MATERIAL TESTING OF COATED ALLOYS IN A SYNGAS COMBUSTION ENVIRONMENT

Year 6 – Activity 1.13 – Development of a National Center for Hydrogen Technology

Topical Report

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ABSTRACT

Modifications were made to the inlet of the existing Energy & Environmental Research Center (EERC) thermal oxidizer to accommodate side-by-side coupon holders for exposure testing. Two 5-day tests with over 200 hours of total exposure time were completed. The first week of testing was conducted in enriched air-blown mode, with coupon temperatures ranging from 128° to 272°F. Carbonyl sampling was conducted, but it was discovered after the fact that the methodology used was producing very low recoveries of iron and nickel carbonyl. Therefore, the data generated during this week of testing were not considered accurate. The second week of testing was conducted in oxygen-blown mode, with coupon temperatures ranging from 220° to 265°F. Two improved methods were used to measure carbonyl concentration during this week of testing. These methods produced results closer to equilibrium calculations. Since both weeks of testing mostly produced a product gas with approximately 15%–18% carbon monoxide, it was felt that actual carbonyl concentrations for Week 1 should be very similar to those measured during Week 2.

The revised carbonyl sampling methodology used during the second week of testing greatly improved the recovery of iron and nickel carbonyl in the sample. Even though the sampling results obtained from the first week were inaccurate, the results from the second week can be used as an estimate for the periods during which the gasifier was operating under similar conditions and producing similar product gas compositions. Specifically, Test Periods 2 and 3 from the first week were similar to the conditions run during the second week. For a product gas containing roughly 15%–18% CO and a coupon temperature of approximately 220°–270°F, the nickel carbonyl concentration should be about 0.05–0.1 ppm and the iron carbonyl concentration should be about 0.1–0.4 ppm.

After each week of testing the coupons were recovered from the coupon holder, weighed, and shipped back to Siemens for analysis.

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EXECUTIVE SUMMARY

Modifications were made to the inlet of the existing Energy & Environmental Research Center thermal oxidizer to accommodate side-by-side coupon holders for exposure testing. Over 200 hours of exposure testing were completed during two 5-day tests. The first test was conducted in enriched air-blown mode, with coupon temperatures of 128°–272°F. The second week was conducted in oxygen-blown mode, with coupon temperatures of 220°–265°F. During both weeks of testing, the gasifier product gas contained 15%–18% carbon monoxide. Iron and nickel carbonyl sampling was performed to determine the concentration of carbonyls in the syngas. After each week of testing, the coupons were weighed to determine the mass of carbonyl deposition and then returned to Siemens for further analysis.

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INTRODUCTION AND BACKGROUND

The gas turbine in the Puertollano integrated gasification combined-cycle (IGCC) power plant experienced performance degradation caused by deposits and corrosion in the burners and first-row expander airfoils. Some of the deposition and corrosion was because of iron and nickel carbonyls, which were apparently formed in the upstream piping and transported to the turbine. The orifice plates immediately upstream of each of the 18 burners experienced considerable deposition.

During 2004 through 2008, Siemens tested a new carbonyl-resistant coating developed by a third party for its ability to operate in its intended environment. The tests by Siemens involved most aspects of normal operation, and the tests by EERC added the additional component of high-velocity to the syngas stream. This project was intended to test coated (coupon samples) in a comparable coal-derived syngas stream to see if carbonyls are deposited on the sample. A comparison set of uncoated samples was also exposed to the same syngas stream as the control samples.

The objective of this project was to test the effectiveness of a new coating to resist deposition of carbonyl compounds present in syngas under realistic IGCC operating conditions and to identify where the coating could be applied in gas turbines and other process equipment that are exposed to carbonyl-laden reducing gases.

This testing was conducted at the laboratories of the University of North Dakota Energy & Environmental Research Center (EERC).

APPROACH

The objective of this activity was to test the effectiveness of a new coating to resist deposition of carbonyl compounds present in syngas under realistic IGCC operating conditions and to identify where the coating could be applied in gas turbines and other process equipment exposed to carbonyl-laden reducing gases.

In Task 1, the thermal oxidizer system components were modified to incorporate side-by-side coupon holders for holding both a coated and uncoated section of the flow equalizer. In addition, various coupons were placed downstream in the thermal oxidizer at the desired temperature range to determine if carbonyl dusting of the gas expander section is appreciable. An electric heater was installed on the syngas inlet line capable of preheating syngas to the desired temperature range specified by Siemens. A high-carbon-monoxide syngas was passed through a

nickel or iron fixed-bed reactor to maximize the carbonyl concentration to speed up the carbonyl deposition process.

Task 2 testing was conducted according to a preapproved test plan developed with Siemens. This task provided 200 hours of exposure to the coal-derived syngas. The high-pressure fluid-bed gasifier (FBG) was utilized to generate the syngas from one or two selected feedstocks. After the first week, the coupons were inspected and weighed and possible samples taken. The internal coupons in the thermal oxidizer were inspected after each week of testing. Siemens and the EERC mutally decided to resume the testing with the same conditions. Since nitrogen is added to the syngas before it passes through the flow equalizers at the Puertollano plant, the FBG operated in an air-blown mode for ease of operation unless the nickel or iron packed-bed reactor is utilized, in which case oxygen-blown conditions were utilized to maximize CO concentrations and reduce syngas flow through the packed bed, thereby minimizing pressure drop across the packed bed. During the two 5-day tests, numerous Dräger tubes for the carbonyl species were taken, along with extractive wet-chemistry samples (U.S. Environmental Protection Agency [EPA] Method [M] 29) being taken every day.

