

PILOT-SCALE TESTING OF MERCURY OXIDATION CATALYSTS FOR ENHANCED CONTROL BY WET FGD

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ABSTRACT

This paper presents results from two projects, which are co-sponsored by DOE-NETL, EPRI, Great River Energy (GRE), City Public Service (CPS) of San Antonio, TXU Generation Company LP (TXU), Duke Energy, and Southern Company. The projects are evaluating at pilot scale catalysts that oxidize elemental mercury in flue gas to promote high mercury removal percentages in downstream wet FGD systems. Results are presented from mercury oxidation catalyst operation at GRE's Coal Creek Station and CPS' Spruce Plant, including short-term pilot FGD tests that document the ability to remove catalytically oxidized mercury in a wet scrubber. Interim results are also presented from ongoing tests at TXU's Monticello Steam Electric Station, as are plans for pilot testing at Southern Company's Plant Yates. Results presented include mercury oxidation across the catalysts as a function of time in service, catalyst regeneration results, mercury removal across the pilot wet FGD absorber, and process economics based on pilot catalyst life data.

INTRODUCTION

The mercury control process under development uses catalysts to promote the oxidation of Hg^0 in flue gas from coal-fired power plants equipped with wet FGD systems. The oxidation reactants are already present in the flue gas and may include chlorine, hydrochloric acid, oxygen and/or other species. Oxidized mercury is removed in wet FGD absorbers and leaves the system with the FGD byproducts.

A project co-sponsored by EPRI and DOE-NETL as part of Cooperative Agreement DE-FC26-01NT41185, "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems" is near completion. The objective of the project has been to test potential mercury oxidation catalysts at pilot scale to provide engineering data for future full-scale designs. The pilot tests were conducted for approximately 1.5 years at two sites to provide catalyst life data. Two utilities provided co-funding and host sites for the project: GRE, which fires North Dakota lignite at their Coal Creek Station (CCS), and CPS of San Antonio, which fires Powder River Basin (PRB) subbituminous coal at their J.K. Spruce Plant.

North Dakota lignite and PRB flue gases typically contain mostly Hg^0 rather than oxidized mercury. The oxidation catalyst technology would have the greatest effect on scrubbed flue gas where most of the mercury is normally present as Hg^0 . Texas lignite also produces mostly Hg^0 in the flue gas. Furthermore, some plants that fire bituminous coal may require additional Hg^0 oxidation to allow high-efficiency mercury capture in their FGD systems. A second Cooperative Agreement, DE-FC26-04NT41992, added two new pilot test sites, TXU's Monticello Steam Electric Station, which fires a Texas lignite/PRB blend, and Southern Company's Georgia Power Plant Yates, which fires low-sulfur Eastern bituminous coal. The pilot units used at CCS and Spruce Plant are being moved to the new sites and charged with fresh catalysts for long-term catalyst activity tests these new sites.

Also as part of the second project, a pilot-scale wet FGD system was built. The mobile, pilot wet FGD absorber is being used to verify the ability to scrub catalytically oxidized mercury at each of the four oxidation catalyst pilot test sites.

This paper covers the pilot test results from oxidation catalyst operation at the CCS and Spruce sites, including pilot wet FGD results from downstream of catalysts and results of in situ catalyst regeneration tests. Also presented are the results from approximately seven months of operation at Monticello. Interim conclusions are made at the end of the paper.

EXPERIMENTAL

Figure 1 illustrates a simplified process flow diagram for the catalytic oxidation process, which has no "moving parts." A catalyst, most likely in honeycomb form, is inserted into the flue gas path upstream of the FGD system. The outlet of the plant's cold-side particulate control device is a likely location for the catalyst, since the velocity is typically low there and the flue gas is relatively clean. The low velocity allows catalyst operation at longer residence time and low pressure drop, while the relatively particulate-free flue gas allows a close-pitched catalyst to be used. This allows a high surface area per volume of catalyst relative to "dirty" gas operation, so less catalyst volume is used. Downstream of the catalyst, the oxidized mercury is scrubbed in the FGD absorber, and leaves with the FGD byproduct.

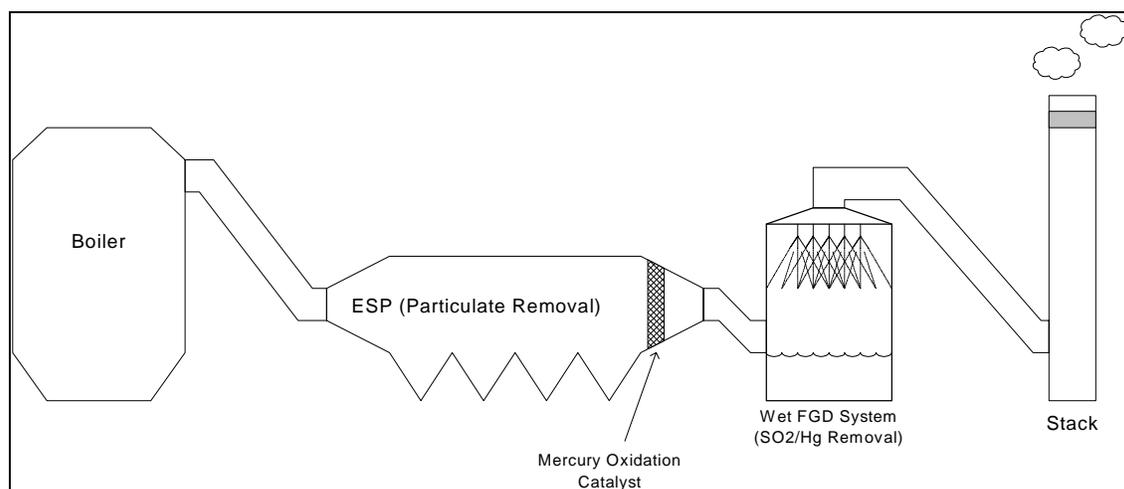


Figure 1. Illustration of low-temperature mercury oxidation catalyst process.

