

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

Quarterly Technical Progress Report

January 1, 2002 – March 31, 2002

Cooperative Agreement No: DE-FC26-01NT41185

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Abstract

This document summarizes progress on Cooperative Agreement DE-FC26-01NT41185, Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems, during the time period January 1, 2002 through March 31, 2002. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-01NT41185. EPRI, Great River Energy (GRE) and City Public Service (CPS) of San Antonio are project co-funders. URS Group is the prime contractor.

The mercury catalytic oxidation process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates in a stable form with the byproducts from the FGD system. The co-precipitated mercury does not appear to adversely affect the disposal or reuse properties of the FGD byproduct. The current project will test previously identified, effective catalyst materials at a larger, pilot scale and in a commercial form, so as to provide engineering data for future full-scale designs. The pilot-scale tests will continue for up to 14 months at each of two sites to provide longer-term catalyst life data.

This is the second full reporting period for the subject Cooperative Agreement. During this period, most of the project efforts were related to pilot unit design and conducting laboratory runs to help select candidate catalysts. This technical progress report provides an update on these two efforts. A Test Plan for the upcoming pilot-scale evaluations was also prepared and submitted to NETL for review and comment. Since this document was already submitted under separate cover, this information is not repeated here.

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1.0 Introduction

This document is the semi-annual Technical Progress Report for the project “Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems,” for the time period January 1, 2002 through March 31, 2002. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-01NT41185. EPRI, Great River Energy (GRE) and City Public Service (CPS) of San Antonio are project co-funders. URS Group is the prime contractor.

The mercury catalytic oxidation process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. The oxidizing species are already present in the flue gas and may include chlorine, hydrochloric acid (HCl) and/or other species. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates in a stable form with the byproducts from the FGD system. The co-precipitated mercury does not appear to adversely affect the disposal or reuse properties of the FGD byproduct.

The objective of the current project is to test previously identified, effective catalyst materials at a larger scale and in a commercial form, so as to provide engineering data for future full-scale designs. The pilot-scale tests will continue for up to 14 months at each of two sites to provide longer-term catalyst life data.

Based on information from the U.S. EPA Mercury Information Collection Request (ICR), the technology under development is probably best suited for plants with a high-efficiency particulate control device upstream of the FGD system, rather than systems that use high-energy scrubbers to achieve combined particulate and SO₂ control. The former represents the majority of FGD systems in the U.S., about 90,000 MW of generating capacity. The ICR results also suggest that catalytic oxidation of elemental mercury would have the greatest effect on the flue gas from subbituminous coal or lignite, where most of the mercury is present in the elemental form. There are approximately 28,000 MW of scrubbed capacity firing these fuels with more systems planned.

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

After successful completion of the project, it is expected that sufficient full-scale test data will be available to design and implement demonstration-scale or commercial-scale installations of the catalytic mercury oxidation technology.

The remainder of this report is divided into three sections. Section 2 provides an account of progress on the project during the current reporting period, including any problems encountered. Section 3 provides a forecast of plans for the next and future reporting periods, and Section 4 provides a detailed discussion of technical results from the project during the current reporting period.

2.0 Progress during the Current Reporting Period

2.1 Summary of Progress

The current reporting period, January 1, 2002 through March 31, 2002, is the second full technical progress reporting period for the project. August 30, 2001 was the start date for the Cooperative Agreement. Several efforts over this period were related to test planning, including holding host site kickoff meetings and preparing an initial test plan.

A site kickoff meeting was held on February 6, 2002, at GRE's CCS. Project team members from URS Group and representatives from CCS and GRE's Elk River, MN home office were in attendance. The primary outcome of the meeting was to agree on a location for the pilot unit near the induced draft fans on CCS Unit 1, and to discuss the project plans and schedule with station personnel.

A similar site kickoff meeting was held on February 22, 2002 at CPS' Spruce Plant.

A draft Test Plan for the project was prepared and distributed to NETL and to other team members for review on March 20, 2002. A detailed design for the pilot-scale catalyst test unit was completed during the quarter, and a request for quotation for fabrication will be sent out in mid-April.

Also during this reporting period, efforts continued on the selection of candidate catalyst materials for evaluation at the pilot scale, and a laboratory evaluation of candidate catalysts was begun. The design of the pilot oxidation system required to conduct the planned tests was completed. The laboratory evaluation of candidate catalyst materials and the design of the pilot unit are discussed further in Section 4 of this report. No pilot-scale testing was conducted during this reporting period.

