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CANMET Gasifier Liner Coupon Material Test Report

TOPICAL REPORT

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Principal Authors

Mark Fitzsimmons Task Development Lead
Dave Grimmett Metallic Materials Engineer
Bryan McEnerney Ceramic Materials Engineer

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Task 1 Cooled Liner Coupon Development and Test

Pratt & Whitney Rocketdyne, Inc.
6633 Canoga Avenue
P.O. Box 7922
Canoga Park, CA 91309-7922

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1.0 ABSTRACT

This report provides detailed test results consisting of test data and post-test inspections from Task 1 “Cooled Liner Coupon Development and Test” of the project titled “Development of Technologies and Capabilities for Coal Energy Resources – Advanced Gasification Systems Development (AGSD)”. The primary objective of this development and test program is to verify that ceramic matrix composite (CMC) liner materials planned for use in an advanced gasifier pilot plant will successfully withstand the environments in a commercial gasifier.

Pratt & Whitney Rocketdyne (PWR) designed and fabricated the cooled liner test assembly article that was tested in a slagging gasifier at CANMET Energy Technology Centre (CETC-O) in Ottawa, Ontario, Canada.

The test program conducted in 2006 met the objective of operating the cooled liner test article at slagging conditions in a small scale coal gasifier at CETC-O for over the planned 100 hours. The test hardware was exposed to at least 30 high temperature excursions (including start-up and shut-down cycles) during the test program. The results of the testing has provided valuable information on gasifier startup and required cooling controls in steady state operation of future advanced gasifiers using similar liners. The test program also provided a significant amount of information in the areas of CMC materials and processing for improved capability in a gasifier environment and insight into CMC liner fabrication that will be essential for near-term advanced gasifier projects.

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2.0 EXECUTIVE SUMMARY

This test report describes the technical work performed by Pratt & Whitney Rocketdyne (PWR) and CANMET personnel at CANMET Energy Technology Centre-Ottawa (CETC-O) on Task 1 “Cooled Liner Coupon Development and Test” of the project titled “Development of Technologies and Capabilities for Coal Energy Resources – Advanced Gasification Systems Development (AGSD)”. The primary purpose of this development and test program is to verify that ceramic matrix composite (CMC) liner materials planned for use in an advanced gasifier pilot plant will successfully withstand the environments in a commercial coal gasifier. The objective was met as described below and in more detail in the body of the report.

The test program commenced in December of 2005, was delayed temporarily between January and April of 2006 due to repair time associated with a damaged facility coal supply system, and was successfully completed in July of 2006. The test program met the major objective of operating the cooled CMC liner in a slagging gasifier environment for 100 hours.

PWR designed and fabricated the cooled liner test assembly article that was tested at CANMET. The test item was a circular cross section, replacing the existing outlet of the gasifier and consisted of a ceramic liner made up of three axial sections with different CMC material compositions fabricated by experienced CMC manufacturers and a two-pass heat exchanger flowing nitrogen coolant to maintain reduced wall temperatures.

The testing consisted of 103 hours of slagging gasifier operation, exposing the CMC liner sections to a highly reducing slag environment to evaluate material survivability in specific gasifier regions. Materials were also exposed to 500 hours of oxygen rich warm-up operation due to the specific nature of the CANMET gasifier operating procedures. The intent of the test article design was to protect the liner with a combination of active cooling and thermal and chemical barriers. The objectives of the test were to obtain life information, to identify infant mortality design issues, and to assess cooling schemes and limits of operation in the reducing environment.

The test was successful in all of these goals. The test program provided a significant amount of information in the areas of thermal control, CMC materials and processing for improved capability in a gasifier environment, and CMC liner fabrication that will be essential for upcoming advanced gasifier projects. There were several areas where the original CMC liner surface was completely intact at the end of the test program. The indication is that, in zones where the cooling was able to maintain the CMC liner within the planned temperature range, a solid layer of slag was formed on the CMC liner inner surface and protected the liner from erosion and corrosion.

Several key "Lessons Learned" were experienced during the test program. The CMC liner survived without catastrophic failure even though the liner was significantly over-tested as a result of low density (high porosity) in the ceramic matrix and exacerbated by damage to thermocouple instrumentation later in the test program which produced ambiguous data.

During post-test Scanning Electron Microscope (SEM) examination, each of the three CMC liner sections was found to have much higher porosity than expected from prior CMC experience at PWR. The excessive porosity resulted in thermal conductivities significantly lower than the baseline values used in the design analysis. This quality control issue experienced with the CMC manufacturer resulted in increased temperature gradients on the CMC liner. In addition, failure of thermocouples in later runs also led to operating the CMC liner at temperatures well above the design range except at the downstream end that experienced the most cooling. The formation of a protective layer of solid slag was not possible under these increased surface temperature conditions for most of the liner axial length, allowing diffusion of corrosive elements into the surface and some loss of material as would be expected. However, the liner did not fail even at these greatly elevated operating temperatures and gradients.

The quality control issue for liner design is one of the more important findings of the test program. Wide variation in ceramic porosity was found from sample to sample and in various locations in the liners. Reasonable process control will be critical to fabricating a successful gasifier liner for future applications.

The material evidence shows that oxygen and slag damaged internal layers of the ceramic, which is to be expected given the material porosity and elevated temperatures. However, future tests at Oak Ridge National Laboratory on a wider range of CMC formulations will guide the design of a suitable ceramic for this application. In addition, the CANMET gasifier operation required extended (18-hour) warm-ups for each test where the CMC liner was exposed to a hot oxidizing environment that is not expected for PWR gasifier operation.

Although loss of liner material due to the over-temp operations was observed, indications are that one of the CMC liner materials/processing options provided superior performance. This provides key insight into which CMC options to carry forward in the ongoing bench-scale testing and in gasifier design activities.

In summary, a great deal of highly useful information has resulted from the PWR cooled CMC gasifier liner test program, leading to a number of larger scale design concepts, improved gasifier liner concepts, and specific direction for further material development. More risk reduction tasks have been started based on the results of these tests to fine-tune material systems for liners, including oxygen susceptibility testing and additional slag tests on some variations of CMC materials.

3.0 EXPERIMENTAL METHODS

3.1 GENERAL TEST PHILOSOPHY

The purpose of these tests was to verify that materials planned for use in an advanced gasifier pilot plant will withstand the environments in a commercial gasifier. Materials used for the hottest portion of the gasifier were tested in static slag adhesion and corrosion oven tests at the US DOE-NETL Albany, but were not subjected to the kinetic atmosphere of a gasifier reactor. The environment in this test program more closely simulated an actual gasifier: temperature, slagging environment, solids loading of the flow stream, hot gas velocity, cooling rates and heat flux of the test article were similar to those expected in future phases of this project. A more detailed discussion on the task objectives is presented in section 4.1.

A section of the gasifier chamber at CANMET Energy Technology Centre-Ottawa (CETC-O) was replaced with the PWR test hardware as described in section 3.2. The test article liner was made up of three axial sections with different CMC material compositions. The test program consisted of 103 hours of slagging gasifier operation, exposing the CMC liner sections to a highly reducing slag environment to evaluate material survivability in specific gasifier regions.

The test was conducted with constant cooling of the ceramic liner. In all tests the objective was to establish that coal slag can be deposited on the surface of the liner and prevent erosion of the ceramic. Furthermore, the test temperatures were defined such that the molten slag would not fill and plug the reactor outlet, as this could prevent completion of the test program. To accomplish this, a temperature range between 815 and 982ºC (1500-1800°F) was chosen as the target CMC liner temperature. The liner was typically kept below 700ºC for refractory warm up (required by the existing facility) and then reached the target temperatures only after slagging operation began.

Thermocouples placed in a variety of locations were used to maintain the desired temperature range (described in sections 3.2 and 3.3, below).

Photos of the as-installed test article were taken of the seals, thermocouples and facility installation. Borescope (fiber optic probe) inspections were performed after every test to evaluate slag coverage and these inspections were used often to diagnose clogging problems with the reactor and coal injector.

3.2 TEST HARDWARE

3.2.1 Test Assembly P/N 7R110019A1

The Test Unit consisted of a 12” SCH 40 pipe with 300# class flanges. The cooling jacket was welded into this outer pressure shell and contained GN_2 coolant through channels to actively cool the CMC liner. See Figure 3.1.

For this test article and specific to the CANMET gasifier, the syngas traveled in from a 5” diameter flow passage into a reducing cone fabricated from castable refractory material, which channeled the flow into a 1.875 inch diameter hole concentric with the same diameter CMC liner. The top ½” of this CMC liner extended above the cooling jacket, and in this relatively uncooled space were placed eight small material samples (see section 4.3.5).

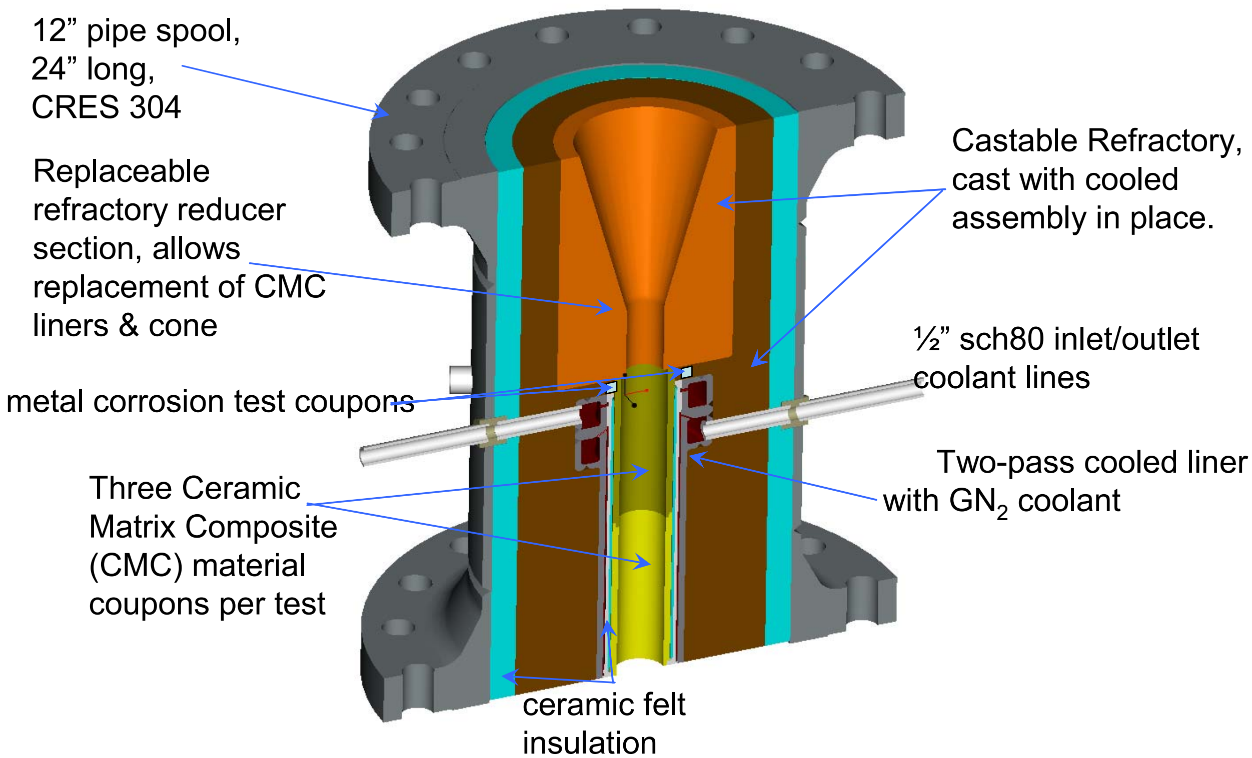


Figure 3.1 Test Assembly P/N 7R110019A1

3.2.2 CMC Liners P/N 7R110022

The Ceramic Matrix Composite liners were made in three sections (Figure 3.2): an inlet (-3) and two outlets (-5). The rabbet joint between the liners is intended to simulate the rabbet joint that would likely be used to assemble a 15 foot long liner for a commercial plant and pilot plant. Each of the three liner segments was of slightly different material. Holes in the first test inlet allowed thermocouples to measure syngas and slag temperatures in the reaction chamber and anchor thermal models.