EQUIPMENT DESCRIPTION

Fluid-Bed Gasifier

This system was designed according to American Society of Mechanical Engineers (ASME) B31.3 Process Piping Code specifications. The internal reactor dimensions are based upon the existing operational continuous fluidized-bed reactor (CFBR) that currently operates up to a maximum operating pressure (MOP) of 1.0 MPa (150 psig). After a review of available alloys, Haynes 556® was selected as the material most suitable for fabrication of this high-temperature, high-pressure system. The reactor was designed with the capability to operate at a MOP of 6.9 MPa (1000 psig) at operational temperatures of 843°C (1550°F), 4.5 MPa (650 psig) at an operational temperature of 917°C (1650°F), and 2.0 MPa (300 psig) at an operational temperature of 1800°F. This system is designed to be externally electrically heated in a similar manner to the CFBR. The 2500-pound 316H stainless steel flanged connections at the top and bottom of the reactor will be limited to a maximum operating temperature of 677°C (1250°F) for a MOP of 6.9 MPa (1000 psig), 732°C (1350°F) for a MOP of 4.5 MPa (650 psig), and an operational temperature of 816°C (1500°F) for a MOP of 2.0 MPa (300 psig). Haynes 556® alloy was selected as the material of construction for the reactor, all the reactor nozzles, and the cyclone.

The feed system uses a K-Tron® loss-in-weight feeder setting inside of the pressure vessel capable of 6.9-MPa (1000-psig) operation. This system allows a real-time measurement of the fuel feed rate to the gasification system. The feed system electronic controls are interfaced to a data acquisition system that allow for local or remote computer control of the fuel feed rate. Power and electronic signals to and from the feeder are through two isolation fittings on the pressure vessel. The upper pressure vessel is the fuel charge hopper. The fuel charge hopper is manually charged with fuel through the top valve while at atmospheric pressure. It is then sealed and pressurized. Finally, the fuel feed material is transferred by gravity feed to the weigh hopper

inside through the lower dual-valve system. The weigh hopper is on an integral platform scale that provides an electronic signal of the overall weight of the fuel feed material. Hopper weights along with feed rates are recorded by the data acquisition system and can be displayed and trended as required.

Additionally, two sets of three (six total) water-cooled quench pots have been designed for condensing moisture and organics from the gas stream. These quench pots have been designed for operation up to 1000 psig. The design of these quench pots is based upon what has been successfully used with the CFBR. This design has been very effective in the removal of organics and moisture while not plugging off. It has evolved over years of operation. Either water or a cooled glycol and water mixture is circulated through the outer jacket of each quench pot to cool the product gas down.

A design drawing of the FBG is shown in Figure 1, and a photograph of the gasifier is shown in Figure 2. A design drawing of the fuel feed system is shown in Figure 3, with a photograph of the feeder vessel given in Figure 4. Photographs of the back-end cleanup systems are shown in Figures 5–8 for the sulfur control reactor, hot-gas filter system, fixed-bed reactors, and water quench systems, respectively.

A thermal oxidizer was added to the FBG outlet so that the syngas could be completely combusted before being vented. For this project, a heated coupon holder was designed and constructed that will enable the four coupons (two coated and two uncoated provided by Siemens) to be exposed to heated syngas from the FBG just before it is enters the thermal oxidizer for combustion. This design compresses the four 2-inch by 4-inch coupons in a vessel that seals the edge of the coupons such that gas flow is forced through the holes (flow diffusers/straighteners) in each coupon. Figure 9 is a schematic of the coupon holder located at the inlet to the thermal oxidizer. Figure 10 is photograph of the coupon holder and thermal oxidizer, while Figure 11 is a photograph of the coupons mounted inside the coupon holder.

RESULTS AND DISCUSSION

Week 1 Testing

The FBG was operated on coal for 103 hours between August 30 and September 3, 2010. The coal was from the Antelope Mine which is a Powder River Basin subbituminous coal from Wyoming. Plum Run dolomite was added at a ratio of 1.25 lb per 25 lb of coal (approximately 4.75 wt%). Table 1 shows the analysis of the baseline Antelope coal utilized for all of the gasification testing. Five steady-state test periods were identified, varying mostly in coal feed rate, steam rate, and O_2 rate in the gasifier, and with different temperatures in the duct where Siemens coupons were located. The average operating conditions and product gas compositions for the steady-state periods are presented in Tables 2 and 3.

