ADVANCED GASIFICATION MERCURY/TRACE METAL CONTROL WITH MONOLITH TRAPS

Final Scientific/Technical Revised Report for Year 1

(for the period of July 1, 2005, through February 28, 2007)

Prepared for:

Jenny Tennant

National Energy Technology Laboratory
U.S. Department of Energy
3610 Collins Ferry Road, MS 921-107
PO Box 880
Morgantown, WV 26507-0880

Contract No. DE-FC26-05NT42461

Prepared by:

Michael L. Swanson
Grant E. Dunham
Mark A. Musich

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, ND 58202-9018

2008-EERC-01-08

January 2008

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

EERC DISCLAIMER

LEGAL NOTICE: This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by the U.S. Department of Energy. Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

ADVANCED GASIFICATION MERCURY/TRACE METAL CONTROL WITH MONOLITH TRAPS

ABSTRACT

Three potential additives for controlling mercury emissions from syngas at temperatures ranging from 350° to 500°F (177° to 260°C) were developed. Current efforts are being directed at increasing the effective working temperature for these sorbents and also being able to either eliminate any potential mercury desorption or trying to engineer a trace metal removal system that can utilize the observed desorption process to repeatedly regenerate the same sorbent monolith for extended use. Project results also indicate that one of these same sorbents can also successfully be utilized for arsenic removal. Capture of the hydrogen selenide in the passivated tubing at elevated temperatures has resulted in limited results on the effective control of hydrogen selenide with these current sorbents, although lower-temperature results are promising. Preliminary economic analysis suggests that these Corning monoliths potentially could be more cost-effective than the conventional cold-gas (presulfided activated carbon beds) technology currently being utilized. Recent Hg-loading results might suggest that the annualized costs might be as high as 2.5 times the cost of the conventional technology. However, this annualized cost does not take into account the significantly improved thermal efficiency of any plant utilizing the warm-gas monolith technology currently being developed.

TABLE OF CONTENTS

LIST OF FIGURES

Continued…

LIST OF FIGURES (continued)

LIST OF TABLES

ADVANCED GASIFICATION MERCURY/TRACE METAL CONTROL WITH MONOLITH TRAPS

EXECUTIVE SUMMARY

A high-pressure laboratory-scale test apparatus has been constructed that allows testing of powdered, granulated, and monolith sorbent samples on bottled syngas mixtures at pressures up to 1200 psig. The data acquisition and control system was installed, and the correct control of the process bottled gases and pressure control were verified. First-year testing has examined the effects of temperature, pressure, space velocity, and gas composition, including trace contaminants, on the removal of mercury, arsenic, and selenium from simulated warm fuel gas mixtures. This test apparatus is able to blend bottled gases to simulate the desired gas composition for any of the major gasifier vendors, including that of entrained-flow slurry feed and dry-feed gasifiers and fluid-bed gasifiers, including transport reactor and GTI U-gas systems.

The Energy & Environmental Research Center (EERC) and Corning team has currently developed three potential additives for controlling mercury emissions from syngas at temperatures ranging from 350° to 500°F (177° to 260°C). Current efforts are being directed at increasing the effective working temperature for these sorbents and also being able to either eliminate any potential mercury desorption or trying to engineer a trace metal removal system that can utilize the observed desorption process to repeatedly regenerate the same sorbent monolith for extended use. Project results also indicate that one of these same sorbents can also successfully be utilized for arsenic removal. Capture of the hydrogen selenide in the passivated tubing at elevated temperatures has resulted in limited results on the effective control of hydrogen selenide with these current sorbents, although lower temperature results are promising. These data show that the first sorbent was achieving a mercury loading that was not saturated and good mercury closures were found. These results are very similar to the mercury loadings reported by other researchers in which Hg sorbent loadings of 114 to 1231 μg/g were achieved. Mercury closures for the SR-liquid sorbent were poor, with 1% Hg recovered and the maximum Hg loading approximately 43 μg/g. There is some concern that the mercury-stabilizing compound in this additive may not be acid-leachable and, therefore, would not be measured by the cold-vapor atomic fluorescence technique utilized to conduct these analyses. The final monolith utilized a more stable form of the additive that had been shown to volatilize in the presence of reducing gases. The relatively lower closure (28%) for this test might indicate that some of the Hg had desorbed from the monolith, resulting in the lower Hg loading of approximately 58 μg/g that was observed.

Preliminary economic analysis suggests that these Corning monoliths potentially could be more cost-effective than the cold-gas presulfided activated carbon beds currently being utilized; however, recent Hg-loading results might suggest that the annualized costs might be as high as 2.5 times the cost of the conventional technology. However, this annualized cost does not take into account the significantly improved thermal efficiency of any plant utilizing the warm-gas monolith technology currently being developed.

ADVANCED GASIFICATION MERCURY/TRACE METAL CONTROL WITH MONOLITH TRAPS

DESCRIPTION OF EQUIPMENT

A high-pressure laboratory-scale test apparatus has been constructed that will allow testing of powdered, granulated, and monolith sorbent samples on bottled syngas mixtures at pressures up to 1200 psig. The data acquisition and control system has been installed, and the correct control of the process bottled gases and pressure control were verified. Shakedown testing on the laboratory-scale unit has shown that the mercury being fed into the laboratory-scale rig is the same as the measured Hg leaving the system, which indicates that the Sulfinert® coating placed on all of the tubing and fittings in contact with the Hg-laden fuel gas is not retaining the elemental Hg. First-year testing has examined the effects of temperature, pressure, and gas composition, including trace contaminants, on the removal of mercury, selenium, and arsenic from simulated warm fuel gas mixtures. This test apparatus is able to blend bottled gases to simulate the desired gas composition for any of the major gasifier vendors, including that of entrained-flow slurry feed and dry-feed gasifiers and fluid-bed gasifiers, including transport reactor and GTI U-gas systems. Appropriately sized mass flow controllers and a high-pressure water pump allows the gas mixture compositions to be set independently. Impurities such as H_2S, COS, HCl, ArH_3, and H_2Se have been added to certain cylinders of bottled gas to get the appropriate concentrations in the simulated bottled gas mixture. A diagram of the designed laboratory-scale test rig is shown in Figure 1. Figures 2 and 3 are photographs of the constructed test rig. The pure and mixed bottled gas cylinders and mass flow controllers are in the right-hand hood, while the preheating tubing and the monolith holding vessel and back-pressure control valve are located in the left-hand hood. Mass flow controllers sized for 6 scfh of CO_2, 8 scfh of H_2, 10 scfh of CO, 1 scfh of CH_4, and 12 scfh of N_2 allow the test apparatus to blend bottled gases to simulate the desired gas composition. These flow rates were calculated as a function of desired space velocities and operating temperature and pressure. Operation at the maximum pressure of 1200 psig resulted in the need for the highest flow rates given a specific desired space velocity in the monolith. All fittings downstream from the mercury injection point have been coated with Restek's Sulfinert coating to reduce any chances for mercury absorption on the metal surfaces.

The mercury concentration in the simulated fuel gas is being measured with a modified PS Analytical (PSA) Sir Galahad cold-vapor atomic fluorescence instrument. The Sir Galahad is equipped with two gold traps. The first trap collects the mercury in the sample gas stream and is desorbed to the second trap with air as the carrier gas. The second gold trap is desorbed to the detector with nitrogen as the carrier gas. A Horiba DM-6B cold-vapor atomic absorption mercury analyzer has also been used at times to verify the results from the PSA Sir Galahad. The water in the sample gas is removed in a chilled bubbler and a gas–liquid separator. A $SnCl_2$–NaOH solution can also be added to the bubbler to reduce all mercury in the sample gas stream to elemental mercury. Arsine and hydrogen selenide tests were completed by blending either 10 ppm arsine in nitrogen or 100 ppm hydrogen selenide in nitrogen gases in at the same point the mercury in carbon dioxide or in nitrogen stream was added to the system while utilizing the same

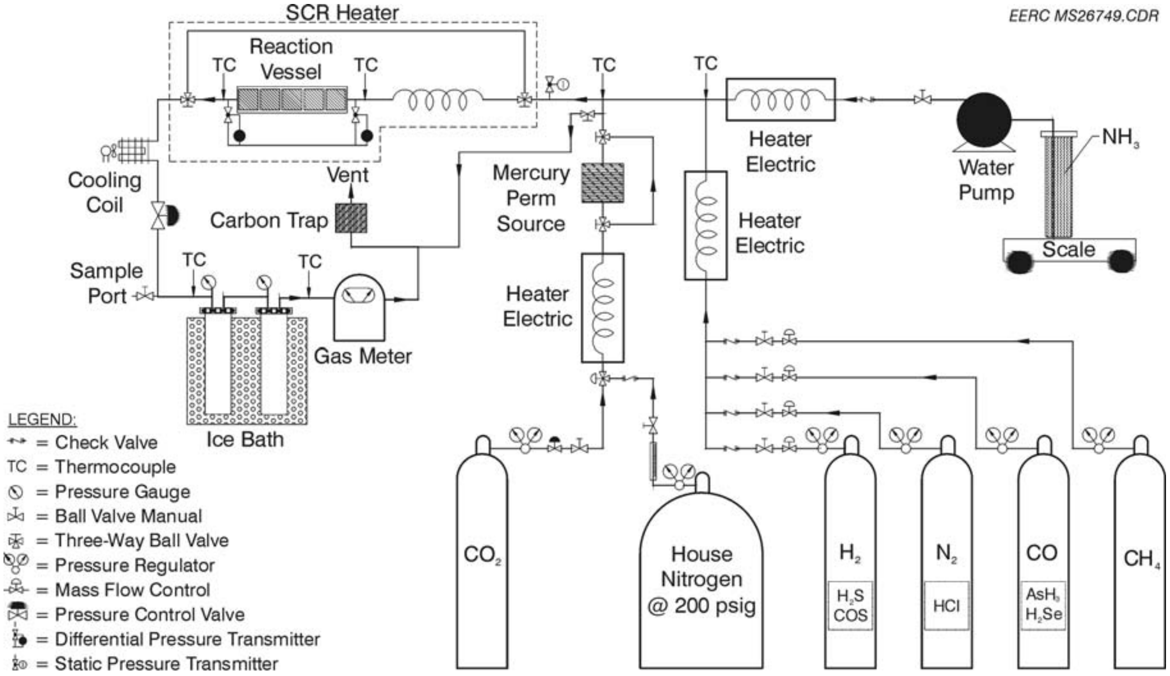

Figure 1. Schematic of the carbon monolith test stand.

Figure 2. Photograph of the carbon monolith test stand.

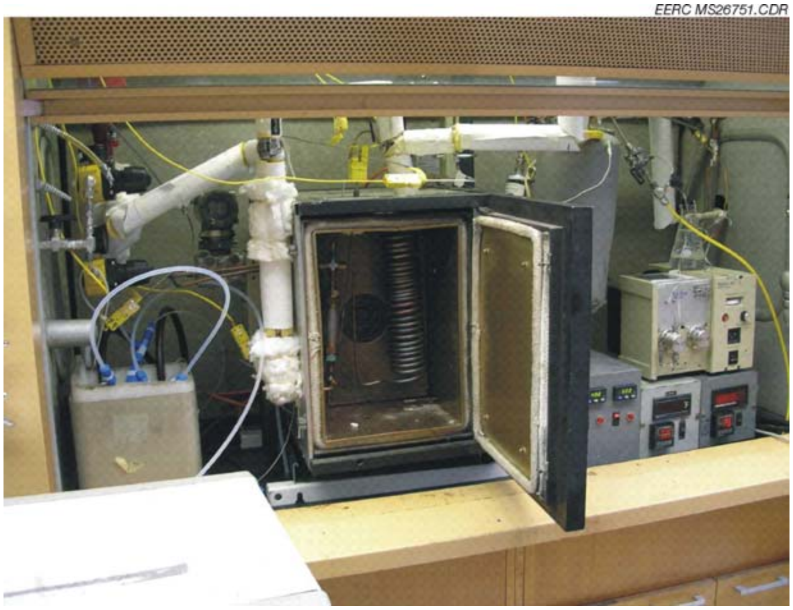

Figure 3. Photograph of the carbon monolith reactor vessel and preheating coil.

mass flow controller. Arsine and hydrogen selenide concentrations were measured with a Honeywell CM-4 hydride analyzer, which is interfaced with the system data acquisition system to provide continuous logging of the concentration data.

RESULTS AND DISCUSSION

Table 1 summarizes the operating conditions from all of the successful tests completed on the bench-scale test rig. The baseline fuel gas mixture used for most tests consisted of 25% H_2, 20% CO, 15% CO_2, 17.5% H_2O, and 5% CH_4 with the balance being N_2, which would closely simulate an air-blown transport reactor operating on a higher-moisture lignite fuel. Some tests were completed in the presence of hydrogen sulfide to determine its effect on the performance of the additive.

The very first tests looked at the mercury captureability of the baseline Corning monolith and a presulfided granulated activated carbon (Calgon F-400) utilizing a baseline fuel gas mixture. In these tests, the carbon-based material did not capture any Hg at the conditions tested. Figure 4 shows the breakthrough curves from these tests. From these tests, it is apparent that carbon by itself is not capable of capturing any Hg at these elevated temperatures.

Tests were then conducted using EERC-treated granular carbon with the baseline fuel gas mixture. Figures 5 and 6 show the breakthrough curves for these tests utilizing these sorbents at temperatures of 500° and 350°F, respectively. These tests show that the sorbent was effective at removing the mercury to very low levels for a significant period of time; however, once the mercury started to break through, the sorbent would start desorbing mercury until the mercury