The cost of the process will depend largely on the catalyst life and required catalyst volume. This project is collecting data that will allow these parameters to be evaluated for several coal types. At each site, four different catalysts are tested in parallel in a divided reactor sized to treat approximately 2000 acfm of flue gas with each catalyst. The pilot reactor treats low-dust flue gas from downstream of the ESP (CCS, Monticello and Yates) or baghouse (Spruce), isokinetically extracted from the unit's induced draft (ID) fan outlet.

The pilot unit is instrumented for temperature, pressure drop and flow rate measurements for each catalyst bed. The gas flow rate through each catalyst is controlled independently. Once flue gas flow is established, the pilot unit is left in automated operation for 14 months or longer. Telemetry equipment allows pilot unit flow rate, temperature, and pressure drop data to be monitored from off site. The pilot unit is automated for all operations except mercury analyses, as described below. Otherwise, no routine operator intervention is required.

On a bimonthly basis, project team members travel to the site and use a mercury semi-continuous emissions monitor (SCEM) to track total Hg and Hg⁰ concentrations upstream and downstream of each catalyst to determine oxidation activity. Periodically, flue gas measurements are conducted using the Ontario Hydro method (ASTM D6784-02) to verify results from the SCEM. Measurements are also made for sulfuric acid and NO₂ concentrations upstream and downstream of each catalyst to quantify whether the oxidation catalysts also oxidize flue gas SO₂ or NO. Significant oxidation of either would be undesirable due to plume opacity and/or corrosion effects.

The two host sites for the initial project, GRE's CCS and CPS' Spruce Plant, each fire low-sulfur, low-chloride coals. CCS fires North Dakota lignite with about a 6300 Btu/lb heat content, 0.7 wt% sulfur content, 0.1 ppm mercury content, and 100 ppm or less chloride content. Spruce fires a Wyoming, PRB subbituminous coal with about 8400 Btu/lb heat content and 0.5 wt% sulfur content. The mercury and chloride contents of the Spruce coal are similar to those at CCS. The two sites each have tangentially fired boilers rated at about 550 net MW (two units at CCS, one at Spruce). CCS has a large cold-side ESP for particulate control, followed by ID fans and an Alstom wet lime FGD system. At Spruce, a reverse-gas fabric filter is used for particulate control, followed by ID fans and an Alstom wet limestone FGD system. The CCS FGD system produces calcium sulfite byproduct that is landfilled, while the Spruce FGD system produces gypsum that is sold for cement production.

The second project (DE-FC26-04NT41992) added a wet FGD pilot unit sized to treat 2000 acfm of flue gas, which corresponds with the flue gas flow treated by of one catalyst in the oxidation catalyst pilot unit. The wet FGD pilot unit has a spray and perforated plate tray contactor, and can be operated with either lime or limestone reagent and with natural or forced oxidation. The pilot wet FGD system does not have reagent preparation equipment, nor does it have byproduct dewatering equipment. In most instances, reagent prepared by the host site wet FGD system is used as makeup to the pilot wet FGD.

Oxidation catalyst pilot testing has been completed at CCS and Spruce. The catalyst pilot unit from CCS was moved to TXU's Monticello Station last fall. Monticello Unit 3 is a 793-MW wall-fired boiler with a cold-side ESP for particulate control and a limestone forced

oxidation (LSFO) wet FGD system. The unit fires a blend of approximately 80% Texas lignite and 20% PRB coal. The oxidation catalyst pilot unit has been in operation at Monticello since January 2005.

Bench-scale evaluations of candidate catalysts were conducted in URS' laboratories, using a mixture of bottled gases to simulate the flue gases at each site. The results were used to determine which catalysts were most active under these simulated flue gas conditions, and to estimate the amount of each catalyst required to achieve high Hg⁰ oxidation percentages in the pilot unit. Table 1 shows the catalyst dimensions used in the pilot units.

Table 1. Catalyst dimensions selected for the pilot units.

| Pilot Unit | Catalyst Type | Cell Pitch (mm) | CPSI (cells per in. ²) | Catalyst Cross-section (in. x in.) | Catalyst Length (in) | Area Velocity (sft/hr) |
|------------|--------------------------------------|-----------------|------------------------------------|------------------------------------|----------------------|------------------------|
| CCS | SCR Catalyst (Argillon) | 3.7 | 46 | 35.4 x 35.4 | 19.7 | 14 |
| | Experimental Activated Carbon (C #6) | 2.9 | 77 | 35.4 x 35.4 | 9 (3 x 3 in.) | 27 |
| | Palladium (Pd #1) | 3.2 | 64 | 29.5 x 29.5 | 9 (3 x 3 in.) | 49 |
| | Fly-ash-based (SBA #5) | 2.9 | 77 | 35.4 x 35.4 | 9 (3 x 3 in.) | 27 |
| Spruce | SCR Catalyst (Argillon) | 3.7 | 46 | 35.4 x 35.4 | 29.5 | 13 |
| | Experimental Activated Carbon (C #6) | 2.9 | 77 | 35.4 x 35.4 | 9 (3 x 3 in.) | 27 |
| | Palladium (Pd #1) | 3.2 | 64 | 29.5 x 29.5 | 9 (3 x 3 in.) | 49 |
| | Gold-based (Au) | 3.2 | 64 | 29.5 x 29.5 | 9 (3 x 3 in.) | 49 |
| Monticello | SCR Catalyst (MHI/ Cormetech) | | | | | |
| | Johnson Matthey Palladium (J-M Pd) | 3.2 | 64 | 29.5 x 29.5 | 9 (3 x 3 in.) | 49 |
| | Regenerated Palladium (from CCS) | 3.2 | 64 | 29.5 x 29.5 | 9 (3 x 3 in.) | 49 |
| | Gold (Au) | 3.2 | 64 | 29.5 x 29.5 | 9 (3 x 3 in.) | 49 |

Argillon GmbH (formerly Siemens) supplied standard NO_x control selective catalytic reduction (SCR) catalysts for the first two sites, while Mitsubishi Heavy Industries supplied the SCR catalyst for Monticello through their joint venture Cormetech. Because the SCR catalyst proved to be less active at CCS than was expected, the catalyst length was increased by 50% for the Spruce and Monticello pilot units.