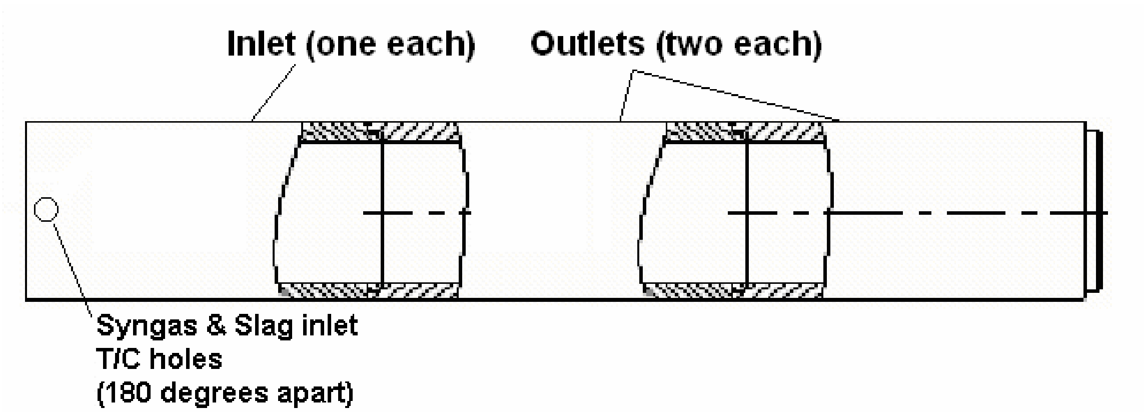


Figure 3.2 CMC Liners 7R110022-3 and -5

3.2.3 Cooling Jacket P/N 7R110023

The cooling jacket, shown in Figure 3.3, is a two-pass heat exchanger using nitrogen to actively maintain a CMC temperature of approximately 815-982°C (1500-1800°F). The cooling control circuit was operated to maintain this temperature, controlled by the coolant flowrate and heat flux through the layers of syngas and ceramic felt (Fiberfrax® -- shown as a thin blue line between the CMC and metal heat exchanger) in the “air gap” area. The metal cooling jacket operated between approximately 300°C and 500°C during testing. Upon completion of the test program, the metal jacket appeared unchanged from the original pre-test condition and no evidence of corrosion was observed.

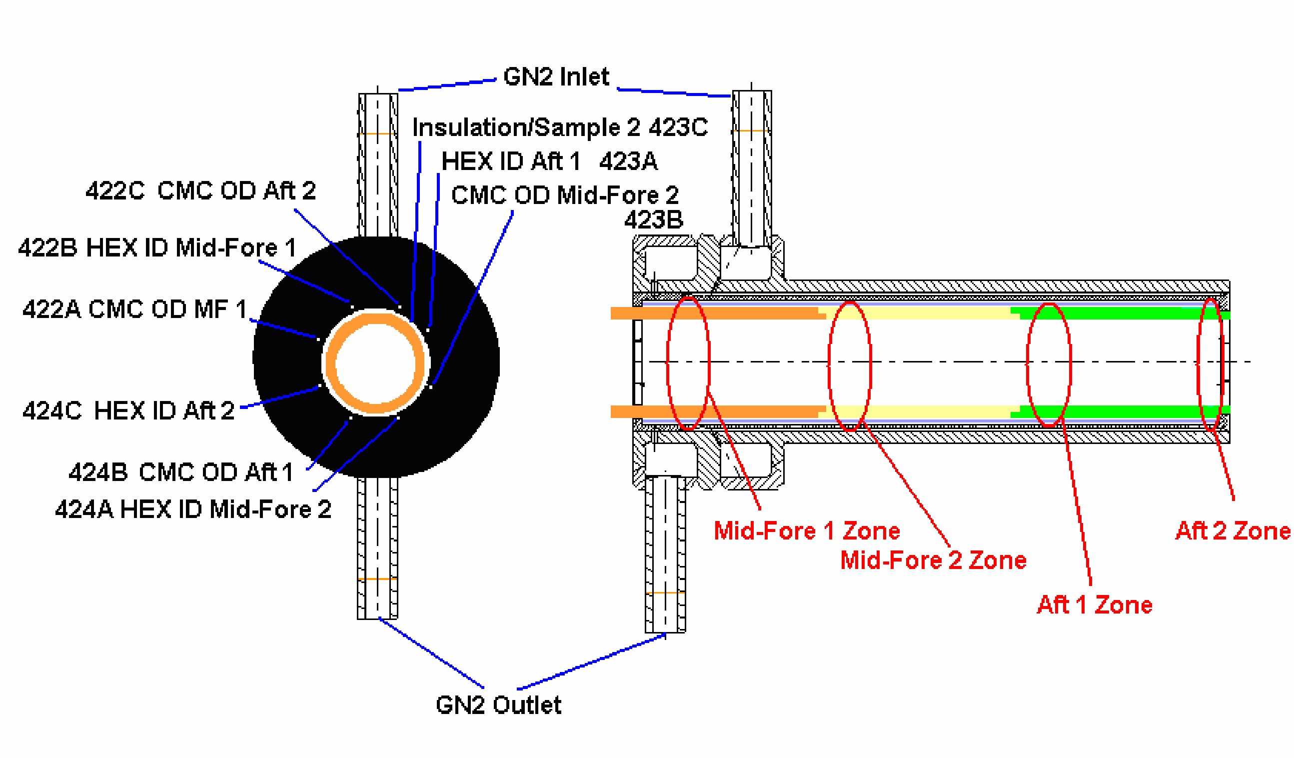


Figure 3.3 Cooling Jacket P/N 7R110023 cooled thermocouple locations

3.2.4 Material Samples and Miscellaneous Thermocouples

Upstream of the cooling jacket the CMC extends 12.5 mm (½ inch) to meet the refractory inlet reducing cone. This section of CMC provided direct access for additional ceramic and syngas temperature measurements and was also intended to give a range of slightly hotter CMC temperatures to assess durability margin.

In this zone several metal coupons were placed to compare with each other as alternate materials to the coated stainless steel used for the cooling jacket. The coupons are shown in Figure 3.4, which also identifies the hot zone thermocouples. The thermocouples which passed through this zone recorded temperatures of samples, CMC, slag and syngas. The locations of these thermocouples are shown in Figure 3.5 and Figure 3.6. Figure 3.6 also shows the metal coupon locations.

