gearbox shaft the bearings and casting of the gearbox cracked open, thus leaving the valve inoperable. It was concluded that something more significant was blocking the valve and that the valve would have to be repaired or replaced at the next plant outage. This valve had already been replaced once before during the oxidation catalyst project at Plant Yates, so a replacement valve would represent the third valve at this location over the life of the project.

Because of continued valve problems and the further delays to the test program that would result if waiting for a unit outage to make valve repairs, the project team reconsidered the project status. At this point the project had been underway for over six years, and a larger-scale demonstration of fixed-structure mercury oxidation catalysts had been completed in Cooperative Agreement DE-FC26-06NT42778. Corning, Inc. had made the decision to discontinue testing of their fixed structure sorbents at Plant Yates. Team member and co-funder EPRI was interested in continuing the development of novel fixed structure mercury sorbents/catalysts, but decided this development was better supported in smaller-scale, shorter-term tests than the pilot unit at Plant Yates was designed to support.

Consequently, the project team decided to not replace the failed valve, but instead to end the pilot-scale testing effort at Plant Yates. This decision was made with concurrence from the host utility, Southern Company, and both the EPRI and the DOE-NETL project managers.

CONCLUSION

This project was conducted over a time period of seven years. It encompassed pilot-scale testing of mercury oxidation catalysts and/or fixed structure sorbents at three sites, and pilot-scale tests of wet FGD for mercury removal at five sites. The project was a follow on to pilot-scale mercury oxidation catalyst tests conducted as part of Cooperative Agreement DE-FC26-01NT41185, and a precursor to a full-scale demonstration conducted as part of Cooperative Agreement DE-FC26-06NT42778.

The objectives of the project were to determine 1). Whether the small-pitched catalyst (typically 64 cpsi [9.9 cells/cm^2]) could be operated long term in flue gas downstream of a cold-side ESP without excessive fly ash buildup and corresponding increases in pressure drop; 2). The effective lives of the catalyst materials in flue gas produced by a range of coal types; and 3). How effectively a conventional wet FGD system could remove catalytically oxidized mercury.

The conclusions that can be made from the current effort are discussed below. Regarding the first two objectives listed above, the results from the project were inconclusive. Operating issues related to the pilot units going unattended for weeks at a time appear to have led to fly ash buildup and loss of catalytic activity that could have been avoided in normal plant operation, where operating and maintenance staff could have addressed these issues as they occurred. The third objective was clearly addressed: catalytically oxidized mercury can be removed by wet FGD systems as effectively as native oxidized mercury formed in the boiler and flue gas path.

Pressure Drop across Oxidation Catalyst Beds

At the completion of the previous, 41185 project, it appeared that a solution had been identified for operating 64 cpsi (9.9 cells/cm^2) catalysts downstream of an ESP – sonic horns operating approximately 10 seconds every half-hour of operation. Sonic energy successfully controlled the pressure drop across the Pd #1 and C #6 catalysts at the Coal Creek site from the time the horns were retrofitted until the end of the test period[1]. At the Spruce site a reverse-gas fabric filter was used by the host site for particulate control upstream of the catalyst pilot unit, and sonic horn cleaning did not appear to be necessary.

It was hoped that with sonic energy cleaning in the current project, catalysts at this cell pitch would operate successfully at low pressure drop and with little fly ash buildup over the entire test period of 14 months or longer. This did not prove to be the case, as pressure drop and fly ash buildup issues were encountered at all three long-term catalyst test sites.

However, these results from the project are somewhat inconclusive. The original plan when the pilot units were designed at the beginning of the 41185 project was that the catalysts would be tested over periods of 14 months or longer in unattended operation, except for periodic visits to the sites by project team members. The retrofit of sonic horns for catalyst cleaning added complexity to the pilot units, and the need to ensure the operation and maintenance of this electromechanical/pneumatic equipment in cyclic operation. At the Coal Creek site, the pilot unit was observed on a daily basis by plant instrument technicians who took a personal interest in the test program. They maintained the horns, their air delivery and control systems, and ensured reliable operation. Also, the power and air supplies to the pilot unit were quite reliable at Coal Creek, so there were no unscheduled outages of the pilot unit and/or sonic horns.

