

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

Quarterly Technical Progress Report

October 1, 2002 – December 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 October 1, 2002 through December 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 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 testing previously identified, effective catalyst materials at a larger, pilot 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.

This is the fifth full reporting period for the subject Cooperative Agreement. During this period, project efforts included starting up the pilot unit with three catalysts at the first site, conducting catalyst activity measurements, completing comprehensive flue gas sampling and analyses, and procuring additional catalysts for the pilot unit. This technical progress report provides an update on these efforts.

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1.0 Introduction

This document is the quarterly Technical Progress Report for the project “Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems,” for the time period October 1, 2002 through December 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 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 this 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 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, October 1, 2002 through December 31, 2002, is the fifth full technical progress reporting period for the project. August 30, 2001 was the start date for the Cooperative Agreement. Efforts over the current reporting period included starting up the pilot unit with catalysts installed, conducting catalyst activity measurements, completing comprehensive flue gas sampling and analyses, and procuring additional catalysts for the pilot unit, all for the first test site. A limited number of laboratory evaluations of catalyst materials were also conducted.

Great River Energy installed the pilot unit near the induced draft (ID) fans on Unit 1 at their Coal Creek Station (CCS), with the flue gas going to the pilot unit being withdrawn from one ID fan outlet duct and returning to the inlet duct on an adjacent fan. The pilot unit was started up with no catalysts loaded during the week of September 16. The first week in October, the pilot unit was shut down and two of the four catalyst materials to be tested, the SCR catalyst and the palladium-based catalyst (Pd #1), were installed. The other two catalysts, the Carbon #6 (C #6) catalyst and the Subbituminous Ash #5 (SBA #5) catalyst, were not yet available. The chambers in the pilot unit for those two catalysts were left empty, and the pilot unit was restarted with the first two catalysts installed on the evening of October 3.

During the weeks of October 14 and October 21, a project team conducted initial catalyst activity tests for the SCR and Pd #1 catalysts, and conducted an initial round of flue gas characterization measurements. Catalyst activity was measured as a function of flue gas flow rate through the catalysts using the EPRI semi-continuous flue gas mercury analyzer. Gas characterization measurements included flue gas mercury concentration and speciation by the draft Ontario Hydro method, metals by Method 29, acid gas species by Method 26a, sulfuric acid by the Controlled Condensation method, and NO_x by gas detection tubes.

The third catalyst to be tested at CCS, SBA #5, was completed in November by a U.S.-based catalyst manufacturer who has requested not to be identified. The catalyst modules were shipped to CCS and installed in the pilot unit the first week in December. At the same time, measurements were made of catalyst activity for the SCR and Pd #1 catalysts, after about 60 days in flue gas service.

Also during this reporting period, laboratory testing continued to support the selection and sizing of catalyst materials for evaluation at pilot scale, now focused on selection for the second site, Spruce Plant. Testing was conducted on Pd #1, SBA #5, and a patented gold-based catalyst that is under consideration to be one of the four catalysts for testing at Site 2.

Two subcontracts were completed during the current reporting period. The U.S.-based catalyst manufacturer completed the preparation of the SBA #5 catalyst for the pilot unit,

and MaxWell Engineering and Consulting completed a subcontract to activate C#6 material in sufficient quantity to prepare the pilot unit catalyst charge. One new subcontract was awarded; the same U.S.-based catalyst manufacturer that prepared the SBA #5 catalyst was awarded a subcontract to prepare the C#6 catalyst using the raw material activated by MaxWell Engineering and Consulting.

2.2 Problems Encountered

One significant problem encountered during the reporting period is a continuing delay in the preparation of the second of the experimental catalysts, C #6, by the U.S.-based catalyst manufacturer. The catalyst is being prepared as an extruded monolith in an alumina substrate. Since this is the first time that the SBA #5 and C #6 materials have been processed into a honeycomb form, the catalyst manufacturer has had to conduct a considerable amount of development work to determine mixing, extruding, drying and firing parameters. Commercial equipment is being used, so these experimental efforts have had to be scheduled between commercial catalyst production runs.

The SBA #5 catalyst was completed in November, and work began on the C #6 catalyst in December. It is expected that the C #6 catalyst will be completed, shipped, and installed in the pilot unit at CCS by the end of the coming quarter. This means that the four catalysts in the pilot unit at CCS will have three different in-service dates – early October for the SCR and Pd #1 catalysts, early December for the SBA #5, and first-quarter 2003 for the C #6. This will tend to complicate catalyst activity comparisons, but should be manageable.

3.0 Plans for Future Reporting Periods

3.1 Plans for Next Reporting Period

The next reporting period covers the time period January 1 through March 31, 2003. Over this time period routine sampling trips will be conducted to evaluate catalyst activity at CCS. In January, the first catalyst activity measurements will be made on the SBA #5 catalyst, and the third set of measurements will be made on the SCR and Pd #1 catalysts. The cause of an apparent loss in activity and increase in pressure drop across the catalyst modules, as described in Section 4, will also be investigated. It is expected that sometime during the quarter, the fourth (C #6) catalyst will be installed. Once this catalyst has been installed and operated in flue gas long enough to achieve mercury adsorption equilibrium (approximately two weeks to one month), initial catalyst performance evaluation tests will be conducted.

One project team member, EPRI, has funded the construction of a second mercury oxidation catalyst pilot unit. That pilot unit will be available to this project for testing mercury oxidation catalysts at Site 2. It is expected that the second pilot unit will be completed in January 2003, and shipped to CPS' Spruce Plant for installation during the quarter. Startup of that pilot unit should commence near the end of the quarter. This will be preceded by Site 2 catalyst selection and procurement activities.

3.2 Prospects for Future Progress

During the subsequent reporting period (April 1 through June 30, 2003) and continuing through calendar year 2003, the pilot unit is slated to remain in operation at CCS, and to be evaluated for elemental mercury oxidation activity through routine (monthly) evaluation trips. An additional intensive flue gas sampling trip will occur after about seven months of pilot unit operation (~May 2003). A final intensive flue gas sampling trip will occur at the end of the 14-month long-term catalyst evaluation period at CCS (~December 2003). Pilot testing should be completed at CCS approximately at the end of calendar year 2003.