Figure 3.4 Thermocouple and Metal Samples Locations

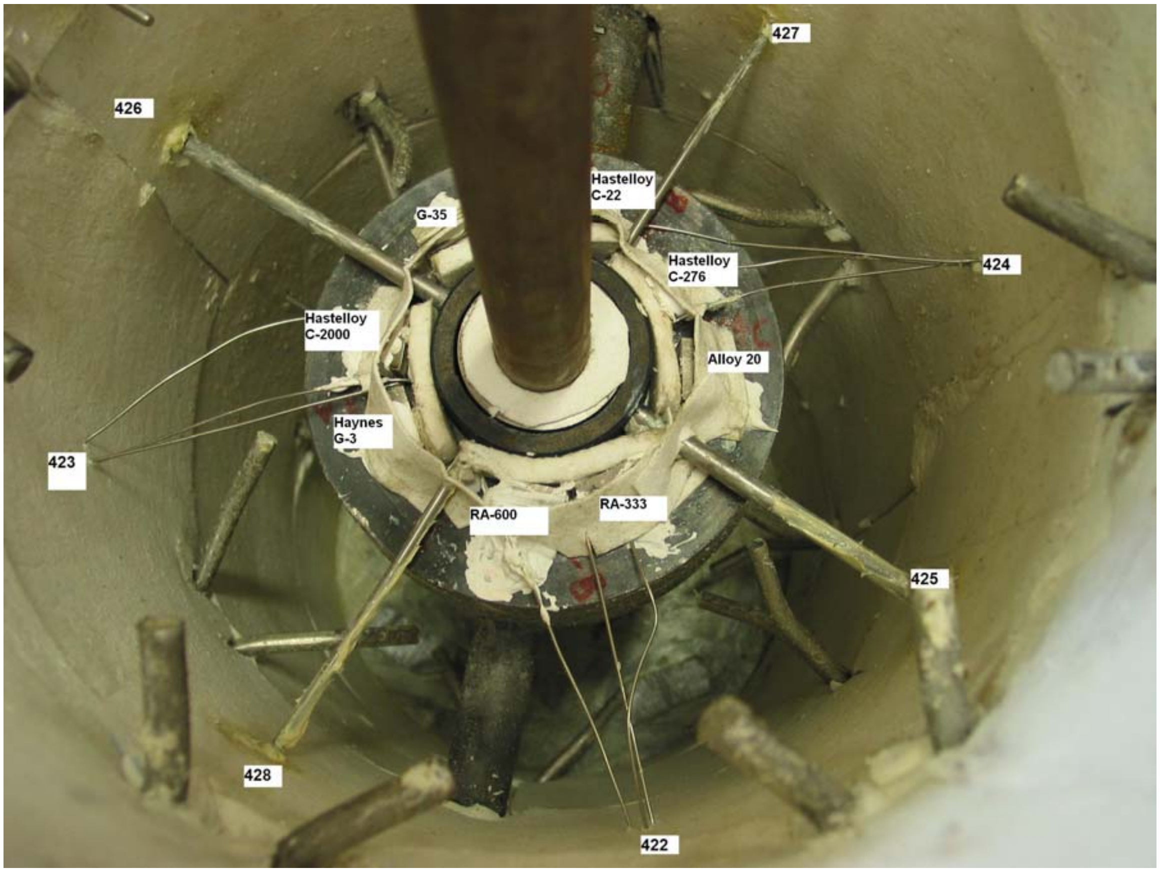


Figure 3.5 Thermocouple Bosses on Coolant Outlet Side

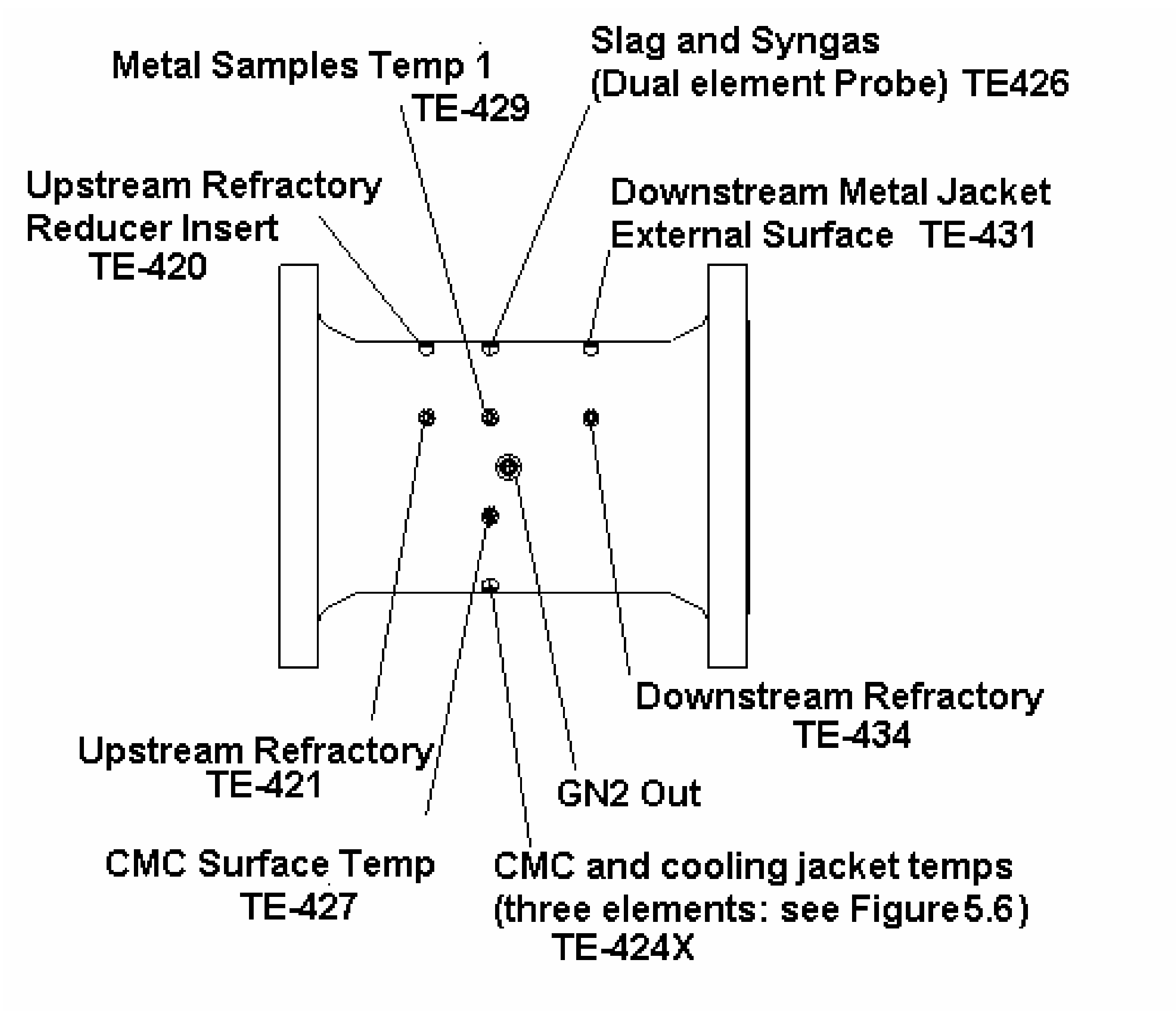
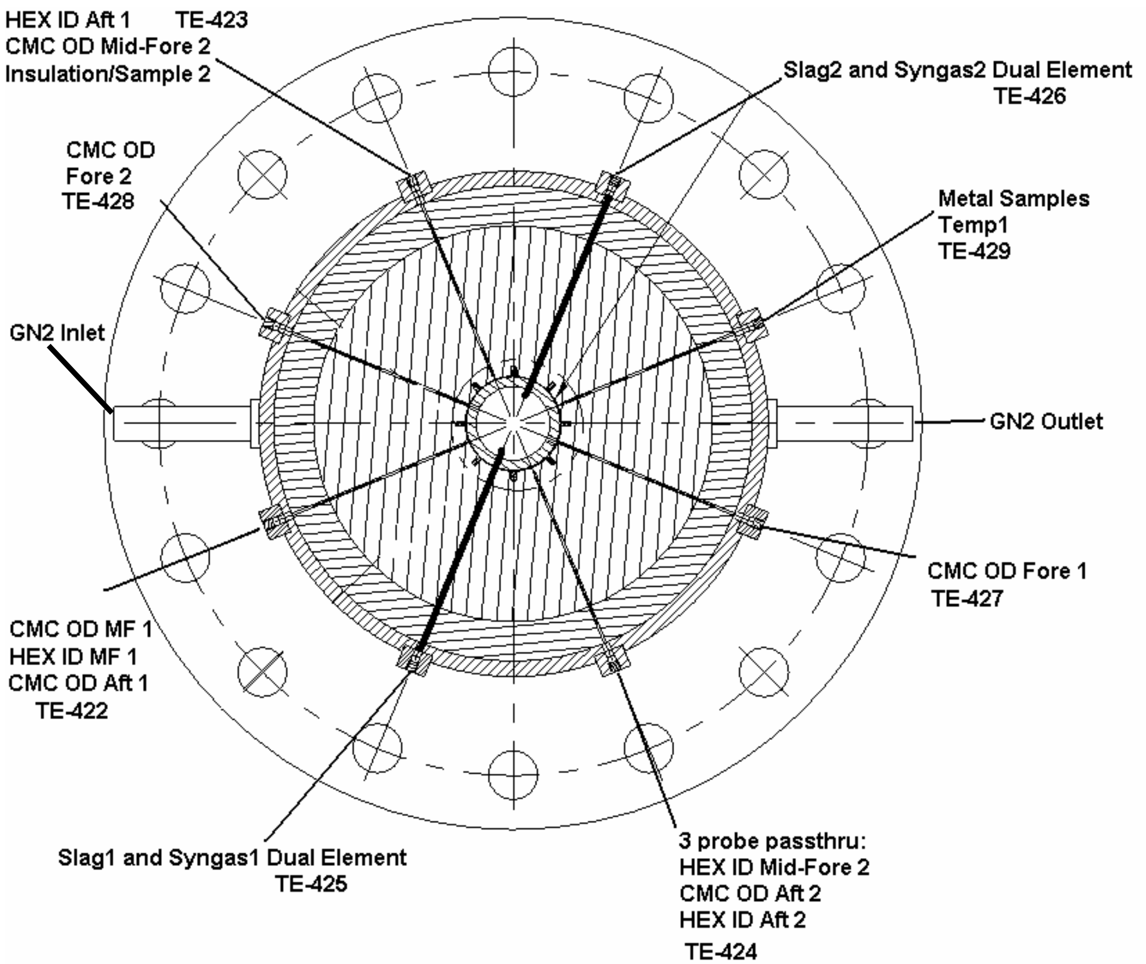


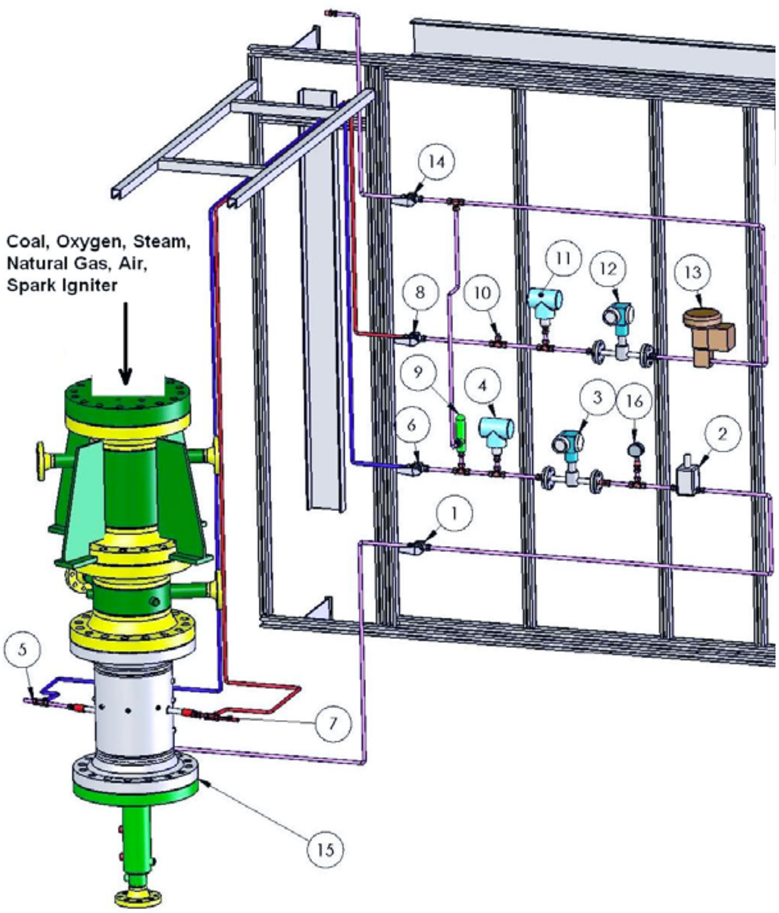
Figure 3.6 Thermocouple Bosses near the CMC Inlet Plane



3.3 TEST FACILITY

3.3.1 General

The gasifier at CANMET is a traditional refractory lined reactor, and as such required a long warm-up and heat soak, usually lasting 16-18 hours. The test article, which did not require this heat soak, was constantly cooled during this heat up time to maintain acceptable temperature. The gasifier and coolant control system is depicted in Figure 3.7 (not including coal, oxygen, steam or igniter feed systems). The CANMET entrained flow slagging gasifier operated at a coal flow rate from 9-11 kg/hr during testing. A photograph of the gasifier with the PWR test article is shown in Figure 3.8.



Equipment List Summary

Find No	Tag	Description
1	HV-250a	Quarter turn ball valve, 1/2", 60 Series Thermal
2	PRV-250	Fairchild Pressure regulator, max input 500 psig, capacity 40 SCFM (78 kg/hr @ 300 psig), Sensitivity 0.125" WC
3	FT-250	AYSIX Sage Thermal Gas Mass Flow Meter, SIE-05-0S-300FLG050-DC24-N2, Max temp 500F, Accuracy 0.2% of reading, 0.5% of full scale over 100:1 turndown
4	PT-250	ABB SMART Gauge Pressure Transmitter model 2600T, output 4-20 mA, pressure range 0-348 psi, Accuracy 0.075% of reading
5	TE-250	Type K thermocouple, 1/4"
6	HV-250b	Quarter turn ball valve, 1/2", 60 Series Thermal
7	TE-251	Type K thermocouple, 1/4"
8	HV-251a	Quarter turn ball valve, 1/2", 60 Series Thermal
9	PSV-251	
10	TE-252	Type K thermocouple, 1/4"
11	PT-251	ABB SMART Gauge Pressure Transmitter model 2600T, output 4-20 mA, pressure range 0-348 psi, Accuracy 0.075% of reading
12	FT-251	AYSIX Sage Thermal Gas Mass Flow Meter, SIE-05-0S-300FLG050-DC24-N2, Max temp 500F, Accuracy 0.2% of reading, 0.5% of full scale over 100:1 turndown
13	TV-251	Badger Research Control Valve, 316SS, 1/2" swagelok process connections, Cv 2.5, CRN OC5007.5, linear trim
14	HV-251b	Quarter turn ball valve, 1/2", 60 Series Thermal
15	R-401F	Boeing Rocketdyne spool piece drwg#
16	PI-250	Wikka Pressure Gauge 0-2500 kPa

Figure 3.7 CANMET Gasifier with PWR coolant control system

3.3.2 Gas Analysis

A mass spectrometer gas analysis was used periodically to establish reactor efficiency through a mass balance. The real-time in line analyzer was also checked with bottled samples which were tested in a laboratory to verify results.

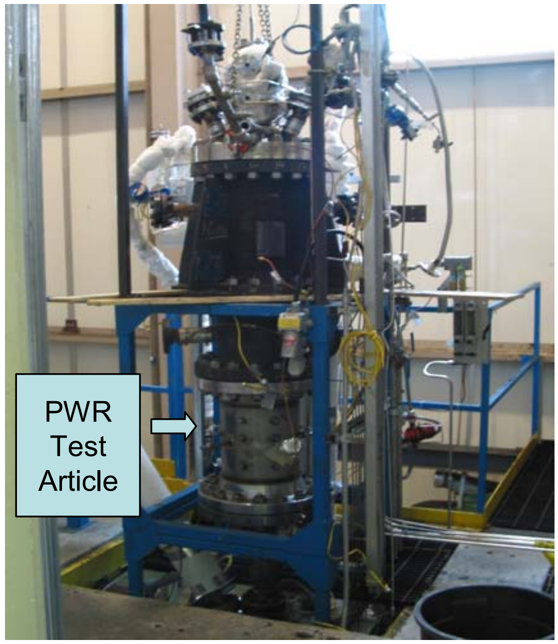


Figure 3.8 CANMET Gasifier with PWR Test Article

3.3.3 Feed Systems

3.3.3.a Coal Feed System

The CETC-O dry feed system was used. The coal hopper experienced auger and bearing damage early in the test programming, delaying the tests for 4-5 months; however it functioned well after repairs were completed.

Pulverized TVA Kentucky Coal #04-RB166 was used throughout the test program. Coal analyses are shown in Table 3.1 through Table 3.3 below.

Ash Fusibility	ºC	ºF
Reducing atmosphere		
Initial deformation	1069	1956
Softening spherical	1122	2052
Softening hemispherical	1138	2080
Fluid temperature	1269	2316
Oxidizing atmosphere		
Initial deformation	1252	2286
Softening spherical	1271	2320
Softening hemispherical	1291	2356
Fluid temperature	1318	2404

Table 3.1 TVA Kentucky Coal Slag Softening Temperatures

Proximate, wt % (dry)	
Ash	9.00
Volatile matter	38.85
Fixed carbon (by difference)	52.15
Ultimate, Wt % (dry)	
Carbon	72.89
Hydrogen	5.11
Nitrogen	1.54
Sulfur	3.28
Ash	9.00
Oxygen (by difference)	8.18
Heating value (dry)	
Cal/gm	7305
MJ/kg	30.58
BTU/lb	13149

Table 3.2 TVA Kentucky Coal Proximate and Ultimate Analysis

Ash analysis - oxides, wt %			
SiO_2	45.04	BaO	0.048
Fe_2O_3	17.22	MnO	0.045
Al_2O_3	17.05	V_2O_5	0.045
SO_3	8.192	SrO	0.014
CaO	6.53	NiO	0.010
K_2O	1.932	Cr_2O_3	0.018
Na_2O	0.913	Cu	0.010
TiO_2	0.89	Cr	0.019
MgO	0.762	Loss on fusion	1.19
P_2O_5	0.076		
Chlorine in coal, mg/g		1302	
Fluorine in coal, mg/g		69	
Bromine in coal, mg/g		< 14	
Mercury in coal, mg/g		0.074	

Table 3.3 TVA Kentucky Coal Ash Analysis

3.3.3.b Other Feed Systems

The oxygen, steam and nitrogen flows were controlled as described in the test plan (November 2005 Topical Report entitled "CANMET Gasifier Liner Coupon Material Test Plan"), however the CANMET injector, being uncooled, was not capable of operating at high pressures, and as pressure increased, the slagging zone of the reactor moved upstream, preventing the PWR test article from reaching the desired slagging operation. This resulted in a change to the test conditions from 1500 kPa to less than 100 kPa for all tests.