The palladium (Pd #1) catalysts for CCS and Spruce were from Sud-Chemie Prototech, who prepared three 3-in.-deep catalyst layers. For Monticello, the Pd catalyst was supplied by Johnson Matthey, who was able to provide a single 9-in. layer rather than three 3-in. layers.

The activated carbon (C#6) and fly ash (SBA #5) catalysts were custom-prepared by a U.S.-based catalyst manufacturer, as extruded monoliths in an alumina substrate, in three 3-in.

layers. The C #6 catalyst is not being tested at Monticello. Instead, the regenerated Pd #1 catalyst from CCS is being tested, to determine how well a regenerated catalyst maintains activity. The C #6 is not being tested at Monticello because preliminary economics based on CCS results showed that the catalyst is not significantly less expensive than palladium catalysts after the increased volume required and the significant production costs for the proprietary process required to prepare the C #6 catalyst are considered. Since the C #6 catalyst did not regenerate at CCS at the conditions tested (as discussed later in the paper), it was seen as offering no advantage over palladium or gold catalysts.

Gold (Au) was tested at Spruce and is being tested at Monticello in the place of the SBA #5 catalyst, which was seen as being unsuitable for commercial catalyst production since it reflects unique properties of the fly ash from a single coal-fired unit. The Tennessee Valley Authority (TVA) has patented the use of gold as a mercury oxidation catalyst in coal-fired flue gases. TVA cost-shared the purchase of the gold catalysts, which were prepared by Sud-Chemie Prototech in dimensions identical to those of the Pd #1 catalysts.

RESULTS AND DISCUSSION

Pilot Unit Operation at CCS

The pilot unit was started up at CCS in September 2002. The first two catalysts (SCR and Pd #1) were installed in early October and long-term evaluation of those catalysts began. The other two catalysts (SBA #5 and C #6) were not yet available and were placed in operation in December 2002 and June 2003, respectively. The pilot unit was operated through June 2004.

Catalyst Pressure Drop Performance

In the first few months of operation, it was observed that catalyst pressure drop was increasing while catalyst activity was decreasing. The cause was fly ash buildup within the catalysts, in spite of them being installed in the “clean” flue gas downstream of the ESP. Sonic horns were retrofitted in June 2003 to limit fly ash buildup in the catalysts.

Pressure drop values from June 2003 through the end of the long-term test in June 2004 are plotted for the Pd #1 and SBA #5 catalysts in Figure 2. The plots show a lot of scatter due to noisy electrical signals. As seen in the figure, in nearly 13 months of operation the average pressure drop across the Pd #1 remained below 1 in. H₂O, showing that the sonic horn was effective in preventing fly ash buildup in this catalyst. The other two catalysts showed similar pressure drop values to those of Pd #1.

The horns were not effective at keeping the SBA #5 catalyst clean. The SBA #5 pressure drop averaged between 3 and 5 in. H₂O during the last six months of operation. This is more than 10 times the initial pressure drop in June 2003. It is possible that there is particle-to-particle electrostatic attraction between the fly ash in the flue gas treated and the fly ash imbedded in the catalysts. Because this catalyst was produced from a single fly ash source and is available in limited quantities, it is of lesser interest for future commercial applications. So, the pressure drop increase across this catalyst is not of great concern.

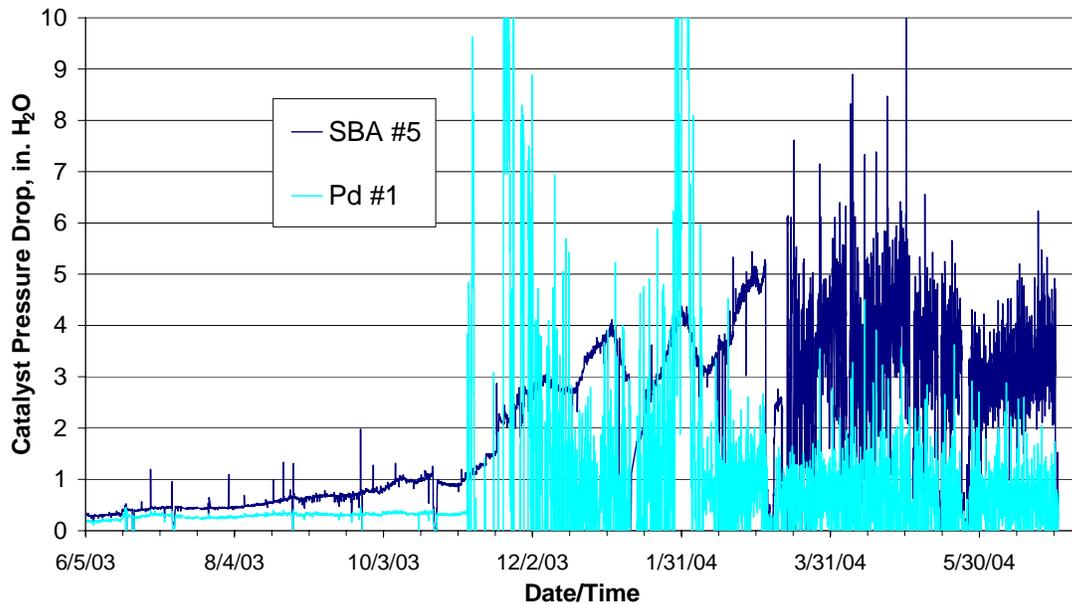


Figure 2. Pressure drop data for the catalysts in service at CCS through June 2004.

Catalyst Activity Results

The “clean catalyst” activity results for the two more active catalysts are plotted versus time in Figure 3. Some data points from late 2002 and early 2003, where the catalysts were obviously plugged with fly ash, have been edited from the plots. Activity results for the Pd#1 and C #6 catalysts in Figure 3 show a linear downward trend in the catalyst activity versus time in service. The June 2004 measurements were considered the “end of test” activity for the catalysts being tested at CCS, so the linear least squares fits of the data shown in the figure were used to make catalyst life projections, as discussed later. The activity data are not shown for the two less active catalysts, the SCR and SBA #5 catalysts. Both were measured at less than 30% Hg^0 oxidation across the catalysts at the end of the test.