Table 1. Test Operating Parameters for Completed Tests

Run No.	Sorbent Type	Sorbent Form	Sorbent Weight, g	Temp., °F	Pressure, psig	H_2, %	CO, %	CO_2, %	CO_2 (Hg), scfh	CH_4, %	H_2O, %	N_2, %
1	No. 412-6	Monolith	2.5773	500	300	25	20	15	0.0155	5	17.5	17.5
2	F2BO	Granular	3.9684	500	300	25	20	15	0.0155	5	17.5	17.5
3	F2HO	Granular	3.6605	500	300	25	20	15	0.0155	5	17.5	17.5
4	F2ZO	Granular	3.7775	500–350	300	25	20	15	0.0155	5	17.5	17.5
5	F2ZO	Granular	2.6219	400	300	25	20	15	0.0155	5	17.5	17.5
6	F2ZO	Granular	3.5600	400	300	25	20	15	0.0155	5	17.5	17.5
7	F2ZO	Granular	3.5193	350	300	25	20	15	0.0155	5	17.5	17.5
8	F2HO	Granular	4.0032	350	300	25	20	15	0.0155	5	17.5	17.5
9	F2HO	Granular	0.5056	350	300	25	0	0	0.0155	0	0	75
10	F2HO	Granular	1.0005	350	300	0	20	15	0.0155	5	0	60
11	CC5BO	Powdered	0.5009	350	300	25	20	15	0.15	5	17.5	17.5
12	CC2BO	Monolith	3.7678	350	300	25	20	15	0.15	5	17.5	17.5
13	CC2BO	Monolith	3.7678	350	300	25	20	15	0.15	5	17.5	17.5
14	CC2ZO	Monolith	4.0873	350	300	25	20	15	0.15	5	17.5	17.5
15	CC2ZO	Monolith	4.0873	350	300	25	20	15	0.15	5	17.5	17.5
16	F2ZO	Granular	3.8158	500	300	25	20	15	0.15	5	17.5	17.5
17	F2ZO	Granular	3.8158	350	300	25	20	15	0.15	5	17.5	17.5
18	CC2ZO	Monolith (2)	6.059	350	300	25	20	15	0.15	5	9.5	25.5
19	FC2BO	Monolith (2)	7.6477	350	300	25	20	15	0.15	5	9.5	25.5
20	TCCAT3	Monolith	3.7482	350	300	25	20	15	0.15	5	9.5	25.5
21	TCCAT3	Monolith	4.1495	500	300	25	20	15	0.15	5	9.5	25.5
22	TCCAT2	Monolith	2.8702	350	300	25	20	15	0.15	5	9.5	25.5
23	TCCAT1	Monolith	3.2218	350	300	25	20	15	0.15	5	9.5	25.5
24	TCCAT1K	Monolith	5.0363	350	300	25	20	14.9	0.15	5	9.5	25.5
25	FC2KO	Monolith	5.2027	350	300	25	20	14.9	0.15	5	9.5	25.5
26	CC2B1	Monolith	5.9067	350	300	25	20	14.9	0.15	5	9.5	25.5
27	F2ZO	Granular	3.016	650	300	25	20	14.9	0.15	5	9.5	25.5
28	F2ZO	Granular	3.003	500	300	25	20	14.9	0.15	5	9.5	25.5
29	F2ZO	Granular	3.0018	350	300	25	20	14.9	0.15	5	9.5	25.5
30	F2ZO	Granular	3.0045	350	150	25	20	14.9	0.15	5	9.5	25.5
31	F2ZO	Granular	3.0045	350	600	25	20	14.9	0.15	5	9.5	25.5
32	FC2PO	Monolith	3.6494	500	300	25	20	14.9	0.15	5	9.5	25.5
33	FCCMO	Monolith	3.0234	350	300	25	20	14.9	0.15	5	9.5	25.5
34	FCZCO	Monolith	4.4818	350	300	25	20	14.9	0.15	5	9.5	25.5
35	TCZO	Monolith	2.229	350	300	25	20	14.9	0.15	5	9.5	25.5
36	FC2PO	Monolith	4.0007	350	300	25	20	14.9	0.15	5	9.5	25.5
37	FCCMSO	Monolith	3.1328	350	300	25	20	14.9	0.15	5	9.5	25.5
39	F2ZO	Granular	3.0216	350	300	25	20	14.9	0.15	5	9.5	25.5
40	Cat. No. 4	Monolith	5.8929	350	300	25	20	14.9	0.15	5	9.5	25.5
41	SR Liquid	Monolith	3.3597	350	300	25	20	14.9	0.15	5	9.5	25.5
42	SR Liquid	Monolith	3.3708	350	600	25	20	14.9	0.15	4	9.5	26.5
43	Cat. No. 2	Monolith	3.2475	350	600	25	20	14.9	0.15	4	9.5	26.5
44	FC2PO	Monolith	4.2448	350	300	25	20	14.9	0.15	4	9.5	26.5
45	Cat. No. 2	Monolith	3.3889	350	600	25	50	5	NA	0	8.75	11.3
46	Cat. No. 2	Monolith	3.6178	500	600	25	50	5	NA	0	8.75	11.3
47	F2ZO	Granular	3.0176	235	300	20	15	15	NA	0	0	50

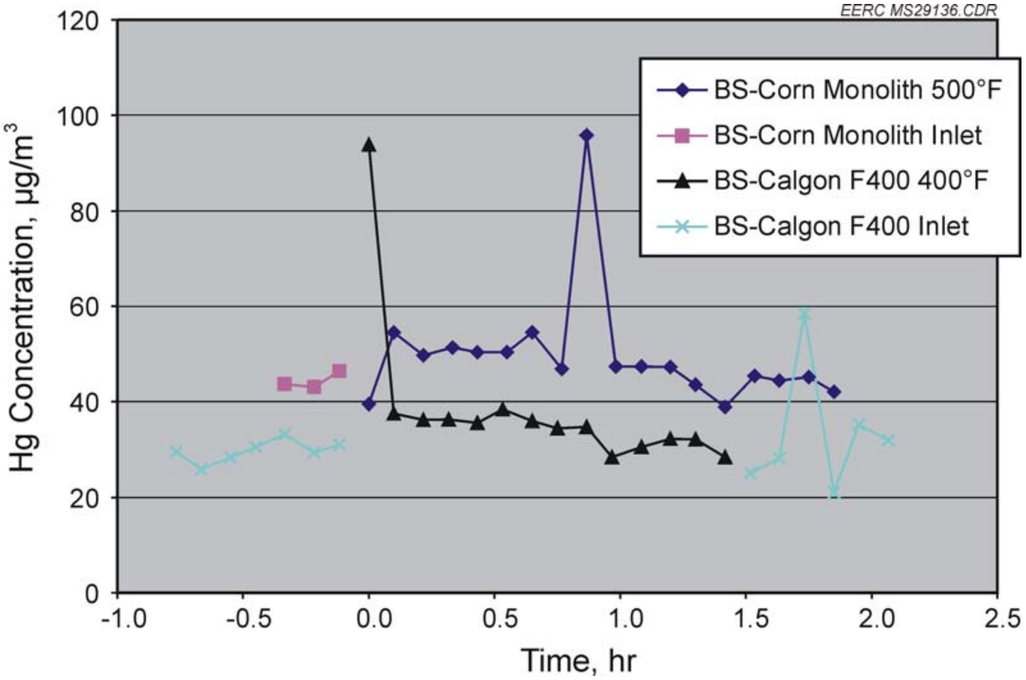

Figure 4. Breakthrough curves for baseline carbon testing at temperature and pressure.

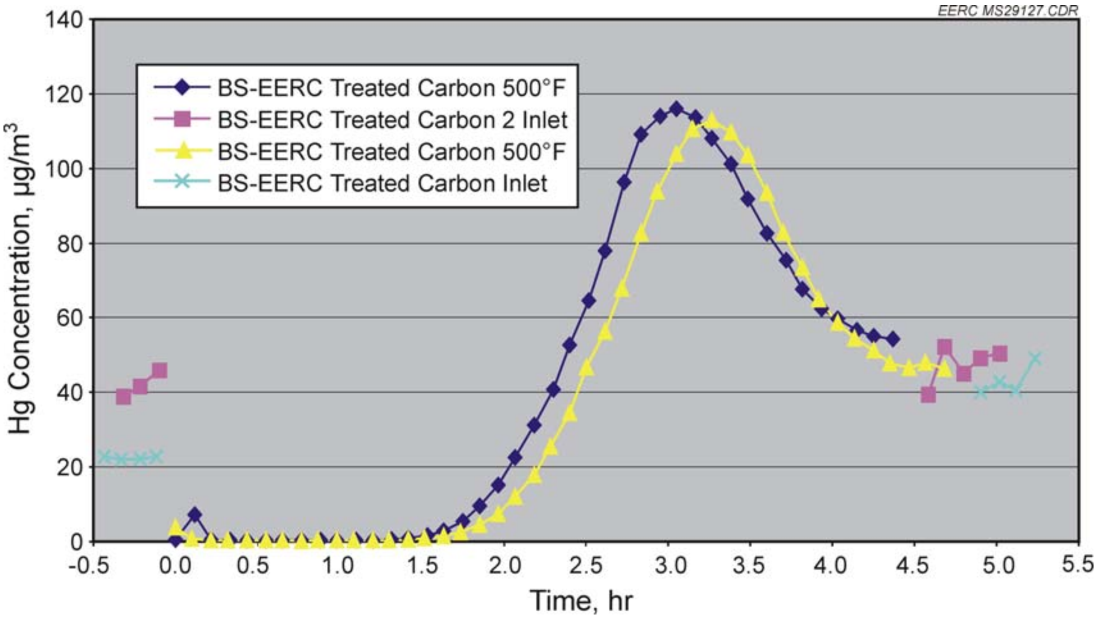

Figure 5. Breakthrough curves for EERC-treated carbon at 500°F and 300 psig with baseline fuel gas mixture.

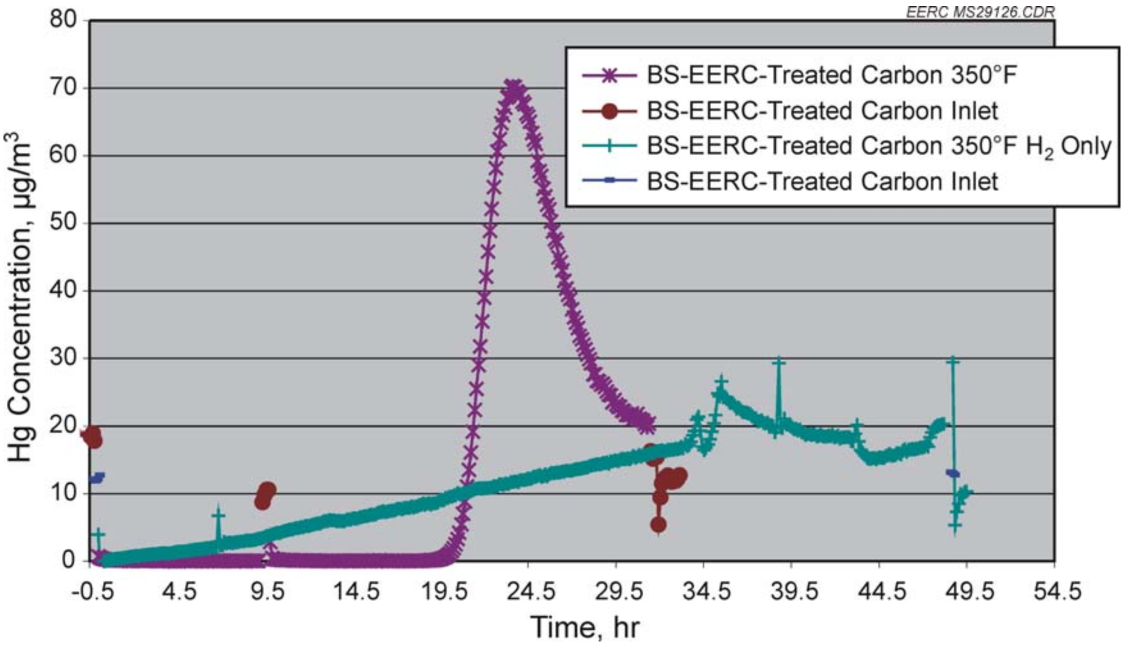

Figure 6. Breakthrough curves for EERC-treated carbon at 350°F and 300 psig with baseline fuel gas mixture and a hydrogen/nitrogen-reducing gas mixture.

was almost completely desorbed. The tests at the lower temperature also indicated that while the sorbent would control mercury for significantly longer periods, eventually the mercury would still desorb. Less desorption appeared to occur when the fuel gas mixture was switched to a H_2/N_2 mixture only. Analysis of the carbon substrate indicated that over 90% of the active ingredient in the EERC-treated carbon had volatilized at these temperatures in the presence of reducing-gas species.

After experiencing the desorption of the mercury at the lower temperatures, another EERC sorbent on granulated activated carbon was tested. The breakthrough curves for these sorbent tests are shown in Figure 7. This figure shows that the sorbent did not work at all at the higher temperature of 500°F, but as soon as the temperature was dropped to 350°F, the sorbent started collecting mercury very well and did not appear to desorb mercury like the previous sorbent. The high spike of Hg seen during the first test and the variability from test to test on the Hg starting concentration led to a decision to replace the saturated Hg sorbent with Hg permeation tubes similar to those utilized on the atmospheric pressure flue gas test rigs utilized at the EERC. This modification required that the system or at least the mercury permeation tubes in the Hg generation section be either pressurized and depressurized very slowly or that a continuous pressurized stream of CO_2 or nitrogen be maintained on the permeation tubes at all times.

As monoliths from Corning became more available, these monoliths were tested with three different additives on the monolith. The breakthrough curves for these different additives on carbon monoliths are shown in Figures 8 through 10. All three figures show a period of 100% mercury capture, which demonstrates that the monoliths are not mass transfer-limited for mercury capture. Figure 8 shows results from a monolith coated with the same additive as shown

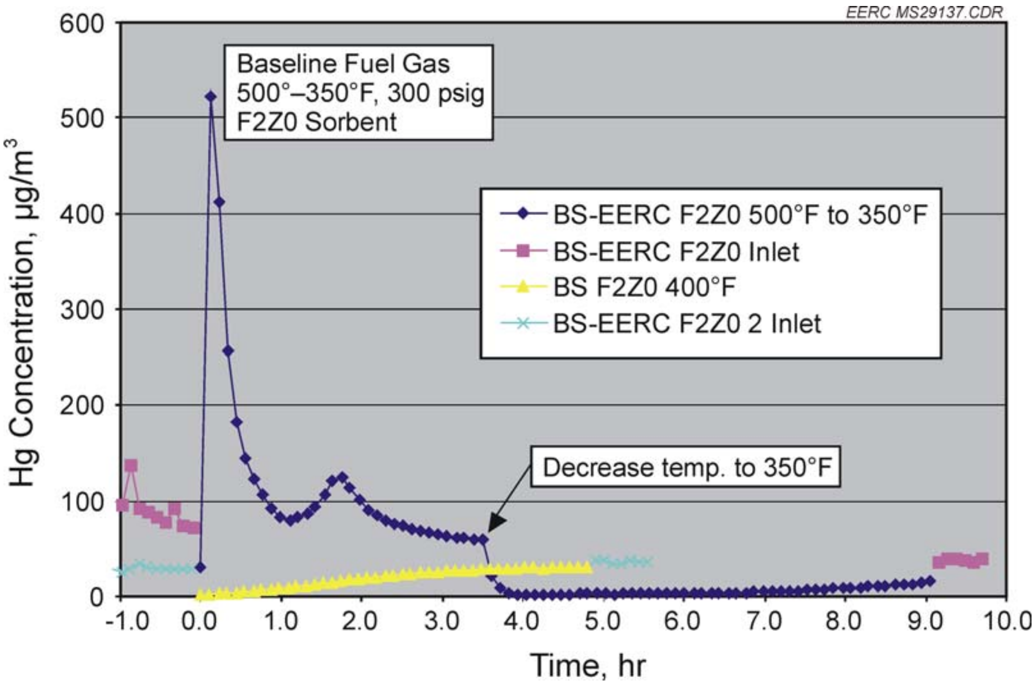

Figure 7. Breakthrough curves for a different EERC-treated carbon as a function of operating temperature.

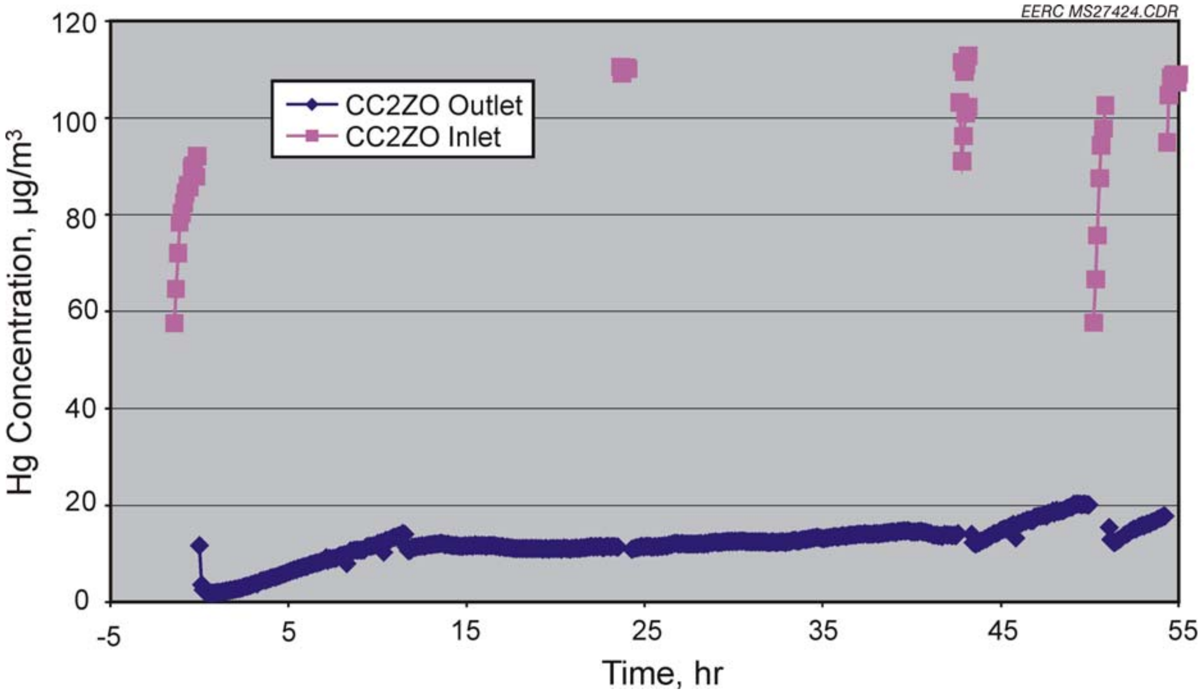

Figure 8. Breakthrough curve for EERC-treated monolith Test 18 (CCZ2O).