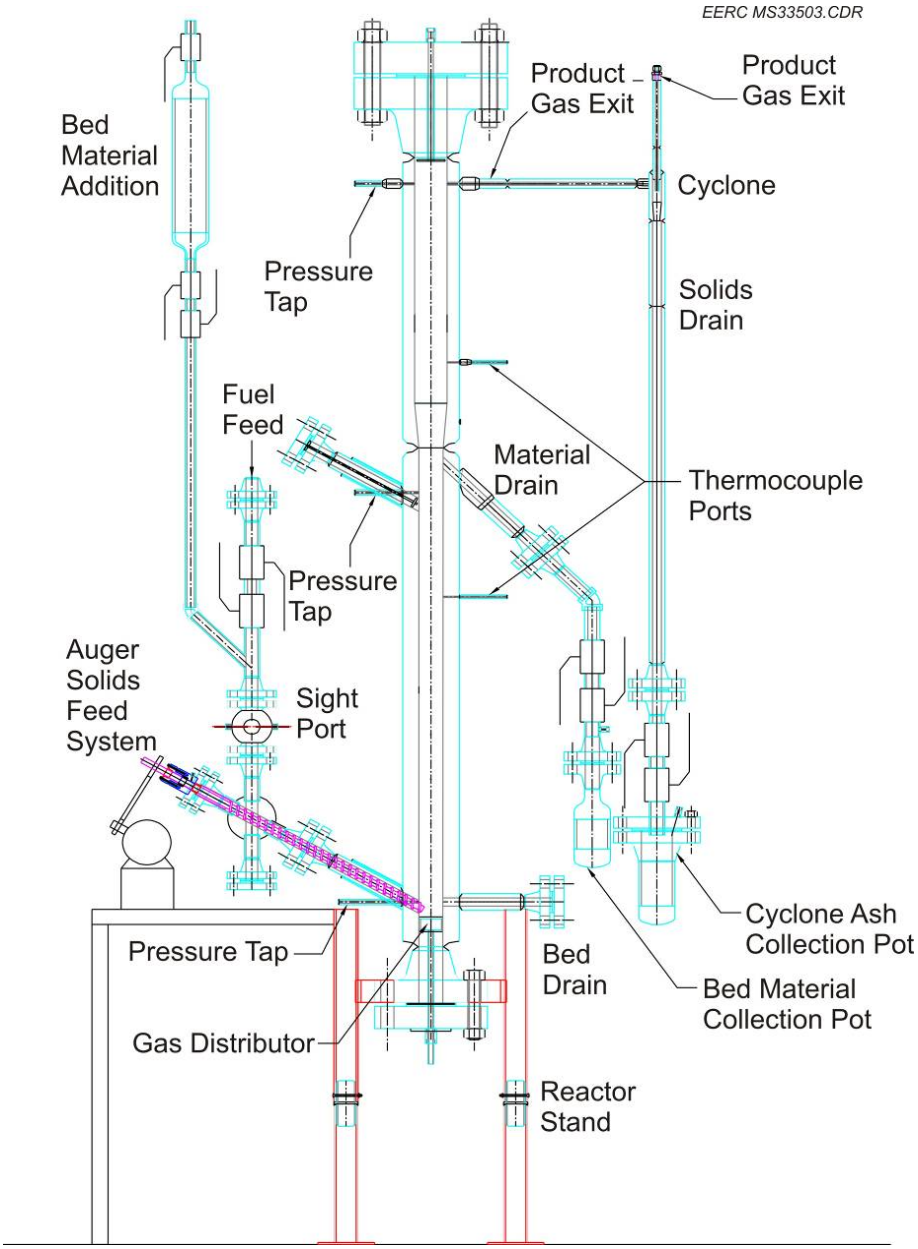

Figure 1. Design drawing of the pressurized, fluidized gasification reactor.

Figure 2. Photograph of the high-pressure FBG.

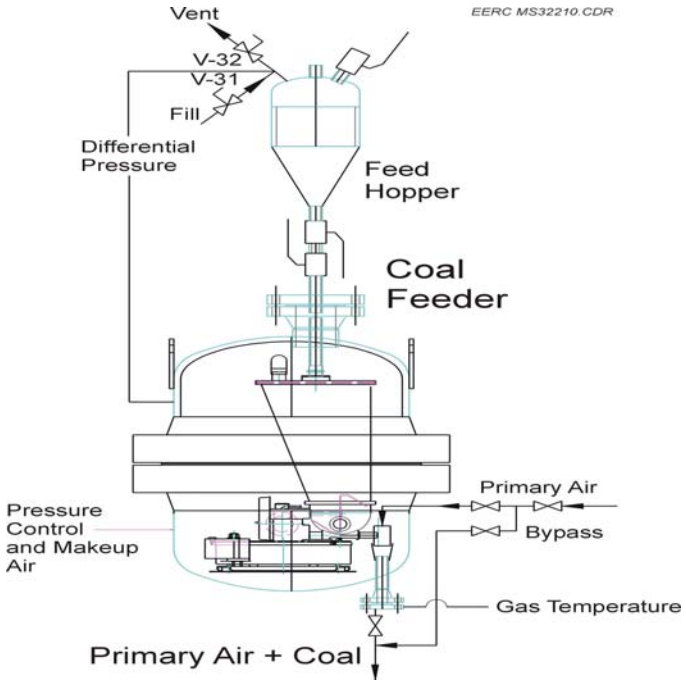

Figure 3. Cross-sectional view of the fuel feed system.

Figure 4. Photograph of the fluid-bed coal feed system.

Figure 5. Photograph of the EERC circulating fluid-bed desulfurizer.

Figure 6. Photograph of the EERC hot-gas filtration system.

Figure 7. Photograph of the EERC fixed-bed reactor/sorbent contactors.

Figure 8. Photograph of the quench system for steam condensation with back-pressure control valve.

The goal was to maintain the temperature at the inlet of the coupon holder between 260°–270°F, but during the last two test periods, the temperature was lowered to 130°–150°F in an attempt to determine if higher temperatures were decomposing carbonyls that might have formed.

Nickel and iron carbonyl testing was performed using a nonisokinetic wet-chemistry method. The method used was a modified M29 sampling train that used the first two impinger solutions of an M29 sample train to capture any nickel carbonyl or iron carbonyl that was present. Nickel and iron carbonyl compounds would exist as a vapor phase at the temperatures sampled (200°F) and would be captured in the hydrogen peroxide/dilute nitric acid impingers of the M29 sample train. All of the sample equipment was either Teflon or glass, and the sample lines as well as the filter holder were rinsed into the combined first and second impinger catches. The samples were then analyzed for nickel and iron, with the assumption that any nickel or iron found would have come from the carbonyl since these metals would not normally show up as vapor-phase compounds at the sampling temperatures used. A filter was analyzed separately just to verify that nothing had collected on it. The results of the sampling indicate nondetects on the filter and nondetects for all of the liquid samples when analyzed for nickel. Analysis for iron indicated amounts below the detection limits on the filter and very low amounts in the liquid samples. The conclusion from this sample program is that no nickel carbonyl was generated and only a limited amount of iron carbonyl was generated. Sample volumes for these tests were fairly large (1.5 to 2 m^3) so the detection limits were relatively low (0.25 ug/m^3 for nickel and 0.5 ug/m^3 for iron). Dräger tubes were also used to determine the carbonyl concentration in the syngas, but the results were inaccurate because of interferences with H_2S.