Catalyst Regeneration

In the summer of 2004, attempts were made to thermally regenerate the SCR, Pd #1 and C #6 catalysts at CCS. After a period of heating each catalyst with 600°F air, catalyst activity was tested on flue gas to determine if the Hg^0 oxidation activity was measurably increased. The results from these tests are summarized in Table 2. The results show that the activities of the Pd #1 and SCR catalysts improved measurably after the thermal regeneration. The Pd #1 activity improved to near the activity of the fresh catalyst (88% vs. 95%) while the SCR catalyst improved to about two-thirds of its original activity (46% vs. 67%). However, the C #6 catalyst showed no measurable improvement in activity after the thermal regeneration. It is possible that the species that cause activity loss by the C #6 catalyst are more strongly adsorbed to the carbon-based catalyst than to the metal-based catalysts.

It is important to note that these regeneration tests were intended to be “proof of concept” tests to determine if the catalysts could be thermally regenerated. The conditions were not

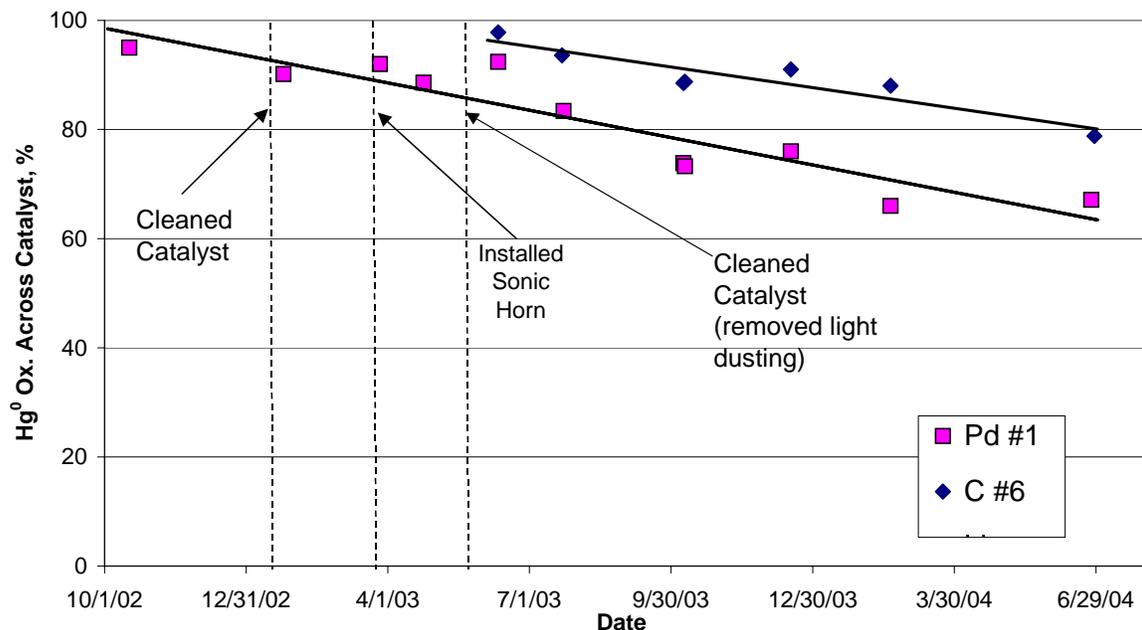


Figure 3. Activity for Hg⁰ oxidation versus time for Pd #1 and C #6 catalysts at CCS.

Table 2. Results of CCS catalyst regeneration tests.

| Catalyst | Elemental Mercury Oxidation Across Catalyst, % | | | |
|----------|--|-----------------------|-----------------------|--------------------|
| | Fresh Catalyst | End of Test (June 04) | Prior to Regeneration | After Regeneration |
| Pd #1 | 95 | 67 | 79 | 88 |
| SCR | 67 | 26 | 25 | 46 |
| C #6 | 98 | 79 | 53* | 48 |

*Estimated because there was not a catalyst inlet Hg⁰ concentration measurement made near the time period the catalyst outlet was measured

optimized to ensure the effectiveness of the thermal regeneration. The regeneration tests were run in batch mode, with the heated air at 600°F flowing through the catalyst chambers overnight. Thus, these results do not indicate what is the minimum heating period required, the optimum air temperature to regenerate the catalysts, or the optimum regenerated activity.

Pilot Wet FGD Tests

In July 2004, the pilot wet scrubber was installed at CCS and used to treat flue gas under baseline (no catalyst) conditions and treating flue gas from downstream of the two more active catalysts (C #6 and Pd #1). Figure 4 shows the FGD pilot installed at CCS.

Example wet FGD results are summarized in Table 3. They show the Pd catalyst increased the mercury oxidation percentage from 34% to 84% at the FGD inlet, which allowed the wet FGD to remove 79% of the mercury in the inlet flue gas. Although oxidized mercury was removed at 100%, there was evidence of mercury re-emissions across the wet FGD, which lowered the FGD mercury capture from the expected 84% (100% of the Hg⁺²) to 79%.