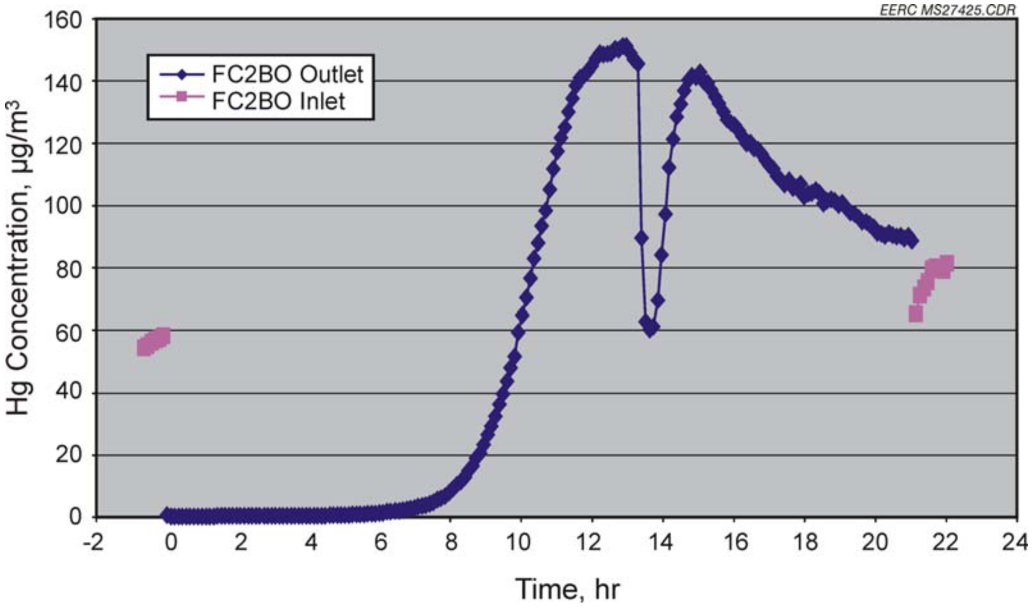

Figure 9. Breakthrough curve for the EERC-treated carbon monolith Test 19 (FC2BO).

in Figure 7. The results indicate that a monolith coated with this material can capture Hg with a high degree of efficiency for an extended period of time. However, the outlet mercury concentration is reduced to less than 5 g/m^3, which is roughly equivalent to the 5 ppbw goal for mercury emissions. The shorter period of high mercury capture may be caused by the sorbent surface becoming saturated with mercury and the diffusion of the Hg into the lower layers of the additive coating controlling the rate of Hg absorption.

Figure 9 shows that the second EERC-treated carbon monolith provided by Corning, Inc., utilizing the same additive shown in Figures 5 and 6 captures the Hg very well for a period of time before the Hg starts to break through and eventually desorb. Again, the desorption of the mercury was attributed to the slow devolatilization of the additive as a function of time. The EERC is still currently investigating less volatile forms of the additive that might permanently hold the additive (and, therefore, the mercury) to the carbon monolith.

Figure 10 shows the breakthrough curve for a Corning-treated carbon monolith that has a relatively slow breakthrough curve that also shows the capability to absorb more mercury after the syngas flow has been stopped to the monolith for a short period of time. This suggests a simple sorbent regeneration procedure might be possible to increase the monolith mercury-loading capacity and period of utilization.

A breakthrough curve test on a carbon monolith that was treated at Corning is shown in Figure 11. An additional breakthrough test completed utilizing one of the Corning monoliths but with just one of the additives from Corning treatment utilized in Figure 11 is shown in Figure 12. The fact that the breakthrough curves for these different additives on the same type of carbon monolith are similar suggests that the one additive might be the key ingredient that is capturing mercury. In fact, the relatively slow reduction of the outlet mercury concentration in Figure 11 as

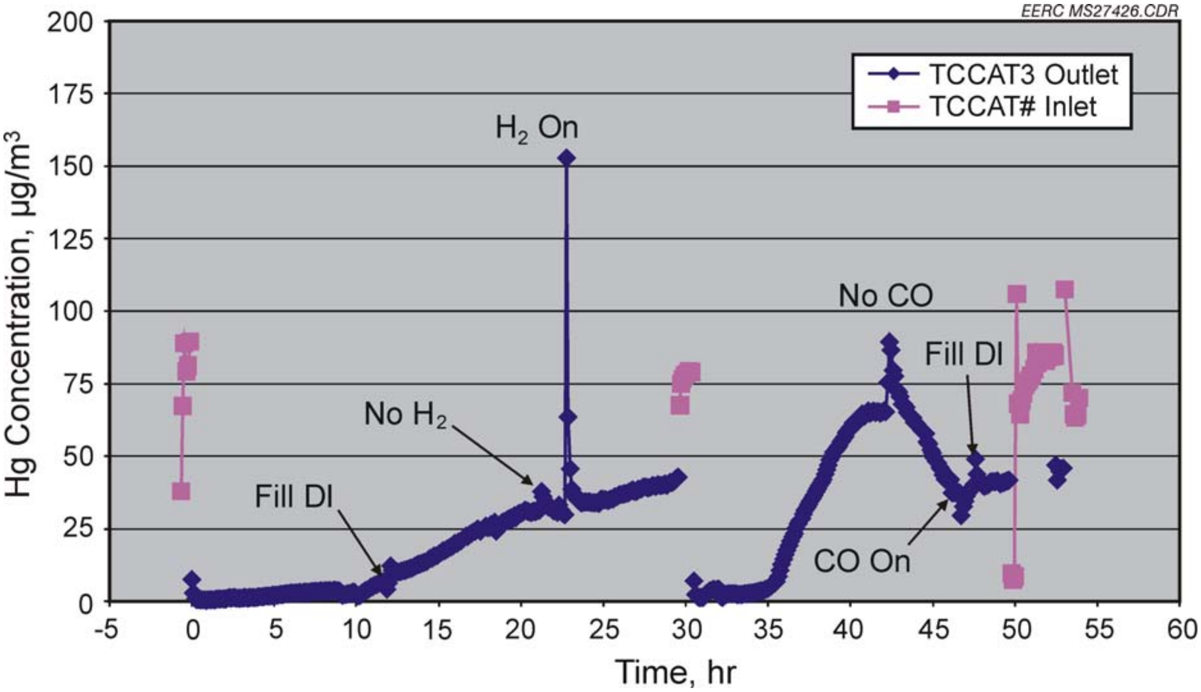

Figure 10. Breakthrough curve for the EERC-treated monolith Test 20 (TCCAT3).

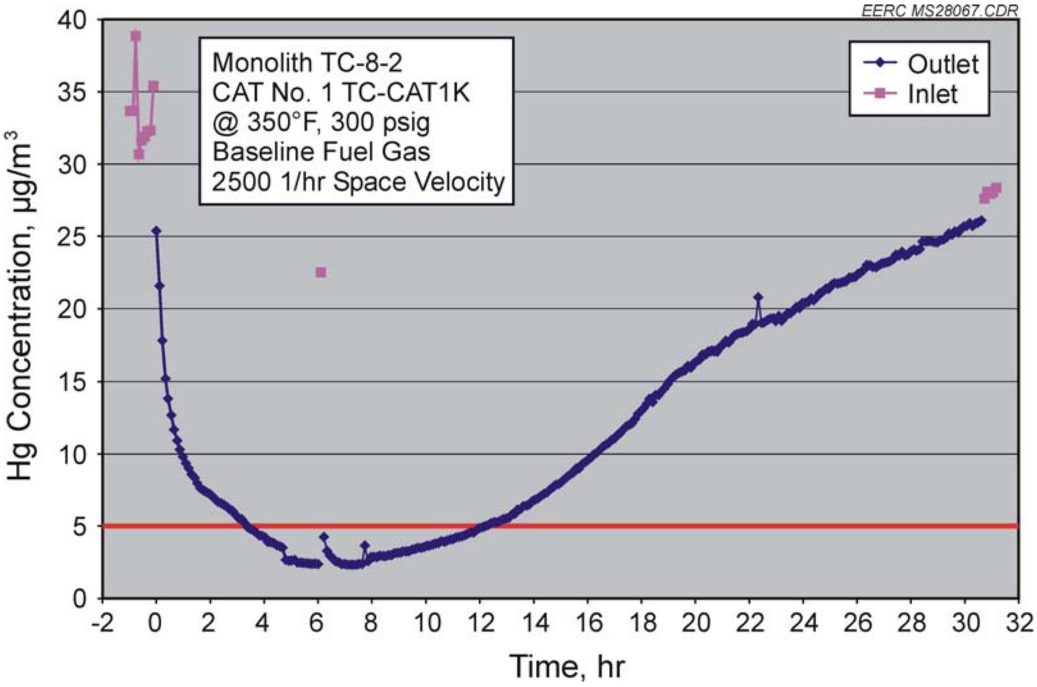

Figure 11. Breakthrough curve for EERC-treated monolith Test 24 (TC-CAT1K).

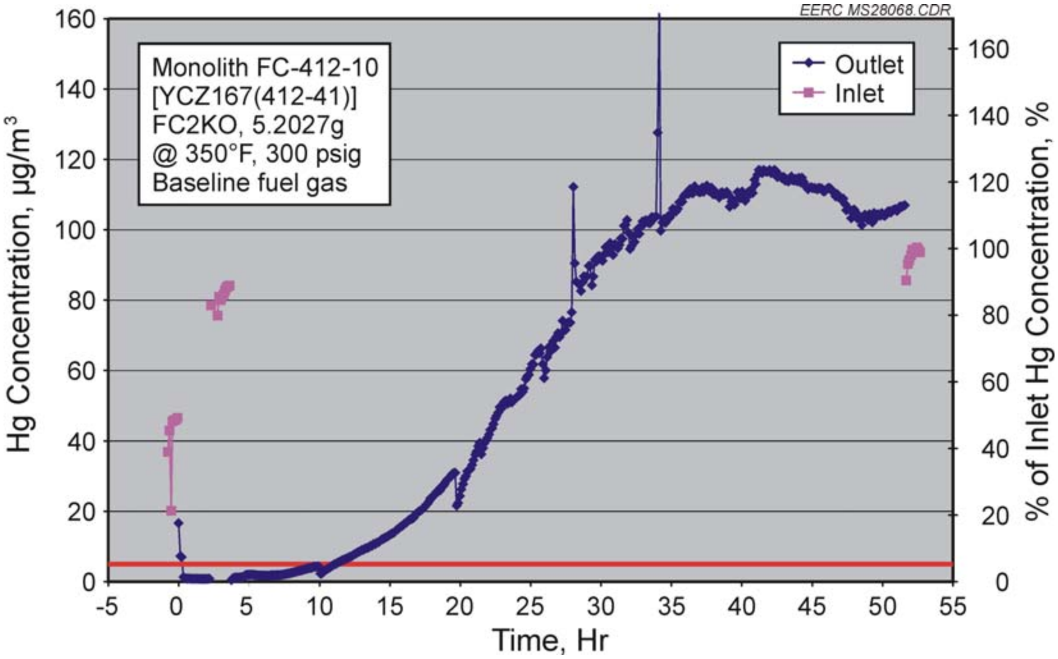

Figure 12. Breakthrough curve for the EERC-treated carbon monolith Test 25 (FC2KO).

compared to Figure 12 may suggest that the extra catalyst material might even be hindering the effectiveness of the one additive. The results indicate that a monolith coated with this material can capture Hg with a high degree of efficiency for an extended period of time with the outlet mercury concentration being reduced to less than 5 µg/m^3, which is roughly equivalent to the 5-ppbw goal for mercury emissions for the given molecular weight of the fuel gas mixture utilized. The shorter period of high mercury capture may be caused by the sorbent surface becoming saturated with mercury and diffusion of the Hg into the lower layers of the additive coating becoming the rate-controlling step.

Figures 13 and 14 show the effect of temperature and pressure on the Hg absorption performance of the EERC-treated carbon F2ZO as a percentage of the inlet concentration. The data were presented as a function of the inlet concentration because the inlet concentration changed at each different test condition since, at a constant space velocity, the volumetric flow of the bottled gases was different; however, the total amount of Hg coming from the permeation tubes was constant. Figure 13 shows that, at 650°F, the sorbent has no effectiveness at capturing Hg, while at 500°F, the sorbent-only captured the Hg for a very short period of time. At 350°F, the sorbent tends to capture the Hg for a greatly extended period of time. Figure 14 shows the effect of system pressure on Hg capture performance. Higher pressures result in lower inlet concentration and, thus, a lower concentration gradient driving force to absorb the Hg on the surface.

Figures 15 and 16 show the results from EERC-treated carbon monolith tests using a less volatile form of the original EERC additive tested in Figures 8, 9, and 12. Previous tests have shown that the EERC additive captures the Hg very well for a period of time before the Hg starts

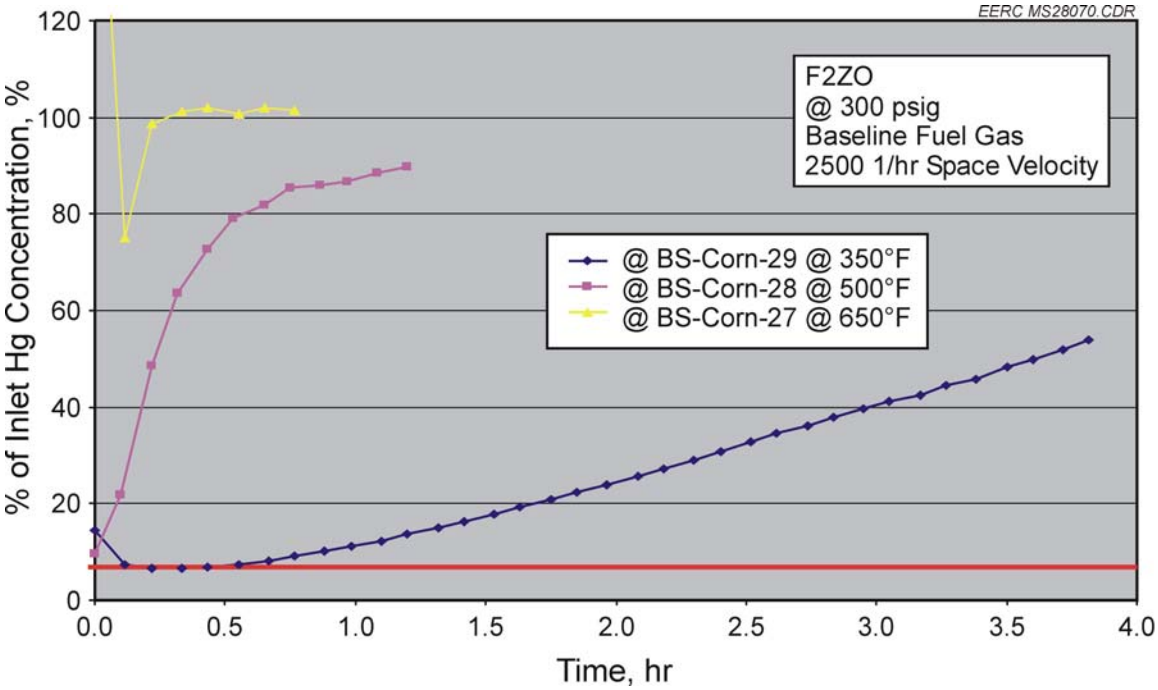

Figure 13. Breakthrough curve for the EERC-treated carbon as a function of temperature Tests 27 through 29 F2ZO.