Catalyst testing should commence at the second site, CPS' Spruce Plant, early in the subsequent reporting period (April 1 through June 30, 2003). An initial intensive gas characterization effort for the Spruce Plant site should also occur during that quarter.

4.0 Technical Results

This section provides details of technical results for the current reporting period (October 1, 2002 through December 31, 2002). The technical results presented include a discussion of the data from pilot operation and results of initial gas characterization efforts at CCS, results of laboratory evaluations of catalyst materials, and a discussion of on-going pilot unit catalyst preparation efforts.

4.1 Pilot Unit Operation

As described in the previous quarterly report, the pilot unit was started up with no catalysts loaded during the week of September 16. The no-catalyst startup was conducted to ensure that desired flue gas flow rates could be attained, and that flue gas temperature, flow rate, and pressure instrumentation and controls worked properly. The pilot unit data acquisition system and telemetry equipment was also checked for proper functionality.

After a successful startup, the pilot unit was left operating with no catalysts loaded until the loading of the SCR and Pd #1 catalysts the first week of October. As described earlier, the other two catalysts (SBA #5 and C #6) were not yet available, so a decision was made to commence testing with only two of the four catalysts installed.

The SCR and Pd #1 catalysts were placed in flue gas service at 2000 acfm through each catalyst the evening of October 3. It was expected that these new catalysts would have a significant capacity for adsorbing mercury from the flue gas, so no catalyst performance measurements were made at that time. With mercury being adsorbed from the flue gas, it is not possible to get an accurate measurement of elemental mercury oxidation. The percent oxidation across the catalyst is based on the drop in elemental mercury across the catalysts, and with mercury being adsorbed it is not possible to distinguish between the drop in concentration due to adsorption and that from oxidization.

The catalysts were left in service at 2000 acfm until the week of October 14, when initial catalyst activity measurements were made using the EPRI semi-continuous flue gas mercury analyzer. Figure 4-1 illustrates the analyzer.

The two catalysts were measured for mercury oxidation percentage at three different flue gas flow rates. The results of these measurements are summarized in Table 4-1. A second catalyst activity measurement trip was made the first week of December. The results from that trip are summarized in Table 4-2. In the two tables and throughout this report, the elemental mercury oxidation percentages across the catalysts are based on the drop in concentration across the catalyst, and do not just reflect the total flue gas mercury oxidation percentage at the catalyst outlet.

The October results show high activity for the Pd#1 catalyst, very near that expected based on previous laboratory and field testing with this material. The SCR catalyst results showed significantly lower oxidation percentages at the same flue gas flow rates, and

lower oxidation performance than had been expected. Figure 4-2 plots the activity results.