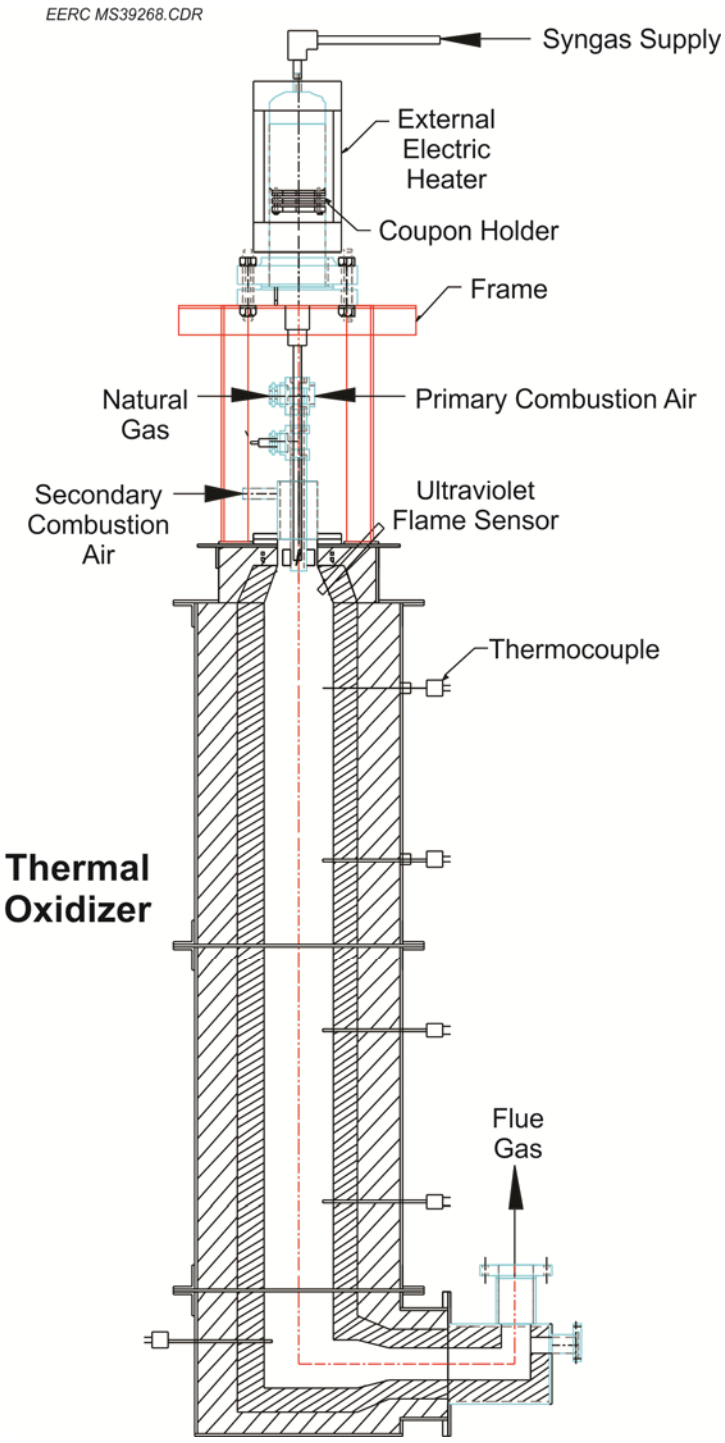

Figure 9. Schematic of the coupon holder in relation to the thermal oxidizer.

Figure 10. Photograph of the coupon holder (top) and thermal oxidizer.

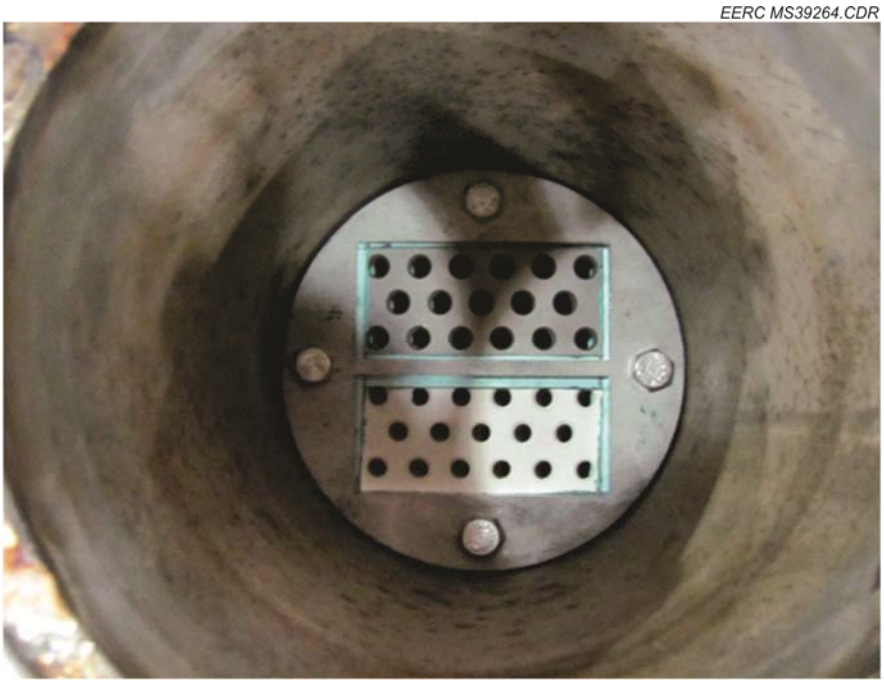

Figure 11. Coupons mounted inside the coupon holder for exposure testing.