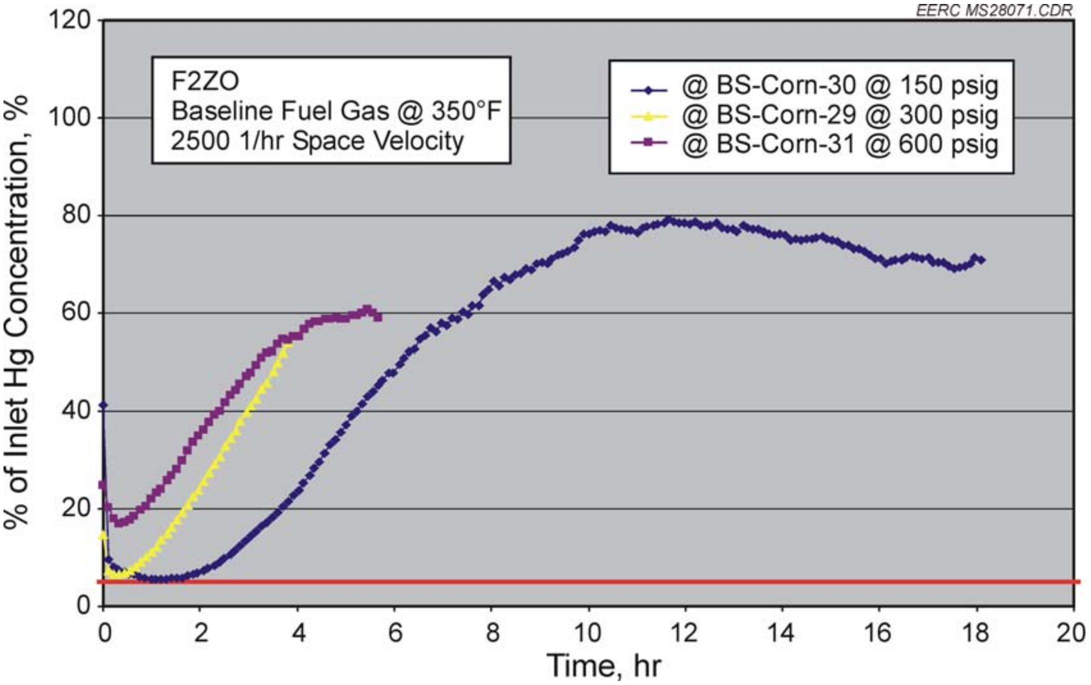

Figure 14. Breakthrough curves for EERC-treated carbon Tests 27 through 29 with F2ZO at various pressures.

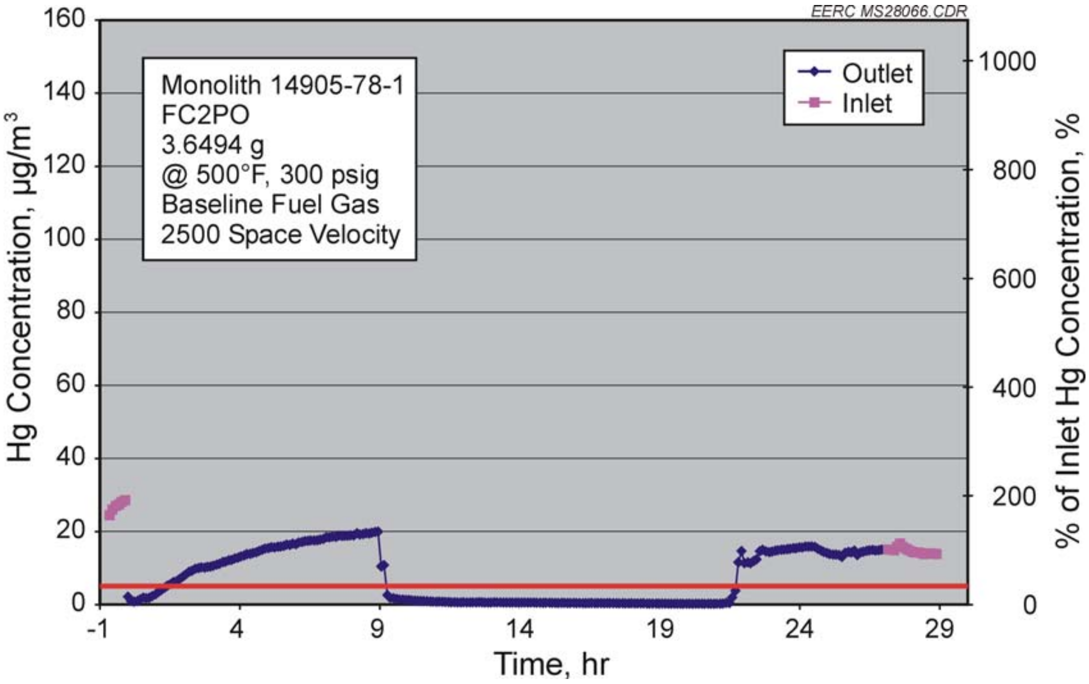

Figure 15. Breakthrough curve for EERC-treated monolith FC2PO at 500°F.

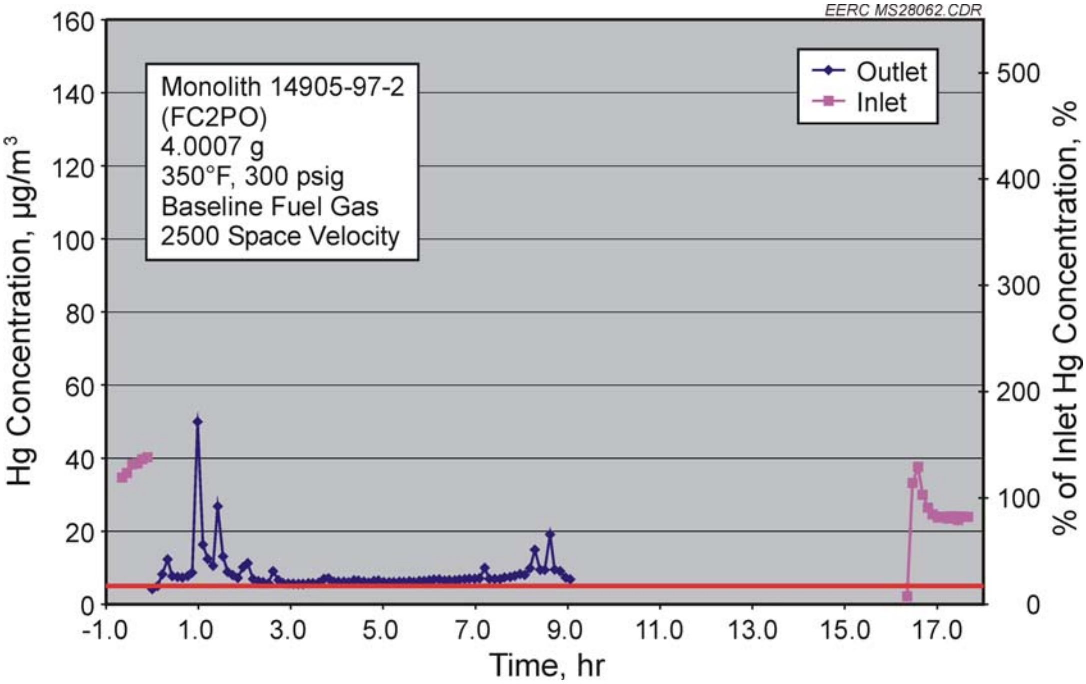

Figure 16. Breakthrough curve for EERC-treated monolith FC2PO at 350°F.

to break through and eventually desorb. The desorption of the mercury was attributed to the slow devolatilization of the additive as a function of time. Both of these figures show that the Hg was captured on the monolith without major desorption of the additive.

Figure 17 shows the breakthrough curve for a Corning-treated monolith utilizing the same additive as the additive for Figures 10 and 11 except the additive was incorporated in the Corning monolith production process. A comparison with other tests suggests that the Corning monolith production process incorporates a curing process at a temperature high enough to decompose the additive. This leads to the poor Hg capture performance shown in Figure 17.

Other tests with FCZCO, FCCMO, and FCCMSO all showed little Hg capture at 350°F and 300 psig. Figures 18 through 21 show the breakthrough curves for these particular sorbents.

A breakthrough curve test, shown in Figure 21, on a treated carbon sample, F2ZO, was tested with the baseline fuel gas mixture except that 1750 ppm of hydrogen sulfide was present in the gas stream. From these results, the additive performance was significantly affected by the presence of the H_2S. This was not entirely unexpected since one part of the additive is known to be potentially reactive toward sulfur.

Figure 22 shows the results from Corning-treated carbon monolith with Cat. 4 that was not a good additive for controlling the mercury; however, Figures 23 and 24 show tests with a Corning-treated monolith that was very effective at controlling the mercury. This SR Liquid additive never did break through on the Hg removal tests in over 150 hours of testing. This

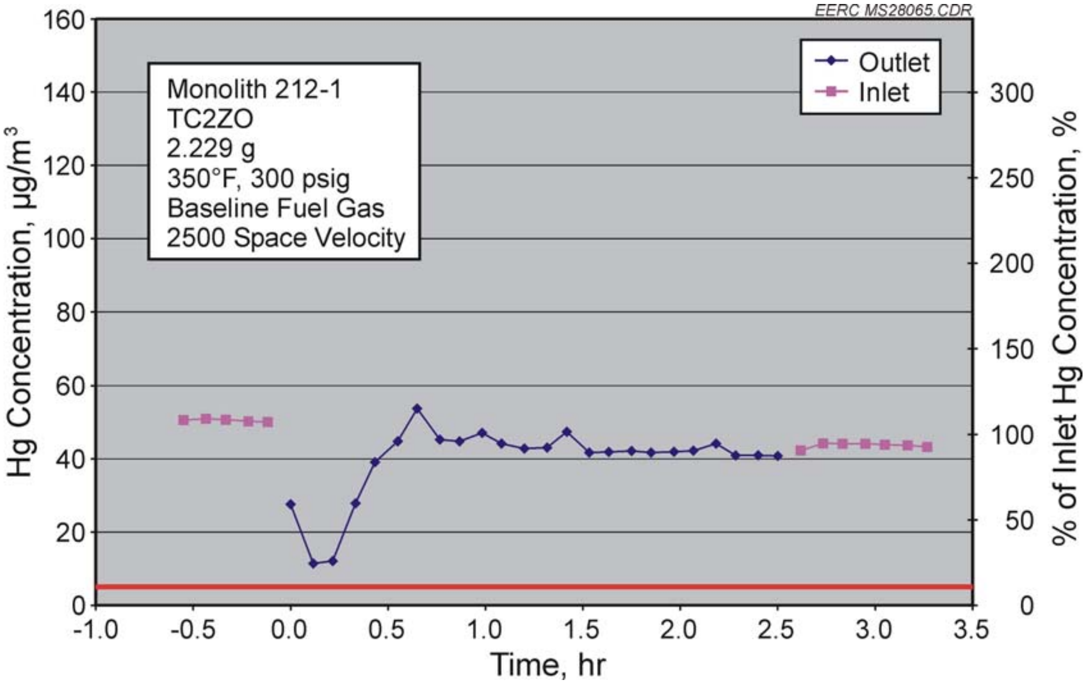

Figure 17. Test with a Corning-treated monolith TCZO.

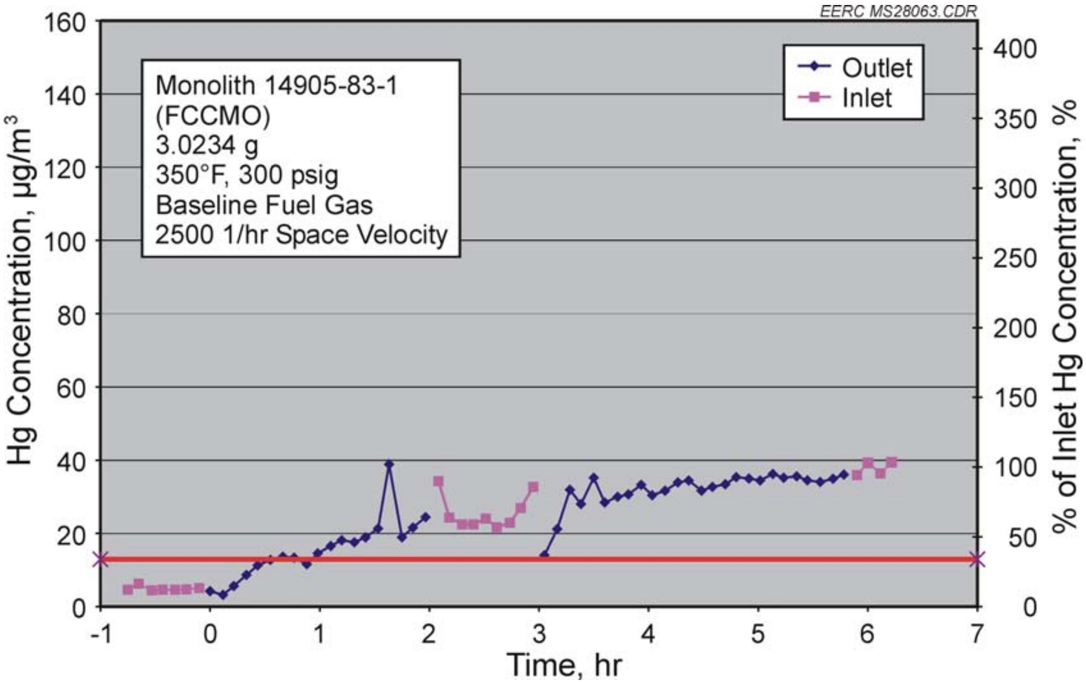

Figure 18. Breakthrough curve for carbon monolith with FCCMO additive.

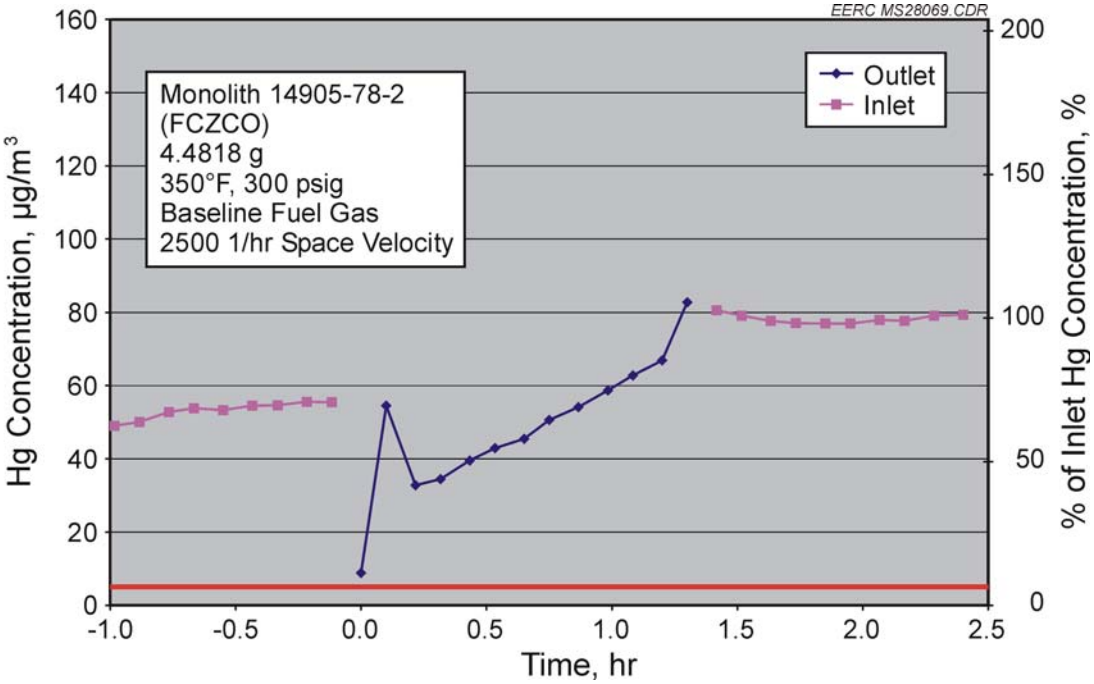

Figure 19. Breakthrough curve for carbon monolith with FCZCO additive.