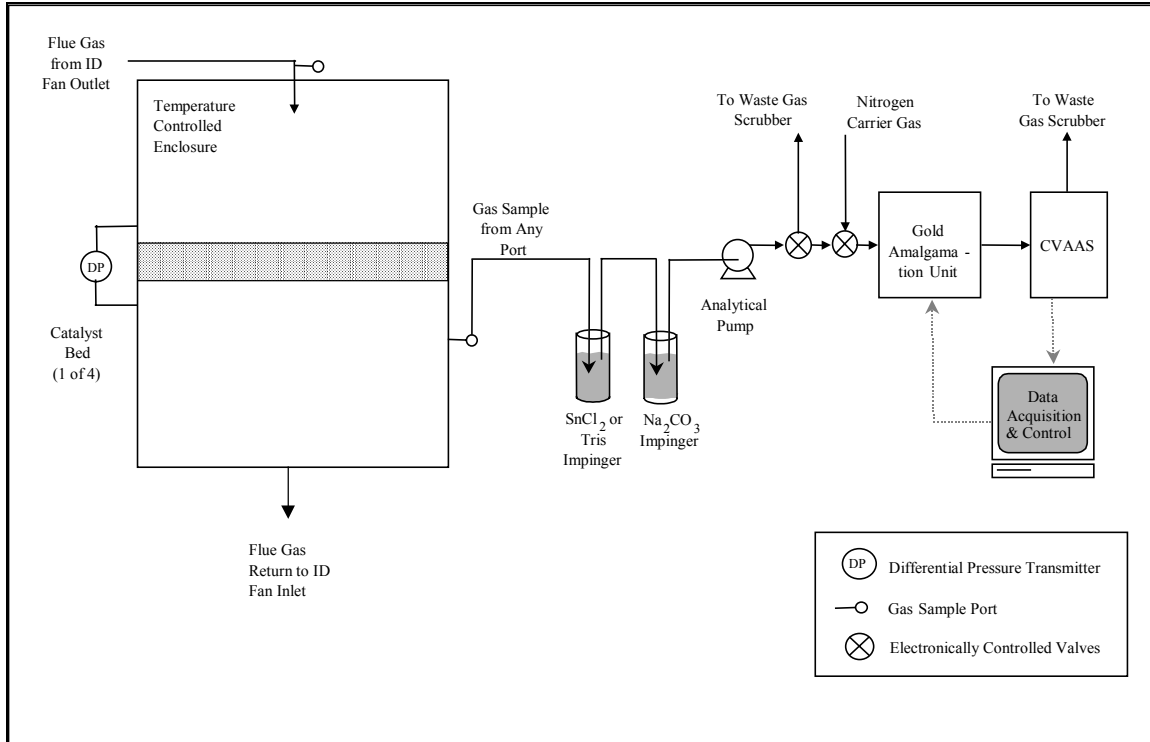


Figure 4-1. Schematic of the EPRI Semi-continuous Mercury Analyzer

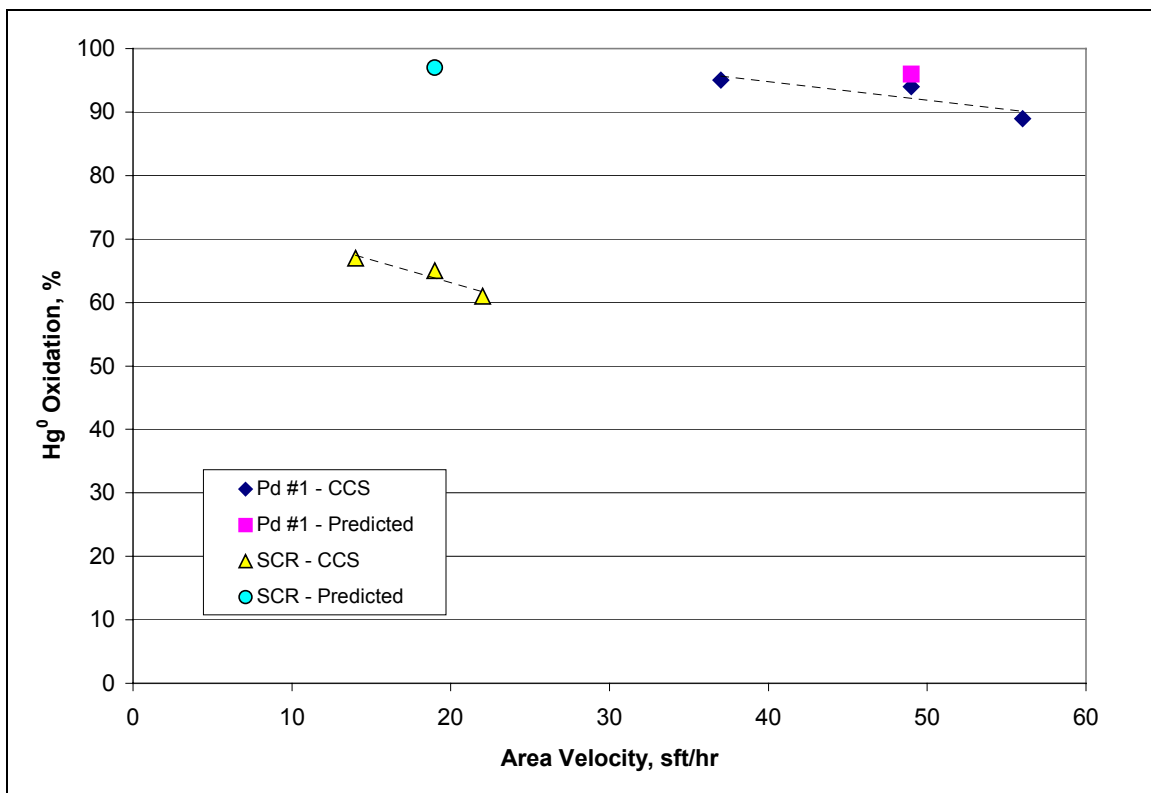


Figure 4-2. Predicted vs. Actual Catalyst Performance at CCS, October 2002

Table 4-1. October Catalyst Activity Results

Flue Gas Rate (acfm)	Inlet Total Hg (µg/Nm ³)	Inlet Hg ⁰ (µg/Nm ³)	Inlet Hg Oxidation (%)	Pd #1 Results			SCR Catalyst Results		
				Catalyst Outlet Hg ⁰ (µg/Nm ³)	Catalyst Hg ⁰ Oxidation (%)	Catalyst Area Velocity (sft/hr)	Catalyst Outlet Hg ⁰ (µg/Nm ³)	Catalyst Hg ⁰ Oxidation (%)	Catalyst Area Velocity (sft/hr)
1500	8.3	4.6	43	0.25	95	37	1.5	67*	14*
2000	10.8	7.4	32	0.52	93*	49*	2.8	62	19
2300	8.0	4.7	42	0.50	89	56	1.8	61	22

*Conditions selected for long-term catalyst operation

Table 4-2. December Catalyst Activity Results

Flue Gas Rate (acfm)	Inlet Total Hg* (µg/Nm ³)	Inlet Hg ⁰ * (µg/Nm ³)	Inlet Hg Oxidation*	Pd #1 Results			SCR Catalyst Results		
				Catalyst Outlet Hg ⁰ (µg/Nm ³)	Catalyst Hg ⁰ Oxidation (%)	Catalyst Area Velocity (sft/hr)	Catalyst Outlet Hg ⁰ (µg/Nm ³)	Catalyst Hg ⁰ Oxidation (%)	Catalyst Area Velocity (sft/hr)
1000	- /14.3	- /9.1	- /36	-	-	-	6.4	30	10
1500	14.3/17.7	9.1/8.8	36/50	3.0	67	37	6.3	28**	14**
2000	17.7/16.7	8.8/8.8	50/47	4.1	53**	49**	7.0	21	19
2200	16.7/ -	8.8/ -	47/ -	3.7	58	54	-	-	-

*First value listed is the inlet condition for the Pd #1 catalyst, second value is for the SCR catalyst

**Denotes normal operating condition for catalyst

In the figure, the October oxidation percentage results for the two catalysts are plotted as a function of area velocity. Projected catalyst performance based on results of previous laboratory tests are also plotted.

The December results shown in Table 4-2 show a marked decrease in activity for both catalysts. The percentage oxidation of elemental mercury across the Pd #1 dropped from greater than 90% in October to approximately 50 to 70% in December. The elemental mercury oxidation across the SCR catalyst dropped from 60 to 70% in October to 20 to 30% in December. Figure 4-3 plots the catalyst activity data as a function of catalyst time in flue gas service, for operation of each catalyst at a flue gas flow rate of 1500 acfm (37 sft/hr for Pd #1 and 14 sft/hr for the SCR catalyst). The data for Pd #1 at its normal flue gas flow rate of 2000 acfm data were not plotted in this figure because the December data for that flow rate appear to be anomalous, showing a lower oxidation percentage than was measured at the higher flue gas rate.

