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

Quarterly Technical Progress Report

April 1, 2002 – June 30, 2002

Cooperative Agreement No: DE-FC26-01NT41185

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July 17, 2002

Disclaimer

Abstract

This document summarizes progress on Cooperative Agreement DE-FC26-01NT41185, Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems, during the time period April 1, 2002 through June 30, 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 third full reporting period for the subject Cooperative Agreement. During this period, most of the project efforts were related to constructing the pilot unit and conducting laboratory runs to help size catalysts for the pilot unit. This technical progress report provides an update on these two efforts.

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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 April 1, 2002 through June 30, 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 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 SO_2 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, April 1, 2002 through June 30, 2002, is the third 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 constructing the pilot unit to be used to evaluate mercury oxidation catalyst activity over time. A detailed design for the pilot-scale catalyst test unit was completed during the previous quarter, and a request for quotation for fabrication was sent out in mid-April. Bids were received in late April, and successful contractors were selected at the end of April as described below. The pilot unit fabrication was nearly completed during the current quarter, with insulation of the pilot unit and running of heat-traced and insulated sample lines for the semi-continuous flue gas mercury analyzer being the only major fabrication efforts remaining. It is expected that all fabrication efforts will be completed by the end of July, and that the pilot unit will be shipped to the first host site in North Dakota at the beginning of August.

Also during this reporting period, laboratory efforts continued to support the selection and sizing of catalyst materials for evaluation at the pilot scale. Three of the catalysts (the Siemens SCR catalyst, the Carbon #6 (C #6) catalyst, and the Subbituminous Ash #5 (SBA #5) catalyst) have been sized based on the laboratory performance data using simulated flue gases. The SCR catalyst was ordered and Siemens began catalyst preparation during the quarter. The laboratory evaluation of the fourth, Palladium #1 (Pd #1) catalyst continued through the quarter. Due to apparent data problems; this catalyst has not yet been sized for the pilot unit. The laboratory evaluation of candidate catalyst materials is discussed further in Section 4 of this report. No pilot-scale testing was conducted during this reporting period.

Several subcontracts were awarded during the current reporting period. Skotz, Inc. of Austin, Texas was awarded the subcontract to complete the mechanical fabrication of the pilot unit. David Bacon Inc. was awarded the subcontract to complete all of the pilot unit wiring, instrument tubing, and sample line installation; and Mid-state Insulation Company was awarded the subcontract to insulate the pilot unit. Thermon Heat Tracing Services was awarded a subcontract to heat trace and insulate the pilot unit inlet duct and the flue gas sample lines for the mercury analyzer. Finally, Applied Ceramics, Inc., was awarded a subcontract to prepare a sample catalyst block of C #6 in a honeycomb extrusion. If this sample block is successfully prepared, Applied Ceramics will prepare the full-pilot unit catalyst load for both the C #6 and the SBA #5 catalysts.

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 July 1 through September 30, 2002. The plans for that period are to complete the pilot unit fabrication and ship the pilot unit to CCS. The pilot unit will be installed at CCS and started up during the quarter.

The three remaining catalyst materials will be procured in sufficient quantity to ensure high elemental mercury oxidation (greater than 95%) at test beginning. The four catalyst materials (including the Siemens SCR catalyst that has already been ordered) will be installed in the pilot unit to begin 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.

3.2 Prospects for Future Progress

During the subsequent reporting period (October 1 through December 31, 2002), it is expected that the four catalysts will be evaluated for elemental mercury oxidation performance during routine monthly evaluation trips. In later reporting periods (January 1 through March 31, 2003 and later periods) the pilot unit will remain in operation at CCS, and will be evaluated for elemental mercury oxidation performance through continuing routine monthly evaluation trips. Two additional intensive sampling trips will occur, one after about 7 months of catalyst operation and the second at the end of the 14-month long-term catalyst evaluation period at CCS. Late in the year 2003, 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 (April 1, 2002 through June 30, 2002). The technical results presented include the results of laboratory evaluations of candidate catalysts applied to honeycomb substrates, and details of the pilot unit design and construction.