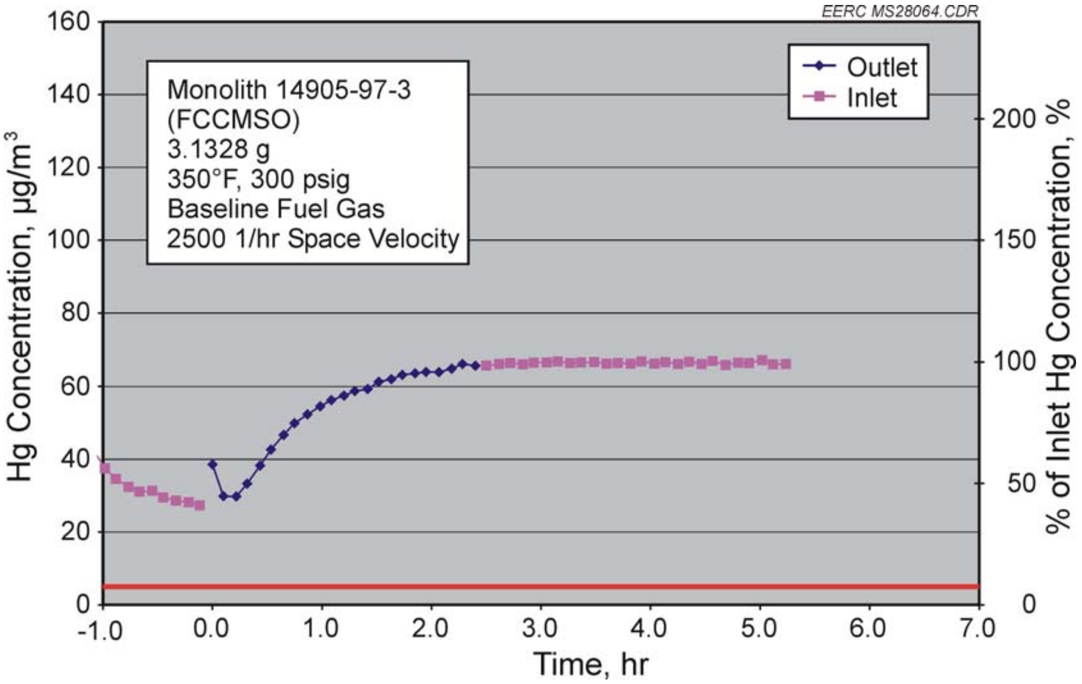

Figure 20. Breakthrough curve for carbon monolith with FCCMSO additive.

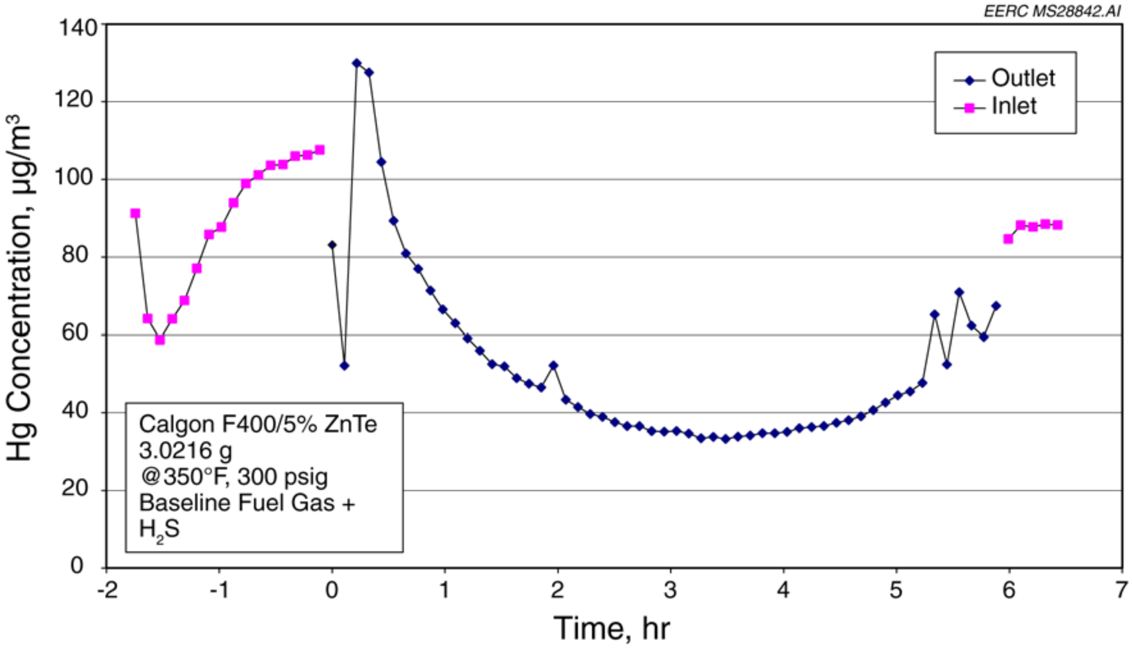

Figure 21. Mercury breakthrough curve for EERC-treated monolith in Test 39 (F2ZO) in fuel gas with high H_2S concentration.

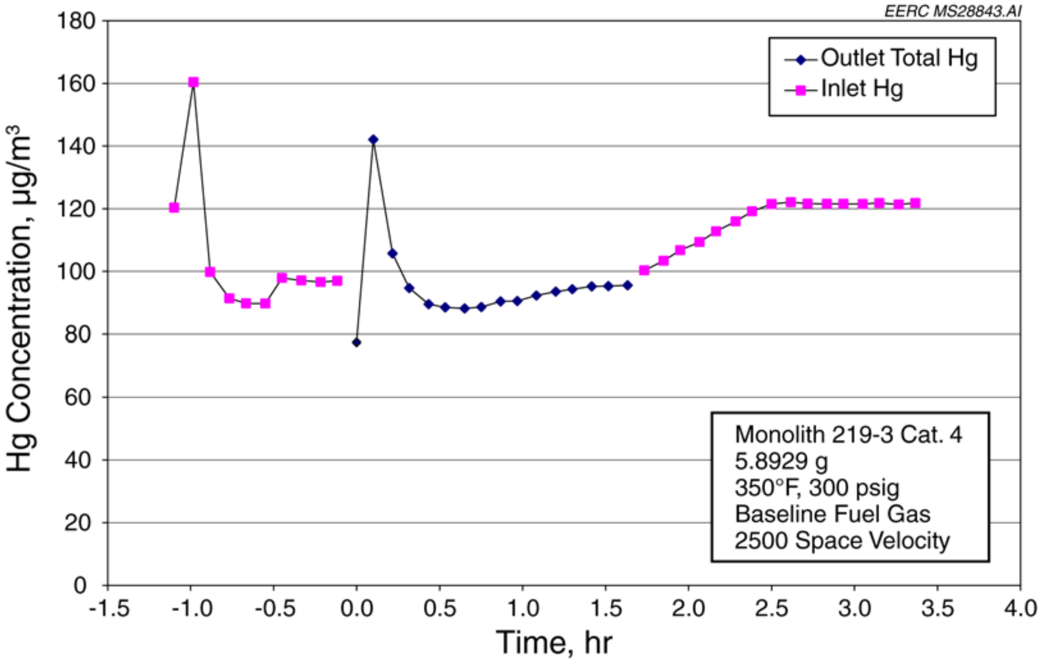

Figure 22. Breakthrough curve for Corning-treated monolith utilizing a Catalyst 4 additive at 350°F.

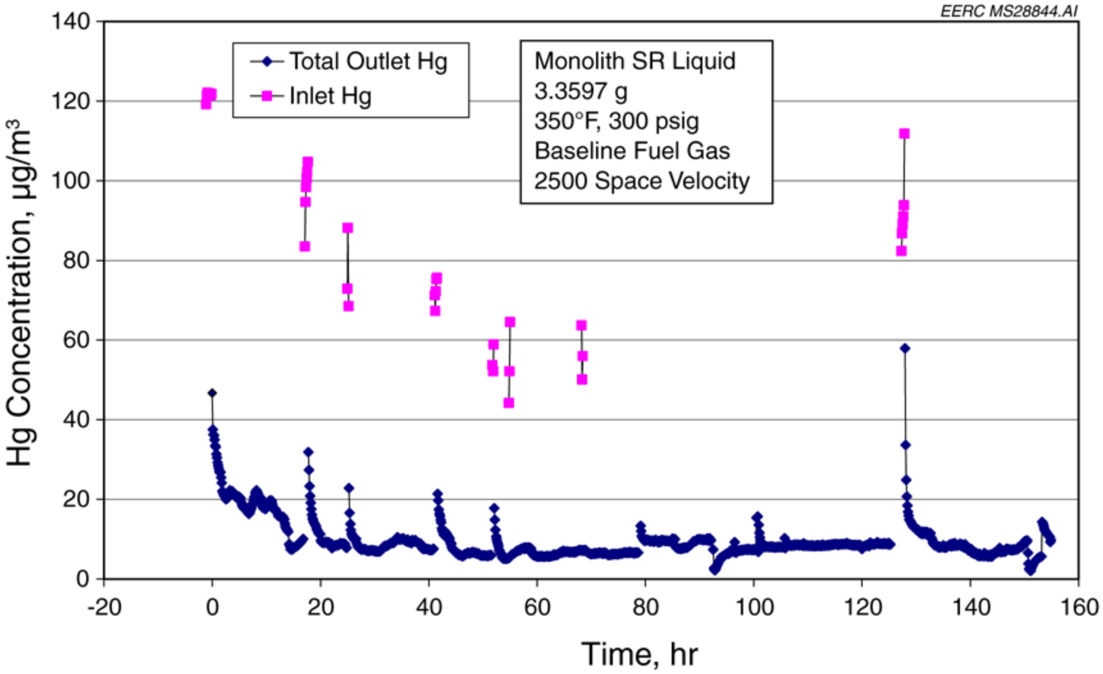

Figure 23. Breakthrough curve for Corning-treated monolith utilizing a SR Liquid additive at 350°F.

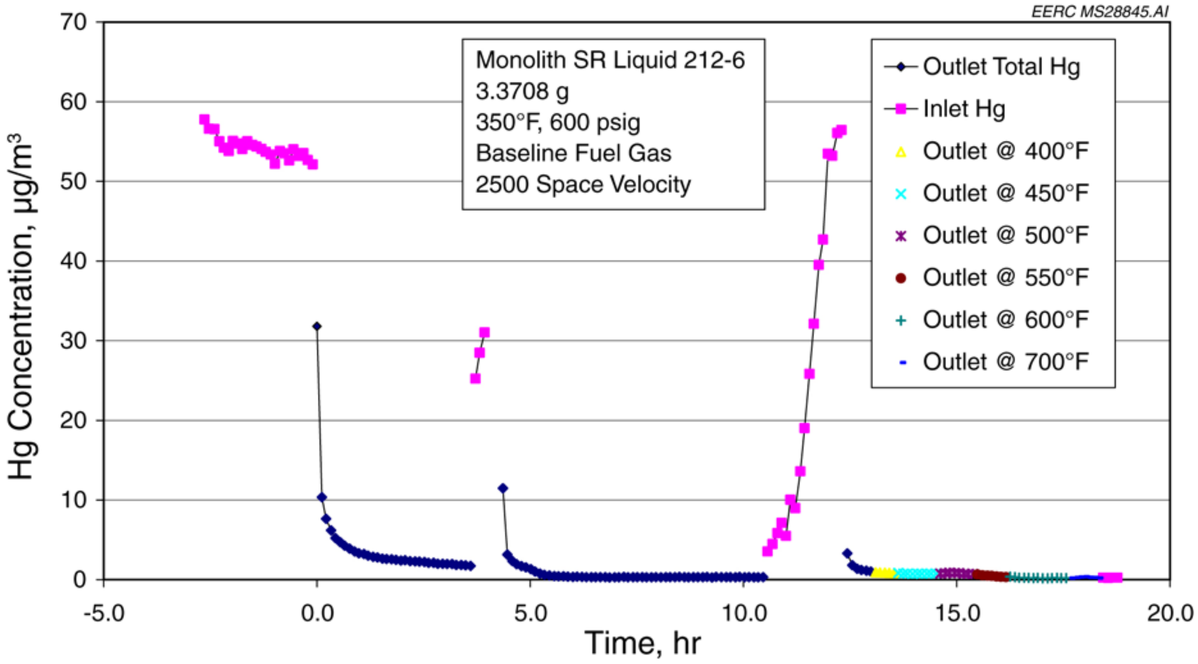

Figure 24. Breakthrough curves for Corning-treated monolith with SR Liquid additive at higher operating pressures and temperatures.

sorbent was tested at higher pressures (up to 600 psig) and higher temperatures up to 700°F and was found to be very effective at controlling the mercury to levels equal to or lower than the concentrations required by the test program.

Figure 25 shows a test which was conducted with the Corning-treated carbon monolith that had Cat. 2, (which is just one of the combined additives present in the SR Liquid additive) in the presence of hydrogen sulfide. This test showed that this additive had some properties similar to the earlier SR Liquid tests (capture at higher temperatures up to 450°F and control to levels close to that desired in the program, even in the presence of H_2S), however, the Hg control is not as effective as the SR Liquid-treated monolith. This test was also completed with $SnCl_2$/NaOH pretreatment steps to ensure that the H_2S had not converted the elemental Hg that the PSA Sir Galahad measures to some form that the analyzer would not detect.

Mercury loadings for three of the best monoliths tested were completed. Table 2 shows the measured Hg loadings as determined by acid leaching into aqua regia and then followed by analysis of the solution by cold-vapor atomic adsorption (CVAA).