Table 1. Analysis of FBG Test Coal for Coupon Exposure Testing

	Antelope PRB Subbituminous Coal
Proximate Analysis, as run, wt%	
Moisture	24.4
Volatile Matter	29.1
Fixed Carbon	42.5
Ash	4.1
Ultimate Analysis, MF[1], wt%	
Carbon	69.54
Hydrogen	4.70
Nitrogen	0.86
Sulfur	0.39
Oxygen	19.11
Ash	5.40
High Heating Value	
MF, Btu/lb	11,668
As-Received, Btu/lb	8820

[1] Moisture-free.

The results obtained from the sampling method are presented in Table 4. Each of the samples yielded carbonyls of less than 1 part per billion (ppb). The fourth sample taken included the mass collected on the filter. Even still, the concentration was less than 3 ppb. However, after the first week of testing was completed, it was discovered that the sampling methodology used

Table 2. Week 1 Gasifier Operating Conditions

Test Period	1	2	3	4	5
Start	8/30 23:08	8/31 17:00	9/1 08:00	9/2 05:00	9/2 20:00
End	8/31 04:37	9/1 07:00	9/1 12:30	9/2 07:00	9/3 08:00
Hours at steady-state	7.0	14.0	4.5	2.0	12.0
Coupon Temperature, °F	272	254	269	128	150
Coal Feed, lb/hr	9.0	7.7	7.7	7.4	6.5
Avg. Gasifier Temp., °F	1550	1575	1575	1570	1570
O_2 Flow, scfh	45	65	65	60	60
N_2 Flow, scfh	36	25	25	30	NA
Steam Flow, lb/hr	8.0	11.5	11.5	15.0	16.0
Recycle Flow, lb/hr	10.2	26.0	26.0	28.0	30.0

Table 3. Week 1 Product Gas Composition

Test Period	1	2	3	4	5
Start	8/30 23:08	8/31 17:00	9/1 08:00	9/2 05:00	9/2 20:00
End	8/31 04:37	9/1 07:00	9/1 12:30	9/2 07:00	9/3 08:00
CO, vol%	9.0	16.4	16.8	16.9	18.7
CO_2, vol%	17.7	41.0	40.7	55.9	60.5
H_2, vol%	20.5	18.6	19.0	22.3	18.6
CH_4, vol%	1.5	2.0	1.9	2.1	1.8
HC, vol%	0.09	0.09	0.04	0.06	0.03
H_2S, vol%	0.060	0.110	0.114	0.146	0.141
N_2, vol%	51.0	22.1	22.3	4.2	2.6

was not accurate, producing a very low recovery of iron and nickel carbonyl from known gas samples. Since these recoveries were less than 8% of known gas samples, a series of laboratory-scale tests were completed until a sampling methodology that accurately measured carbonyl concentrations was developed. Previous sampling during the first week of testing had called into question the sampling techniques used to sample for both iron and nickel carbonyl. In an effort to resolve the sampling protocols, a couple of cylinders of a calibration gas containing approximately 20 ppm of iron carbonyl were obtained (nickel carbonyl was considered too toxic for use in the current lab space) and a series of bench-scale tests were conducted. Bench-scale tests using a wet-chemistry method with 70% nitric acid as a trapping solution provided recoveries in the 70% range. Bench-scale tests using sorbent tubes resulted in recoveries averaging around 85%. A literature search for sampling methods turned up a note in one paper that stainless steel regulators and materials could provide a negative bias in these measurements. Since all of the previous work used stainless steel parts, the low recoveries may have been due to the materials of construction rather that the methods themselves. Because of time constraints, further work in this area was halted and it was decided to continue with the second week of testing using both the wet-chemistry method and the sorbent tube method in parallel, sampling from the same probe. Week 2 carbonyl sampling was conducted using the two revised methods that showed much higher recoveries. Table 5 shows the recorded weights for the coupons for the first week of testing.

Table 4. Week 1 Carbonyl Sampling Results

Sample No.	$Fe(CO)_5$, ppb	$Ni(CO)_4$, ppb
1	0.2504	<0.0953
2	0.4983	<0.0948
3	0.6983	<0.1329
4*	<2.8746	<1.6263

* Includes carbonyl on Sample 4 filter.

Table 5. Coupon Weight Data for First Week of Testing

	Pretest	Posttest
Coupon A – Uncoated Top	328.477 g	328.485 g
Coupon B – Coated Top	331.062 g	331.070 g
Coupon D – Coated Bottom	329.972 g	329.975 g
Coupon E – Uncoated Bottom	330.741 g	330.745 g

Week 2 Testing

During the second week of testing, the FBG was operated on coal for 110 hours between April 24 and April 29, 2011. For this week of testing, the gasifier was operated in oxygen-blown mode, with the exception of a 10-hour period during which the recycle compressor was inoperable. The coal was from the same Antelope Mine (a Powder River Basin subbituminous coal from Wyoming) as was utilized in the first week of testing. Ten steady-state test periods were identified, varying mostly in coal feed rate, steam rate, O_2 rate in the gasifier, syngas composition, and temperatures in the duct where Siemens coupons were located. After completion of the testing, the coupon samples were recovered from the coupon holder and weighed and sent back to Siemens for further analysis. Figure 12 is a photograph of the coupons taken after completion of the second week of testing.