3.3.3.c Heat Exchanger Control System

GN2 coolant flow was maintained on a temperature control algorithm during testing. This control was managed with a series of thermocouples, with a pre-assigned priority in case one or more thermocouples should fail. An alternate method (flow control) was used during initial and some later tests in order to establish heat flux into the coolant and to provide some assurance that coolant flow was not interrupted before the temperature algorithm was proven.

There were several control screens available on the data acquisition and control system, some were designed for real time views of data parameters, others for push button control of valves, motors, igniter and programmed control sequences. As an example, the heat exchanger control system screen is shown in Figure 3.9, below. Some purges and redundant parameters have been removed for clarity.

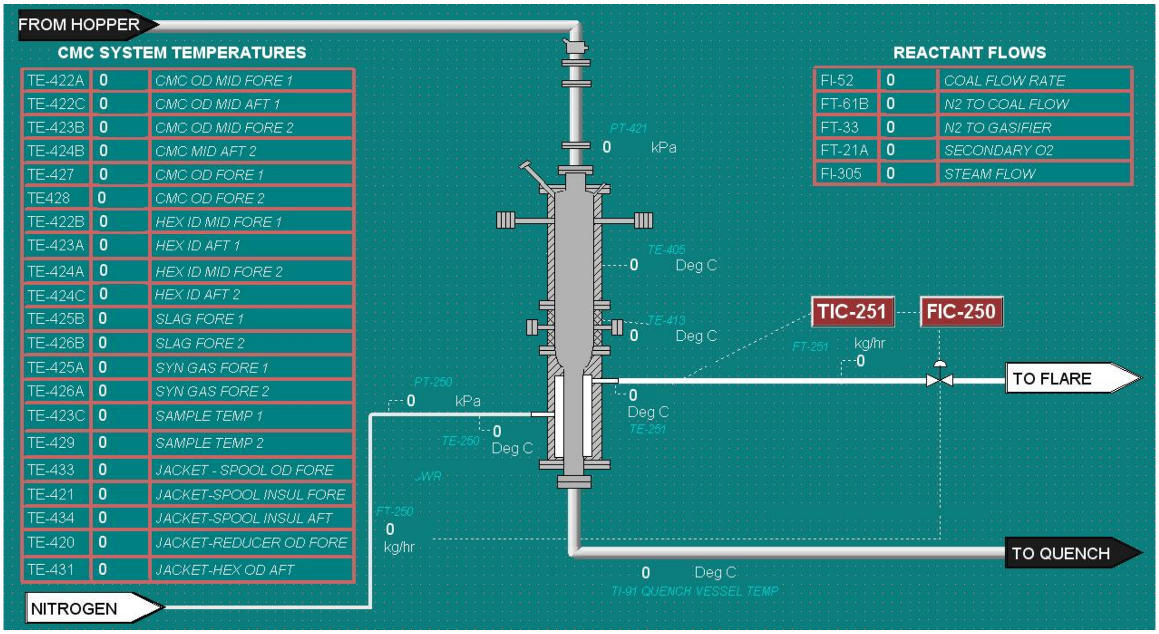


Figure 3.9 Test Control Page for Coolant Subsystem at CANMET

4.0 RESULTS AND DISCUSSION

4.1 OBJECTIVES

The test objectives are summarized below. A short summary of how well each objective was met is also included in the second column.

Objective	Summary (see RESULTS for details)
✓ Demonstrate the concept of a gasifier arrangement with slag frozen onto a ceramic liner surrounded by a cooling jacket.	Concept works, however the design approach for this bench-scale test of controlling temperature by controlling thermal resistance through a gap proved difficult and led to specific improvements in the cooling approach that will be used for subsequent PWR gasifier liner designs.
✓ Demonstrate that at least one of the materials selected for the ceramic liner will adhere to the frozen slag layer and prevent rapid deterioration of the liner.	All materials showed that they will survive with proper thermal control. One CMC material was shown to provide better performance. Quality control issues were identified to provide the desired density and thermal conductivity needed to maintain the design heat transfer.
✓ Develop flow and operational criteria for cooling of the CMC for optimal slag coating, including startup and shutdown procedures and limits.	Operational criteria were close to predicted values. Upper temperature limits for long life should also be adequate for startup. Near-injector zones need to be tested with similar injector elements of advanced design.
✓ Gather data for thermal analysis and design for pilot plant and commercial gasifiers.	Data will be used to support pilot plant and commercial designs.
✓ Acquire data to project a useful life for these larger scale gasifiers.	Sections of liner with adequate thermal control to allow the formation of a protective solid slag barrier showed no loss of material after 103 hours of slagging operation.
✓ Evaluate at least three ceramic liner materials and coating processes.	Three liners tested and evaluated.
✓ Evaluate a variety of corrosion resistant alloys and/or diffusion coatings.	Eight alloys tested and evaluated.
✓ Establish the range of operation to prevent overcooling (plugging gasifier with slag) or undercooling (corrosion of the ceramic liner).	Undercooling limit is the slag spherical softening temperature. Overcooling limit is predicted by the thermal analysis developed for this test program.

4.2 TEST SUCCESS CRITERIA

Overall success of the CANMET tests was established. This is a summary. The details are covered in the RESULTS AND DISCUSSION section.

✓ CMC liners and cooling jacket remain intact at the end of the test campaign.	All were intact. Some regions of ceramic liner erosion due to over-test temperatures demonstrate the upper limit of acceptable operation.
✓ Either no wear is seen on the liners and jacket, or the combination of materials leaves a clear choice with the best performance for pilot plant testing (based on least erosion on CMC, corrosion of surfaces on metal sample coupons – to be determined by a combination of visual/borescope inspection and destructive examination post-test).	Wear patterns show that one CMC material tested was less susceptible to erosion, however post test destructive examination shows that some fabrication errors on the other two materials are strong contributors to the damage seen by them, and the lower cost options are also viable provided manufacturing quality controls are incorporated.
✓ Tests provide useful data on startup and shutdown, particularly with respect to slag adhesion, material thermal shock, and slag surface buildup and morphology.	Thermal shock was not an issue; however slag adhesion relies on good slagging operation. Buildup for small bench-scale diameter cylinders can be problematic, but should be less so with larger reactors.
✓ Slag spalling data and/or metal corrosion data provide useful input to statistical analysis of CMC useful life.	Slag damage shows that even if controls are exceeded, new layers of slag are still protective, making liner life primarily a thermal control issue.
✓ Provide data to select CMC materials.	See RESULTS AND DISCUSSION
✓ Provide data to select cooling jacket materials.	See RESULTS AND DISCUSSION
✓ Thermal control of cooling jacket methodology can be applied to pilot plant testing.	Thermal control (as designed) worked but is problematic due to some design details. The test results indicate that a modified cooling scheme will be more reliable in pilot plant and commercial applications.

4.3 Test Data

4.3.1 Test Program Overview

A run summary is shown in Table 4.1. The syngas and CMC temperatures are thermocouple readings only; thermal conductivity and slag on surfaces has not been taken into account in these values. Corrected syngas and CMC temperatures will be shown graphically in the thermal analysis section, 4.3.3.

Test #	Date	Slagging Test duration	Oxygen Flow (kg/hr)	Coal Flow (kg/hr)	Steam Flow (kg/hr)	GN2 Flow (kg/hr)	Velocity, ft/sec	Reactor inner surface temp max (ºC)	CMC temp measured (ºC)	Likely CMC temp(ºC)	Cumulative Slagging Duration
1	11/30/2005	0.0						956	504	505	0
2	12/1/2005	1.0	8-18	10-15	7-10			1100-1296	690-865	690-866	1.0
3	12/7/2005	3.5	7-9	14	3-4			1500	963	963	4.5
4	1/7/2006	0.0						1600-1800	480	480	4.5
5	4/25/2006	0.0						1072	751	751	4.5
6	4/27/2006	0.0						1460	666	666	4.5
7	5/2/2006	0.8	10	12.5	0.5	2.5	55-60	1374	971	971	5.3
8	5/4/2006	1.7	10	12.5	0.7-3.2	3	50-70	1606	947	947	7.0
9	5/9/2006	3.2	8.8	10	0.1	2.5	45-60	1562	1024	1024	10.2
10	5/11/2006	0.9	9	9.9	0	2.5	50-60	1501	936	936	11.1
11	5/24/2006	4.9	8.7	9.9	1.6	2.5	40-60	1496	946	1050	16.0
12	5/31/2006	6.5	9.1	9.3	0	2.5	40-55	1516	938	1138	22.5
13	6/2/2006	6.0	9.3	10	0.9	3.3	25-60	1500	931	1050-1150	28.5
14	6/6/2006	6.0	9	10.1	1.3	3	24-50	1500	921	1050-1150	34.5
15	6/9/2006	6.0	9.2	10.6	1.0	2.5	30-56	1402	961	1050-1200	40.4
16	6/14/2006	1.4	9.2	10.3	1.1	2.5	35-48	1334	909	1100-900	41.8
17	6/16/2006	7.2	9.5	10.2	0.8	2.5	40-50	1424	974	1050-1150	49.0
18	6/21/2006	6.5	9.5	9.2	1.7	5	40-50	1360	917	1100-1200	55.5
19	6/23/2006	5.9	9.3	10	0	2.5	40-55	1580	938	1050-1150	61.3
20	6/27/2006	6.5	9.3	9.8	1.4	2.6	35-50	1390	850	1100-1250	67.9
21	6/29/2006	6.0	9.3	10.4	1.2	4.8	37-51	1360	768	1200-1300	73.8
22	7/5/2006	6.7	9.5	10.7	1.0	3.9	35-55	1476	721	1150-1250	80.5
23	7/11/2006	0.7	9.5	10.6	2.1	3	40-50	1229	623	1000-1100	81.2
24	7/13/2006	7.4	9.1	8.5	1.4	3	40-60	1442	715	1100-1250	88.6
25	7/18/2006	7.1	9.4	9.9	1.2	4.4	40-58	1453	620	1100-1200	95.6
26	7/20/2006	7.3	9.4	9.7	1.3	4.2	32-55	1626	930	1200-1400	102.9

Table 4.1 Test Program Run Summary

"Slagging operation" has been defined as any test time when the syngas temperature was over 1000ºC while coal and oxygen were on and there was flame indication. Since the actual temperature was usually higher than these thermocouple readings, the full slagging test duration was likely between 103 and 104 hours.

Each test began the day before with a pre-test warm up, operating on natural gas and air, typically for 18 hours to completely warm the large volume of refractory. This warm up was run slightly lean, with typically 1% to 2% oxygen detected in the exhaust stream molecular analyzer.

Some run days had more than one coal start, and since active cooling was always on, the CMC was cooled between starts, but the cooling was not enough to require a full day of refractory warm up. The total number of CMC thermal cycles (from below 600ºC back up to slagging conditions) was 31.

Over 200 parameters were recorded several times a second for each test. Only measurements relevant to understanding the CMC thermochemical environment will be discussed in detail here. In general, the measurements are those shown on the process control diagram shown in Figure 3.9.

4.3.2 Typical Test Operations

Initial tests of the gasifier were short; in part to frequently inspect the liner, but also because there were problems with the coal hopper, which had a damaged bearing and some unsuspected damage to the auger that was eventually discovered during bearing replacement. Once operation for long durations began, runs would typically go for 5-7 hours and end with stable refractory temperatures in the 600-900ºC range (referring to refractory temperatures taken at various places around the cast cone leading into the CMC test article).