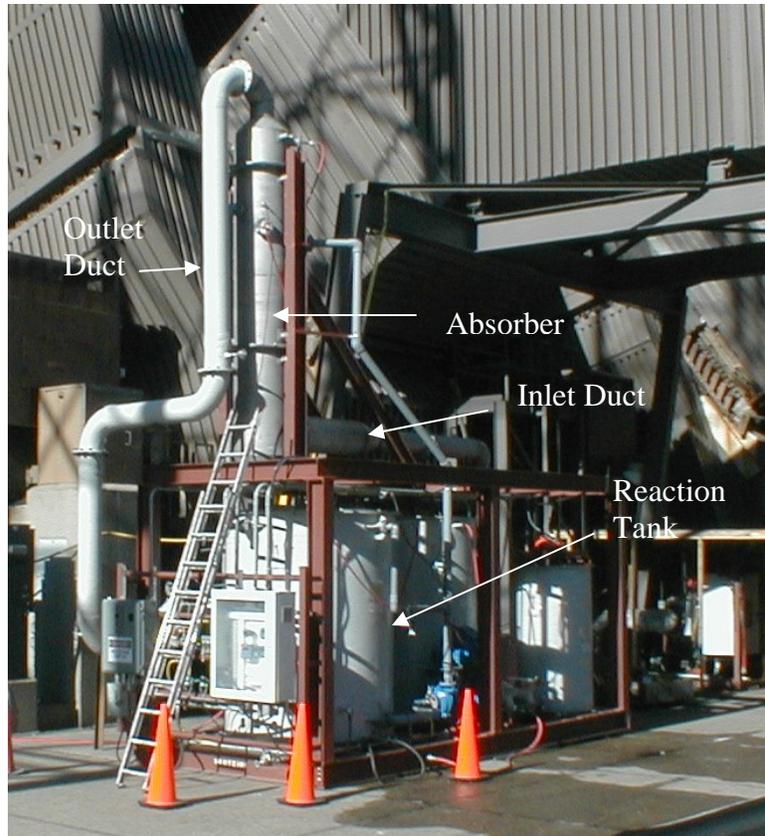


Figure 4. Wet FGD pilot unit installed at CCS.

Table 3. Results of LSFO pilot wet FGD tests at CCS downstream of Pd #1 catalyst.

| | Total Hg | Hg ⁰ | Hg ⁺² | Hg Oxidation, % |
|---|-----------|-----------------|------------------|-----------------|
| Catalyst Inlet ($\mu\text{g}/\text{Nm}^3$) | 18.0 | 11.9 | 6.1 | 34 |
| FGD Inlet ($\mu\text{g}/\text{Nm}^3$) | 17.4 | 2.7 | 14.7 | 84 |
| FGD Outlet ($\mu\text{g}/\text{Nm}^3$)[lb/Tbtu] | 3.7 [2.5] | 3.8 | -0.03 | 0 |
| FGD Hg Removal (%) | 79 | -39 | 100 | - |

Preliminary Catalytic Oxidation Economics

The CCS results were used to estimate the economics of the oxidation catalyst technology for a single, 500-MW plant in North Dakota that fires North Dakota lignite. The required mercury control percentage was based on the minimum specified in NETL solicitation DE-PS26-03NT41718 (Large-scale Mercury Control Technology Field Testing Program – Phase II), 55% for lignite fuels. This percentage represents a mercury removal increase beyond the “baseline” removal for the plant being considered.

The plant was assumed to be configured like CCS, with a large, cold-side ESP for particulate control and a wet FGD system for SO₂ control. The wet FGD system was assumed to treat 100% of the flue gas from the unit. Many FGD systems on plants that fire North Dakota lignite bypass some flue gas around the FGD system. However, for this evaluation it was assumed that the Clean Air Interstate Rule and increased SO₂ credit values will lead most

scrubbed plants to upgrade to 100% scrubbing, independent of mercury co-removal drivers. Consequently, costs to upgrade an existing FGD system to scrubbing 100% of the flue gas were not included in this evaluation.

The costs for oxidation catalyst technology were compared to projected costs for injecting Norit FGD carbon to achieve the same minimum mercury capture level. Several assumptions had to be made regarding the base plant before developing these cost estimates, such as:

- The flue gas at the ESP outlet contains a minimum of 15% oxidized mercury, with the balance being elemental mercury;
- The wet FGD system will remove a net amount of 90% of the oxidized mercury in the flue gas entering the FGD; and
- The plant currently sells all of its fly ash, and fly ash sales would be lost if activated carbon is injected upstream of the ESP for mercury control.

For the catalytic oxidation case, these assumptions meant an overall mercury capture of 61% would be required, and a minimum catalyst oxidation percentage of 62%. This, in turn, corresponds with a catalyst useful life of two years based on the CCS results. For the Norit FGD carbon, full-scale data from GRE’s Stanton Station Unit 1 were used to estimate the required carbon injection rate to achieve 61% Hg capture. A value of 5 lb/mmacf of flue gas was used. Table 4 summarizes the base case economics for the Pd and C #6 catalysts.

Table 4. Base case economics for catalytic oxidation on a North Dakota lignite plant.

| Parameter | FGD Carbon Injection | Palladium-based Oxidation Catalyst | C #6 Oxidation Catalyst |
|--|-----------------------------|---|--------------------------------|
| Catalyst Cost, \$1000 | - | \$5,360* | \$5,220* |
| Delivered Carbon Cost, \$1000/yr | \$3,110 | - | - |
| Lost Fly Ash Sales, \$1000/yr | \$1,120 | - | - |
| Increased Landfill Disposal Costs, \$1000/yr | \$940 | - | - |
| Subtotal O&M Costs, \$1000/yr | \$5,170 | - | - |
| Capital Equipment Amortization, \$1000/yr | \$270 | \$150 | \$150 |
| Catalyst Amortization Costs, \$1000/yr | - | \$3,010 | \$2,930 |
| Total First-year Costs, \$1000/yr | \$5,440 | \$3,160 | \$3,080 |
| First-year Cost, % of Activated Carbon Cost | - | 58 | 57 |

*Includes delivery, installation, and disposal costs

With these assumptions, the catalytic oxidation technology cost estimate shows about 60% of the annual cost of carbon injection. No significant difference was seen between the estimate for the palladium versus the carbon-based catalyst. Considering that the palladium catalyst appears to be regenerated more easily than the carbon, and that the palladium has recovery value at the end of the catalyst life (not considered in these economics) it becomes apparent that there is little incentive to continue development of the experimental carbon catalyst.

A number of sensitivity cases were run to determine the effects of different assumptions on the relative costs of the two technologies. A plant that does not sell its fly ash was considered as one case, and a configuration where the palladium catalyst could be regenerated to double the catalyst life to four years was considered as another case.

Results from these sensitivity cases are summarized in Table 5. They show that if the plant does not currently sell its fly ash, it would be about the same cost to apply carbon injection to control mercury as to apply catalytic oxidation technology. However, if the palladium catalyst can be regenerated once after two years of operation, to extend the catalyst life to four years, the catalytic oxidation technology shows a cost advantage over carbon injection regardless of whether or not the plant sells its fly ash.