These data show that the first sorbent was achieving a mercury loading that was not saturated and good mercury closures were found. These results are very similar to the mercury loadings reported by Alptekin et al. (1) in which Hg sorbents loadings of 114 to 1231 μg/g were achieved. Mercury closure for the SR Liquid sorbent were poor with 1% Hg being recovered and the maximum Hg loading being approximately 43 µg/g. There is some concern that the mercury stabilizing compound in this additive may not be acid leachable and, therefore, would not

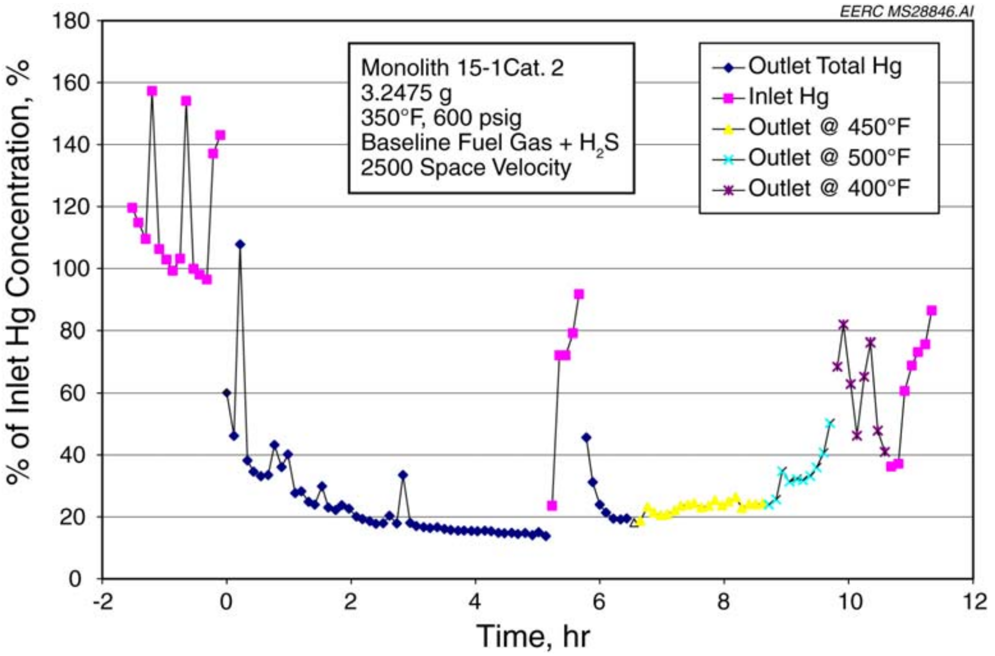

Figure 25. Breakthrough curve for Corning-treated carbon monolith with Catalyst 2 additive for Hg control.

measured by the CVAA technique utilized to conduct these analyses. The final monolith utilized a more stable form of the additive that had been shown to volatilize in the presence of reducing gases. The relatively lower closure (28%) for this test might indicate that some of the Hg had desorbed from the monolith, resulting in the lower Hg loading of approximately 58 µg/g that was measured.

Control of Arsine

Figures 26–28 show some of the breakthrough curves generated utilizing the Corning-treated monolith with the Catalyst 2 additive for the control of arsine gas being added to the baseline fuel gas mixture. The initial test (Test 45 utilized an initial AsH_3 concentration of 50 ppb) was controlled to approximately 5 ppb for over 5 hours; however, the arsine did not recover right away after the reactor was bypassed again. Figure 26 shows the next test (Test 46) where the arsine concentration was increased to 250 ppb and the level of control was only down to approximately 50 ppb. The second part of the test, shown in more detail in Figure 27, shows where the system pressure was increased from 300 to 600 psig and the temperature was increased from 350° to 500°F without affecting the sorbent performance (in fact, perhaps slightly improving performance). However, a further increase in temperature above 500°F results in a significant amount of arsenic release, indicating the maximum operating temperature for arsine removal with this sorbent is approximately 500°F.

Table 2. Monolith Mercury-Loading Data on Selected Long-Term Samples

Monolith Section			
Hg Loading on CC2ZO	Section Weight, g	Section Hg Concentration, µg/g	Section Hg, µg
1a	1.031	74	76.3
2a	0.825	90.2	74.4
3a	0.669	149	99.7
4a	0.829	405	335.7
1b	0.843	206	173.7
2b	0.593	158	93.7
3b	0.828	138	114.3
4b	1.11	108	119.9
Total			1087.6
Closure			90%
Hg Loading on SR-Liquid	Section Weight, g	Section Hg Concentration, µg/g	Section Hg, µg
1	0.904	1.05	1.0
2	0.598	1.14	1.1
3	0.731	42.9	37.3
4	0.795	34.3	29.9
Total			69.3
Closure			1%
Hg Loading on FC2PO	Section Weight, g	Section Hg Concentration, µg/g	Section Hg, µg
1	0.956	6.8	6.1
2	0.964	6.52	3.9
3	0.87	14.2	10.4
4	0.871	57.9	46.0
Total			66.5
Closure			28%

Control of Hydrogen Selenide

Hydrogen selenide control testing was attempted in the same manner that the arsine testing was completed. However, as the hydrogen selenide was fed to the reactor at higher temperatures, the hydrogen selenide being measured by the Honeywell CM4 hydride analyzer would disappear. Temperatures below 230°F gave H_2Se concentrations around 500 ppb; however, as temperatures were increased to 275°F, the H_2Se concentrations decreased to 75 ppb. By 350°F, the hydrogen selenide had dropped to less than 5 ppb. Figure 29 shows the results from a test conducted at 235°F where the H_2Se still had a significant concentration. The breakthrough curve for the EERC-treated carbon in this test shows that the hydrogen selenide is almost completely removed at these lower temperatures with this additive. Subsequent Method 29 wet-chemistry sampling on the empty reactor system heated to 400°F was completed with a known concentration of hydrogen selenide, and only 1% of the total selenium was found to be exiting the Sulfinert-

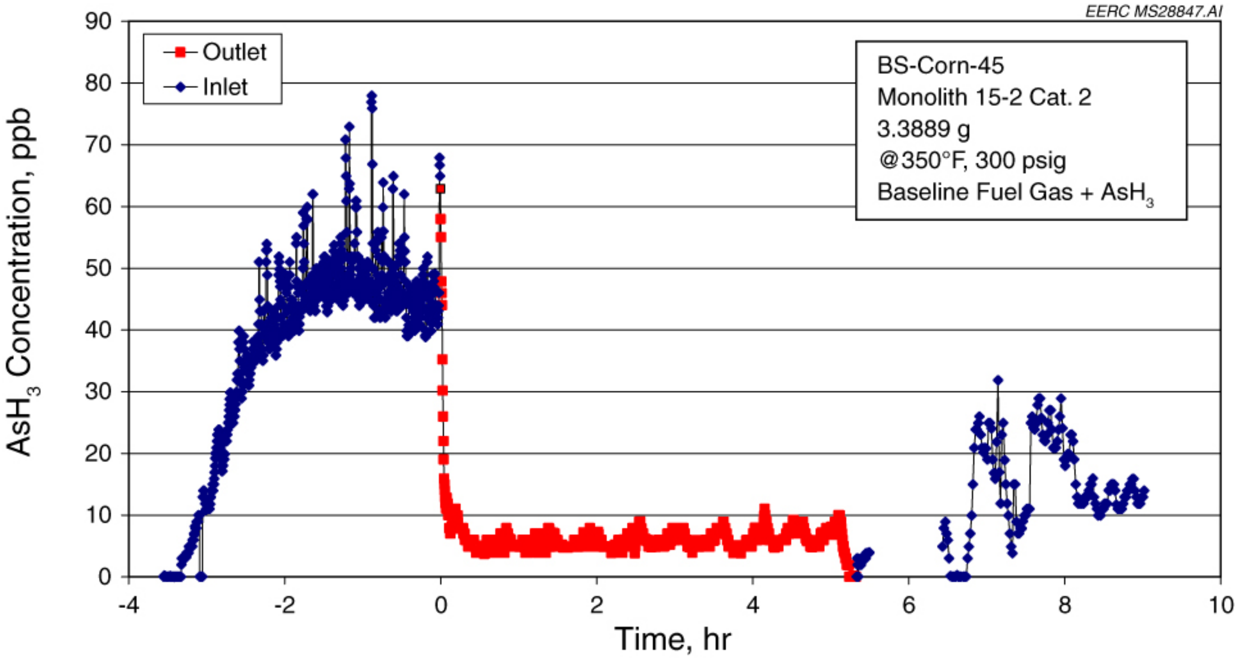

Figure 26. Breakthrough curve for Corning-treated carbon monolith with Catalyst 2 additive for AsH_3 control.

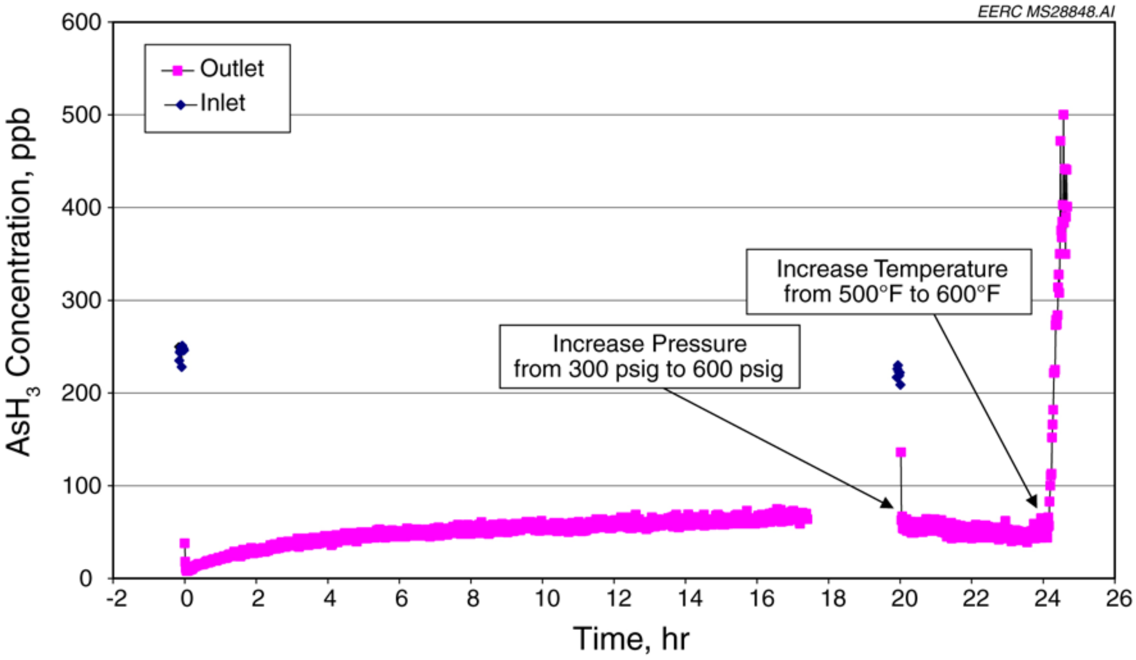

Figure 27. Breakthrough curve for the Corning-treated monolith with Catalyst 2 additive for the control of AsH_3 at various pressures and temperatures.

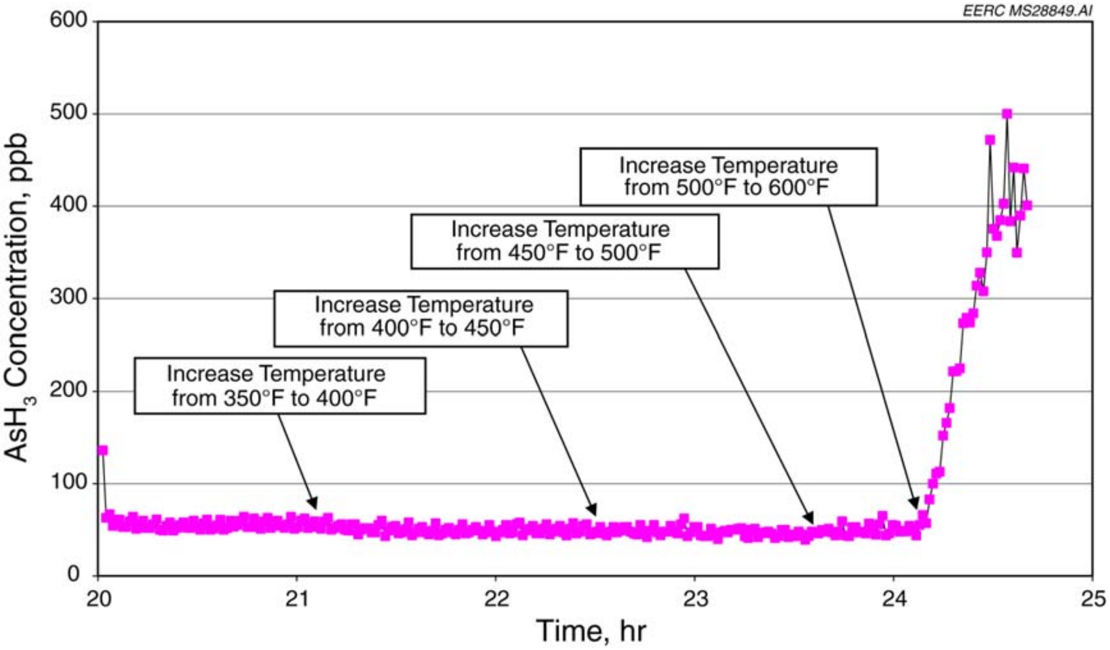

Figure 28. Breakthrough curve for Corning-treated monolith with Catalyst 2 additive for the control of AsH_3 at various pressures and temperatures.

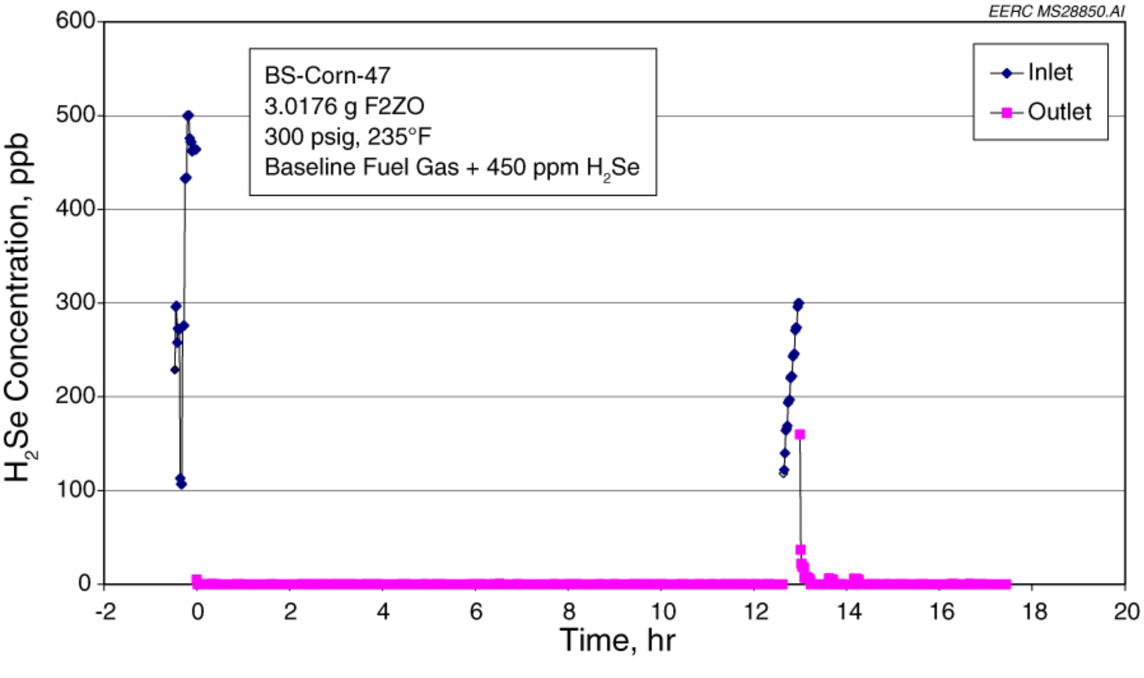

Figure 29. Breakthrough curve for EERC-treated carbon with F2ZO for H_2Se control at lower operating temperatures.

coated tubing and reactor. This result suggests that high-silicone coatings such as Sulfinert are not inert to hydrogen selenide at elevated temperatures and appears to be absorbing or reacting with the H_2Se. Other testing with non-passivated stainless steel tubing provided similar results. However, low-pressure tests with Teflon tubing at temperatures up to 400°F did not result in the disappearance of the hydrogen selenide.

These results led to conversations with Dr. Gokhan Alptekin at TDA Research, Inc., in which he reported that they did not see the hydrogen selenide react with their quartz tube liner inside their metal reactor. Another conversation with Dr. Rachid Slimane about GTI's trace gas sampling systems which utilize Sulfinert-coated tubing revealed that GTI has not conducted any selenide sampling with its trace gas-sampling system. The EERC is currently working with Restek Corporation on its coated stainless steels to determine whether a more appropriate coating is available.

