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

Quarterly Technical Progress Report

July 1, 2002 – September 30, 2002

Cooperative Agreement No: DE-FC26-01NT41185

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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 July 1, 2002 through September 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 fourth full reporting period for the subject Cooperative Agreement. During this period, most of the project efforts were related to completing, installing and starting up the pilot unit, completing laboratory runs to size catalysts, and procuring 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 July 1, 2002 through September 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, July 1, 2002 through September 30, 2002, is the fourth 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 were related to constructing, installing and starting up the pilot unit to be used to evaluate mercury oxidation catalyst activity over time, laboratory evaluation of candidate catalysts, and procuring the catalyst materials to be tested.

The pilot unit fabrication was completed during the current quarter. Insulation of the pilot unit and running of heat-traced and insulated sample lines for the semi-continuous flue gas mercury analyzer were the only major fabrication efforts that remained at the beginning of the quarter. All fabrication efforts were completed by the first week in August, and that the pilot unit was shipped out to the host site in North Dakota on August 9.

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 installation was completed by late August.

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.

Also during this reporting period, laboratory testing continued to support the selection and sizing of catalyst materials for evaluation at the pilot scale. Three of the catalysts (the SCR catalyst, the Carbon #6 (C #6) catalyst, and the Subbituminous Ash #5 (SBA #5) catalyst) were previously sized based on the laboratory performance data using simulated flue gases. The laboratory evaluation of the fourth, Palladium #1 (Pd #1) catalyst continued into the quarter due to apparent laboratory data problems. Early in the quarter, the laboratory data problems were resolved, and the catalyst was sized for the pilot unit.

The SCR catalyst was ordered during the previous quarter. Ceramics Gmbh and Company (was Siemens) prepared the catalyst and shipped it to CCS during the current quarter. At the completion of the laboratory effort mentioned above, the Pd #1 catalyst for the pilot unit was ordered from Prototech, prepared by them, and was shipped to CCS by the end of the quarter. The C#6 and SBA #5 catalysts were also ordered, and will be custom-prepared by Applied Ceramics, Inc. During the current quarter, Applied Ceramics conducted an experimental extrusion of the SBA #5 catalyst, as a preparation for the “production” run to prepare enough material for the pilot unit, and efforts continued to source enough of the C#6 experimental carbon to allow catalyst production.

Several subcontracts were awarded or completed during the current reporting period. Skotz, Inc. of Austin, Texas completed the subcontract for the mechanical fabrication of the pilot unit. David Bacon Inc. completed the subcontract for all of the pilot unit wiring, instrument tubing, and sample line installation; and Mid-state Insulation Company completed the subcontract to insulate the pilot unit. Thermon Heat Tracing Services completed a subcontract to heat trace and insulate the pilot unit inlet duct and the flue gas sample lines for the mercury analyzer.

Prototech, Inc., was awarded a subcontract to prepare the Pd #1 catalyst for the pilot unit, and MaxWell Engineering and Consulting was awarded a subcontract to activate enough of the C#6 material to provide a sufficient quantity of the raw material to Applied Ceramics.

2.2 Problems Encountered

The only significant problem encountered during the reporting period that would warrant discussion in this report is a delay in the preparation of the experimental catalysts, C #6 and SBA #5, by Applied Ceramics. These catalysts are being prepared as extruded monoliths in an alumina substrate. Since this is the first time that either of these materials has been processed into a honeycomb form, Applied Ceramics has had to conduct a considerable amount of development work to determine mixing, extruding, drying and firing parameters. Commercial equipment is being used for the extrusion, drying and firing of catalyst blocks for the pilot unit, so these experimental efforts have had to be scheduled between commercial catalyst production runs.

A "phase 1" test batch of the SBA #5 catalyst was prepared in September, as a means of evaluating extrusion, drying and firing parameters. After some trial and error, appropriate parameters were established, and the "production" extrusion of the pilot unit catalyst blocks was completed at the end of the month. During October, these catalyst blocks will be dried, fired, and "canned" into metal containers of appropriate dimensions for the pilot unit. The preparation of the C #6 catalyst will follow in November.