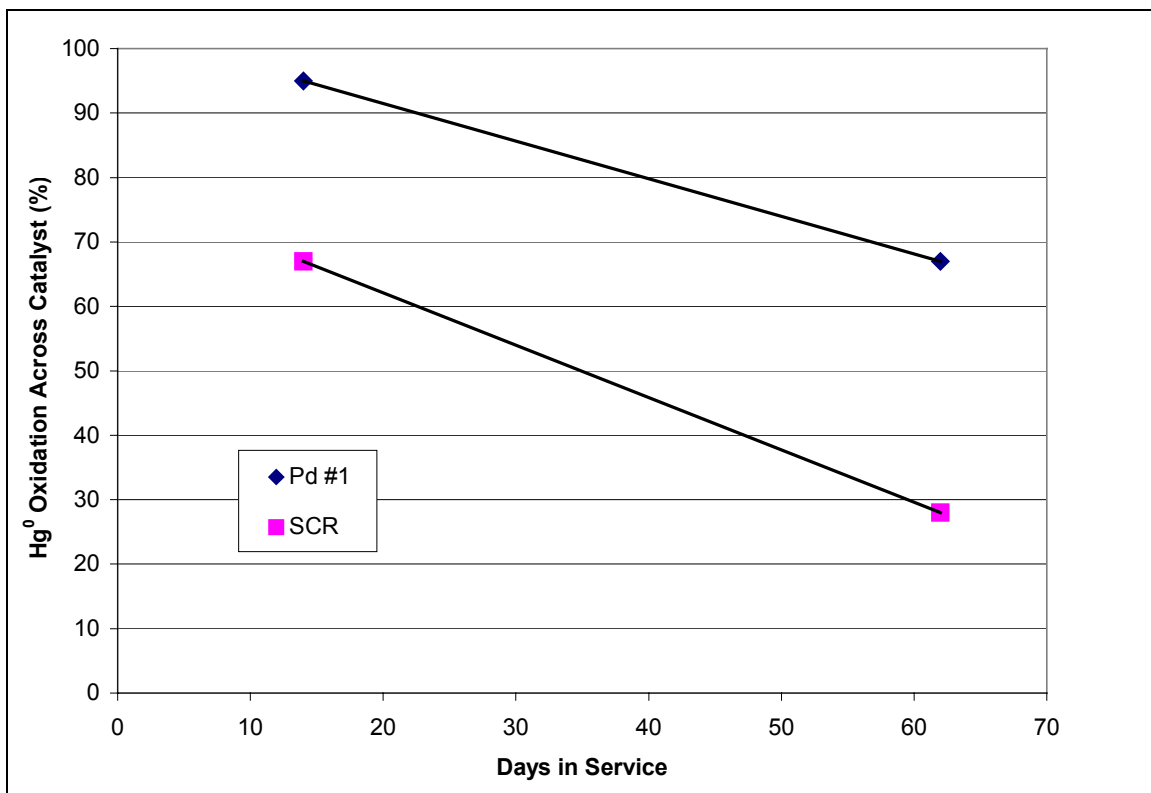


Figure 4-3. Apparent Loss of Activity versus Time in Service at CCS at 1500 acfm Flue Gas Flow Rate

There are several possible explanations for this apparent loss of activity:

1. The catalyst outlet elemental mercury concentration data from December could be biased high due to an undetected measurement problem, although this does not seem likely given the normal appearing inlet values.
2. The catalyst surfaces may be becoming fouled due to a buildup of fly ash, in spite of the catalyst being installed downstream of a high-efficiency ESP.
3. Some species in the lignite-fueled flue gas at CCS may be causing rapid loss of catalyst activity.

It seems likely that explanation number 2 is the cause of the apparent activity loss. At the measured particulate loading of 0.004 gr/dscf in the pilot unit inlet gas, approximately 60 lb of fly ash would have passed through the Pd #1 catalyst at 2000 acfm for 62 days. If much of that fly ash accumulated within the catalyst chamber and/or on the honeycomb surfaces, this could account for the observed loss of apparent activity.

Further evidence of fly ash buildup is seen in the measured pressure drop across the catalyst chambers. When the two catalysts were put into service in October, the initial clean catalyst pressure drop across each chamber was less than 0.5 in. H₂O. Since that time, the indicated pressure drop across the chambers has steadily increased, to about 1.5 in. H₂O across the SCR catalyst and over 3 in. H₂O across the Pd #1 catalyst. The third catalyst, SBA #5, also showed a dramatic increase in pressure drop over time since it was placed in service in early December. Figure 4-4 shows pressure drop versus time for all four catalyst chambers (including the empty chamber) since the beginning of October. The pilot unit instrumentation is scaled to read a maximum of 3 in. H₂O differential, hence the pressure drop data for the SBA #5 and Pd #1 catalysts are currently pegged at full scale.