In contrast, in the current project there was less interest in the project by site personnel, and the pilot units generally went unattended if project personnel were not on site. Interruption of sonic horn operation typically went unnoticed until project personnel visited the site or noticed anomalies in logged data and requested plant personnel to investigate. At Monticello, a significant plant capital construction project took place in the vicinity of the pilot unit during the test program. This meant that power, compressed air, and flue gas flow to the pilot unit were frequently interrupted, and that project personnel access to the pilot unit was limited. These interruptions meant the sonic horns did not operate and/or that moist flue gas was trapped in the catalyst chambers and allowed to cool and condense. At Plant Yates there were frequently other tests being conducted on Unit 1, which meant power was disconnect from the pilot unit and/or the unit was shut down for extended periods. Also, flue gas temperatures at the Plant Yates pilot unit proved to be low at times, often below the flue gas acid dew point, which exacerbated tendencies for acid/moisture condensation and fly ash buildup. At Coronado, there were fewer documented issues, but the pilot unit did not have a data logger and went unattended by project personnel for long periods at a time. Consequently there is no record of what disturbances may have occurred that might have impacted pressure drop performance. Thus, for each site there are uncertainties as to how effective the sonic horns might have been at controlling fly ash buildup and pressure drop increases had the unit operated at typical flue gas temperatures, with reliable sonic horn operation, and proper shut down and flue gas purging procedures.

In retrospect the project team should have sought a stronger commitment from the host stations' personnel to regularly observe and maintain pilot unit operation. Also, it is now obvious that the sonic horns and their controls were critical equipment items, and equipment status should have been logged and alarmed to avoid continued pilot unit operation with inoperable horns. The fail-closed flue gas flow control valves on the pilot units led to several instances where moist flue gas was trapped in the catalyst compartments on loss of compressed air and/or power to the units. These valves should have instead been set up to fail open, and perhaps valving should have been provided to allow for automated purging of the units on loss of power and/or compressed air.

A later full-scale demonstration of oxidation catalyst technology was also limited by fly ash buildup and pressure drop increases across 64 cpsi (9.9 cells/cm^2) catalysts[7]. However, in this case it was theorized that the problems were related to process scale-up issues (e.g., poor flue gas velocity distribution and non-ideal sonic horn placement) rather than clearly representing a limitation on the technology.

Elemental Mercury Oxidation Performance

Pilot-scale mercury oxidation catalyst tests were conducted at three sites over durations ranging from 14 to 19 months (less unit outage time). At all three sites, it was determined that high mercury oxidation percentages (>90%) could be achieved with as little as a 9-in. (23-cm) catalyst depth of the 64 cpsi (9.9 cells/cm^2) catalyst and at a superficial flue gas velocity of 5.5 ft/s (1.7 m/s). This is about the same velocity as flue gas flowing through ESPs. Both gold-based and palladium-based catalysts were shown to be effective in several flue gas matrices, including low-sulfur Eastern bituminous, PRB, and PRB/Texas lignite flue gases. SCR catalysts were shown to be less active for mercury oxidation in this lower-temperature operating regime (about 300°F, 150°C).

Regenerated gold and regenerated palladium catalysts also proved to be very active in these flue gas matrices, even though they had originally been tested as fresh catalysts in different flue gas types at previous sites. In some cases regenerated catalysts were measured to be more active than similar catalysts installed as fresh catalysts at a test site. However, the comparison between fresh and regenerated catalysts was generally confounded by the catalysts being from different vendors, of different geometries, and possibly having different levels of fly ash buildup.

In the previous 41185 project, it proved possible to use periodic catalyst activity measurement data to determine a rate of catalyst activity loss versus time in flue gas service. Rate loss equations were developed for both the carbon-based and palladium-based catalysts at Coal Creek Station[1]. The intent was to develop similar activity loss rate correlations in the current project, to see if the loss rates would prove to be specific to the different flue gas matrices tested. However, because of observed fly ash buildup and pressure drop increases at all three sites, such correlations are not seen as being representative and were not developed and presented in this report. Neither was it seen as worthwhile to use these data to develop process economics.

Laboratory-scale regeneration tests were conducted on gold- and palladium-based catalyst blocks recovered from the pilot unit at Monticello, and laboratory-regenerated blocks were returned and tested for mercury oxidation activity in the Monticello flue gas. These data were used to develop regression equations that predict the mercury oxidation activity of regenerated catalysts as a function of regeneration temperature and regeneration gas throughput (volumetric flow rate times duration of regeneration). The results show that optimum regeneration appears to occur with a regeneration gas temperature of approximately 550-650°F (290-340°C). The results also show that over the range of values tested, regenerated catalyst activity improved with increasing regeneration gas throughput.

The laboratory-scale regeneration tests were conducted using heated air as the regeneration gas. However, successful regeneration was conducted at pilot scale at Coronado Station using heated flue gas. The Coronado results also showed that there is a finite benefit to increasing the regeneration gas throughput that was not achieved in the laboratory-scale tests.