The gasifier operating conditions for each test period, as well as the number of hours at steady-state conditions, are shown in Table 6. The average product gas compositions are shown in Table 7, and the average thermal oxidizer emissions are shown in Table 8. Because of mechanical issues with the recycle compressor, the fourth test period was run without recycle syngas. Overall, the operation of the gasifier was very steady outside of a few upsets due to slight agglomeration problems at the bottom of the bed. The inlet to the coupon holder was maintained from 220°–265°F. In an effort to increase carbonyl formation, a small amount of supplemental deionized (DI) water (2–10 mL/min) was injected upstream of the packed-bed contactor filled with nickel and iron pellets which is located at the top of the coupon holder.

Iron and nickel carbonyl sampling was conducted at the outlet of the coupon holder. Two sampling methods were run in parallel, and the results are presented in Tables 9 and 10. Table 11 shows the gasifier operating conditions and product gas composition at the time samples were taken. In all cases, the values for both iron and nickel carbonyl were below 0.4 ppm, and most of the data fall below 0.2 ppm. There does not appear to be any significant correlation between

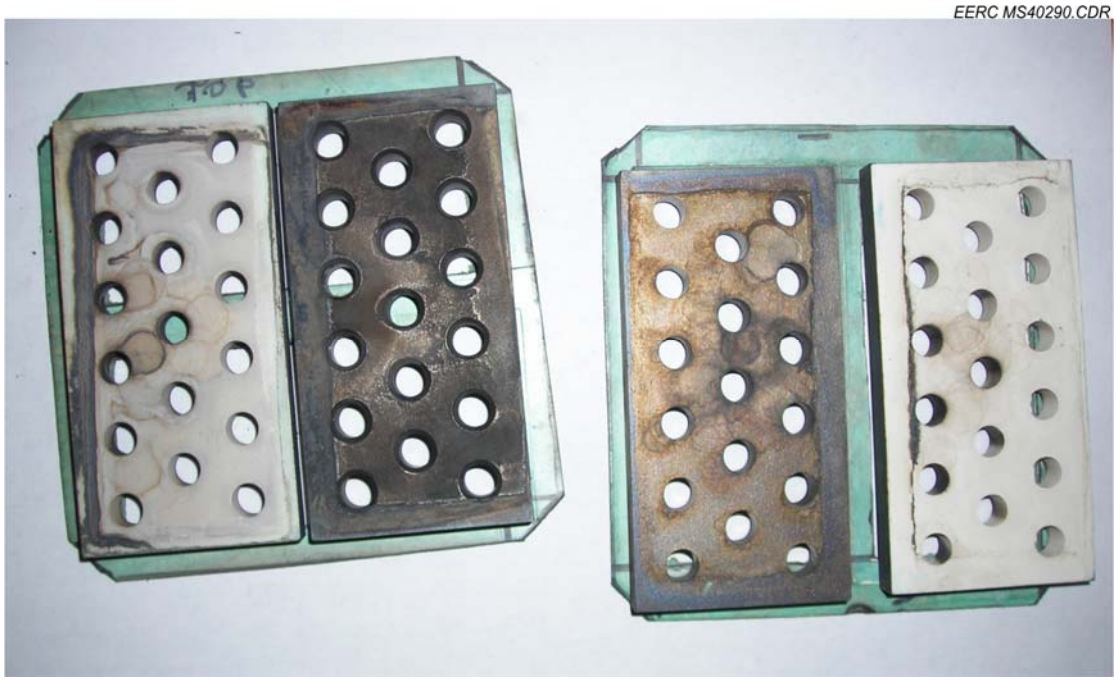

Figure 12. Coupons after the completion of Week 2 testing.

carbonyl concentration and coupon temperature or carbon monoxide concentration over the ranges tested here.

The wet-chemistry sample trains consisted of two 70% nitric acid impingers followed by a DI impinger and a silica gel impinger to remove the moisture. A tee was placed in the sample line to allow a sorbent tube sample to be collected simultaneously with the wet-chemistry sample. All sample lines after the sample port exit valve were Teflon, and the impingers were borosilicate glass. The sorbent tubes were obtained from Frontier GeoSciences and were specifically designed for trace metal sampling. The analytical was done by atomic adsorption.

As a further test of the wet-chemistry method, iron carbonyl was spiked into the port that normally was connected to the sorbent tube for one test. This arrangement allowed for a dynamic spike of iron carbonyl into the sample stream during the sample on April 28 at 12:20. The iron carbonyl results for this sample are calculated based on a 100% subtraction of the sample spike. Based on the value of the iron carbonyl in the flue gas after subtracting the full spike value, it was determined that the wet-chemistry test method was indeed capturing a very high percentage if not all of the iron carbonyl. Because iron carbonyl and nickel carbonyl are closely related compounds, it was felt that the validation of the method for iron carbonyl would also provide some indication as to the effectiveness for collecting nickel carbonyl.

The tests were very consistent considering the fact that concentrations were near the detection limit for both methods. One of the problems with the data is how to handle the “less than” values that were generated. All of these samples consisted of more than one fraction, and