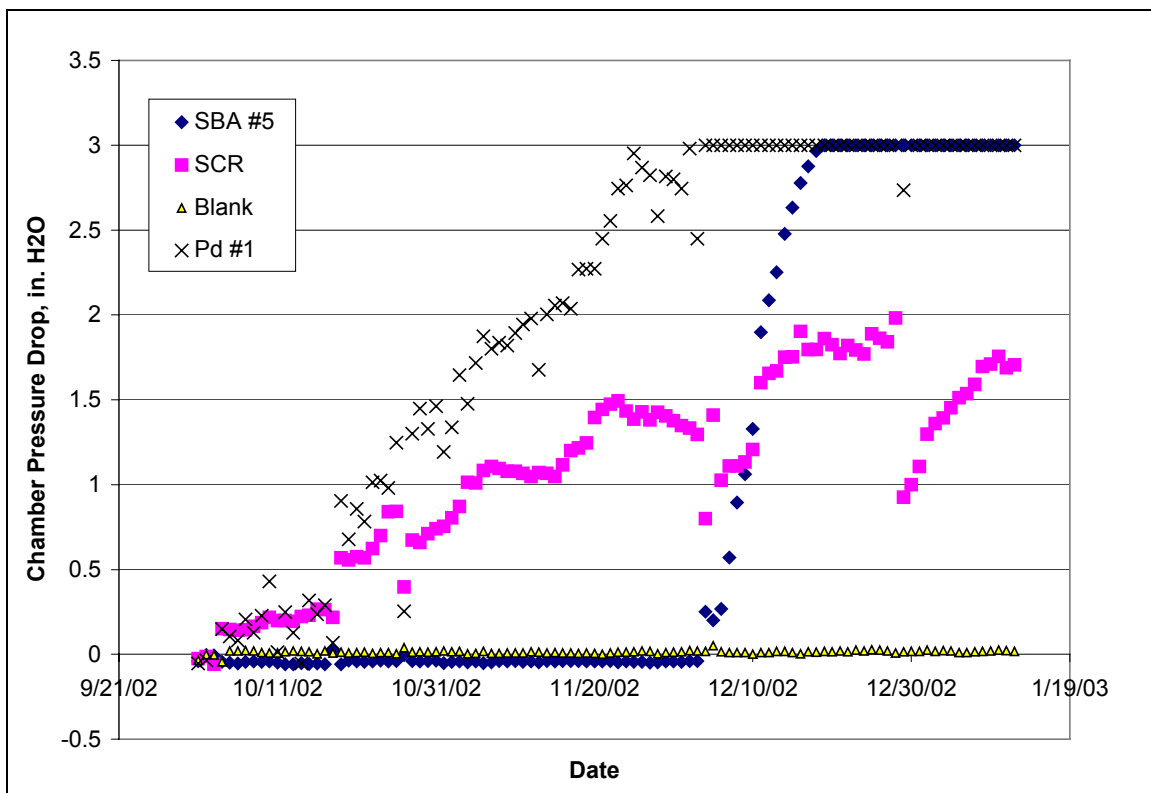


Figure 4-4. Catalyst Chamber Pressure Drop versus Time in Service.

The next catalyst activity measurement trip is scheduled to occur in January. At that time, it will be determined whether the apparent loss of activity has continued with time, stabilized, or has reversed. Also, the catalyst pressure drop indications by the pilot unit instrumentation will be verified and the instruments will be re-scaled to read higher differential pressures. If the activity loss has continued and the pressure drop increase is confirmed, it is likely that one or more of the catalyst chambers will be opened to observe whether there is significant fly ash buildup. If so, we will likely attempt to clean the catalyst surfaces with dry compressed air. Also, we are considering removing one 6-in. by 6-in. by 3-in. block of Pd #1 honeycomb catalyst from the pilot unit (about 1.3% of the pilot catalyst surface area) for laboratory evaluation.

The January trip will also provide the first opportunity to measure the activity of the SBA #5 catalyst, assuming that catalyst has achieved mercury adsorption breakthrough (i.e., the catalyst inlet and outlet total mercury concentrations are approximately equal). However, it too may be adversely affected by fly ash buildup, based on the observed pressure differential readings.

4.2 Flue Gas Characterization at CCS

As part of the initial catalyst activity characterization trip conducted in October, a number of manual flue gas characterization measurements were made. The measurements included:

- CCS FGD system inlet and outlet mercury by the draft Ontario Hydro method,
- Pilot unit inlet and catalyst outlet mercury by the draft Ontario Hydro method,
- Pilot unit inlet metals by Method 29,
- Pilot unit inlet halogens by Method 26a,
- Pilot unit inlet and catalyst outlet sulfuric acid by the Controlled Condensation method, and
- Pilot unit inlet and catalyst outlet NO and total NO_x by the gas detection tube method.

These results are presented and discussed in the following paragraphs.

4.2.1 Ontario Hydro Results

Table 4-3 summarizes the results of measurement made at CCS by the draft Ontario Hydro method. Table 4-4 compares the results of the Ontario Hydro method results for the pilot unit to those measured by the EPRI semi-continuous mercury analyzer (also called the mercury semi-continuous emissions monitor or SCEM) during the same time period.

The results in Table 4-3 show that the mercury in the FGD inlet/pilot unit inlet flue gas at CCS is not very highly oxidized (less than 50% oxidation), and that the total mercury concentrations are typically in the range of 10 to 20 µg/Nm³. This agrees with the

Table 4-3. Summary of Ontario Hydro Results from CCS, October 2002 (all values represent the average from three individual measurement runs)

	Hg Concentration ($\mu\text{g}/\text{Nm}^3$)			Total Hg Oxidation (%)	Hg ⁰ Oxidation Across Catalyst (%)
	Hg ⁺²	Hg ⁰	Total		
FGD Inlet	7.1	11.6	18.7	38	-
FGD Outlet	0.2	11.7	11.8	1.4	-
Pilot Inlet	6.0	11.3	17.3	35	-
Pilot Outlet:					
SCR Catalyst (1500 acfm)	11.5	3.5	15.0	77	69
Pd #1 Catalyst (2000 acfm)	15.4	0.7	16.1	96	94

Table 4-4. Comparison of Ontario Hydro Results with EPRI Mercury Semi-continuous Emissions Monitor Results from CCS, October 2002

	Hg Concentration ($\mu\text{g}/\text{Nm}^3$)			Total Hg Oxidation (%)	Hg ⁰ Oxidation Across Catalyst (%)
	Hg ⁺²	Hg ⁰	Total		
Pilot Inlet – OH	6.0	11.3	17.3	35	-
Pilot Inlet – SCEM	7.5	9.1	16.6	45	-
Pilot Outlet:					
SCR Catalyst – OH (1500 acfm)	11.5	3.5	15.0	77	69
SCR Catalyst – SCEM (1500 acfm)	12.7	2.9	15.6	81	68
Pd #1 Catalyst – OH (2000 acfm)	15.4	0.67	16.1	96	94
Pd #1 Catalyst – SCEM (2000 acfm)	15.2	0.85	16.1	95	91

measured coal mercury concentration of 0.08 mg/kg. Combustion calculations using this coal mercury concentration predict a flue gas concentration of 15 $\mu\text{g}/\text{Nm}^3$, assuming all of the coal mercury is present in the gas phase at the FGD inlet.

Also, the data show that oxidized mercury is removed across the FGD absorbers at high efficiency (97.6% removal) and that little or no elemental mercury is re-emitted. That is, the increase in elemental mercury concentration across the FGD absorber is negligible (a measured 0.6% increase in concentration, or an increase of less than 0.1 $\mu\text{g}/\text{Nm}^3$).

The results in Table 4-4 show excellent agreement between the EPRI SCEM and the draft Ontario Hydro method. The measured total mercury concentrations at each of the three pilot unit measurement locations are very close between the two methods, and the measured elemental mercury oxidation percentages across the two catalysts also agree well.

Some relative error is seen when comparing the pilot unit inlet oxidation percentages between the two methods. However, some error might be expected considering that the Ontario Hydro method takes an integrated, speciated sample at each location over the sampling period while the EPRI SCEM had to cycle through four measurement locations and between elemental and total mercury measurements over that same period. The SCEM data may reflect temporal changes in inlet flue gas speciation that were averaged out over time in the Ontario Hydro results.