Because the first two catalysts (SCR and Pd #1) were already prepared and available for testing by the end of September, it was decided to load these catalysts and start up the pilot unit in early October. The SBA #5 and C #6 catalysts will be loaded and started in operation later, approximately at the end of November, after both have been prepared by Applied Ceramics and shipped to CCS.

3.0 Plans for Future Reporting Periods

3.1 Plans for Next Reporting Period

The next reporting period covers the time period October 1 through December 31, 2002. The plans for that period are to install the SCR and Pd #1 catalysts and start up the pilot unit with two of the four catalysts. Once these two catalyst materials have 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. Towards the end of the quarter (late November or early December) it is expected that the other two catalysts (SBA #5 and C #6) will have been completed and shipped to the site, and they will be installed and started up in flue gas service.

3.2 Prospects for Future Progress

During the subsequent reporting period (January 1 through March 31, 2003), it is expected that the four catalysts will be evaluated for elemental mercury oxidation performance during routine monthly evaluation trips. In later reporting periods (April 1 through June 30, 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 (~May 2003) and the second at the end of the 14-month long-term catalyst evaluation period at CCS (~December 2003). At the end of the year 2003, pilot testing should be completed at CCS.

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 by the end of December 2002, and that testing will commence at the second site, CPS' Spruce Plant, early in the year 2003.

4.0 Technical Results

This section provides details of technical results for the current reporting period (July 1, 2002 through September 30, 2002). The technical results presented include a discussion of the pilot unit installation and start up at CCS, the results of laboratory evaluations of the Pd #1 catalysts applied to honeycomb substrates, and a discussion of catalyst preparation efforts.

4.1 Pilot Unit Installation and Start Up

The pilot unit fabrication was 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 that remained at the beginning of the quarter. All fabrication efforts were completed by the first week in August, and that the pilot unit was shipped out to the first host site in North Dakota on August 9.

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 installation was completed by late August. Figure 4-1 shows the completed pilot unit as installed at CCS. This photograph was taken before the pilot unit inlet and outlet duct runs were insulated.

Figure 4-1. Pilot Skid as Installed at CCS (inlet duct is in the foreground).

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.

The start up went well. Pilot unit flow rates were readily controlled at 2000 acfm per compartment (although with no catalysts installed to add pressure drop) and pilot unit flue gas temperatures could be controlled above 300°F even before the inlet ductwork was insulated. No flue gas leaks of any significance were observed, and no problems were encountered dialing up the pilot unit's data acquisition system from off site and downloading process data files. The pilot unit was left operating with no catalyst load until the planned loading of the SCR and Pd #1 catalysts the first week of October.

4.2 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 (°F)	350

Catalyst testing during the quarter was with Pd #1 wash-coated at two different palladium loadings on the honeycomb. The results of the laboratory simulation runs are summarized in Table 4-2, and plotted as a function of area velocity in Figure 4-2. Figure 4-2 includes laboratory simulation data for Pd #1 that were reported in previous quarterly technical progress report (January through March 2002, and April through June, 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.

Table 4-2. Laboratory Simulation Results (all tests with KCl instead of Tris impingers when measuring elemental mercury concentrations)

Catalyst	Gas Flow Rate (l/min)	Inlet Hg^0 ($\mu g/Nm^3$)	Outlet Hg^0 ($\mu g/Nm^3$)	Hg^0 Oxidation (%)
Pd #1 5x; 2" core	0.98	22.3	0.52	97.7
Pd #1 5x; 2" core	1.3	16.7	0.30	98.2
Pd #1 5x; 2" core	1.7	12.9	0.00	100
Pd #1 3x; 2" core	0.98	23.6	0.00	100
Pd #1 3x; 2" core	1.3	17.8	0.70	96.1
Pd #1 3x; 2" core	1.7	13.6	0.32	97.7
Pd #1 3x; 1" core	0.98	23.4	0.41	98.2
Pd #1 3x; 1" core	1.3	17.7	1.17	93.4
Pd #1 3x; 1" core	1.7	13.5	1.31	90.3