No subcontracts were awarded during the current reporting period. As the pilot unit design effort was completed, a number of purchase orders were issued during the period, though, for pilot unit instrumentation and controls, valves, and isokinetic "scoops" for withdrawing flue gas at a representative location from the utilities' ID fan outlet ductwork.

2.2 Problems Encountered

There were no significant problems encountered during the reporting period.

3.0 Plans for Future Reporting Periods

3.1 Plans for Next Reporting Period

The next reporting period covers the time period April 1 through June 30, 2002. The plans for that period are to select a subcontractor for the pilot unit fabrication, complete the fabrication and ship the pilot unit to CCS. Depending on the timing of the fabrication subcontract, the pilot unit may be installed at CCS and started up during the next quarter or during a subsequent quarter.

Additional samples of candidate catalyst materials for the 14-month test at Site 1 will be procured, and laboratory testing of all candidates will be completed. These results will be used to select four catalysts with the highest mercury oxidation activity at simulated CCS flue gas conditions. Four catalyst materials will be procured in sufficient quantity to ensure high elemental mercury oxidation (greater than 95%) at test beginning

3.2 Prospects for Future Progress

Early in the subsequent reporting period (July 1 through September 30, 2002), it is expected that the completed mercury oxidation pilot unit will be installed and started up at GRE's CCS plant. The four catalyst materials will be installed in the pilot unit at the beginning of the long-term test period. Once the catalyst material has been installed and operated in flue gas long enough to achieve mercury adsorption equilibrium (approximately one to two weeks), an initial host site flue gas characterization effort and catalyst performance evaluation test will be conducted. Later in the period, the four catalysts will be evaluated for elemental mercury oxidation performance during one or two routine monthly evaluation trips.

In later reporting periods (October 1 through December 31, 2002, and later periods) it is anticipated that the pilot unit will remain in operation at CCS, and will be evaluated for elemental mercury oxidation performance through routine monthly evaluation trips. Eventually, pilot testing will commence at the second site, CPS' Spruce Plant.

4.0 Technical Results

This section provides details of technical results for the current reporting period (January 1, 2002 through March 31, 2002). The technical results presented include the results of initial laboratory evaluations of candidate catalysts applied to honeycomb substrates, and details of the pilot unit design.

4.1 Laboratory Evaluation Candidate Catalysts

Four catalyst cores were received during the period and tested in the laboratory for mercury oxidation activity under simulated North Dakota lignite flue gas conditions. Table 4-1 summarizes the simulation gas conditions. The percent moisture is lower than what would be expected in the flue gas from North Dakota lignite (about 15%). The value listed (9%) represents the practical upper limit on the laboratory gas mixing apparatus. This difference in expected actual versus simulation gas moisture content is not thought to affect the results.

Table 4-1. Gas Conditions for CCS Simulations

Species	Condition
SO ₂ (ppm)	500
NO _x (ppm)	200
HCl (ppm)	6
O ₂ (%)	5
CO ₂ (%)	12
H ₂ O (%)	9
N ₂ (%)	Balance
Temperature (°F)	350

The catalysts tested included Pd#1 at two different palladium loadings on the honeycomb, SCR catalyst sample S#1, and Carbon #6 applied to a honeycomb substrate. The results of the laboratory simulation runs are summarized in Table 4-2, and plotted as a function of area velocity in Figure 4-1. Table 4-3 shows honeycomb substrate dimensions for each catalyst sample, and the actual versus predicted performance of each compared to a mass transfer model. Using the model to predict mercury oxidation performance is based on a simplifying assumption that mercury oxidation is instantaneous once the mercury has diffused to the catalyst surface. If the actual performance is close to the model prediction, this is an indicator of very rapid catalytic oxidation at the catalyst surface, whereas if the actual performance is well below the model prediction it is an indicator of a slower surface reaction. The actual versus predicted oxidation is compared on the basis of “number of transfer units” (NTU), a mass transfer performance term, rather than on the basis of percent oxidation.