A typical run (Test 17, on June 16, 2006) will be used as an example to describe the test environment. Test 17 occurred after the coal system repairs were complete and long test days could be accomplished, but before some data channels were lost to heat or chemical attack.

Figure 4.1 shows the various flows: coal, oxygen, steam, nitrogen, etc. Figure 4.2 shows the major system pressures (revealing that the event causing a temporary shutdown at 310 minutes for this specific test was a coal line plug).

These parameters are typical for the various runs. In general, the coal, oxygen, nitrogen and steam flows did not vary more than 15% from these values over the entire test program, except for transients, and the run-to-run repeatability was very close. The parameter that was allowed to vary, gasifier pressure, only was allowed to do so in runs 13, 14 and 26. More discussion will follow on this information in section 4.3.3b, as it could have altered the thermochemical environment; however it is unlikely this had a large effect on the overall results of this test program.

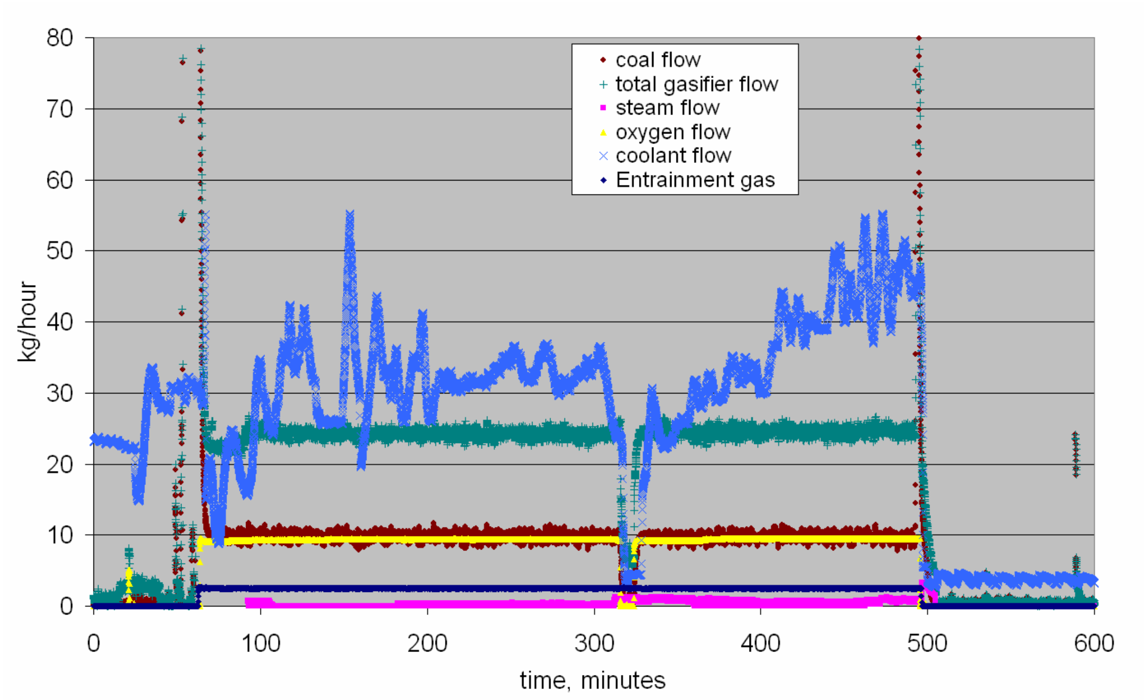


Figure 4.1 Test 17 Flow Rates

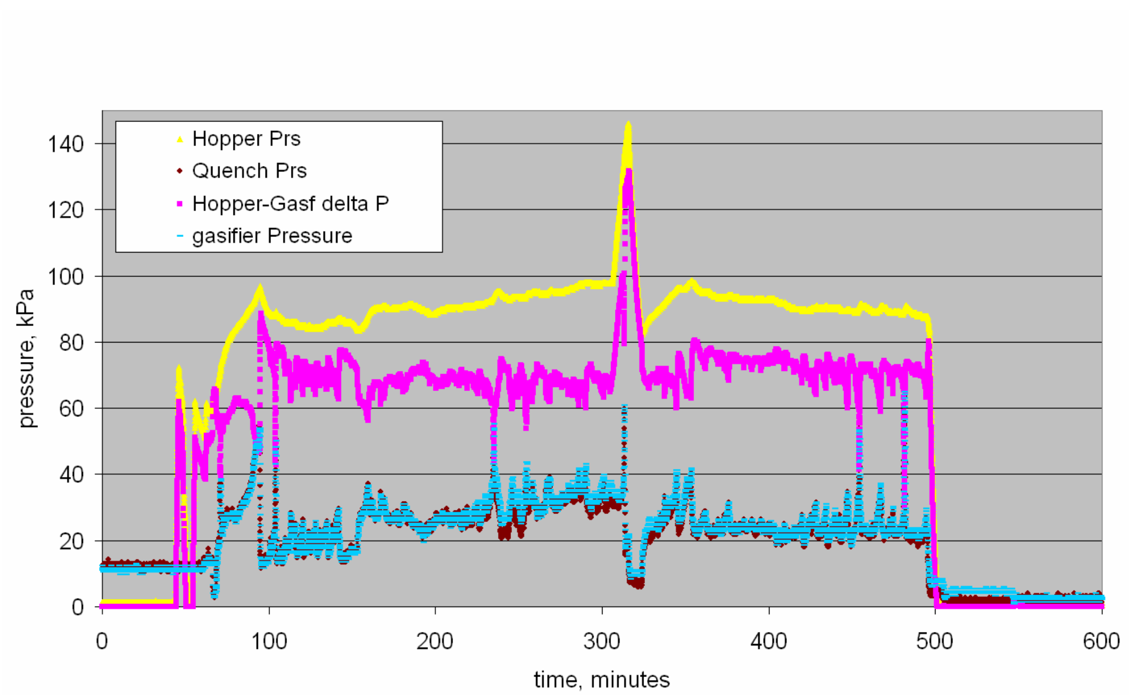


Figure 4.2 Test 17 Pressures

Coolant flow rates vary considerably because the control system was operating on a closed loop temperature control, keeping the cooling jacket temperatures constant during the test. Figure 4.3 shows various hot wall and coolant system temperatures, and Figure 4.4 shows refractory temperatures for this run.

TE-423A, 424A and 424C were thermocouples originally glued to the inner diameter of the cooling jacket metal wall and were used as primary temperature controls in the closed loop system. The thermocouple temperatures were fairly constant, which was attributable to a stable, properly tuned control system. The thermal analysis of this test rig indicated that as long as the cooling jacket was kept at the proper temperature, the CMC wall temperature ought to be maintaining a hot face below the slag softening temperature, and hence a frozen protective slag layer.

Figure 4.3 illustrates a number of other important features of the gasifier cross section and cooling system. Thermocouples 422C, 423B, 424A, 424B and 427 were all originally placed on the outer surface of the CMC liners in various locations. It can be seen that a significant variation existed between the different metal OD and CMC ID thermocouples, which was due to loosening of glue and relaxing of thermocouple sheaths at higher temperatures. The thermocouples lose contact with their respective surfaces and become “air gap” temperatures and can only be relied on for an indication of approximate conditions in the gap between the metal and CMC walls.

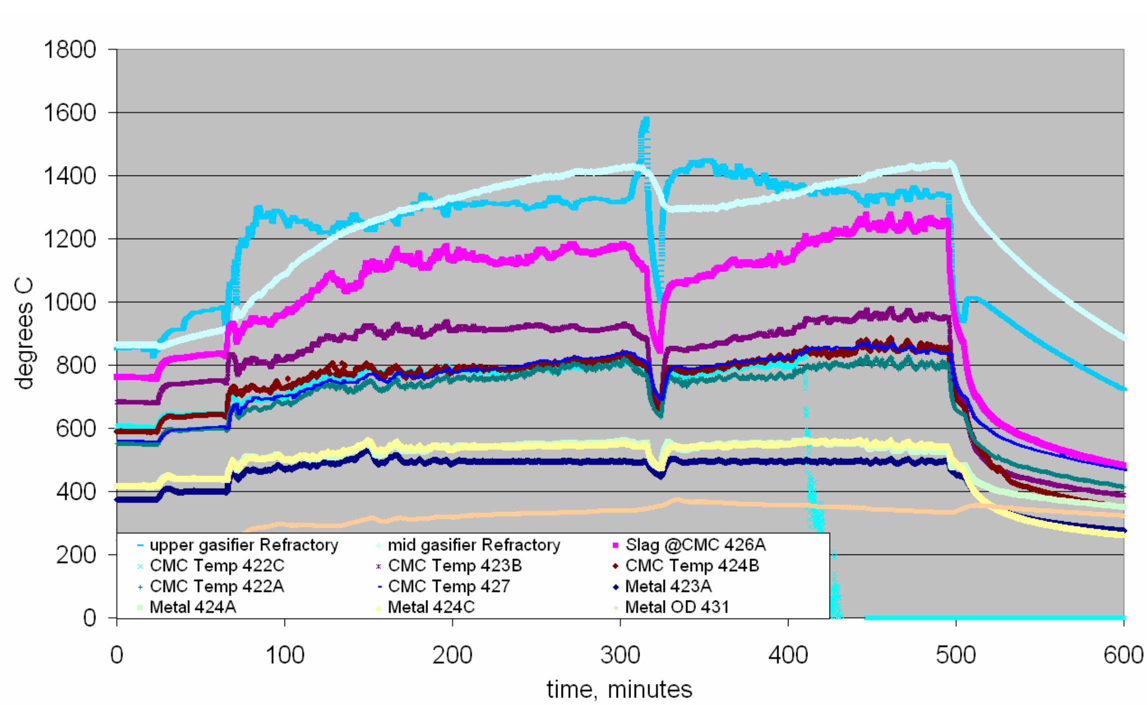


Figure 4.3 Test 17 Inner Wall Temperatures

TE-422C can be seen to fail at about 420 minutes. This was at the time determined to be a failure of the connector outside of the gasifier. Similarly, TE-422B (not shown) also had a bad connection in Test 17, but was repaired in test 21, displaying a temperature consistent with previous tests. A different sort of thermocouple failure was observed in subsequent tests. See the next section on long term trends.

TE-431 was a thermocouple placed on the outer diameter of the cooling jacket and represented the most accurate and stable indication of cooling jacket bulk temperature, however it was very slow to respond to changes which may occur due to syngas changes, leaks in the CMC wall, loss of insulation, etc.

TE-426A was one of four thermocouples placed into the syngas stream through the CMC walls. All of the other three had since been destroyed, but 426A survived throughout the entire test program. It was originally placed so that its junction was just at the OD wall of the CMC, however it is clear from early borescope inspections that, when the thermocouples were damaged and as slag deposited over them, it was probably somewhere inside the wall of the CMC cylinder. For most of the tests, 426A was probably indicating a temperature somewhere within the slag layer which had penetrated the through hole in the CMC wall. It can be seen by comparison with Table 3.1 that this thermocouple is reading a temperature well into the soft region of the slag most of the time, and into the fluid region for nearly an hour. This was the case for most of the tests, as will be seen in the next section.

TE-405 and 413 represent the upper gasifier and middle gasifier wall temperatures, respectively. For most of the tests, the thermocouples were placed flush with the wall. In tests 24-26 these thermocouples were replaced and in the last test (Test 26) TE-413 was placed so that it was well immersed in the syngas flow. Discussion will follow in the next sections on these temperatures.

In Figure 4.4, TE-420 was the temperature of the refractory cone directing gas into the test section, and was hottest due to the direct impingement of hot gas and slag onto the cone. The other four thermocouples were for the metal sample temperatures, and were all placed close to the upper coolant gas manifold. The amount of heat which flowed through this refractory cone into the coolant manifolds accounts for about 25% of the total heat picked up by the coolant circuit, which will be discussed in the section 4.3.3, Thermal Analysis.