Table 6. Week 2 Steady-State Gasifier Operating Conditions

Test Period	1	2	3	4	5	6	7	8	9	10
Start	4/25 04:00	4/25 12:00	4/25 22:00	4/26 05:40	4/26 20:54	4/27 22:00	4/28 03:00	4/28 14:00	4/29 00:00	4/29 05:00
End	4/25 08:00	4/25 14:30	4/26 02:00	4/26 11:00	4/27 15:00	4/28 01:00	4/28 10:20	4/28 17:20	4/29 03:15	4/29 14:00
Hours at Steady-State	4.0	2.5	4.0	5.3	18.1	3.0	7.3	3.3	3.2	9.0
Inlet Coupon Temp., °F	221.9	235.4	234.1	250.8	263.3	252.2	254.0	256.5	265.2	265.2
Avg Gasifier Temp., °F	1564	1556	1540	1529	1545	1553	1553	1556	1548	1542
Coal Feed Rate, lb/hr	8.1	8	8.2	8	7.8	7.9	8.1	7.9	7.7	7.7
O_2 Flow Rate, scfh	89.9	89.9	84.9	79.8	69.9	74.8	74.7	74.8	74.8	74.7
N_2 Flow Rate, scfh	0	0	0	208.2	0	0	0	0	0	0
Recycle Syngas Flow Rate, lb/hr	25.0	25.2	25.2	0	16.8	19.2	17.0	15.9	16.6	15.9
Steam Flow Rate, lb/hr	14.1	14.1	14.1	18.3	17.6	17.6	17.6	17.5	19.3	19.3
Velocity, ft/s	0.92	0.89	0.89	0.79	0.83	0.88	0.86	0.86	0.89	0.87
Carbon Conversion, %	94.5	95.0	92.8	97.3	93.2	94.7	96.4	92.7	89.9	97.5

Table 7. Week 2 Product Gas Composition

Test Period	1	2	3	4	5	6	7	8	9	10
Start	4/25 04:00	4/25 12:00	4/25 22:00	4/26 05:40	4/26 20:54	4/27 22:00	4/28 03:00	4/28 14:00	4/29 00:00	4/29 05:00
End	4/25 08:00	4/25 14:30	4/26 02:00	4/26 11:00	4/27 15:00	4/28 01:00	4/28 10:20	4/28 17:20	4/29 03:15	4/29 14:00
CO, vol%	15.9	15.8	18.3	4.1	15.4	17.3	17.9	17.5	16.4	16.2
H_2, vol%	18.7	18.7	25.7	14.7	31.6	29.1	31.4	31.8	32.1	32.3
CO_2, vol%	48.6	50.0	45.4	17.7	44.5	45.5	43.1	42.1	45.2	45.3
CH_4, vol%	2.3	2.2	2.8	0.6	3.1	2.8	3.1	3.0	2.8	3.0
N_2, vol%	5.7	5.4	2.9	59.4	2.8	3.0	3.3	2.9	2.8	2.9
H_2S, ppm	1005	994	929	253	910	937	943	732	722	703

Table 8. Week 2 Thermal Oxidizer Emissions

Test Period	1	2	3	4	5	6	7	8	9	10
Start	4/25 04:00	4/25 12:00	4/25 22:00	4/26 05:40	4/26 20:54	4/27 22:00	4/28 03:00	4/28 14:00	4/29 00:00	4/29 05:00
End	4/25 08:00	4/25 14:30	4/26 02:00	4/26 11:00	4/27 15:00	4/28 01:00	4/28 10:20	4/28 17:20	4/29 03:15	4/29 14:00
O_2, vol%	16.9	15.8	13.1	10.5	10.4	10.4	10.0	10.8	10.4	9.6
CO_2, vol%	1.2	9.2	11.3	10.9	11.6	11.4	11.5	11.0	11.1	11.1
CO, ppm	197	193	18	50	15	14	15	13	14	15
NO_x, ppm *	N/A	N/A	13	8	26	23	25	23	22	51
SO_2, ppm	77	70	73	76	67	72	81	61	70	111

* NO_x analyzer was not working properly during Tests 1 and 2.

Table 9. Week 2 Iron Carbonyl Sampling Results

	Iron Carbonyl Concentration, ppm (dry)	Iron Carbonyl Concentration, ppm (dry)	Iron Carbonyl Concentration, ppm (dry)	Iron Carbonyl Concentration, ppm (dry)
	Wet-Chemistry Method	Sorbent Tube Method	Wet-Chemistry Method	Sorbent Tube Method
Sample Date and Time	Min. Values	Min. Values	Max. Values	Max. Values
4/25 11:00	0.000	0.071	0.131	0.071
4/26 14:00	0.138	0.150	0.146	0.150
4/27 11:20	0.145	0.085	0.145	0.085
4/27 12:20	0.098*	–	0.098*	–
4/28 13:50	0.394	0.126	0.394	0.126
4/29 10:30	0.321	0.151	0.321	0.151

* Sample was spiked with iron carbonyl to test the yield.

Table 10. Week 2 Nickel Carbonyl Sampling Results

	Nickel Carbonyl Concentration, ppm (dry)	Nickel Carbonyl Concentration, ppm (dry)	Nickel Carbonyl Concentration, ppm (dry)	Nickel Carbonyl Concentration, ppm (dry)
	Wet-Chemistry Method	Sorbent Tube Method	Wet-Chemistry Method	Sorbent Tube Method
Sample Date and Time	Min. Values	Min. Values	Max. Values	Max. Values
4/25 11:00	0.000	0.000	0.175	0.025
4/26 14:00	0.000	0.022	0.021	0.035
4/27 11:20	0.000	0.014	0.067	0.062
4/27 12:20	0.000	–	0.340	–
4/28 13:50	0.000	0.024	0.177	0.024
4/29 10:30	0.000	0.027	0.130	0.035

some of these fractions were “less than” values. The data are presented as a maximum and a minimum value. The values are calculated as follows:

- To calculate the minimum values, all “less than” values were treated as zeros, values above the detection limits were reported as real numbers, and the calculated values for each run were based on the sum of the reported values plus the sum of the “less than” values (“less than” values were assigned 0.0 as a value). For example, a real value of 4 ng in the first section of a trap and <4 ng in the second section of a trap would result in the following, 4 + <4 = 4.