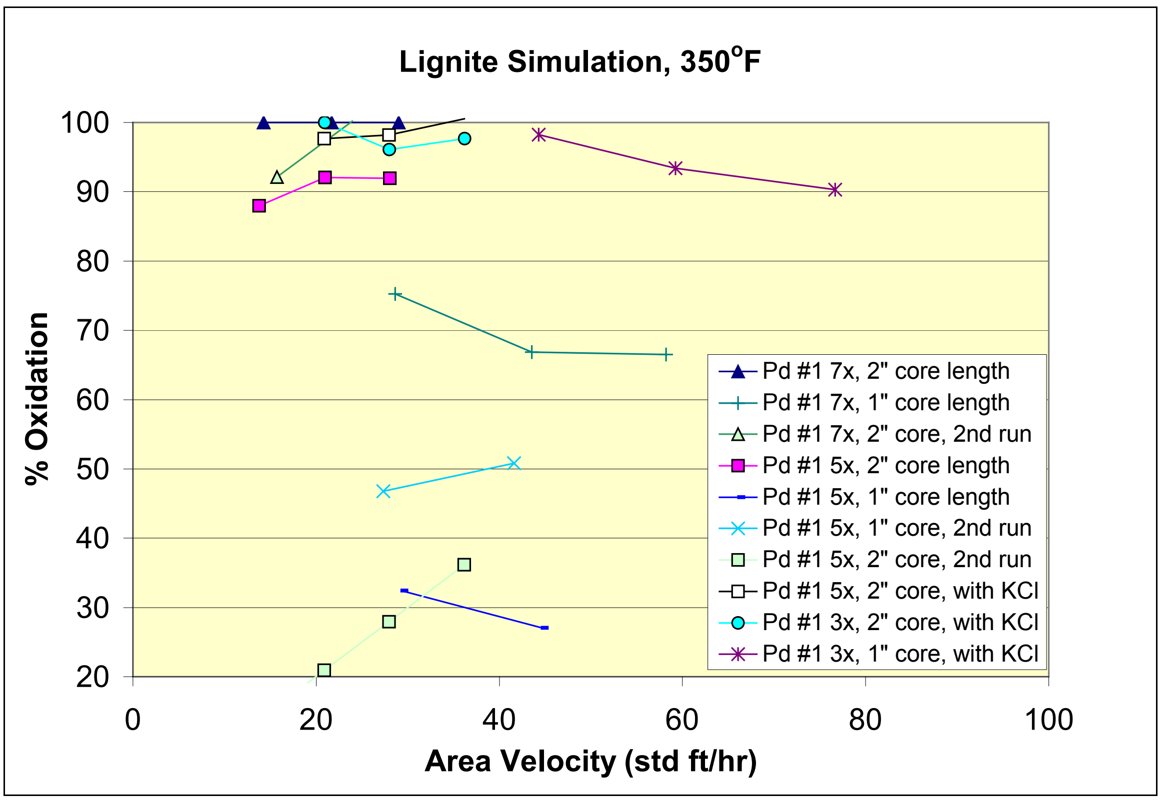
Lignite Simulation, 350°F
% Oxidation
Area Velocity (std ft/hr)
100
90
80
70
60
50
40
30
20
0
20
40
60
80
100
Pd #1 7x, 2" core length
Pd #1 7x, 1" core length
Pd #1 7x, 2" core, 2nd run
Pd #1 5x, 2" core length
Pd #1 5x, 1" core length
Pd #1 5x, 1" core, 2nd run
Pd #1 5x, 2" core, 2nd run
Pd #1 5x, 2" core, with KCl
Pd #1 3x, 2" core, with KCl
Pd #1 3x, 1" core, with KCl

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

The current test results in Table 4-1 and plotted in Figure 4-2 show high oxidation percentages (>90%) for both palladium loadings when tested at either the 2-inch or 1-inch core lengths, and area velocities in the range of 20 to 80 sft/hr. The previous results for Pd#1 plotted in Figure 4-2, for palladium applied at higher loadings on the honeycomb and for both core lengths, show a great deal of scatter and generally lower performance. The major factor contributing to this scatter 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 previous catalyst performance results in Figure 4-2 to be suspect.