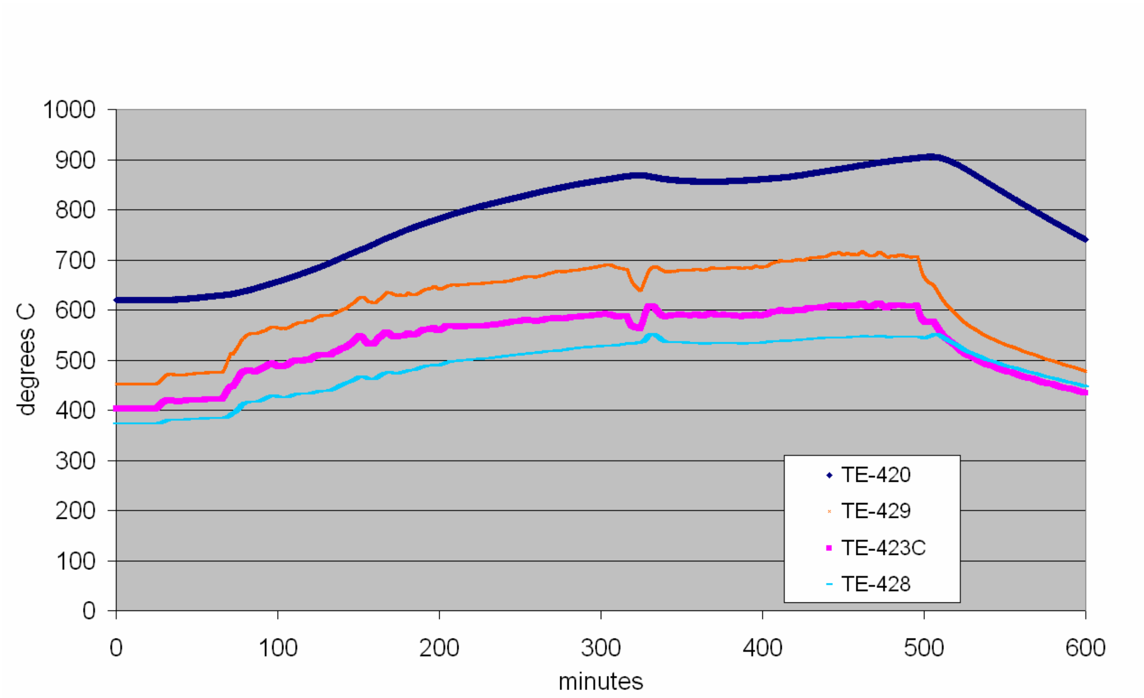


Figure 4.4 Test 17 Refractory Temperatures

4.3.3 Long Term Temperature and Heat Flux Trends

Figure 4.5 (Test 20) and Figure 4.6 (Test 21) provide the best illustration of the thermocouple damage that was mentioned in the previous section.

In Test 20, CMC temperature TE-423B and metal wall temperature TE-424C show some dramatic changes in temperature. The other “air gap” temperatures show similar step changes, but these two are the largest and most sudden. Several explanations exist for these changes, and all were investigated, but no firm conclusion was reached until the end of the test program when destructive inspections revealed the root cause.

The possibilities that were investigated included:

- CMC cracks, slag cracks or refractory cracks have allowed hot gas to flow behind the CMC, equalizing temperatures.
- Cracks in the coolant containment vessel (braze joint or hot wall cracks) have caused gas to flow behind the wall, equalizing temperatures.
- Insulating felt between the CMC and metal wall was disintegrating, equalizing temperatures in the air gap.
- Thermocouples were moving (bending), measuring different locations in the air gap.
- Thermocouples were melting and re-fusing, creating junctions at different locations in the air gap.

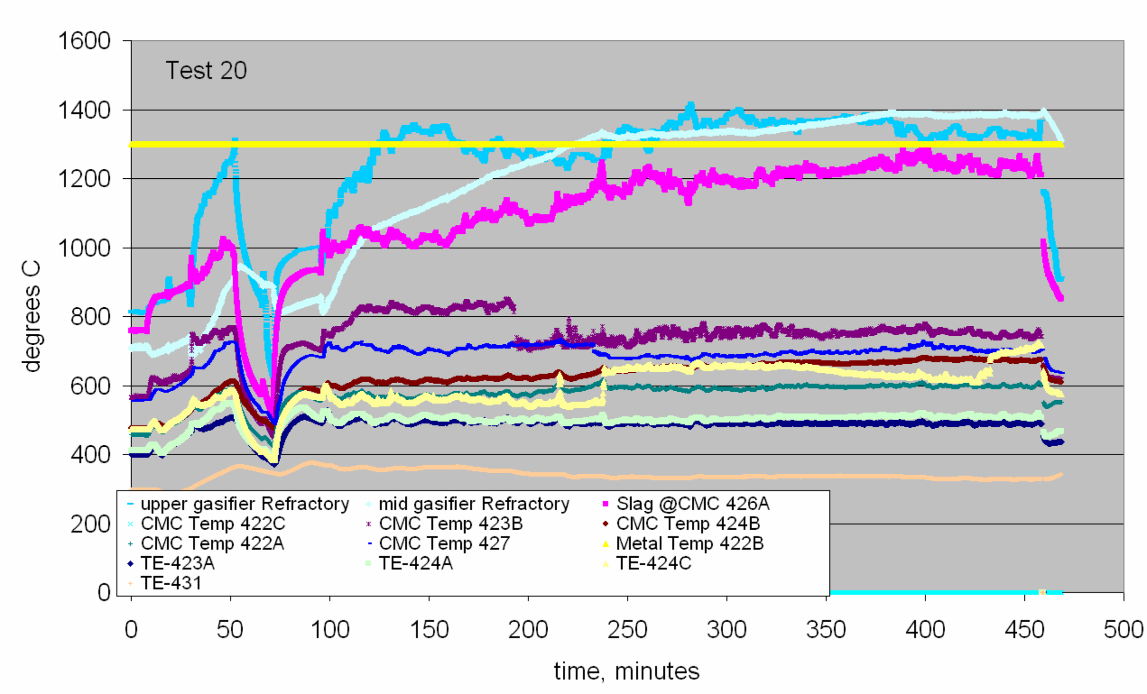


Figure 4.5 Test 20 Inner Wall Temperatures

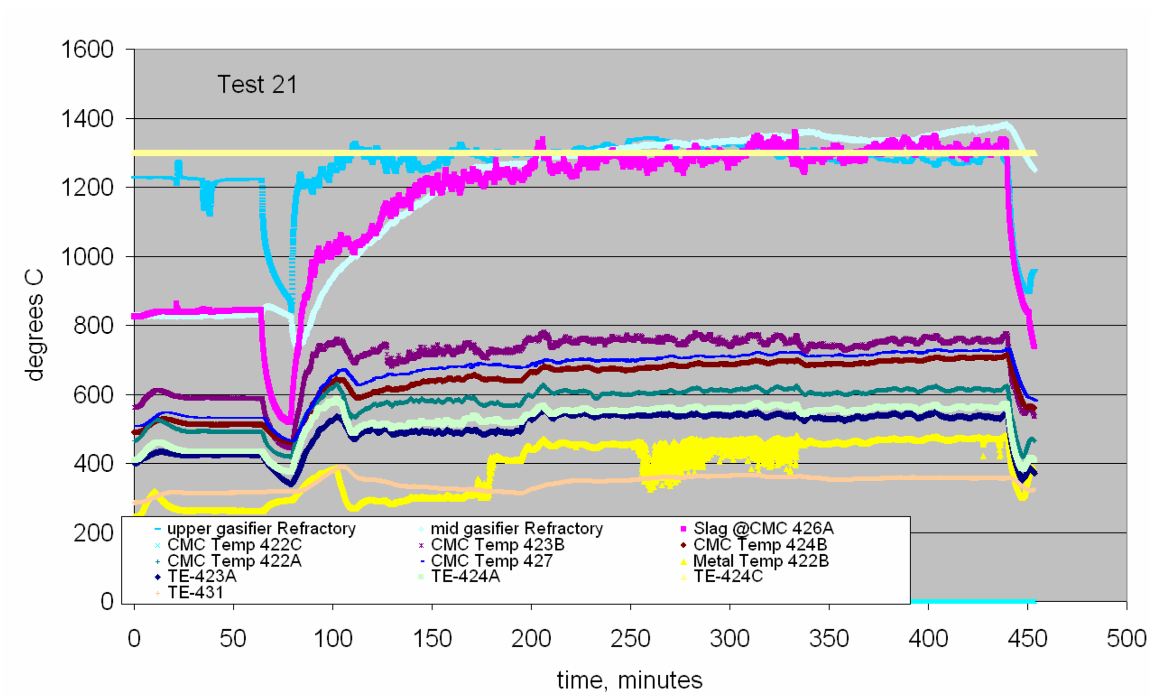


Figure 4.6 Test 21 Inner Wall Temperatures

In Test 21, CMC temperature TE-423B again and metal wall temperature TE-422B (repaired from its earlier bad connector joint) are seen to exhibit similar behavior. Leak tests on the coolant circuit eliminated the possibility of a coolant leak, and borescope examinations appeared to show that slag was filling in and covering up the joints between CMC pieces where syngas leaks would occur (post test examinations appear to show that leaks of this type may have actually taken place, would help to explain the high heat flux into the coolant and could be a contributor to thermocouple failures, but there is no conclusive evidence of this).

Thermocouple melting and re-fusing was considered unlikely, though possible (this was eventually proven to be the actual cause, but the evidence was ambiguous). Insulation degradation was considered unlikely at this time, since the manufacturer's literature didn't suggest a strong reaction with the syngas to be likely, although it was given further strong consideration later when long term heat flux numbers were compared. Thermocouple bending and movement, however, was seen from the very beginning of the test program and was considered to be the most likely cause when it first occurred.

The decision was made to stick to the temperature control method, choosing the lowest reading of the several metal wall thermocouples, but adjusting the control value up to account for the fact that the actual temperature was likely to be the temperature of the gas between the CMC and the metal wall.

Beginning with tests 21 and 22, the control system was switched to run on flow control for long periods to obtain cleaner steady state heat flux data and compare long term trends. This practice continued to the end of the test program. At this point it is illustrative to show graphs for all test days combined.

Figure 4.7 shows a few wall thermocouples and total coolant heat flux for all of the runs. Test 20 begins at about 62 hours. The convergence of the CMC wall and metal wall thermocouples is very clear. There is also a subtle but definite increase in the heat flux into the coolant. This was compared to the thermal model of the through-wall heat flux and it was found to be consistent with the removal of the felt insulation layer, so for test 26, the coolant flow was decreased slightly and temperatures were allowed to rise above their prior set points.

The true cause of the increase in heat flux was later found to be a combination of factors: loss of insulator material, some loss of CMC thickness, and greater CMC thermal conductivity due to slag infiltration which filled some existing voids in the CMC wall, however this was not known at the time.

The conclusion that the liner was overcooled in later runs was supported by the thermocouple TE-427, which was not of the same type as the other small diameter probes with A, B and C designations, and was installed in close contact with the CMC OD. TE-427 was later found to have melted back at least ¼ inch as well yet still had a closed electrical junction, further lending support to the possibility of racetrack leaks around the back side of the CMC.

If the assumptions had been correct, this would appear to have brought the CMC wall temperatures back up to the original planned temperature zone of 750-900ºC. The thermocouple TE-426A was not given much weight in this analysis for the reason that the three other identical junctions (426B, 425A & 425B) in similar locations were intermittent, and worked only when hot (600-800ºC or higher). Thus 426A was possibly an electrical connection inside the slag that was dubious, and it was unknown if a hot slag junction would be accurate. However, after reviewing the data, it appears that the temperature reading may have been accurate and not a slag junction. Thus it is likely that the actual temperature of the slag near the leading edge of the CMC cylinder was close to the reading of TE-426A. If true, the CMC temperature was probably well over the intended test temperature beginning with the very first test, making this a significant overtest of the intended environment.

The thermal analysis (section 4.4.2) and material destructive examination (section 4.4.3) tend to support this conclusion.