ECONOMIC ANALYSIS

A preliminary economic analysis was performed for the control of mercury emissions using the Corning monolith system in a gasification combined-cycle scenario. The economic analysis centered only on the monolith technology and did not attempt to quantify improvements to cost, system design and operation, or efficiency (heat rate) of the entire gasification combined-cycle process. A limited sensitivity analysis was also performed. The mercury control costs for the Corning monolith technology were compared against a "conventional" mercury removal technology that is based on granular packed-bed sorbent carbon.

The economic analysis results for the "conventional" mercury removal technology is from the 4-year-old Parsons study, "The Cost of Mercury Removal in an IGCC Plant" (2). The "conventional" technology consists of parallel cylindrical vessels with internal diameters of approximately 7 ft, each containing granular carbon beds with depths of 20 ft. The application is well proven for mercury capture, based on Tennessee Eastman experience at their Kingsport, TN acetyl chemicals plant that employs coal gasification as a precursor for syngas-to-chemicals production. For utilization in an IGCC scenario, Parsons used in-house data to estimate equipment costs. The "conventional" packed-bed sorbent—Calgon Carbon Corporation's HGR-P sulfur-impregnated carbon pellets—is commercially available with an established cost history.

For the preliminary comparison of the Corning monolith against the "conventional" technology, a number of the plant as well as mercury control parameters were maintained at levels used in the Parsons study. These parameters and their values include:

- Plant load: 250 MW_e
- Plant capacity factor: 80%
- Mercury inlet concentration: 52 ppbw
- Mercury reduction by technology: 90% (131 lb/yr)
- Sorbent life: 1.5 years (10,502 hours)

In addition, the operations and maintenance shift labor requirements for the add-on mercury control technology, as well as economic parameters (e.g. capital cost, labor and overhead rates, taxes, etc.) were also kept constant relative to the Parsons study. As a matter of reference, values for these parameters are listed in Appendix A. Design and operating parameters for the Corning monolith technology that are different from those of the "conventional" technology are presented in Table 3.

The initial configuration of the Corning technology, envisioned for this analysis, consists of cylindrical monoliths, approximately 12 inches in diameter and up to 1 foot in length. The monoliths would be stacked within containment tubes that are arranged in parallel within a pressure vessel. Inlet and outlet tube sheets, sealed to the containment tubes would function to distribute flow to the tubes and through the channels of the monoliths. The number of parallel tubes (and pressure vessels) would depend upon the total volume rate of gas to be treated, and the height of stacked monolith within a containment tube would depend upon the desired space velocity (or residence time) for gas contacting.

Based on the gas flow rate for the 250 MWe plant (6.76 million scfh) and the assumed space velocity (41,200 hr^{-1}), the present configuration consists of 14 monolith tubes with a stacked monolith height of 15 ft, all within a single pressure vessel. Without the benefit of a rigorous vessel design effort, for this first-level analysis, it was assumed that the single vessel for the Corning monolith technology (with headers and monolith tubes) would have a capital cost equivalent to that required for the two pressure vessels of the "conventional" technology. Further, it was presumed that maintenance labor requirements for recharging structured monoliths in the Corning technology would be similar to the maintenance labor requirements for recharging loose, granular carbon used in the "conventional" technology.

The breakdown of the capital costs is presented in Figure 30. The total capital cost (TCC) was $834,400 or $3.34/kW with approximately 50% of the TCC consisting of the purchased equipment. The first-year O&M cost was estimated to be $173,800 with approximately 44% of this value due to monolith replacement costs. Other significant contributors to the annual O&M cost include taxes/insurance/administration at 19% and overhead at 12%. A breakdown of the annual O&M is presented in Figure 31.

The estimated total annual cost was approximately $299,000 based on a capital recovery factor of 15%. This equates to an incremental electricity cost of $0.171/MWh (or 0.171 mills/kWh) for the baseline monolith configuration. For the assumed mercury removal level of 90 wt% (131 lb/yr), the cost of mercury reduction was estimated at $2290/lb Hg removed. This latter value is approximately an order of magnitude less than estimates for mercury removal in pulverized coal (PC) systems.

The costs for the monolith technology were also compared against those of the "conventional" technology with the results graphically presented in Figures 32 and 33. The economics for the conventional technology is based upon an assumed 0.4 wt% mercury loading on the granular carbon sorbent (2). The granular sorbent apparently can hold up to 20 wt%

Table 3. Technology Operating Parameters – Monolith vs. Conventional

		Value	
Parameter	Units	Monolith	Conventional
Plant Net Capacity	MWe	250	
Capacity Factor	%	80	
Molecular Weight	lb/lb mol	21.0	
Gas Temperature	°F	350	105
Pressure	psia	415	378
Mercury Concentration	ppbw	52	
Monolith Density	lb/ft^3	30	
Space Velocity (actual volume)	hr^{-1}	2400	178
Monolith Void Area	%	0	
Monolith ID	inches	12	
Stacked Monolith Height	ft	15	
Monolith Life	hr	10,502	
Monolith Life	cycles	1	
Output Parameter	Units	Value	
Syngas Molar Rate	lb-mol/hr	18,824	
Syngas Mass Rate	lb/hr	396,099	
Syngas Volume Rate	sft^3/hr	6,757,816	
Syngas Volume Rate	aft^3/hr	394,090	
Sorbent Charge Volume	ft^3	164	1689
Space Velocity (standard volume)	hr^{-1}	41,200	4000
Initial Monolith Charge Mass	ton	2.5	25.0
Monolith ID	ft	1.00	
Number of Monolith Elements (parallel)		14	
Gas Superficial Velocity	ft/sec	10	1
Gas Residence Time	sec	1.5	20
Monolith Replacement Cycle	yr	1.50	
Sorbent Replacement Rate	ton/yr	1.6	16.9
Sorbent Replacement Rate	ft^3/yr	109.6	1142
Hg Loading on Sorbent	lb Hg/lb monolith	0.0397	0.0039
Plant Parameters	Units	Value	
Plant Net Capacity	MWe	250	
Gas Rate	lb/hr	396,099	
Hg Level Before Fixed Bed	ppbw	52	
Mercury Reduction	%	90	
Hg Level after Monolith Bed	ppbw	5	
Capacity Factor	%	80	
Mercury Reduction	lb/yr	131	
Labor	hrs/shift	1	
Maintenance	hrs/shift	0.5	
Monolith Utilization Rate	lb/yr	3287	
Electricity Consumption	kWh/yr	100,000	~1,000,000
Monolith/Carbon Cost	\$/ft^3	700*	193

* Initial preliminary cost estimate from Corning based on small-scale development work.

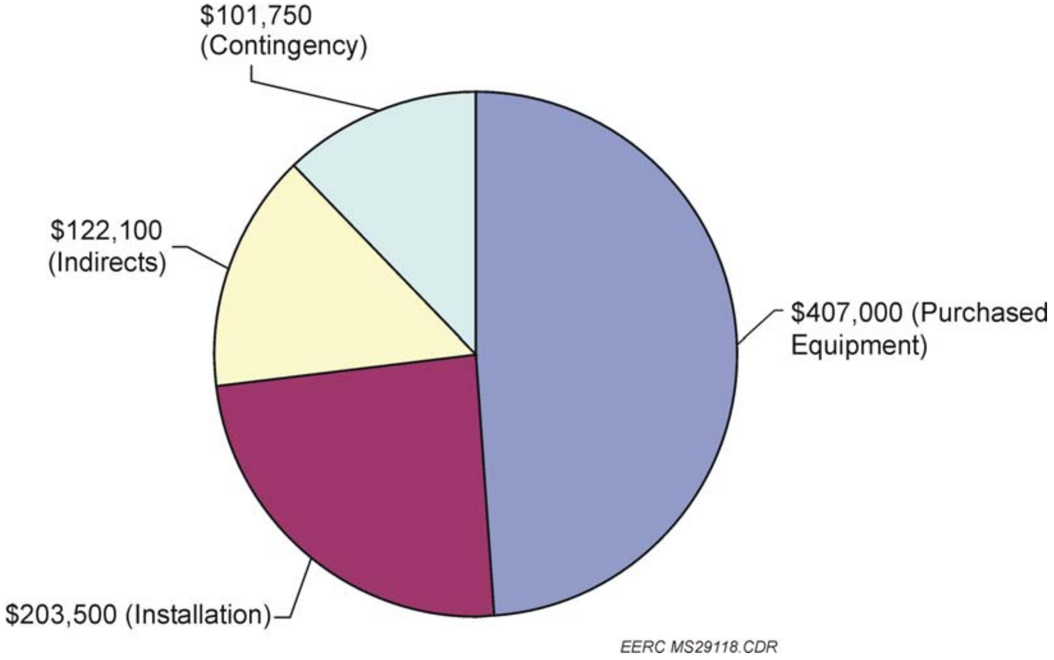

Figure 30. Breakdown of capital costs for monolith technology.

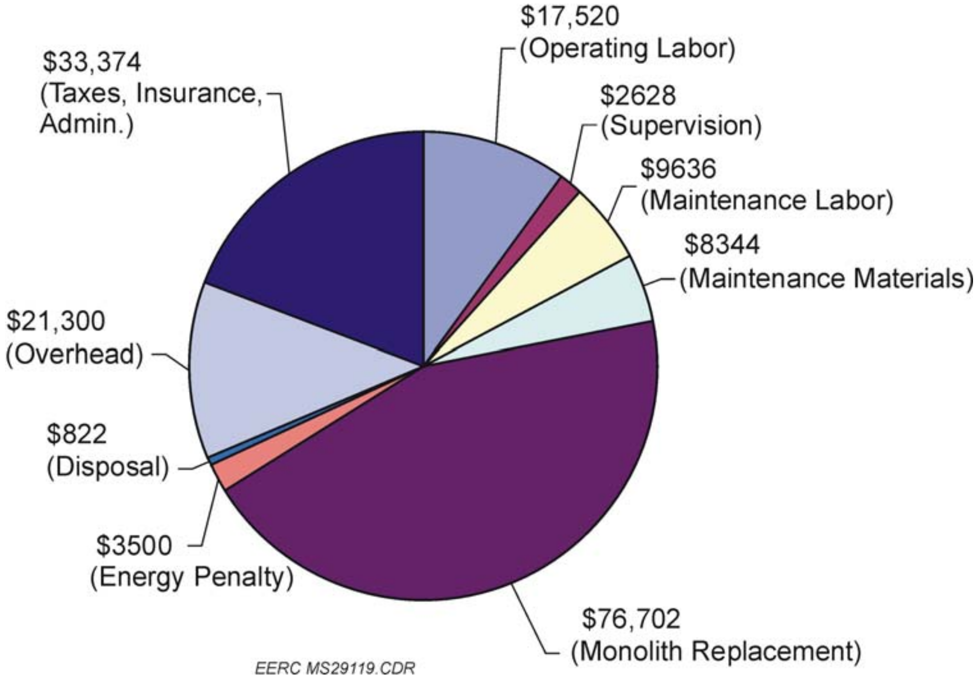

Figure 31. Breakdown of operating and maintenance costs for monolith technology.

mercury, also as reported by Parsons (2). Our baseline economics for the monoliths assumed a 4 wt% capacity, thus allowing the ten fold reduction in sorbent mass used. Based on the preliminary assumptions for the system design and operation, the Corning monolith technology provides the potential for a 33% reduction in cost, principally through the reduction of O&M costs (see Figure 32). The majority of the O&M cost reduction is due to the 10-fold reduction in sorbent charge (and replacement rate) relative to the “conventional” technology based on the higher space velocities utilized in the EERC testing. This would require that Hg levels would approach 4 wt% in the monolith, which is still considerably less than mercury levels up to 20 wt%.

A limited sensitivity analysis was also performed using monolith cost, purchased equipment cost, monolith life, and monolith charge as the sensitivity variables. The ranges of values used in the sensitivity analysis are shown below.

- Initial estimated monolith cost ($450/ft^3 and $1200/ft^3)
  - Baseline = $700/ft^3
- Purchased equipment cost ($203,500 and $814,000)
  - Baseline = $407,000
- Monolith life (0.75 and 3.0 years)
  - Baseline = 1.5 years (10,502 hours)
- Monolith charge (25 ton with 16.9 ton/yr replacement rate; same as conventional)
  - Baseline = 2.5 ton

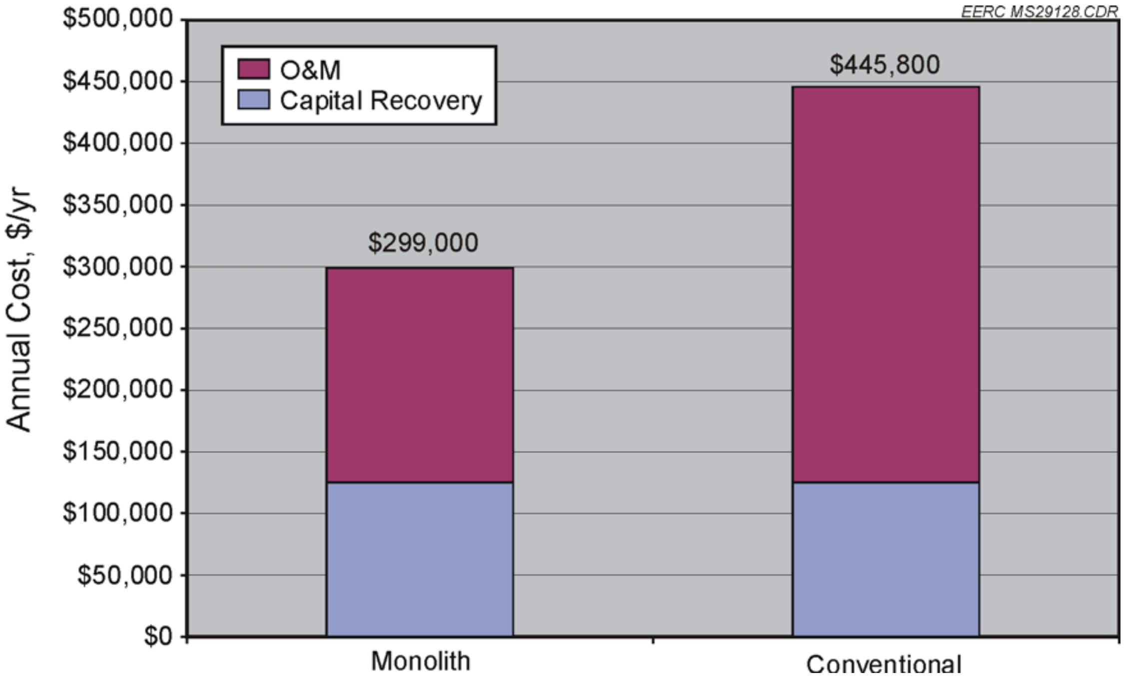

Figure 32. Total annual cost ($/yr) – monolith vs. conventional.