Table 4-2. Laboratory Simulation Results

Catalyst	Gas Flow Rate (l/min)	Inlet Hg ⁰ (ng/Nm ³)	Outlet Hg ⁰ (μg/Nm ³)	Hg ⁰ Oxidation (%)
Pd#1 7x; 2" core	0.64	147	0.01	100
Pd#1 7x; 2" core	1.0	94.9	0.01	100
Pd#1 7x; 2" core	1.3	71.3	0.01	100
Pd#1 5x; 2" core	0.64	118	14.1	88
Pd#1 5x; 2" core	1.0	75.9	6.02	92
Pd#1 5x; 2" core	1.3	57.1	4.59	92
S#1 SCR; 2" core	0.64	118	5.01	96
S#1 SCR; 2" core	1.0	75.9	3.39	96
S#1 SCR; 2" core	1.3	58.4	3.13	95
S#1 SCR; 1" core	0.64	110	14.8	87
S#1 SCR; 1" core	1.0	70.6	10.1	86
S#1 SCR; 1" core	1.3	54.3	9.16	83
Carbon #6; 0.8" core	0.64	84.0	0.94	99
Carbon #6; 0.8" core	1.0	54.1	2.61	95
Carbon #6; 0.8" core	1.3	40.7	1.55	96

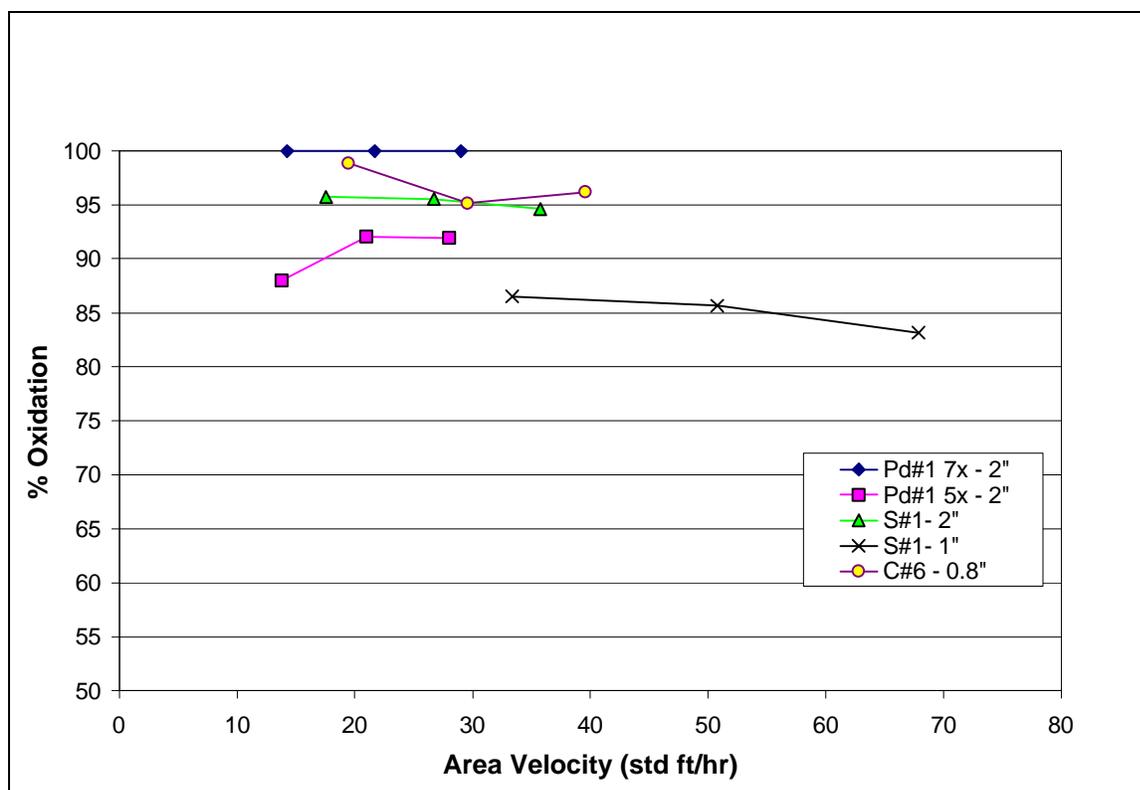


Figure 4-1. Catalyst Sample Oxidation Percentage vs. Area Velocity

Table 4-3. Honeycomb Dimensions and Actual vs. Predicted Catalyst Performance

Catalyst Type	Core Diameter (in)	Core Length (in)	Cell Pitch (mm)	Cell Wall Thickness (mm)	Measured Hg ⁰ Oxidation (%)	Predicted Hg ⁰ Oxidation (%)	Measured NTU/ Predicted NTU (%)
Pd#1 7x	0.54	2.0	3.17	0.35	100	100*	98
Pd#1 7x	0.54	2.0	3.17	0.35	100	100*	>100
Pd#1 7x	0.54	2.0	3.17	0.35	100	100*	>100
Pd#1 5x	0.55	2.0	3.17	0.35	88	100*	22
Pd#1 5x	0.55	2.0	3.17	0.35	92	100*	35
Pd#1 5x	0.55	2.0	3.17	0.35	92	100*	41
S#1	0.56	2.0	4.15	0.51	96	100*	45
S#1	0.56	2.0	4.15	0.51	96	100*	59
S#1	0.56	2.0	4.15	0.51	95	99	67
S#1	0.56	1.1	4.15	0.51	87	99	45
S#1	0.56	1.1	4.15	0.51	86	96	59
S#1	0.56	1.1	4.15	0.51	83	94	64
C#6	0.56	0.8	1.75	0.45	99	100*	31
C#6	0.56	0.8	1.75	0.45	95	100*	28
C#6	0.56	0.8	1.75	0.45	96	100*	36

*Predicted number is less than 100.00 but greater or equal to 99.50; the value is shown as 100 in the table due to rounding.

The results plotted in Figure 4-1 show high oxidation percentages for all of the catalysts. Note that the oxidation results shown were all measured after the catalysts had reached mercury adsorption equilibrium, so the performance shown truly represents the oxidation of elemental mercury across the honeycomb sample and no elemental mercury adsorption. The data clearly show that the higher palladium loading on the honeycomb improved the oxidation performance for Pd#1.

Other than for the 1-inch sample of the S#1 catalyst, the samples were typically tested at area velocities in the range of 15 to 40 sft/hr. However, the expectation is that in a full-scale application, the catalysts will be installed to operate at higher area velocities, in the range of 70 sft/hr or greater. In the next quarter, tests will be conducted on shorter catalyst cores and at slightly higher gas rates (the gas rate is limited by the capacity of the bench-scale simulation gas mixing apparatus) to allow operation at higher area velocities. Also in the next quarter, additional tests will be conducted on a fly-ash-based catalyst (SBA#5) applied to a honeycomb substrate and to Pd#1 with the palladium applied at other loadings.