Table 5. Results of sensitivity cases for catalytic oxidation on a N.D. lignite plant.

| Sensitivity Case | Palladium-based Oxidation Catalyst, Annual Cost in % of Carbon Injection Cost | C #6 Oxidation Catalyst, Annual Cost in % of Carbon Injection Cost |
|--|--|---|
| Plant does not currently sell fly ash | 93 | 91 |
| Catalyst regeneration to extend life from 2 to 4 years, for plant that sells fly ash | 38-42* | - |
| Catalyst regeneration to extend life from 2 to 4 years, plant that does not sell fly ash | 60-68* | - |

*Range represents low and high regeneration cost estimates

Results from Pilot Unit Operation at Spruce Plant

The second oxidation catalyst pilot unit was operated at CPS' Spruce Plant from September 2003 through April 2005. After considering unit outage time, two catalysts (gold and palladium) saw approximately 18 months of operation.

Pilot unit inlet flue gas Hg⁰ concentrations were much lower at Spruce than were expected, given that Spruce fires PRB coal. The low Hg⁰ concentrations have been attributed to mercury oxidation and removal across the reverse-gas fabric filter used for particulate control. At first it was speculated that high mercury oxidation across the baghouse was because of the age of the bags (over 11 years) and the fact that petroleum coke had been co-fired with the PRB in the past, depositing vanadium and other oxidation catalyst metals on bag surfaces. However, the fabric filter was rebagged in the middle of the test program, in January and February 2004, with no apparent affect on the high mercury oxidation percentages and mercury removal seen across the baghouse.

Catalyst Pressure Drop Results

The pressure drop across the four catalyst chambers at Spruce remained nearly constant between 0.2 and 0.3 in H₂O over the entire operating period, most likely because a high-efficiency reverse-gas fabric filter is used for particulate control at this site. The fabric filter resulted in a low dust loading in the pilot unit inlet flue gas, and a dust loading that has less residual electrostatic charge than in flue gas downstream of an ESP.

Catalyst Activity Results

The data collected over 18 months of operation were used to generate a plot of measured catalyst activity versus time for the four catalysts in service at Spruce. The plot is shown in Figure 5. The data do not show a consistent trend for activity versus time in flue gas service. Only for the Pd #1 catalyst is there an apparent linear decrease in activity over time, for the period May 2004 through April 2005 (shown as a dashed line on the figure). Even for this catalyst, the data prior to May 2004 do not fit this apparent linear relationship, and there are prior data that showed lower activity than the “end-of-test” data.

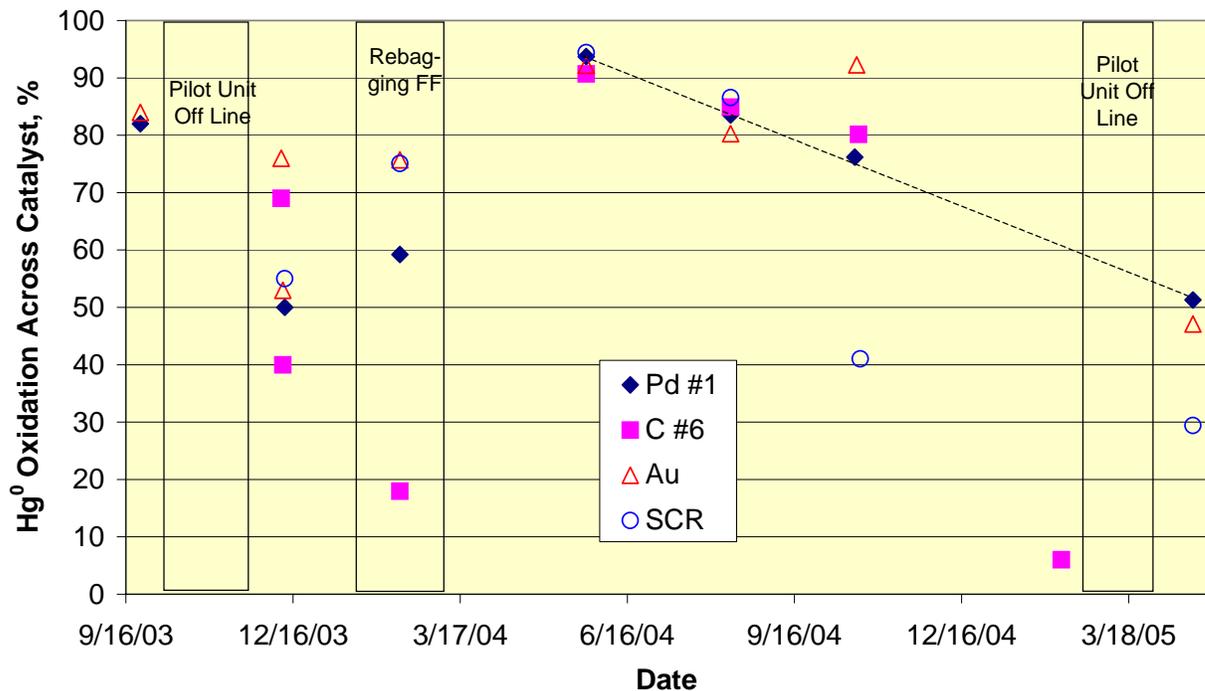


Figure 5. Spruce catalyst activity vs. time in service.

For the gold and C #6 catalysts, the end-of-test data show considerably lower performance than might have been expected based on trends seen in the data collected between May and October 2004. The SCR catalyst end-of-test data were consistent with a significant drop in activity seen in October 2004.

The scatter in the data has been at least partially attributed to extremely low catalyst inlet Hg⁰ concentrations encountered frequently at Spruce. With the inlet Hg⁰ concentration at or below 1 µg/Nm³, this made it difficult to measure catalyst outlet Hg⁰ concentrations to be

able to calculate meaningful oxidation percentages. Also, catalyst inlet total mercury concentrations and oxidation percentages were observed to be quite variable, most likely tied to fabric filter cleaning cycles, which made it difficult to measure catalyst performance.