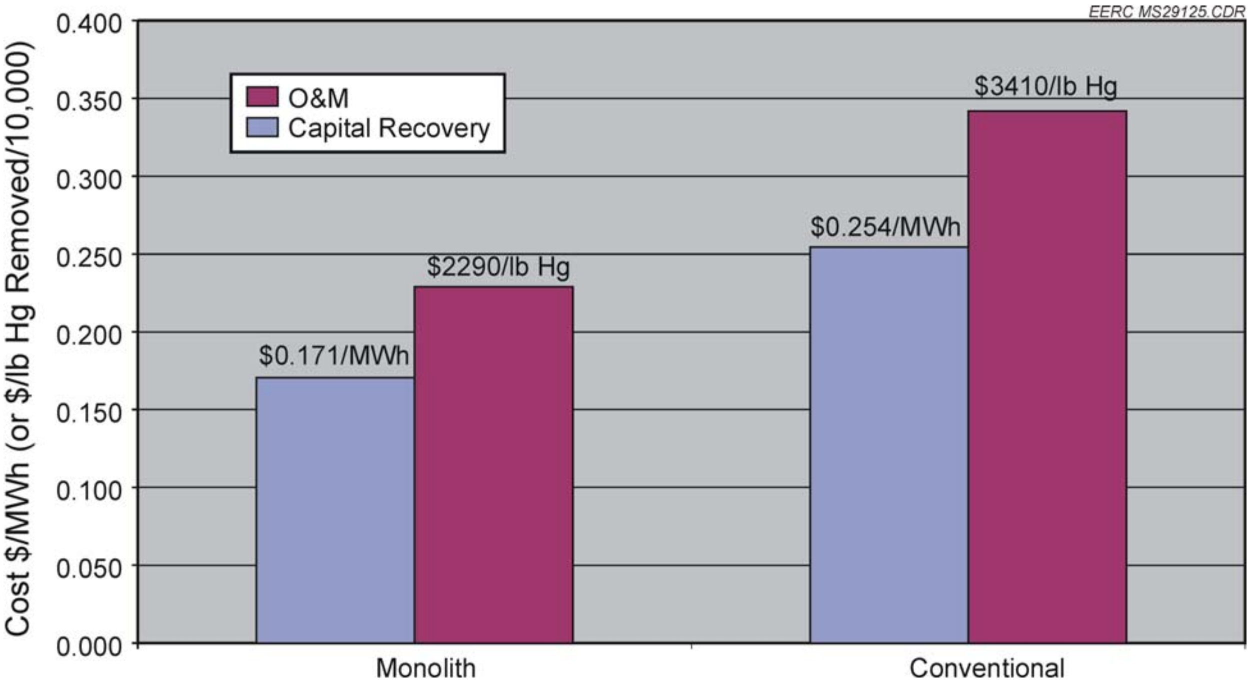

Figure 33. Incremental electricity cost ($/MWh) and mercury removal cost ($/lb Hg) – monolith vs. conventional.

Baseline refers to the parameter value used in the initial analysis. Corning provided the initial preliminary monolith cost data. The purchased equipment values of $203,500 and $814,000 are simply 50% and 200%, respectively, of the baseline value of $407,000. Similarly, the monolith life values of 0.75 years and 3.0 years are 50% and 200%, respectively, of the baseline value of 1.5 years. A tenfold increase in monolith charge, from a baseline of 2.5 up to 25 tons, was evaluated in case future analysis shows that the mercury capacity of the treated monolith at process conditions will be limited to a value—~0.4 wt%—similar to that assumed for the "conventional" activated carbon technology.

Figures 34 and 35 show the impact of monolith cost, purchased equipment cost, and monolith life on the Corning mercury control technology cost. At a monolith charge ~1/10 of the "conventional" sorbent charge, the purchased equipment cost has the greatest influence on annual mercury control cost, with low and high values ranging from ~-30% to ~+60% of the baseline cost. Therefore, subsequent analysis needs to define the gas contacting/pressure containment device that would utilize the monoliths.

Figure 36 presents the results of sensitivity analysis comparing total annual cost of the baseline monolith scenario to a scenario utilizing a monolith mass charge equivalent to that of the "conventional" sorbent technology. This would be the case if the maximum sorbent loading of the monolith is equivalent to the "conventional" sorbent. The results show the potential for an approximate 240% increase in total annual cost because of the tenfold increase in monolith charge. Further testing is required to determine the maximum mercury loading of the monoliths.

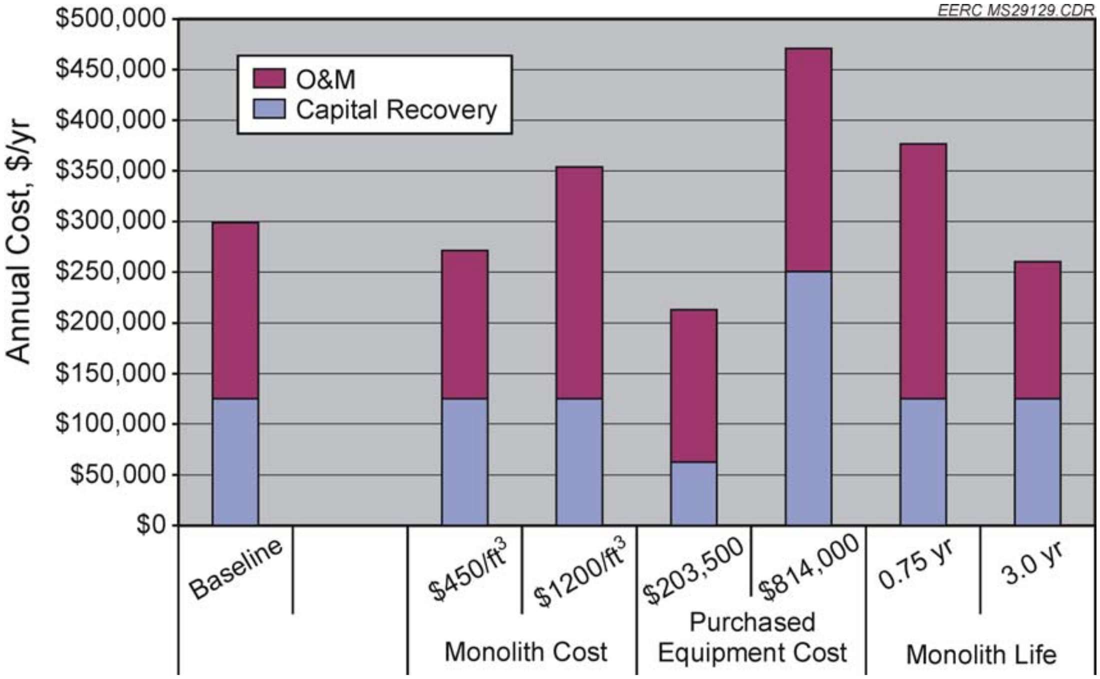

Figure 34. Sensitivity analysis results – impact on total annual cost ($/yr).

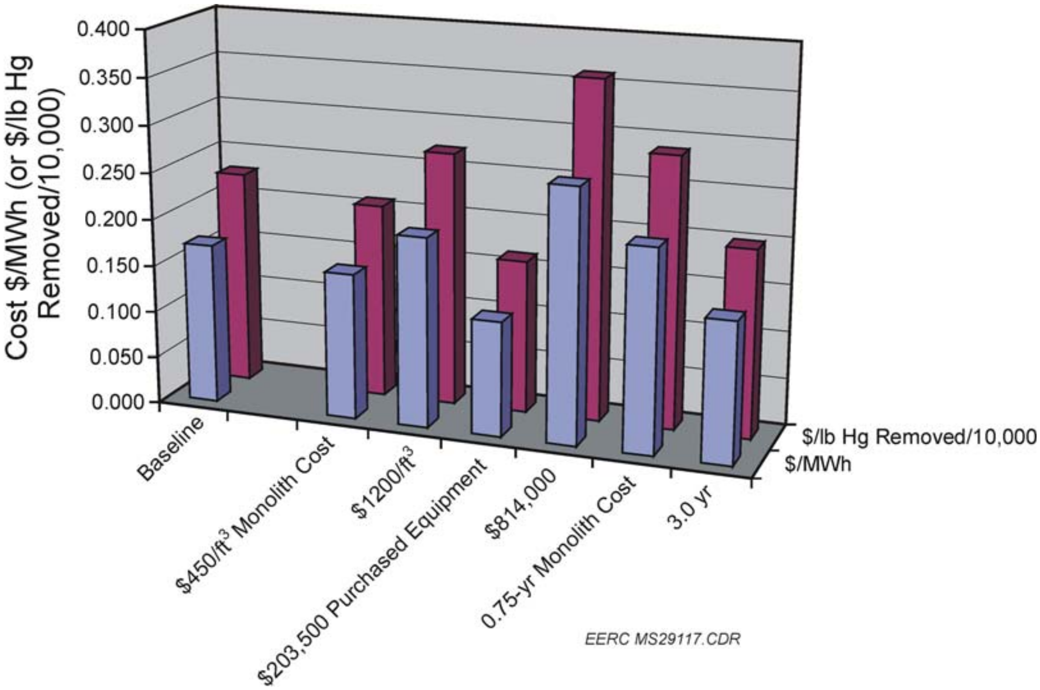

Figure 35. Sensitivity analysis results – impact on incremental electricity cost ($/MWh) and mercury removal cost ($/lb Hg).

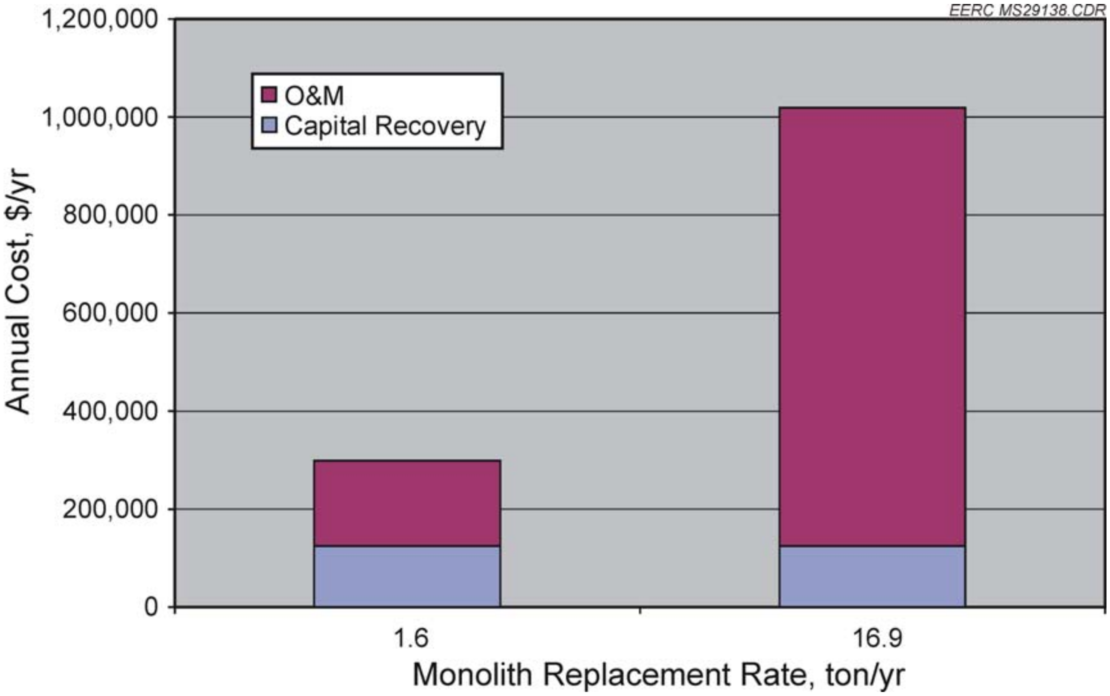

Figure 36. Sensitivity results – impact of monolith mass charge on total annual cost ($/yr).

Additionally, it is presumed that there would be a greatly reduced or eliminated gas cooling/reheat requirement with the monoliths as they would operate at higher temperature relative to the "conventional" sorbent. These system improvements would lead to lower capital and O&M costs as well as combined-cycle system thermal efficiency improvements.

CONCLUSIONS

The EERC and Corning team has currently developed three potential additives for controlling mercury emissions from syngas at temperatures ranging from 350° up to 500°F (177° up to 260°C). Current efforts are being directed at increasing the effective working temperature for these sorbents and also being able to either eliminate any potential mercury desorption or trying to engineer a trace metal removal system that can utilize the observed desorption process to repeatedly regenerate the same sorbent monolith for extended use. Project results also indicate that one of the same sorbents can also successfully be utilized for arsenic removal. Capture of the hydrogen selenide in the passivated tubing at elevated temperatures has resulted in limited results on the effective control of hydrogen selenide with these current sorbents although lower temperature results are promising. Preliminary economic analysis suggests that these Corning monoliths potentially could be more cost-effective than the cold-gas presulfided activated carbon beds currently being utilized; however, recent Hg loading results might suggest that the annualized costs might be as high as 2.5 times the cost of the conventional technology. However, this annualized cost does not take into account the significantly improved thermal efficiency of any plant utilizing the warm gas monolith technology currently being developed.

FUTURE WORK

The EERC is currently calibrating different arsenic and selenium measurement techniques against known wet-chemistry methodologies under a separate EPA-funded program. This information will be incorporated into the Year 2 project. Year 2 work will focus on laboratory-scale bottled gas testing at higher temperatures (>400°F) and at higher pressures (>600 psig) to test monoliths at more commercially relevant conditions. Two weeks of lower pressure testing on an existing fluid-bed gasifier will also be completed to determine monolith performance on an actual coal-derived syngas. This bench-scale testing will allow the more difficult cadium control testing to be completed. A more comprehensive economic analysis will be performed at the end of the second year to determine whether the monolith-based trace element control technology is cost-effective.

REFERENCES

1. Alptekin, G.; Amalfitano, R.; Dubovik, M.; Cesario, M. Sorbents for Trace Metal Removal from Coal-Derived Synthesis Gas, Proceedings of the 22nd Annual Pittsburgh Coal Conference; Sept 12–15, 2005.

2. Rutkowski, M.; Klett, M.; Maxwell, R. The Cost of Mercury Removal in an IGCC Plant. Presented at the Gasification Technologies 2002 Conference, San Francisco, CA, October 27–30, 2002.

APPENDIX A

PARAMETERS FOR COST ANALYSIS

Table A-1. Parameters for Cost Analysis

Parameter	Units	Value
Plant Net Capacity	MWe	250
Capacity Factor	%	80
Molecular Weight	lb/lb mol	21.0
Gas Temperature	°F	350
Pressure	psia	415
Mercury Concentration	ppbw	52
Monolith Density	lb/ft^3	30
Space Velocity (actual volume)	hr^{-1}	2400
Monolith Void Area	%	0
Monolith ID	inches	12
Stacked Monolith Height	ft	15
Monolith Life	hr	10,502
Monolith Life	cycles	1
Output Parameter	**Units**	**Value**
Syngas Molar Rate	lb mol/hr	18,824
Syngas Mass Rate	lb/hr	396,099
Syngas Volume Rate	sft^3/hr	6,757,816
Syngas Volume Rate	aft^3/hr	394,090
Sorbent Charge Volume	ft^3	164
Space Velocity (standard volume)	hr^{-1}	41,155
Initial Monolith Charge Mass	ton	2.5
Monolith ID	ft	1.00
Number of Monolith Elements (parallel)		14
Gas Superficial Velocity	ft/sec	10
Gas Residence Time	sec	1.5
Monolith Replacement Cycle	yr	1.50
Sorbent Replacement Rate	ton/yr	1.6
Sorbent Replacement Rate	ft^3/yr	109.6
Hg Loading on Sorbent	lb Hg/lb monolith	0.0397
Plant Parameters	**Units**	**Value**
Plant Net Capacity	MWe	250
Gas Rate	lb/hr	396,099
Hg Level Before Fixed Bed	ppbw	52
Mercury Reduction	%	90
Hg Level After Monolith Bed	ppbw	5
Capacity Factor	%	80
Mercury Reduction	lb/yr	131
Labor	hrs/shift	1
Maintenance	hrs/shift	0.5
Monolith Utilization Rate	lb/yr	3287
Electricity Consumption	kWh/yr	100,000
Economic Parameters	**Units**	**Value**
Installation	% of PE	50

Continued…

Table A-1. Parameters for Cost Analysis (continued)

Indirects	% of PE	30
Contingency	% of PE	25
Supervision	% of OL	15
Maintenance Materials	% of TCC	1
Overhead	% of L & M	60
Taxes, Insurance, Administration Rate	% of TCC	4
Disposal Fee	\$/ton	500
Labor Rate	\$/hr	20
Maintenance Rate	\$/hr	22
Monolith Cost	\$/ft^3	700
Energy Cost	\$/kWh	0.035
Discount Rate	%	0
Escalation	%/yr	0
Capital Recovery Factor	%	15
Economic Life	yr	0