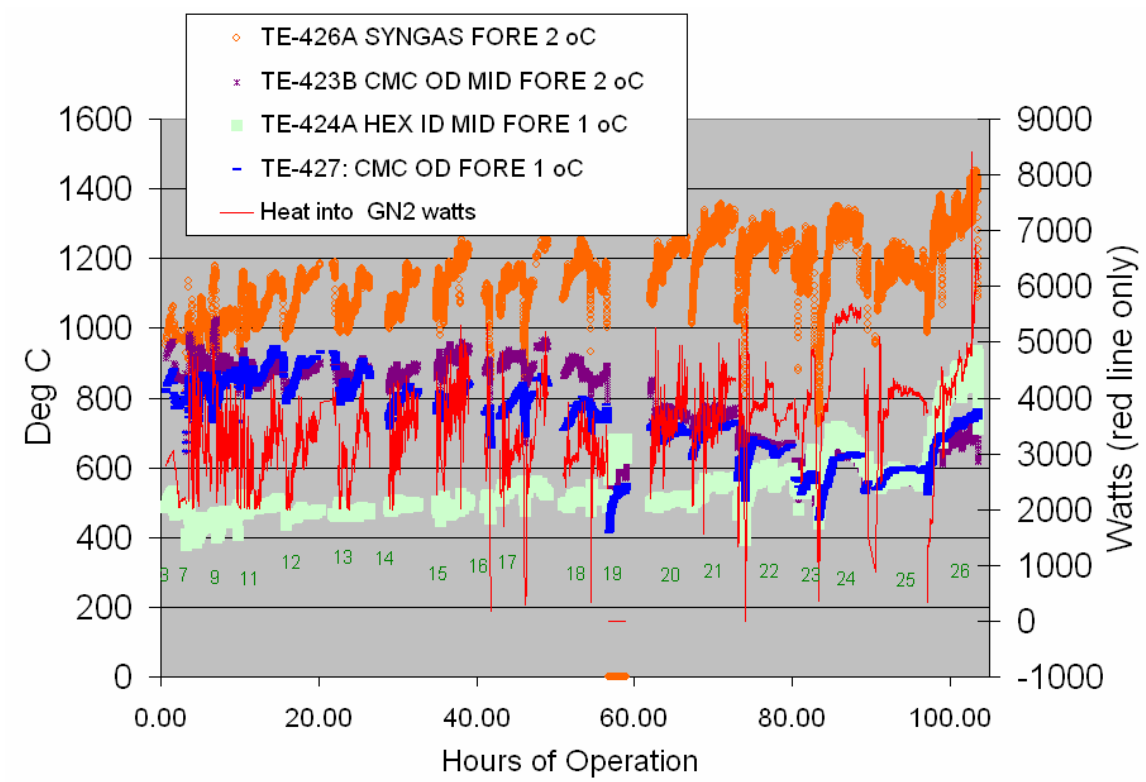


Figure 4.7 All Tests: Wall Temperatures and Heat Flux

(Test numbers in Green)

4.3.4 Borescope Photographs

Both wide angle and close up photographs of the inner surfaces of the gasifier were taken after every test with a small diameter flexible fiber optic video camera. The intent of these inspections was to determine if the CMC liner was in good shape after each test, and it turned out to be very useful for general inspections. It was difficult to determine from the pictures how thick the slag was, but it was possible to see that there had been slagging operation. Surface inspections were not capable of telling whether the CMC diameter had changed during the test, however on close inspection of a few frames some of the last tests appear to show surface damage near the upstream edge of the cylinder which was also obvious on disassembly.

Figure 4.8 shows a typical view of the cylinder joints, with slag partially filling the seam between liner cylindrical sections.

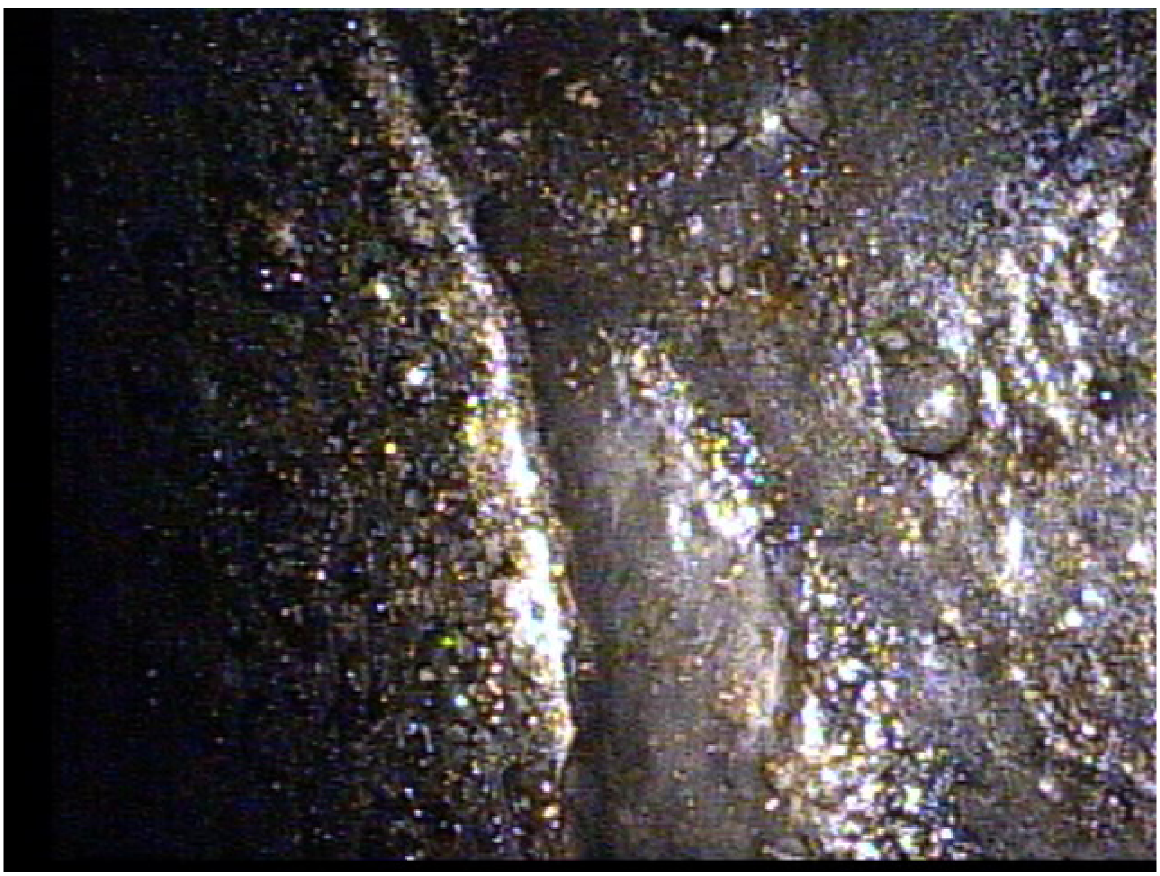


Figure 4.8 Slag over CMC joint after Test 10

Figure 4.9 shows the “rivers” of slag that were running down the CMC cylinder from the outlet of the gasifier chamber upstream of the PWR test article. This was due to the large diameter change from the gasifier to the test section and quench vessel diameter. A lot of slag was deposited in the exit cone, and from there would drip down the surface into the smaller hole. The shape of the hole would change from test to test as this slag melted and was replaced by fresh slag flowing down the surface. Figure 4.10 shows a similar wide angle view after test 24, demonstrating the dynamic nature of the test conditions. Although both indicate that slag is always present, the fact that it changed in every test indicates that the slag was in a softened state during the tests.

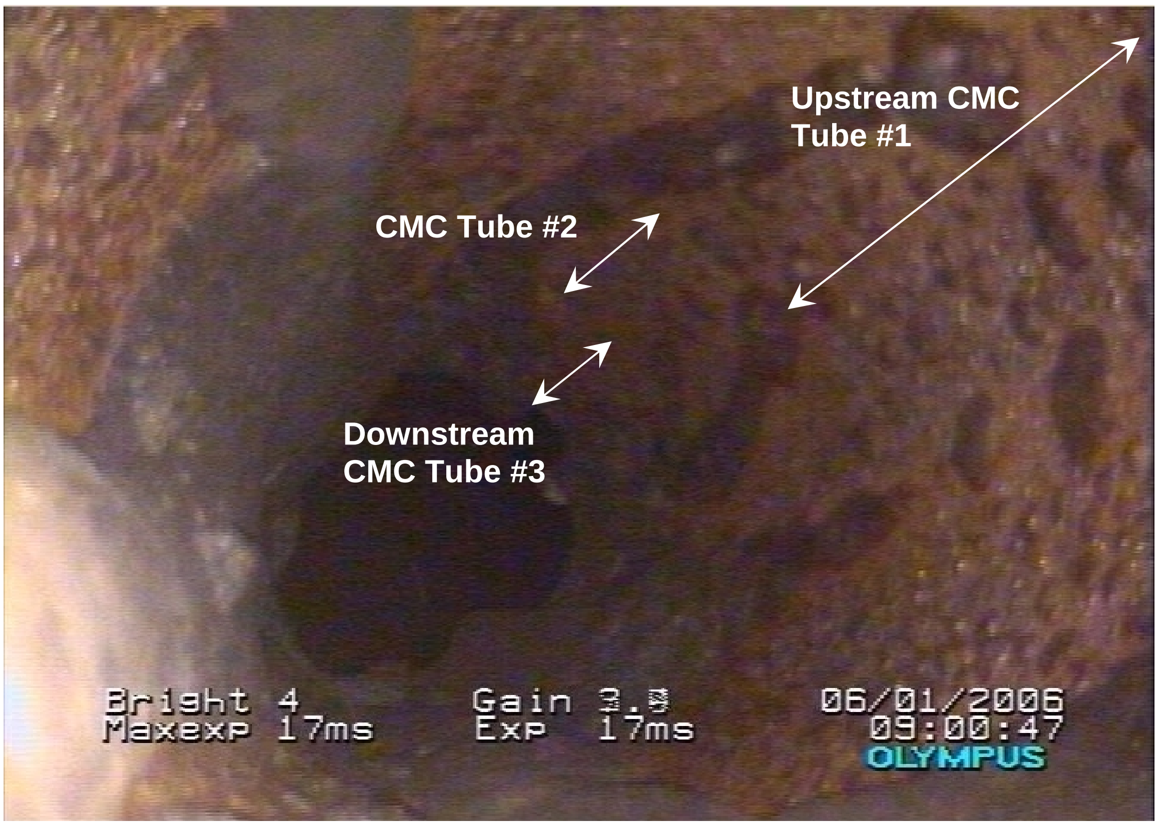


Figure 4.9 Wide Angle View of CMC Liner After Test 12

(View from Upstream End Down into CMC Liner Section)

Figure 4.10 Wide Angle View After Test 24

Figure 4.11 Close up view after Test 24, thick region

Figure 4.12 Close up View After Test 24, showing CMC fabric edges

Figure 4.11 and Figure 4.12 show two very different, but typical views of the slag surface. In the first picture, the slag is quite thick, though bumpy, and the CMC is not visible. In the second, the slag is in drops, with well defined edges, and the CMC surface is visible, including what appear to be edges of layers of fabric (confirmed in post test inspections). This is the upstream edge of the first cylinder, and these fabric edges were visible to the naked eye after disassembly.

4.3.5 Mass and Energy Balance

A real-time mass spectrometer was used to analyze the output gas from the gasifier quench vessel. On several days this data was compared to a separate gas analysis done at a separate laboratory on a bottled gas sample. In general the gas analyses were similar from day to day, although samples were not available for all days while the mass spectrometer was being calibrated.

For the days in which analyses were performed, the carbon conversion for the CANMET gasifier under test conditions ranged from 56% to 68%. Table 4.2 summarizes the output and performance for several tests.