Catalyst Regeneration Test Results

Given the extremely low and variable catalyst inlet Hg⁰ concentrations seen at Spruce, there was even some question as to whether these end-of-test performance values truly represent a loss of catalyst activity, or just that the catalyst outlet Hg⁰ concentrations were too low to reliably measure by SCEM. Catalyst thermal regeneration tests were conducted, and those results indicate that the end of test values do represent activity losses that could be recovered by thermal regeneration.

The tests were conducted by introducing heated air through a port in the catalyst inlet duct. Each catalyst was regenerated individually, and each regeneration test was run from one morning to the next, with nearly 24 hours of elapsed time during the regeneration. The catalyst activity data for the regenerated catalysts are shown in Table 6. The Pd catalyst was the most active after regeneration, increasing from 51% elemental mercury oxidation prior to regeneration to 84% afterward. The gold catalyst saw nearly as great an improvement, going from 47% oxidation to 78%. The other two catalysts, which were considerably less active prior to regeneration, also saw substantial improvements in catalyst activity.

Table 6. Spruce post-regeneration catalyst oxidation activity data.

| Catalyst | Catalyst Inlet Hg⁰ (µg/Nm³ corrected to 3% O₂)* | Catalyst Outlet Hg⁰ (µg/Nm³ corrected to 3% O₂)* | Observed Hg⁰ Oxidation Across Catalyst (%) |
|-----------------|---|--|--|
| Pd #1 | 1.17 | 0.19 | 84 |
| C #6 | 0.94 | 0.41 | 56 |
| Au | 0.88 | 0.19 | 78 |
| SCR | 0.90 | 0.30 | 66 |

*Note – 1.0 µg/Nm³ at 3% O₂ equals 0.67 lb/10¹² Btu heat input

Results from Pilot Unit Operation at Monticello Station

The catalyst pilot unit from CCS was moved to TXU’s Monticello Station and had new catalysts (one regenerated catalyst) installed as described in the previous section. The pilot unit was started up on flue gas in mid-January 2005. At the time this paper is being written, the catalysts have been in service for seven months.

Catalyst Pressure Drop Results

In the catalyst testing at CCS, 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 and were generally effective in preventing fly ash buildup. Since Monticello, like CCS, has an ESP for particulate control, it was expected that

sonic horns would be necessary to prevent fly ash buildup there. The sonic horns were placed in service on the catalyst pilot unit at the end of January, two weeks after initial catalyst startup. However, the sonic horns did not operate properly over the next two months due to a number of component failures. Solenoid valve and air pressure regulator changes, along with minor wiring and tubing changes, resulted in all four valves cycling properly beginning in late April. The four horns appear to have cycled properly through mid-June.

Figure 6 shows full load pressure drop data for all four catalysts from start up through June 2005. 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 is 2000 acfm for all four catalysts. The data show that the pressure drop across the Johnson Matthey Pd and gold catalysts remained low (about 0.5 in. H₂O) while the SCR and regenerated Pd catalysts show excursions to higher pressure drop.

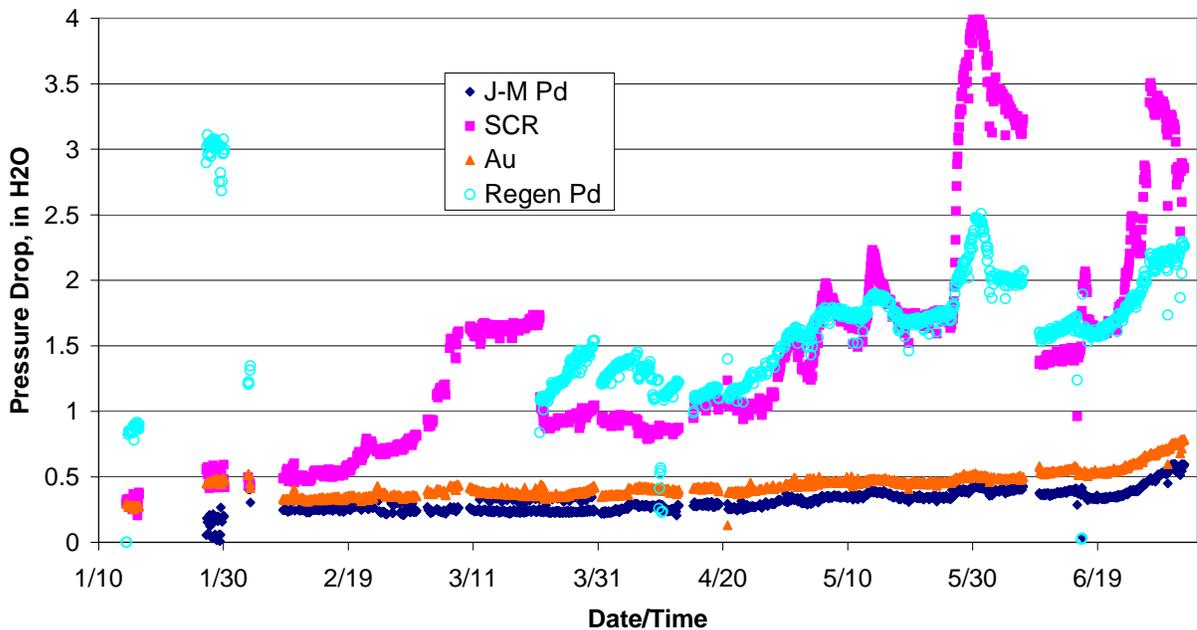


Figure 6. Full-load catalyst pressure drop data from the Monticello pilot unit.

Some early excursions where the pressure drop across the SCR and regenerated Pd catalysts increased appeared to correspond with periods where the sonic horns were not operating properly. This does not appear to be the case later. 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. This may be due to debris from the plant compressed air line plugging the regulator controlling air flow to the horns, which was discovered and corrected in early August.

It is possible that improperly functioning horns have led to fly ash buildup in the SCR and regenerated Pd catalysts, that has not been removed with fully functional horns. The SCR

catalyst may be more sensitive to horn operation because of its greater catalyst length, and the regenerated Pd may be more sensitive because of residual fly ash remaining on the catalyst surfaces from its 20+ months of service at CCS. It is possible that these two catalysts will have to be shut down and cleaned if their pressure drops continue to see high excursions.