Table 11. Week 2 Gasifier Operating Conditions and Gas Composition During Carbonyl Sampling

	4/25	4/26	4/27	4/28	4/29
Date and Time of Sample	11:00	14:00	11:20	13:50	10:30
Inlet Coupon Temp., °F	233.0	239.0	264.1	248.0	265.8
Avg Gasifier Temp., °F	1562	1545	1557	1558	1540
Coal Feed Rate, lb/hr	8.0	8.0	8.0	8.0	8.0
O_2 Flow Rate, scfh	90	85	70	75	75
N_2 Flow Rate, scfh	0	0	0	0	0
Recycle Syngas Flow Rate, lb/hr	25.1	25.5	15.0	16.1	15.9
Steam Flow Rate, lb/hr	14.7	14.3	18.2	17.9	18.6
Velocity, ft/s	0.92	0.86	0.80	0.86	0.87
CO, vol%	15.8	17.8	15.0	17.5	16.2
H_2, vol%	18.8	23.5	32.5	32.0	32.6
CO_2, vol%	49.4	47.3	44.4	42.1	46.0
CH_4, vol%	2.2	2.4	3.0	3.0	3.0
N_2, vol%	5.9	4.1	2.6	3.4	2.1
H_2S, ppm	1020	835	880	800	665

- To calculate the maximum values, all less than values were treated as real numbers, values above the detection limits were reported as real numbers, and the calculated values for each run were based on the sum of the reported values plus the sum of the less than value. For example, to calculate the maximum value for a trap with a real value of 4 ng in the first section of the trap and <4 ng in the second section of the trap would result in the following, 4 + <4 = 8.

- If both sections of a trap had real values they were added together to get a total. For example, to calculate the maximum value for a trap with a real value of 4 ng in the first section of the trap and 4 ng in the second section of the trap would result in the following, 4 + 4 = 8; in this case the data would show minimum and maximum values that were the same.

Several nickel carbonyl Dräger tube samples were also taken at the coupon holder outlet. Concentration was determined by comparing the intensity of the pink discoloration to a standard color scale. However, there is a cross-sensitivity with iron carbonyl that causes a brown discoloration. No color scale is provided for the iron carbonyl, but the indicator is slightly less sensitive to iron than it is to nickel carbonyl. A small sorbent trap was used to remove H_2S prior to sampling because of interferences that cause inaccurate readings. With the first couple of samples, very slight brown discoloration occurred, indicating the presence of very small amounts of iron carbonyl. However, no pink discoloration was observed, indicating the presence of little or no nickel carbonyl. Even after 100 pumps on the N = 20 tubes, very little discoloration occurred. A last Dräger sample was taken using a mechanical pump and a gas meter to get a larger volume of gas through the tube. The volume of gas passed through the tube was equal to

29 times the volume during the normal N = 20 pumps. The tube showed significant brown discoloration, but no pink discoloration. Using a very rough estimation based on the intensity of the brown color as compared to the changes in the pink standard color scale and the factor of 29, the concentration of iron carbonyl during this sample was approximately 0.1 ppm. Sorbent trap and wet-chemistry sampling confirm this approximation.

Table 12 shows the coupon weights before and after the test was completed. It appears that the top coupons had significantly more weight gain the lower coupons independent of whether the coupon was coated or not. Siemens substituted two of the coupons in the second test run in order to increase the number of samples with 100 hours of exposure time.

CONCLUSIONS

Two 5-day tests with over 200 hours of total exposure time were completed. The first week of testing was conducted in enriched air-blown mode, with coupon temperatures ranging from 128° to 272°F. Carbonyl sampling was conducted, but it was discovered after the fact that the methodology used was producing very low recoveries of iron and nickel carbonyl. Therefore, the data generated during this week of testing were not considered accurate. The second week of testing was conducted in oxygen-blown mode, with coupon temperatures ranging from 220° to 265°F. Two improved methods were used to measure carbonyl concentration during this week of testing. These methods produced results closer to equilibrium calculations. Since both weeks of testing mostly produced a product gas with approximately 15%–18% carbon monoxide, it was felt that actual carbonyl concentrations for Week 1 should be very similar to those measured during Week 2.

The revised carbonyl sampling methodology used during the second week of testing greatly improved the recovery of iron and nickel carbonyl in the sample. Even though the sampling results obtained from the first week were inaccurate, the results from the second week can be used as an estimate for the periods during which the gasifier was operating under similar conditions and producing similar product gas compositions. Specifically, Test Periods 2 and 3 from the first week were similar to the conditions run during the second week. For a product gas containing roughly 15%–18% CO and a coupon temperature of approximately 220°–270°F, the nickel carbonyl concentration should be about 0.05–0.1 ppm and the iron carbonyl concentration about 0.1–0.4 ppm.

Table 12. Coupon Weight Data for Second Week of Testing

	Pretest	Posttest
Coupon A – Uncoated Top	328.487 g	328.635 g
Coupon B – Coated Top	331.072 g	331.204 g
Coupon C – Uncoated Bottom	329.665 g	329.701 g
Coupon F – Coated Bottom	330.006 g	330.046 g

After each week of testing, the coupons were recovered from the coupon holder, weighed, and shipped back to Siemens for analysis. It appears that the top coupons had significantly more weight gain than the lower coupons independent of whether the coupon was coated or not.

The coupons that were placed further downstream in the thermal oxidizer to test carbonyl dusting in the gas expander section have not been removed and are being left in place for more exposure testing.

SUMMARY OF SIGNIFICANT ACCOMPLISHMENTS

A coupon holder was constructed to expose the coupons to syngas right before the gas was combusted in the thermal oxidizer. A revised carbonyl sampling methodology was developed to allow accurate carbonyl concentration to be measured. Over 200 hours of coupon exposure to syngas was achieved. Coupon weight changes were recorded and the coupons returned to Seimens for analysis. Carbonyl concentrations were in the range of 0.1 to 0.4 ppm.