4.1 Laboratory Evaluation of Candidate Catalysts

Testing of catalyst cores in the laboratory for mercury oxidation activity under simulated North Dakota lignite flue gas conditions continued during the period. 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 North Dakota Lignite Simulations

Species	Condition
SO_2 (ppm)	500
NO_x (ppm)	200
HCl (ppm)	6
O_2 (%)	5
CO_2 (%)	12
H_2O (%)	9
N_2 (%)	Balance
Temperature (^oF)	350

The catalysts tested during the quarter included Pd #1 wash-coated at two different palladium loadings on the honeycomb, C #6 extruded into a honeycomb substrate, and SBA #5 extruded into 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 Figures 4-1 and 4-2. Figures 4-1 and 4-2 include laboratory simulation data that were reported in the previous quarterly technical progress report (January through March 2002). Note that the oxidation results shown in the table and figures 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 results plotted in Figure 4-1 show high oxidation percentages (>90%) for all three catalysts (SCR, C #6, and SBA #5) when tested at the longer core lengths and area velocities in the range of 20 to 60 sft/hr. When the Siemens' SCR and C #6 catalysts were tested at shorter core lengths (1-inch vs. 2-inch for the SCR catalyst, 0.4-inch vs. 0.8-inch for the C #6 catalyst) to allow operation at higher area velocities, the oxidation performance of each dropped off considerably. It is speculated that at these shorter core

Table 4-2. Laboratory Simulation Results

Catalyst	Gas Flow Rate (l/min)	Inlet Hg^0 ($\mu g/Nm^3$)	Outlet Hg^0 ($\mu g/Nm^3$)	Hg^0 Oxidation (%)
C #6; 0.4" core	0.64	50.5	6.66	87
C #6; 0.4" core	1.0	32.5	6.49	80
C #6; 0.4" core	1.3	24.4	6.99	71
Pd #1 7x; 1" core	0.64	96.6	23.9	75
Pd #1 7x; 1" core	1.0	63.1	20.9	67
Pd #1 7x; 1" core	1.3	47.6	15.9	67
Pd #1 5x; 1" core	0.64	102	68.7	32
Pd #1 5x; 1" core	1.0	66.8	48.7	27
Pd #1 5x; 1" core	0.64	97.7	52.0	47
Pd #1 5x; 1" core	1.0	63.8	31.4	51
SBA #5; 0.6" core	0.64	102	6.77	93
SBA #5; 0.6" core	1.0	66.8	1.00	99
SBA #5; 0.6" core	1.3	50.3	1.53	97
Pd #1 5x; 2" core	0.64	39.1	10.9	72
Pd #1 5x; 2" core	1.0	25.5	2.4	91
Pd #1 5x; 2" core	1.3	19.3	4.3	78
Pd #1 5x; 2" core	1.6	15.7	5.2	67
Pd #1 7x; 2" core	0.64	38.1	3.0	92
Pd #1 7x; 2" core	1.0	24.9	0.0	100