Catalyst Activity Results

The activity data for these catalysts are plotted versus time in Figure 7. The figure is illustrated to show linear trends for activity versus time for each of the four catalyst types, extrapolated back to the time they were initially placed in operation. However, there is quite a bit of scatter for the data for all but the gold catalyst. More time in service will determine whether the linear correlations shown in the figure prove true.

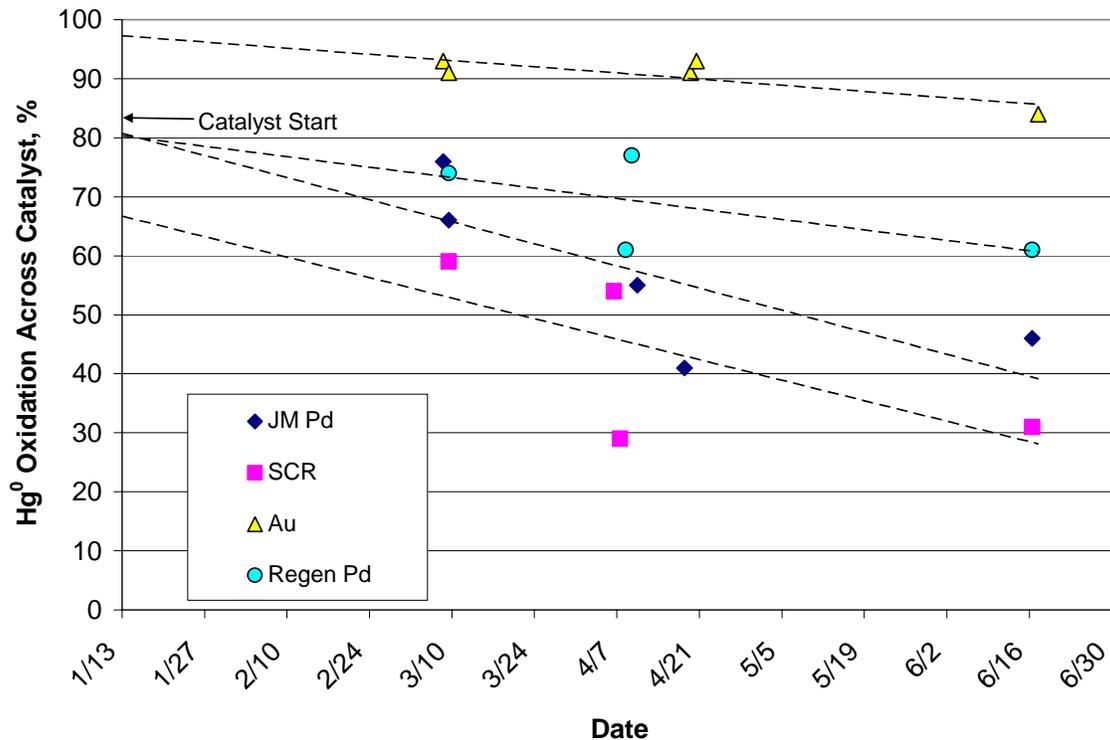


Figure 7. Elemental mercury oxidation activity vs. time for catalysts at Monticello.

The apparent oxidation across all four catalysts had dropped measurably by June 2005, indicating a loss of activity with time in service in this flue gas. The gold dropped from greater than 90% to 84% Hg⁰ oxidation in June, while the SCR catalyst dropped to only 31% oxidation. The performance of the SCR catalyst and regenerated palladium may have been adversely affected by fly ash buildup, as indicated by the pressure drop across these two catalysts. The Johnson Matthey palladium and gold apparently remained clean, as seen by the pressure drop values of approximately 0.5 in. H₂O or less for these two catalysts in mid-June, and were less likely to have been impacted by fly ash buildup. The Johnson Matthey palladium catalyst was measured to be less active than the regenerated palladium from CCS. This may be in part due to the different geometry (one 9-in. layer rather than three 3-in.

layers), as laminar-flow mass transfer calculations indicate a small benefit from having three separate layers.

CONCLUSIONS

The pilot plant results from CCS indicate that sonic horns or soot blowers will be required to keep the horizontal gas flow catalysts clean of fly ash buildup. The palladium and C #6 catalysts can apparently remain active for up to two years in North Dakota lignite flue gas, and the palladium catalyst can be readily regenerated. The life of regenerated catalyst compared to fresh catalyst still remains to be evaluated. The CCS pilot wet FGD results showed that the catalytically oxidized mercury can be scrubbed at high efficiency, with overall mercury capture limited only by re-emissions.

Preliminary economic evaluations based on the CCS results show that catalytic oxidation technology applied to scrubbed plants can be very competitive with injection of activated carbon, even if the catalyst life is assumed to be only two years, if the plant currently sells all of its fly ash. If the plant currently landfills its fly ash, catalytic oxidation technology does not show a cost advantage over carbon injection. Catalyst regeneration to extend its life can greatly improve the economics of the process. Even one regeneration cycle, to extend the catalyst life to four years, was estimated to lower the cost of the catalytic oxidation process by 20 percentage points relative to the estimated cost for conventional activated carbon injection.

Results from Spruce Plant are difficult to interpret, because of the high amount of Hg⁰ oxidation that was observed across the reverse gas fabric filter upstream of the oxidation catalyst pilot unit there. The strongest conclusion that can be made from the Spruce results is that plants that fire PRB and that have reverse gas fabric filters to particulate control may not need additional catalysts to promote mercury oxidation upstream of the FGD system.

The oxidation catalyst testing at Monticello is at about the mid-point of the planned 14-month duration. Results to date show that the gold is the most active of the four catalysts being tested. However, the loss of activity versus time is greater than was measured at CCS, which suggests that the Texas lignite flue gas may be a more severe environment for the catalysts than North Dakota lignite. However, the activity loss experienced at Monticello may be exacerbated by fly ash buildup as a result of intermittent sonic horn malfunctions.