Table 4-3 shows the dimensions of the various honeycomb core samples. This table illustrates why the catalyst performance was plotted as a function of area velocity rather than space velocity. The cores supplied are on substrates with varying cell pitches and wall thickness, and thus varied active surface area per unit volume. Space velocity is defined as the standard gas flow rate divided by the catalyst volume, but at similar space velocities the smaller-pitched

catalysts would have more active surface areas than the coarser-pitched catalysts. The area velocity is defined as the standard gas flow rate divided by the catalyst external surface area, and thus better accounts for varied cell pitch and wall thickness. Since any of the catalyst materials could conceivably be applied on any substrate, the area velocity is the more equitable parameter for catalyst comparison, and less influenced by the cell pitch at which the particular samples were available for testing.

Table 4-3 also shows the actual versus predicted performance of each catalyst. At higher oxidation percentages, this comparison becomes imprecise. Due to the exponential form of the NTU calculation, the NTU values become large as the oxidation percentage approach 100%. Normal experimental error in quantifying performance at high oxidation percentages can make big differences in the observed NTU values, and can skew the actual versus predicted performance comparison.

Notwithstanding these potential errors, the comparison of actual to predicted NTU shows that the higher palladium loading for Pd#1 resulted in nearly instantaneous oxidation at the catalyst surface (measured performance near 100% of the mass-transfer limit). Pd#1 at the lower loading had measured performance that was 22 to 41% of the mass-transfer limit, S#1 measured 45 to 67% of the mass transfer limit, and C#6 measured 28 to 36% of the mass transfer limit. These percentages suggests that Pd#1 at the higher palladium loading was the most active catalyst tested, S#1 was the next most active, and Pd#1 at the lower loading and C#6 showed the lowest activity, with the two being about equal in performance. This ranking is not obvious in the plots of performance versus area velocity in Figure 4-1, because the mass transfer model better takes into account the effects of differing catalyst geometry than does a simple area velocity calculation. These comparisons will be made again after data at higher area velocities become available, and after all catalyst types have been tested.