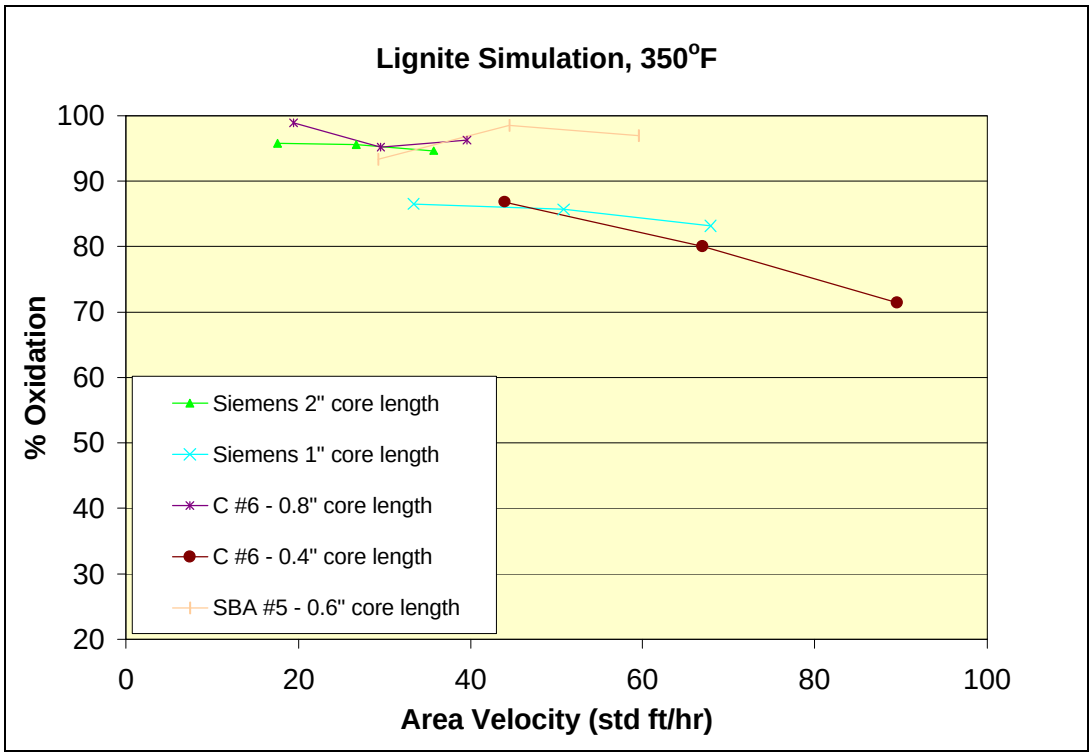

Figure 4-1. Effect of Area Velocity on Catalyst Oxidation of Mercury

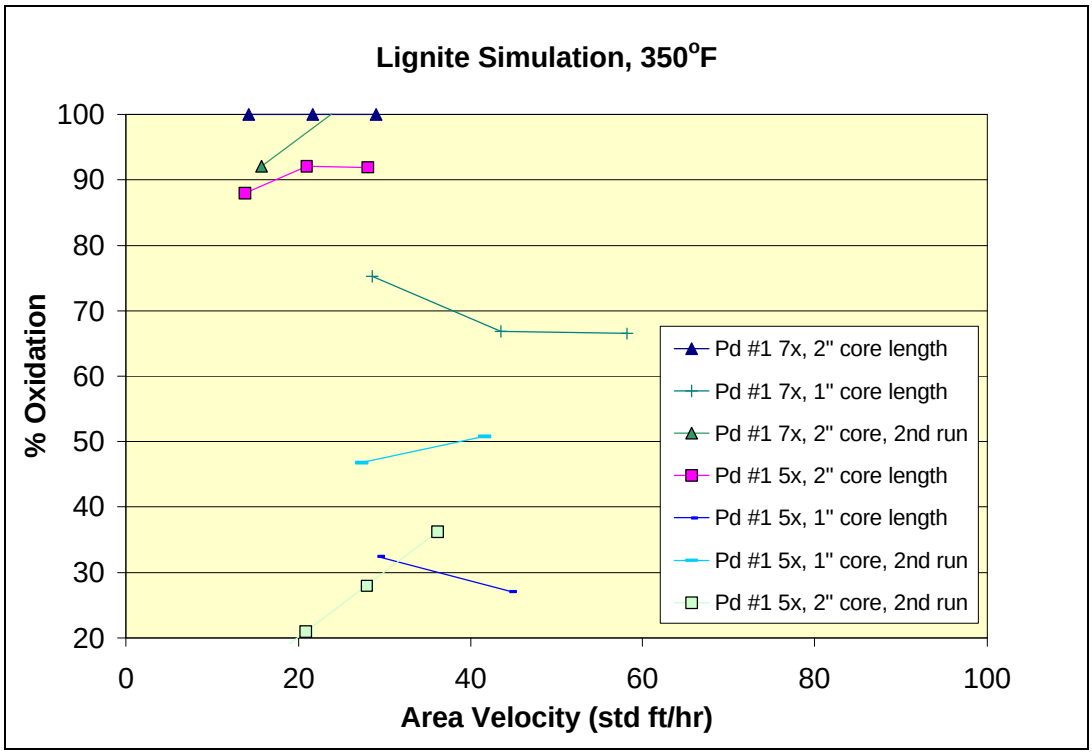

Figure 4-2. Effect of Area Velocity on Pd #1 Catalyst Oxidation of Mercury

lengths, the gas distribution across the face of the honeycomb was adversely affected, lowering the overall oxidation activity from what would have been realized with a more ideal gas distribution.