In the tests conducted this quarter, summarized in Table 4-1, the Pd #1 tests were repeated 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. Potassium chloride solution is used to capture oxidized forms of mercury in the draft Ontario Hydro gas sampling method and has been shown to prove similar results as the Tris solution in previous URS tests. The apparent interference was eliminated by the solution change, and these new results were used to determine the palladium loading and the catalyst volume required for the pilot unit for the Pd #1 catalyst.

Table 4-3 shows the planned honeycomb cell pitch dimensions for each catalyst as required for the pilot unit and the overall dimensions of each. The overall catalyst dimensions required for the pilot unit were predicted by an empirically adjusted mass transfer model previously developed by URS. The model was described in the previous technical progress report, but basically 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 includes the dimensions of the honeycomb core samples tested in the laboratory.

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	3.7	46	3.7	46	35.4 x 35.4	19.7	19
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	30 x 30	9	49

In general, the catalysts were sized to achieve a predicted 95% oxidation of elemental mercury in the flue gas treated, as determined by laboratory results and the mass transfer model mentioned above. The planned catalyst sizing is considered to be conservative (e.g., area velocities in the range of 19 to 49 sft/hr). It is hoped that the field performance for these catalysts will be above 95% oxidation of elemental mercury at design conditions. 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.

4.3 Catalyst Supply

Ceramics Gmbh and Co. (was Siemens) has proceeded with the preparation of a block of SCR catalyst based on the dimensions in Table 4-3. The completed catalyst block was shipped to CCS in late July. Figure 4-3 shows a photograph of the completed catalyst block, ready for installation in the pilot unit.

Figure 4-3. Ceramics Gmbh & Co. Catalyst Block Ready for Installation in Pilot Unit.

At the completion of the laboratory effort mentioned above, the Pd #1 catalyst for the pilot unit was ordered from Prototech, prepared by them, and was shipped to the CCS site by the end of the quarter.

The C#6 and SBA #5 catalysts were also ordered, and will be custom-prepared by Applied Ceramics. These catalysts are being prepared as extruded monoliths in an alumina substrate. Since this is the first time that either of these materials has been processed into a honeycomb form, Applied Ceramics has had to conduct a considerable amount of development work to determine mixing, extruding, drying and firing parameters. Commercial equipment is being used for the extrusion, drying and firing of catalyst blocks for the pilot unit, so these experimental efforts have had to be scheduled between commercial catalyst production runs. During the current quarter, Applied Ceramics conducted an experimental extrusion of the SBA #5 catalyst, as a preparation for the "production" run to prepare enough material for the pilot unit. Figure 4-4 is a photograph of a sample 6-inch by 6-inch by 3-inch deep catalyst block of the SBA #5 test extrusion, prepared by Applied Ceramics at the requested cell pitch.