4.2 Pilot Unit Design

During the quarter, the detailed design of the pilot catalyst skid was completed. The pilot unit is depicted in Figure 4-2, and the pilot unit instrumentation is summarized in Table 4-4.

The skid will have four catalyst chambers, each representing a cube that is one meter in all three directions. Each “cube” will have a removable side panel that provides full access to the chamber, for installing and retrieving catalysts. The amount of catalyst in each chamber will be varied as necessary to achieve desired elemental mercury oxidation, based on the laboratory screening results as discussed above. For any catalyst where the cross-section of the honeycomb “block” installed is less than one meter by one meter, a “picture frame” spacer will be installed around the catalyst block that will fit snugly against the chamber side, top and bottom walls. This spacer will center the catalyst block in the chamber, and reduce the effective opening size of the catalyst chamber to ensure that all of the flue gas flows through the honeycomb and not through the annular space between the honeycomb and the chamber walls.

Table 4-4. Summary of Pilot Unit Instrumentation

Parameter	Sensor Type	Number of Each
Pilot Unit Inlet Temperature	Type K thermocouple	1
Catalyst Outlet Temperature	Type K thermocouple	1 per chamber (4 total)
Catalyst Pressure Drop	Differential pressure transducer	1 per chamber (4 total)
Catalyst Outlet Gauge Pressure	Differential pressure transducer	1 per chamber (4 total)
Catalyst Flow Rate	Venturi flow meter, Differential pressure transducer (corrected for temperature and gauge pressure)	1 per chamber (4 total)
Pilot Unit Inlet and Catalyst Outlet Hg Concentrations, Speciation	Semi-continuous Hg analyzer	1 (cycled between pilot unit inlet and individual catalyst outlets, for Hg ⁰ and total Hg)

The design flue gas flow rate through each chamber is 2000 acfm, for a total of 8000 acfm to the skid. The skid inlet piping is 20-inch diameter pipe, and the return to the utility duct is 12-inch pipe. On the inlet side of the chambers, the 20-inch common feed pipe splits to a 10-inch diameter feed pipe for each followed by a 30° transition to each cube opening. The low velocity in the 10-inch line and the shallow angle on the 30° transition are intended to ensure good flue gas flow distribution across the face of each catalyst. On the outlet side the transition is much steeper, at 45°, and the outlet piping is also smaller at 6-inch diameter. The smaller diameter is to increase the gas velocity, to improve the signal strength for the venturi flow meters in the outlet run from each chamber. Butterfly-style dampers are used to control flue gas flow. Damper position will be automatically modulated to control flow rate based on feedback from the venturi flow meter pressure differential, corrected for the total gauge pressure and measured gas temperature in the outlet duct.

The pilot unit inlet gas will be pulled from a 5-foot-long “scoop” installed in the host unit’s ID fan outlet duct. The “scoop” is a straight piece of pipe cut at a 45° angle at the end, facing into the flue gas flow, to result in pulling gas at approximately isokinetic conditions. The 5-foot length is to ensure a representative gas sample, from near the center of the duct. The pilot unit can be isolated from the host unit with wafer-style butterfly dampers at the pilot unit inlet penetration (20-inches) on the ID fan outlet duct and return penetration (12-inches) on the ID fan suction 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 entrance to the inlet transition for that chamber.

The pilot unit will have a total of five control loops. Four will be for flow rate through the individual catalyst chambers, as described above, and the fifth will be for pilot unit inlet flue gas temperature. The inlet temperature will be controlled with heat tracing on the 20-inch diameter inlet pipe run, to match the host unit ID fan outlet gas temperature at full load (nominally 350°F at CCS and 300°F at Spruce). A slight positive offset will be required to account for temperature losses across the catalyst enclosures. The pilot unit piping runs and catalyst enclosures will be insulated with at least a 2-inch thickness of mineral wool or fiberglass insulation to minimize heat losses.

Mercury concentrations and speciation will be measured at the pilot unit inlet and at the outlets of each catalyst chamber with the EPRI semi-continuous mercury analyzer, which has been described in our original proposal and in the test plan. The analyzer will be cycled between the five measurement locations and between measuring elemental mercury and total mercury to determine the elemental mercury oxidation across each catalyst.