This speculation highlights a limitation of the current laboratory simulation setup. The catalyst core testing is being conducted with an existing apparatus that was set up to test mercury sorbent and catalyst materials in a “sand bed” reactor. To test honeycomb catalyst cores, the sand bed is replaced with a catalyst core of round cross section, typically about 5/8-inch diameter. The catalysts tested were acquired from the various vendors in whatever pitch was available. With the diameter of the catalyst core holder fixed at 5/8-inch, the core pitch being fixed, and the gas mixing flow rate range of the existing apparatus limited to about 1.3 l/min, the only variable that can be adjusted to increase area velocity is the core length. As can be seen in Figure 4-1, to achieve higher area velocities (approaching 100 sft/hr) the corresponding core lengths can become very short, particularly for the C #6 and SBA #5 catalyst cores, which were available in a very tight cell pitch pattern. In spite of this limitation, the data for the longer core lengths for the SCR catalyst and for the C #6 catalyst should be adequate for determining catalyst quantities for the pilot unit.

The results for Pd#1 plotted in Figure 4-2, for palladium applied at two loadings on the honeycomb and for two core lengths, show a great deal of scatter. Two factors appear to cause this data scatter. One is the core length issue as described above. The 2-inch core length data are probably more representative than the 1-inch data. Another factor is that there appears to have been an interference between some component in the sample gas

exiting the Pd #1 cores and the Tris(hydroxymethyl)aminomethane (Tris) solution used to remove oxidized mercury from the sample gas. This apparent interference caused a high degree of variability in the measured catalyst outlet elemental mercury concentrations, and thus caused the catalyst performance results in Figure 4-2 to be suspect. During the next quarter, the Pd #1 tests will be repeated using only 2-inch core lengths and using potassium chloride rather than Tris solution to remove oxidized mercury from the sample gas going to the laboratory mercury analyzer when measuring for elemental mercury. Assuming the apparent interference can be eliminated by the solution change, these additional results should allow the palladium loading and the catalyst volume required for the pilot unit to be selected for the Pd #1 catalyst.

The results plotted in Figure 4-1 were adequate to estimate the amount of each of three catalysts (SCR, C #6, and SBA #5) required to achieve high elemental mercury oxidation percentages in the pilot application. Table 4-3 shows the planned honeycomb substrate dimensions for each catalyst and the overall catalyst dimensions required for the pilot unit as predicted by a mass transfer model previously developed by URS. The model predicts mercury oxidation performance based on a simplifying assumption that mercury oxidation is instantaneous once the mercury has diffused to the catalyst surface.

Table 4-3. Honeycomb Dimensions for the Laboratory Testing Proposed for the Pilot Unit

	Core Tested		Pilot Unit Catalyst				
Catalyst Type	Cell Pitch (mm)	CPSI (cells per in^2)	Cell Pitch (mm)	CPSI (cells per in^2)	Catalyst Cross-section (in x in)	Catalyst Length (in)	Area Velocity (sft/hr)
Siemens SCR	4.2	37	4.2	37	35.4 x 35.4	19.7	21
Carbon #6	1.8	211	3.2	64	36 x 36	12	19
SBA #5	1.7	217	3.2	64	36 x 36	12	25
Pd#1	3.2	64	3.2	64	35.4 x 35.4	TBD*	TBD*

*To be determined based on laboratory results in the next quarter.

To use the model to predict the expected performance of each catalyst in the pilot unit, the actual performance of each catalyst in the laboratory simulations was compared to model predictions. If the actual performance was close to the model prediction, this is an indicator of very rapid catalytic oxidation at the catalyst surface; whereas if the actual performance was 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. This comparison is used to develop an empirical correlation between the lab results and the model prediction, expressing the actual NTU as a percentage of the "theoretical" NTU. This correlation should account for the differing surface activity among the catalyst types. The empirically adjusted model was then used to predict the performance of each catalyst at different cell pitches, catalyst cross-sectional area, and catalyst depth.

Table 4-3 includes the dimensions of the honeycomb core samples tested in the laboratory. This table illustrates why the catalyst performance was plotted in Figures 4-1 and 4-2 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 in 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, area velocity is the more equitable parameter for catalyst comparison and is less influenced by the cell pitch at which the particular samples were available for testing.