Pilot-scale Wet FGD Mercury Capture Co-benefit Tests

Pilot-scale wet FGD tests were conducted at five sites, with four of those being conducted downstream of oxidation catalysts and the fifth conducted on untreated ESP outlet flue gas. In each test, capture of oxidized and elemental mercury was measured across the pilot wet FGD system. Tests were conducted in both limestone forced oxidation and lime reagent, natural oxidation modes. The objective of these tests was to determine whether catalytically oxidized mercury in flue gas could be removed by wet FGD systems at high efficiency, or whether some alternate form of oxidized mercury might be produced that would not be scrubbed.

Results from this testing were somewhat mixed. The pilot wet FGD system was designed to treat 2000 acfm (3400 m^3/h) of flue gas, all of the flue gas flow through one oxidation catalyst pilot chamber, yet be compact enough to be moved between test locations on one semi-trailer. This meant the absorber vessel needed to be relatively short. Although the short vessel was designed with a tray and is able to achieve upwards of 95% SO_2 removal, there was room for only one stage of mist elimination at the top of the absorber.

This proved to be a limitation on the ability to measure co-benefit mercury capture across the pilot scrubber, as carryover of absorber liquor, particularly during mist eliminator washing, produced a high bias in outlet flue gas mercury concentration measurements. With time, workarounds were developed for this problem, including suspending measurements during mist eliminator washing, using two IGS filter loops in series, and lowering the operating temperature of the IGS filter loops. However, data from the first three tests sites are of questionable accuracy because these workarounds had not yet been developed and implemented.

Regardless of this limitation, the results clearly show that the catalytically oxidized mercury can be removed by wet FGD systems at the same efficiency as mercury oxidized by native effects in the boiler and flue gas path. High oxidized mercury removal efficiencies (≥95%) were measured across the pilot scrubber in several tests. However, high *total* mercury removal efficiencies (>90%) were only measured in one test, although removal efficiencies between 85% and 89% were measured on several other occasions. In some cases, much lower total mercury removal efficiencies were measured. The limitations on total mercury removal were generally due to lowered mercury oxidation percentages downstream of the catalyst, a result of fly ash buildup and/or activity loss; mercury re-emission from the wet scrubber; or both effects. However, both of these limiting effects can be addressed through optimization of catalyst and FGD design and operating conditions, and do not appear to represent limitations on the effectiveness of low-temperature mercury oxidation catalyst technology.

Investigation of Fixed-structure Mercury Sorbents/Catalysts

The second round of testing at Plant Yates, in flue gas from Unit 1 firing low-sulfur Eastern bituminous coal, was focused on fixed-structure materials that have a high capacity for adsorbing mercury and that promote oxidation of the mercury in the flue gas treated that is not adsorbed. This round of pilot-scale testing was somewhat limited, so few conclusions can be made. One is that a honeycomb-structure adsorbent developed by Corning, Inc., had adequate structural integrity to survive in a flue gas environment, and exposure to sonic cleaning energy. However, Corning decided not to pursue additional pilot-scale testing of their fixed-structure sorbent at Plant Yates.

A second conclusion is that parallel plates of granular carbon inserted in a flue gas stream had a limited capacity for adsorption of mercury, but significant activity for mercury oxidation (~50% oxidation across the parallel plates) after three months of operation. The parallel plate configuration operated at very low pressure drop (~0.1 in. H_2O [0.025 kPa]). Parallel plates of an activated carbon fiber cloth showed significantly lower capacity for adsorption and activity for oxidation, in spite of promising performance in the laboratory in synthetic flue gas.

REFERENCES

1. *Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems. Draft Final Report*. DOE-NETL Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. October 2006.

2. Carey, Todd R., O.W. Hargrove, Jr., C.F, Richardson, R. Chang, and F. B. Meserole. "Factors Affecting Mercury Control in Utility Flue Gas Using Activated Carbon," *Journal of the Air & Waste Management Association,* December 1998, Vol. 48, pp 1166-1174.

3. "Standard Test Method for Elemental, Oxidized, Particulate-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)", ASTM International, West Conshohocken, PA, June 2002. D 6784 – 02.

4. *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems*, EPRI, Palo Alto, CA, and U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA, June 2001.

5. *FGD Chemistry and Analytical Methods Handbook, Volume 2: Chemical and Physical Test Methods, Revision 1.* EPRI CS-3612, Volume 2, Revision 1. EPRI, Palo Alto, CA. November 1988.

6. Blythe, Gary M. and Marijon Owens. *Field Testing of a Wet FGD Additive for Enhanced Mercury Control, Final Report.* DOE-NETL Cooperative Agreement No. DE-FC26-04NT42309, URS Corporation, Austin, Texas 78729. March 2008.

7. Blythe, Gary M., and Jennifer Paradis. *Full-scale Testing of a Mercury Oxidation Catalyst Upstream of a Wet FGD System. Final Report*. DOE-NETL Cooperative Agreement No. DE-FC26-06NT42778, URS Group, Austin, Texas 78729, September 2010.