4.2.2 Flue Gas Metals (Method 29)

Table 4-5 summarizes the results of flue gas metals concentration measurements made at CCS in October by Method 29. The results in the table represent averages of three individual measurement runs. Also shown in the table are gas phase metals concentrations measured at two sites at which mercury oxidation catalysts were previously evaluated in a DOE project, but at a much smaller scale. Site 1 fires a Texas lignite fuel, and Site 2 fires a Powder River Basin coal.

The results in Table 4-5 show that the flue gas at CCS contains considerably higher vapor-phase metal concentrations than the two previous sites for the following metals: aluminum, arsenic, barium, calcium, chromium, iron, magnesium, molybdenum, nickel, titanium, and vanadium. It is interesting to note that selenium, which was theorized to have played a role in the rapid loss of catalyst activity at Site 1 in the PRDA project, is present at much lower concentrations at CCS than at either PRDA site.

Also, of the vapor-phase metals present at higher concentration at CCS, arsenic is known to be a strong poison for SCR catalysts. It could be theorized that the relatively high vapor-phase arsenic concentrations at CCS are contributing to the apparent loss of activity in the SCR (titanium-vanadium) and palladium-based catalysts. However, because the mechanisms for elemental mercury oxidation on the catalysts are not known at this time, it is not apparent whether arsenic poisoning would also affect these catalysts in this service.

4.2.3 Flue Gas Halogen Species (Method 26a)

Table 4-6 summarizes the results of flue gas halogen species concentration measurements made at CCS in October by Method 26a. The results in the table represent averages of three individual measurement runs.

Table 4-5. Flue Gas Metals Concentrations at CCS by Method 29 (Pilot Unit Inlet Location) – all values in ppbv (dry gas basis)

Metal	Site 1 Gas Phase Concentration	Site 2 Gas Phase Concentration	CCS Gas Phase Concentration	CCS Particulate Phase Concentration*
Aluminum	20.2	10.2	569	35.3
Antimony	0.17	0.07	0.71	0.49
Arsenic	ND	0.01	0.53	0.16
Barium	0.09	0.08	28.2	0.26
Beryllium	0.27	0.06	0.28	<0.77
Cadmium	0.05	0.02	<0.06	0.01
Calcium	41.0	15.7	509	121
Chromium	0.19	0.12	0.43	0.16
Cobalt	ND	0.02	<1.14	<1.18
Copper	0.48	0.56	0.39	1.32
Iron	9.08	8.62	146	19.3
Lead	0.11	0.05	0.12	0.04
Magnesium	3.02	3.05	177	11.3
Manganese	0.49	2.24	1.94	0.72
Molybdenum	0.01	0.02	1.13	<0.59
Nickel	0.41	0.17	1.48	0.15
Potassium	89.3	3.17	66.3	169
Selenium	26.8	2.94	0.70	0.51
Silver	0.01	0.01	<0.25	<0.05
Sodium	191	120	235	337
Strontium	0.09	0.04	-	-
Thallium	4.52	0.40	0.13	<0.14
Tin	-	-	0.34	18.8
Titanium	0.64	0.16	12.5	0.54
Vanadium	0.06	0.00	1.41	<1.37
Zinc	2.09	2.30	0.84	3.79

*Mass present in the particulate (solid phase) has been converted to an equivalent gas-phase concentration.

Table 4-6. Flue Gas Halogen Species Concentrations at CCS by Method 26a (Pilot Unit Inlet Location)

Species	Concentration (ppmv, dry basis)
HCl	1.56
Cl ₂	<0.04
HF	5.31
F ₂	0.12

As expected, the halogen species concentrations are quite low. It is a bit surprising to see that the HF concentrations in the flue gas are higher than the HCl concentrations. In bituminous and subbituminous coals, the opposite is typically the case.

Compared to the flue gases at three previous PRDA sites, the HCl concentrations at CCS are similar to those at Site 1 (Texas lignite) and Site 2 (PRB), but over an order of magnitude lower than at Site 3 (bituminous coal). The chlorine (Cl₂) concentrations are lower than the values at all three PRDA sites. The HF concentrations at CCS are higher than at PRDA Sites 1 and 2, but lower than at Site 3, while the fluorine concentrations are higher than at any of the PRDA sites.

4.2.4 Flue Gas Sulfuric Acid Concentrations (Controlled Condensation Method)

Flue gas sulfuric acid concentrations were measured for two reasons. One is that in the previous PRDA project, sulfuric acid was identified as a possible contributor to loss of mercury oxidation catalyst activity, perhaps due to adsorption or precipitation of sulfates that block active catalyst sites. Consequently, pilot unit inlet sulfuric acid concentrations were measured for comparison to values at other sites where mercury oxidation catalysts have been tested.

The second reason is that there has been some concern that catalysts active for oxidizing elemental mercury might also be active for oxidizing flue gas SO₂ to SO₃. SO₃ combines with flue gas moisture to form vapor-phase and/or condensed sulfuric acid. Sulfuric acid in the flue gas can lead to undesirable effects such as duct corrosion and increased plume opacity. Also, conversion of SO₂ to SO₃ could produce acid sulfates that can plug the honeycomb catalysts. Thus, oxidation of SO₂ to SO₃ across these mercury oxidation catalysts would be undesirable.

The results of flue gas sulfuric acid concentration measurements, by the Controlled Condensation method, are summarized in Table 4-7. Each data point represents the average of three runs. The average SO₂ concentration measured simultaneously over the course of the three Controlled Condensation runs at each location is also shown. The measured values agree reasonably well with the results of combustion calculations for a coal sample from October 21, which predict an SO₂ concentration of 940 ppmv (dry basis).