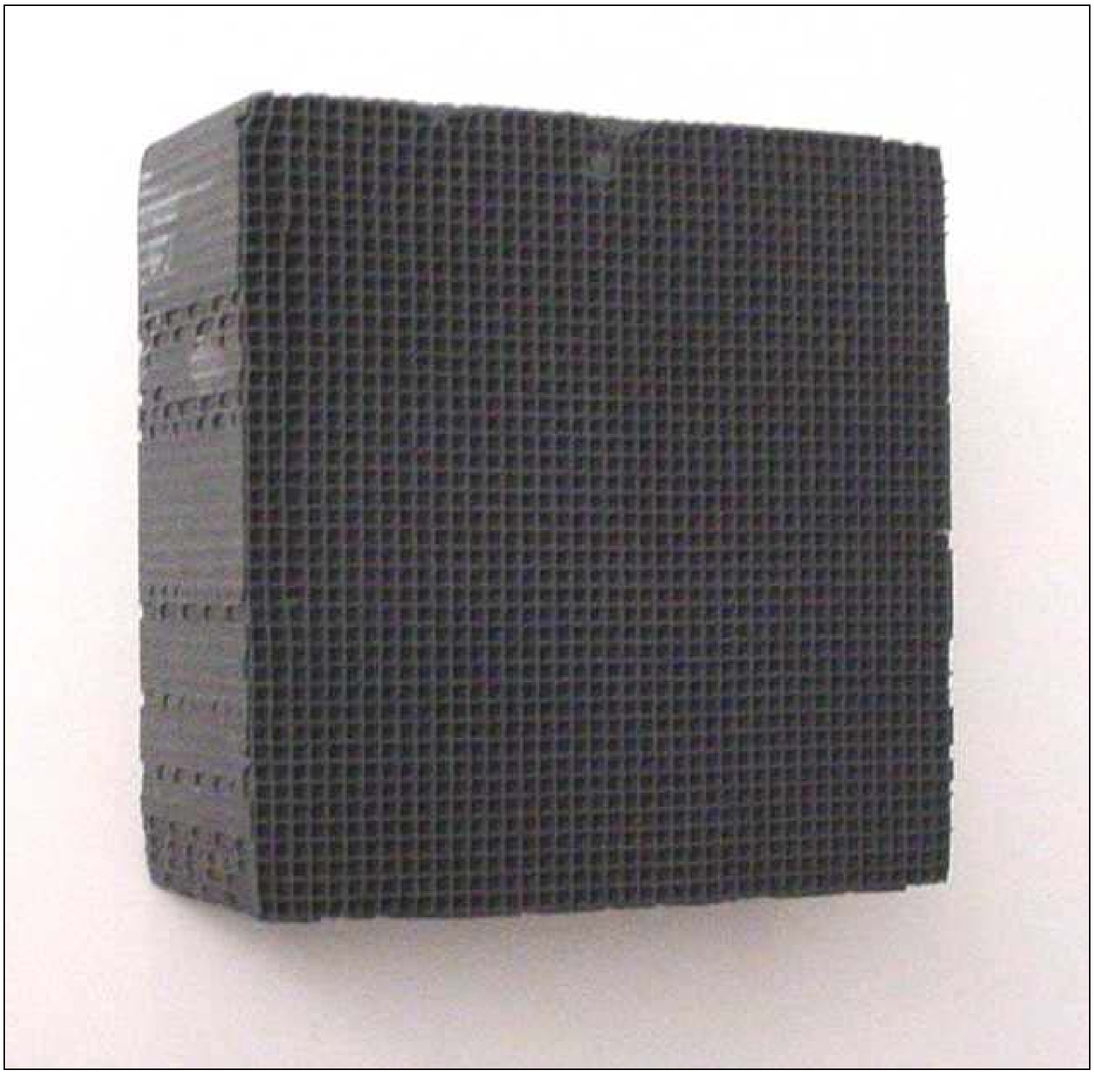

Figure 4-4. Sample Catalyst Block for SBA #5, as Prepared by Applied Ceramics

Now that this block has been successfully prepared, Applied Ceramics will prepare enough blocks of these sizes for both the C #6 and SBA #5 to produce composite catalyst blocks of each of the overall dimensions shown in Table 4-3. The "production" extrusion of the pilot unit SBA #5 catalyst blocks was completed at the end of September. During October, these catalyst blocks will be dried, fired, and "canned" into metal containers of appropriate dimensions for the pilot unit.

The preparation of the C #6 catalyst will follow in November. During the current quarter, efforts continued to source enough of the C#6 experimental carbon to allow production of the C #6 catalyst extrusions. In September, the Illinois State Geological Survey and MaxWell Engineering and Consulting prepared and activated approximately 300 lb of the C#6 material, to provide a sufficient quantity of the raw material to Applied Ceramics.

Because the first two catalysts (SCR and Pd #1) were already prepared and available for testing by the end of September, it was decided to load these catalysts and start up the pilot unit with these catalysts in early October. The SBA #5 and C #6 catalysts will be loaded and started in operation later, approximately at the end of November, after both have been prepared by Applied Ceramics and shipped to CCS.