Table 4-3 also shows the planned cell pitch dimensions for each catalyst as required for the pilot unit and the overall dimensions of each. Note that the planned catalyst sizing is considered to be conservative (e.g., area velocities in the range of 20 to 25 sft/hr). It is hoped that the field performance for these catalysts will be well above 95% oxidation of elemental mercury at the design conditions for the values in the table. If so, it will be possible to operate the catalysts at somewhat higher flue gas flow rates through the individual catalyst chambers, and hence allow them to operate at higher area velocity values.

Siemens has proceeded with the preparation of a block of SCR catalyst based on the dimensions in Table 4-3. The completed catalyst block will be shipped to CCS in late July. Applied Ceramics is under contract to make one 6-inch by 6-inch by 3-inch deep catalyst block of the SBA #5 extrusion, at the cell pitch we have requested. If this block is successfully prepared, we will have them prepare enough blocks of these sizes for both the C #6 and SBA #5 to produce a composite catalyst block of each of the overall dimensions shown in Table 4-3. In the interim, we have procured a sufficient quantity of both C #6 and SBA #5 to prepare the required number of individual catalyst blocks of each, and are shipping those materials to Applied Ceramics.

4.2 Pilot Unit Design

During the previous quarter, the detailed design of the pilot catalyst skid was completed, and bids for its fabrication were solicited. Bids were received in late April, and successful contractors were selected as described in Section 2. The pilot unit fabrication was nearly completed during the current quarter, with insulation of the pilot unit and running of heat-traced and insulated sample lines for the semi-continuous flue gas mercury analyzer being the only major fabrication efforts remaining. It is expected that all fabrication efforts will be completed by the end of July, and that the pilot unit will be shipped to CCS in North Dakota at the beginning of August.

The pilot unit was described in the previous technical progress report, but for the reader’s convenience the description is repeated below. The pilot unit instrumentation is summarized in Table 4-4. Figures 4-4 through 4-6 are photographs that depict the status of the pilot unit fabrication as of the end of the quarter.

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)

Figure 4-4. Photograph of the Pilot Skid from the Side on the Inlet End, Near the Completion of its Mechanical Fabrication

Figure 4-5. Photograph of the Pilot Skid from the Exit End, Near the Completion of its Mechanical Fabrication

The skid has four catalyst chambers, each representing a cube that is one meter in all three directions. Each "cube" has 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 described in Table 4-3 to achieve desired elemental mercury oxidation based on the laboratory screening results discussed above. The catalyst honeycomb "block" cross-sections installed will each be less than one meter by one meter, so a "picture frame" spacer will be installed around the catalyst block to 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.

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-in pipe. On the inlet side of the chambers, the 20-inch common feed pipe splits to 10-inch diameter pipe for each followed by a 30^{o} transition to each cube opening. The low velocity in the 10-inch line and the shallow 30^{o} transition angle 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^{o}, and the outlet piping is also smaller at a 6-inch diameter. The smaller diameter is to increase the gas velocity, which improves 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

Figure 4-6. Photograph of Pilot Unit Control Panel Prior to Installation on Pilot Skid

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^{o} angle at the end (facing into the flue gas flow) that results 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 "scoop" was fabricated and installed in the CCS ID fan outlet duct during an outage in April.

The pilot unit can be isolated from the host unit with wafer-style butterfly dampers at the pilot unit inlet penetration (20 inch) on the ID fan outlet duct and return penetration (12

inch) on the ID fan suction duct. These two isolation valves were also installed on the CCS ductwork during the April outage. 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 has 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 a 15-foot length, prefabricated and heat-traced 20-inch diameter inlet spool piece. The set point temperature will match the host unit ID fan outlet gas temperature at full load (nominally 350^{o}F at CCS). A slight positive offset will be required to account for temperature losses across the catalyst enclosures. The pilot unit piping and catalyst enclosures will be insulated with at least a 2-inch thickness of fiberglass insulation to minimize heat losses. Aluminum sheathing will provide weather protection for the insulation.

Mercury concentration 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 was 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. Solenoid valves will be installed on sample ports at each location, and heat-traced and insulated Teflon tubing will connect each sample with a common manifold to feed sample gas to the analyzer. The analyzer controller will select which sample solenoid is opened and hence which location is being sampled and analyzed.