Table 4-7. Flue Gas Sulfuric Acid Concentrations at CCS by the Controlled Condensation Method

Location	Sulfuric Acid Concentration (ppmv, dry basis)	SO₂ Concentration (ppmv, dry basis)
Pilot Unit Inlet	0.21	933
SCR Catalyst Outlet	0.09	1040
Pd #1 Catalyst Outlet	0.04	836

The results in Table 4-7 do not indicate oxidation of SO₂ to SO₃ across the catalysts. In fact, the catalyst outlet sulfuric acid concentrations are slightly lower than the inlet values. This may indicate some adsorption of sulfuric acid across the catalysts, either on the catalyst substrate itself or on fly ash collected on catalyst surfaces, but could just as well represent run-to-run measurement variability. Concentrations of 0.2 ppmv and lower are at the practical lower detection limit for the method. The measured concentrations at the pilot unit inlet are lower than at PRDA Sites 1 and 3 (Texas lignite and bituminous coal, respectively) and about the same as at Site 2 (PRB).

4.2.5 Flue Gas NO₂ Concentration by Gas Detection Tubes

Flue gas NO₂ concentrations were measured upstream of the pilot unit and downstream of both catalysts using gas detection tubes. As for the oxidation of SO₂ to SO₃ as discussed above, there was concern that the oxidation catalysts used in the pilot unit might similarly catalyze the oxidation of NO to NO₂. While NO is a colorless gas, NO₂ has a brown color that can lead to flue gas plume coloration and increased opacity at concentrations as low as 10 ppm. Since significant oxidation of NO to NO₂ would be an undesirable side effect of mercury oxidation catalysts, this was an important measurement regarding the viability of a mercury oxidation process.

The project plan calls for measurement of flue gas NO and NO₂ concentrations upstream and downstream of each catalyst using a continuous or semi-continuous NO_x analyzer. Since there would be a significant effort involved to temporarily set up this analyzer, and since only two of the four catalysts were in service in October, it was decided to delay the analyzer measurements. Instead, gas detection tubes were used to provide an indication of any NO to NO₂ conversion across the two catalysts in service. Unfortunately, there is an interferent in the flue gas with the NO₂ detection tube, so changes in NO₂ concentration across the catalysts had to be determined by difference using NO and NO_x detection tubes. The results of these measurements are summarized in Table 4-8.

Table 4-8. Flue Gas NO_x Concentration Data Using Gas Detection Tubes

	NO_x (ppmv wet)	NO (ppmv wet)	NO₂ (ppmv wet, by difference)
Pilot Unit Inlet	150	150	0
SCR Catalyst Outlet	150	140	10
Pd #1 Catalyst Outlet	150	140	10

These results indicate the possibility that approximately 10 ppmv of the flue gas NO was oxidized to NO₂ across each catalysts (about 7% of the inlet NO). A concentration of 10 ppmv of NO₂ in the stack flue gas might result in some visible plume coloration. However, it is likely that any NO₂ formed would be scrubbed along with oxidized mercury in the downstream wet scrubber.

The apparent NO₂ concentrations shown in Table 4-8 were measured by a relatively imprecise method (the gas detection tubes results are read to the nearest 10 ppmv). Also, the NO₂ concentrations are calculated as the difference between two much larger numbers. Consequently, the indicated NO₂ concentrations should be considered to have a significant error band. It is estimated that the actual NO₂ concentrations downstream of the two catalysts are in the range of 0 to 20 ppmv.

In a future reporting period, once all four catalysts are in service, a NO_x analyzer will be brought to the pilot unit site and set up to quantify NO and NO₂ concentrations upstream and downstream of all four catalysts on a semi-continuous basis. This should provide a better measure of any NO to NO₂ oxidation across the catalysts. The above results suggest that any such oxidation is relatively minor on a percentage basis, though.

4.3 Laboratory Evaluation of Candidate Catalysts

Testing of catalyst cores in the laboratory for mercury oxidation activity continued during this quarter, under simulated North Dakota lignite and PRB coal (Spruce) flue gas conditions. In previous technical progress reports for this project we reported scatter in laboratory results that appears to have been caused by an interference between some component in the sample gas exiting Pd #1 cores and the Tris(hydroxymethyl)amino-methane (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 much of the previous catalyst performance results for Pd #1 sample cores to be suspect.

In the preceding quarter (July 1 through September 30, 2002), Pd #1 tests were repeated using potassium chloride (KCl) rather than Tris solution to remove oxidized mercury from the sample gas going to the laboratory mercury analyzer, when measuring for elemental mercury. KCl solution is used to capture oxidized forms of mercury in the draft Ontario Hydro gas sampling method and has been shown to produce similar results as the Tris solution in previous URS tests. The apparent interference was eliminated by the solution change, and new results reported last quarter were used to predict the palladium loading and the catalyst volume required for the pilot unit for the Pd #1 catalyst. As shown previously in this report, the field results for Pd #1 agreed quite well with the laboratory results measured using KCl impingers.

During the current reporting period, laboratory tests were conducted at simulated CCS and Spruce Plant flue gas conditions with current catalysts and with a new candidate

catalyst material, gold. Gold has been patented by TVA as a flue gas elemental mercury oxidation catalyst.

The results of tests conducted at CCS conditions early in the quarter appear to indicate that the gold catalyst compares favorably with Pd #1 for elemental mercury oxidation activity. However, late in the quarter, it was determined that the KCl impinger solutions were being depleted very rapidly during these laboratory runs. The result of this depletion is a low bias in the indicated elemental mercury concentration. Thus, there is concern that the favorable results for the gold catalyst from early in the quarter were biased by depleted KCl impinger solutions. These questionable results are not reported here.

Because of concern over depletion of the KCl impinger solutions, midway through the quarter the laboratory run procedures were modified so the performance of each catalyst core was measured both with fresh Tris and fresh KCl solutions. Good agreement between results with the two impinger solution types was taken as an indicator that potential biases with each solution type were avoided. If the results with the two impinger solution types did not agree well, the test was repeated.

This procedure was used to begin evaluation of candidate catalyst materials for the pilot testing to be conducted at Site 2, CPS' Spruce Plant, which fires PRB coal. Table 4-9 compares the simulation gas compositions for CCS versus Spruce Plant simulations.

Table 4-9. Gas Conditions for Host Site Simulations

Species	CCS Conditions	Spruce Conditions
SO ₂ (ppm)	500	200
NO _x (ppm)	200	200
HCl (ppm)	6	6
O ₂ (%)	5	5
CO ₂ (%)	12	12
H ₂ O (%)	9	7
N ₂ (%)	Balance	Balance
Temperature (°F)	350	300

Table 4-10 summarizes the results of laboratory tests conducted late in the quarter under simulated Spruce Plant conditions. The result shown for the gold catalyst are still considered suspect, because the results with gold catalyst did not agree well between the Tris and KCl impinger trains. The gold tests are currently being repeated. The results for gold catalyst in Table 4-10 should be considered preliminary at this time.

If the gold catalyst laboratory performance holds up when the data are re-analyzed, it is likely that gold will be selected as one of the four catalysts for evaluation at Spruce Plant.

Table 4-10. Laboratory Simulation Results (average results using KCl and Tris impingers for measuring elemental mercury concentrations)

Catalyst	Gas Flow Rate (l/min)	Inlet Hg⁰ (µg/Nm³)	Outlet Hg⁰ (µg/Nm³)	Hg⁰ Oxidation (%)
Pd #1 3x; 1" core	0.94	31.1	2.88	90.8
Pd #1 3x; 1" core	1.3	21.7	2.61	88.0
Pd #1 3x; 1" core	1.7	15.9	1.75	89.0
SBA #5; 0.5" core	0.94	24.8	2.73	89.0
SBA #5; 0.5" core	1.3	18.9	2.63	80.8
SBA #5; 0.5" core	1.7	15.2	2.73	82.0
Au 1x; 1" core	0.94	34.0	0.94*	97.2*
Au 1x; 1" core	1.3	12.4	0.61*	95.1*
Au 1x; 1" core	1.7	9.48	1.30*	86.3*

*Value is suspect because of poor agreement between Tris and KCl impinger results

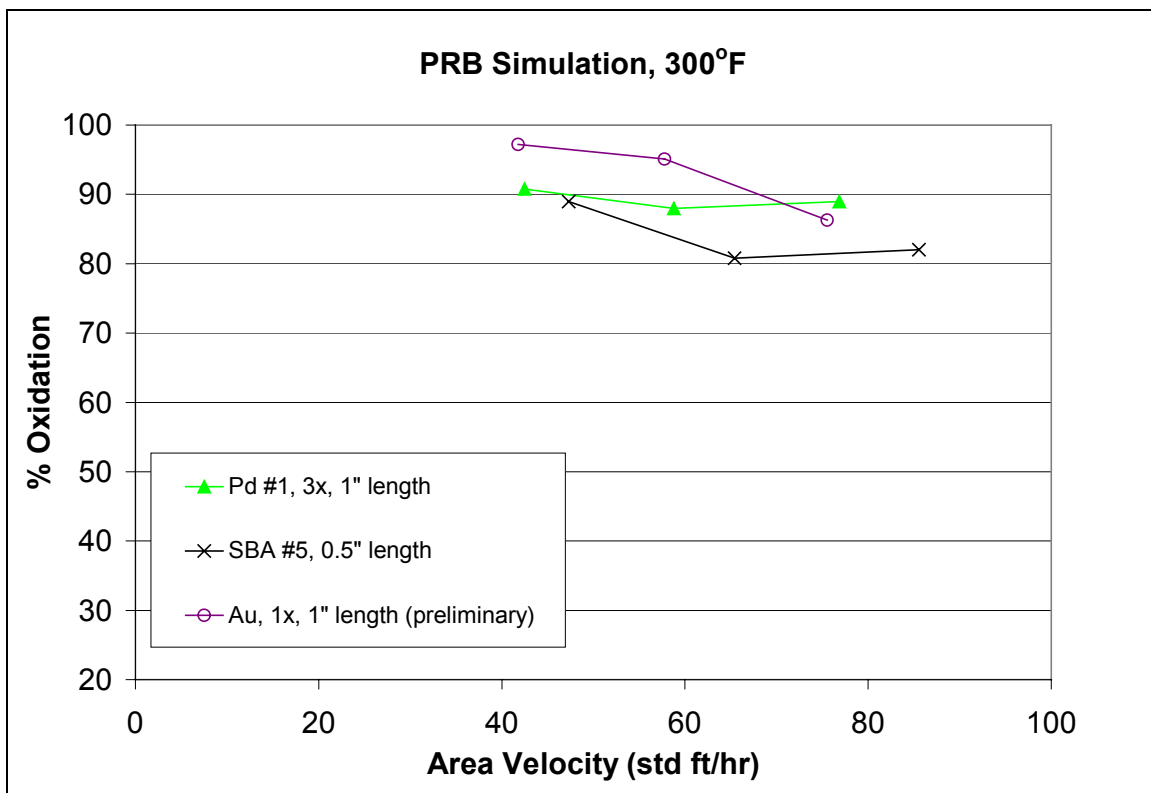


Figure 4-5. Effect of Area Velocity on Catalytic Oxidation of Mercury under Site 2 Conditions

4.4 Catalyst Supply

During the quarter, the SBA #5 catalyst was custom-prepared by a U.S.-based catalyst vendor, as extruded monoliths in an alumina substrate. Since this is the first time that this material has been processed into a honeycomb form, the vendor had to conduct a considerable amount of development work to determine mixing, extruding, drying and firing parameters. Commercial equipment was used, so these experimental efforts had to be scheduled between commercial catalyst production runs.

The “production” extrusion of the pilot unit SBA #5 catalyst blocks was completed at the end of September. During October, these catalyst blocks were dried and fired, and in November they were “canned” into metal containers of appropriate dimensions for the pilot unit. Figure 4-5 shows an overall view of one of the three SBA #5 catalyst cans that were installed in the pilot unit in December. Figure 4-6 is a close-up shot of the same can, which shows how individual 6-in. by 6-in. blocks were stacked to produce the 36-in. by 36-in. cross section.

In December, the preparation of the C #6 catalyst began. A 300-lb lot of activated C #6 material, prepared the Illinois State Geological Survey and MaxWell Engineering and Consulting, was ground to size for extrusion. The extrusion, drying, firing and canning of these catalyst blocks are expected to occur during the upcoming quarter. It is hoped that the C #6 catalyst will be installed in the pilot unit at CCS by the end of the next quarter.



Figure 4-6. Photograph of One of Three SBA #5 Catalyst Cans



Figure 4-7. Close-up of One of Three SBA #5 Catalyst Cans