Table 4.2 Mass Balance and Approximate Carbon Conversion

	Test 13	Test 18	Test 21	Test 21	Test 22	Test 25	Test 25	Test 26
	6/2/06 (online)	6/21/06 (online)	6/29/06 (online)	(Lab Sample)	(Lab Sample)	7/18/06 (online)	(Lab Sample)	7/20/06 (online)
Inputs	kg/hr							
O2	9.32	9.53	9.33	9.33	9.33	9.43	9.42	9.40
N2	3.32	5.01	4.82	4.82	4.82	4.37	4.37	4.22
Coal	9.96	9.23	10.35	10.35	10.35	9.87	9.88	9.72
H2O	0.85	1.69	1.18	1.18	1.18	1.18	1.18	1.28
Total:	23.46	25.46	25.68	25.68	25.68	24.84	24.85	24.63
Outputs	vol % from online mass spectrometer or post test lab analysis of sample gas							
H2*	8.51	19.24	12.69	12.28	12.28	18.29	13.94	15.27
N2	24.00	21.22	21.90	29.11	29.11	19.72	25.98	20.22
CO	20.44	11.61	14.56	26.26	26.26	12.29	33.41	13.09
CO2	46.05	32.29	32.09	30.95	30.95	27.85	24.03	29.15
O2	0.08	0.50	0.12	0.00	0.00	0.88	2.17	0.08
H2S	0.01	1.47	0.96	0.39	0.39	1.08	0.47	0.87
CH4	0.02	0.04	0.04	0.02	0.02	0.02	0.00	0.02
	kg/hr (N2 averaged, H2 corrected & scaled to total)							
C	3.95	4.57	4.41	4.20	4.07	3.81	4.14	3.78
H*	0.63	0.68	0.69	0.69	0.69	0.66	0.66	0.67
N	3.47	5.15	4.98	4.98	4.98	4.51	4.51	4.37
S	0.00	0.41	0.24	0.08	0.07	0.27	0.09	0.21
Ash	4.21	1.36	3.24	2.88	5.42	5.34	5.31	4.16
O	11.20	13.29	12.12	12.87	10.46	10.25	10.13	11.44
Total	23.46	25.46	25.68	25.68	25.68	24.84	24.85	24.63
Carbon conversion	56.9%	71.0%	61.1%	58.2%	56.5%	55.4%	60.2%	55.9%

*Missing hydrogen assumed to be in steam captured in quench vessel, and a small amount in ammonia. Nitrogen in coal assumed to go to ammonia.

Using an average carbon conversion value of 60%, the PWR kinetic model calculated the following hot syngas information within the cylindrical CMC liner prior to quench. The kinetic model shows that there is some free oxygen and steam within the gas at very high temperature (4,600ºF).

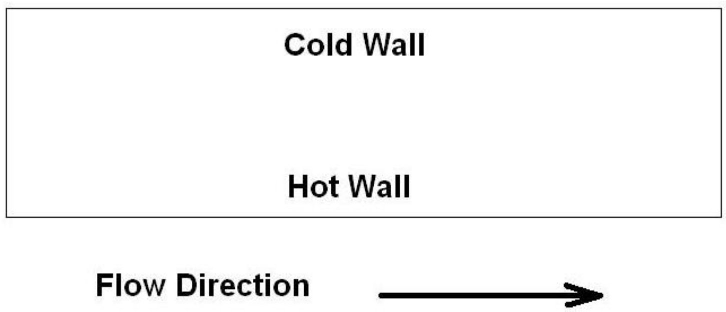
Temperature:	2540ºC (4600ºF--design condition was 2,700ºF)	
Pressure:	124 kPa (18 psia--design condition was 220 psia)	
Velocity:	24 m/s (80 ft/sec--design condition was 30 ft/sec)	
Gas Properties:		
Molecular Weight:		26.0 g/mol
Specific Heat:		1.77 kJ/kg/K (0.425 Btu/lbm-ºF)
Dynamic Viscosity:		0.080 centipoise
Thermal Conductivity:		0.209 W/m/K (0.121 Btu/ft/hr/ºF)
Prandtl Number:		0.677
Composition:		
CO (vol%)		24.77
CO2 (vol%)		17.58
H (vol %)		1.87
H2 (vol%)		5.84
H2O (vol%)		27.37
NH3 (vol%)		0.70
NO2 (vol%)		0.25
N2 (vol%)		19.41
O (vol%)		0.64
O2 (vol%)		1.38
SO2 (vol%)		0.19

The reactor mass balance shows that 40 wt% of the initial coal carbon exited the gasifier as char (with a composition of roughly 60-80 wt% carbon), and the fly ash analyzed did show a carbon content of 75%, however the slag found on the CMC liner's entrance was essentially 100 wt% ash as determined using ASTM ultimate analysis procedures. CANMET explained this interesting result by the fact that probably most, if not all, of the ash material on the CMC liner wall can be attributed to the molten slag originally deposited on the gasifier's upper walls. This slag subsequently flows down along the walls of the gasifier and convergent cone section before entering the CMC liner test section. It is estimated that the residence time of this wall slag is on the order of seconds due to frictional hold-up of this highly viscous and quasi-liquid material along the walls of the upper gasifier's low velocity regions. This extended residence time within the upper gasifier section allows the wall slag to reach near 100 wt% carbon conversions before flowing over the CMC walls. One should note that the residence time of the bulk coal char within the reactor is probably less than 10 milliseconds.

4.4 CMC Liner Assessment

In all of the CMC liner dissections that follow, a simple convention is used to maintain an orientation of the parts, shown in Figure 4.13. For radial transverse cuts, the curvature of the part should be visible, identifying the hot wall as the I.D. of the tube. When the curvature is not obvious, the hot wall will be down.

Figure 4.13 Section Orientation, longitudinal-radial cuts



The three CMC liner sections are identified as follows. Tube #1 is the upstream liner cylindrical section, Tube #2 is the middle section, and Tube #3 is the downstream section.

The cooled liner test program successfully met all primary objectives. As discussed in more detail in section 4.4.3, there were several areas where the original CMC liner surface was completely intact at the end of the test program. The indication is that, in regions where the cooling was able to maintain the CMC liner within the planned temperature range, a solid layer of slag was formed on the CMC liner inner surface and protected the liner from erosion and corrosion as expected. The test program provided a significant amount of information in the areas of thermal control, CMC materials and processing for improved capability in a gasifier environment, and CMC liner fabrication that will be essential for upcoming advanced gasifier projects.

The CMC liner survived over 100 hours of slagging operation and 31 thermal cycles (from below 600ºC back up to slagging conditions) without catastrophic failure even though the liner was significantly over-tested as a result several contributing factors.

One of the primary factors resulting in over-test conditions was associated with the manufacturing of the CMC liners. During post-test scanning electron microscope (SEM) examination, each of the CMC liners was found to have much higher porosity than expected from prior CMC experience at PWR and from CMC manufacturer reports. The excessive porosity found to be present in the liners manufactured for the CANMET testing resulted in thermal conductivities significantly lower than the baseline values used in the design analysis. This CMC liner manufacturing issue is detailed in section 4.4.1.

Two additional factors were associated with the specific nature of the CANMET gasifier under the test conditions: (1) as described in section 4.3.5, the bench-scale gasifier provided carbon conversion dramatically lower than that expected for the PWR advanced gasifier and resulted in gas temperatures in the CMC liner region nearly 2,000ºF higher than the baseline value used during design; and (2) the actual radial thermal heat flux was approximately 35% higher than the design value due primarily to the actual gas flow rates at the final test conditions. This topic is further discussed in section 4.4.2.

Failure of thermocouples in later runs (as discussed in section 4.3.3) also led to operating the CMC liner at temperatures well above the design range except at the downstream end that experienced the most cooling.

Due to the combination of factors specific to the CANMET test program, the formation of a protective layer of solid slag was not possible under these increased surface temperature conditions for most of the liner axial length, allowing diffusion of corrosive elements into the surface and some loss of material as would be expected. The material evidence shows that oxygen and slag damaged internal layers of the ceramic, which is to be expected given the material porosity and elevated temperatures. However, the liner did not fail even at these greatly elevated operating temperatures and gradients. Section 4.4.3 details the CMC-slag interaction evaluation and section 4.4.4 provides an evaluation of the design and specific recommendations for improvements.

4.4.1 CMC Material Properties

During post-test inspection and examination, all three of the CMC liner materials showed surface degradation and loss of some thickness, however upon initial visual examination the 2nd and 3rd cylinders were noticeably thinner than the 1st. Cross sections of the liner sections revealed porosity described above (section 4.4), and attempts to anchor thermal analysis indicated conductivity was probably low, so thermal conductivity was measured with pristine samples (cut off ends from the manufacturing process which had not been exposed to the slag).

The thermal diffusivity of the three sample materials was determined at Teledyne Scientific using a NETSCH Laser Flash device at room temperature. The density of each sample was also measured so that thermal conductivity could be determined by the following formula,

$$\kappa = \alpha \times \rho \times Cp$$

,where κ is thermal conductivity, α is the thermal diffusivity, ρ is the density and Cp is the heat capacity of the material. The heat capacity of the materials was estimated based upon previous work and is within range of similar composites. These measurements were made after the CANMET testing was complete and utilized excess materials from CMC1, CMC2 and CMC3. It is important to note that these samples did not undergo the final seal-coating that the service specimens did, however, due to the heavy internal porosity, the seal coating would have had a negligible effect on thermal conductivity. Porosity values of the liner sections removed from the test rig appear to be similar from measures of open area in cross section.

Thermal conductivity of the samples is shown in Table 4.3 below.

Table 4.3 Liner Density and Conductivity

	Density g/cc	Open Porosity %	Conductivity W/m/K	Conductivity BTU/ft/hr/ºF
Cylinder 1	2.32	19%	4.7	2.7
Cylinder 2	2.06	25%	1.0	0.6
Cylinder 3	1.89	32%	0.8	0.5

The net result in these low thermal conductivities (target was 4 BTU/ft/hr/ºF) is higher temperature on in ID, a larger temperature gradient through the thickness and a higher internal stress in the material. Calculations of the thermal stress for a typical run (anchoring Test 17) show thermal stresses as high as 248 MPa (36 ksi). Since the expected strength of a pristine, fully dense liner is expected to be only 46 ksi it is reasonable to deduce that the materials could have been at or above their stress limits, and this high stress may have contributed to the material lost during the test program either from brittle failure at the surface as the slag freezes, or simply from thermal stress during operation.

The excessive porosity resulting in poor thermal conductivity has been assessed to be a quality control issue during the manufacturing process with the subcontractor on this specific project. PWR past experience with other CMC manufacturers has shown that the design baseline thermal conductivity values of 7 W/m/K (4 BTU/ft/hr/ºF) are achievable with realistic quality control methods. This is not viewed as a generic and inherent issue with CMC liners.

4.4.2 Thermal Analysis

Based on the physical state of the CMC liner, a detailed thermal analysis of the test article was performed to better understand the operational environment.

As noted in section 4.3.5, based on the results of a mass and energy balance, the gas temperature in the test article section was calculated to be 2,540ºC (4,600ºF) compared to the design condition of 1,482ºC (2,700ºF). This is due primarily to the relatively low carbon conversion (60%) associated with this bench-scale CANMET gasifier under the test conditions. The design condition was calculated based on a nearly-complete carbon conversion value associated with the PWR advanced gasifier. Thus, the CMC liner was exposed to the syngas at a significantly higher temperature than planned for this test program and expected for the PWR advanced gasifier.

Additionally, the CMC liner system was designed for an outward radial thermal heat flux of approximately 4.7 W/cm^2 (0.029 Btu/in^2-sec) at the slag/CMC interface. The actual measured radial thermal heat flux was 6.4 W/cm^2 (0.039 Btu/in^2-sec) – approximately 35% higher than design conditions due primarily to the actual gas flow rates at the final test conditions.

The non-porous "design" thermal conductivity for the CMC liner test hardware is 7.0 Watts/m/K (4.0 Btu/hr/ft/ºF). With the higher heat flux measured during testing, this thermal conductivity should have produced a slag/CMC interface temperature of about 1050ºC (1900ºF) – somewhat higher than the design's 930ºC (1700ºF) interface temperature but still below the slag's solidus temperature of approximately 1100ºC (2,000ºF). However, as discussed in section 4.4.1, the CMC liners manufactured by a subcontractor for this test program had significant porosity and correspondingly significantly lower values of thermal conductivity than the design value.

The measured thermal conductivities for each of the three liner segments are provided in Table 4.3, above. A lower CMC thermal conductivity produces significantly higher slag/CMC interface temperatures. For example, a CMC thermal conductivity of 1.6 W/m/K (1.0 Btu/hr/ft/ºF) would increase the slag/CMC interface temperature to about 2,300ºF. This temperature is well above the slag's solidus temperature and would allow for the wicking of molten slag into the CMC's pore structure (as seen in many of the micrographs presented in section 4.4.3). The analysis indicates that if the CMC's thermal conductivity was as measured in the samples described above, the majority of the CANMET tests were conducted under conditions which prevented the use of a "solid" protective slag coating on the CMC's inside diameter during operation. Hence, the test conditions were significantly worse than the design condition.

A post test thermal analysis anchoring the data from Test 17 was performed using the average thermal conductivity of 2.2 W/m/K (1.3 Btu/hr/ft/ºF). The result is shown in Figure 4.14. The transition from green to yellow in the figure is just below the softening temperature of the slag. Therefore, only the last inch or so of the CMC was likely to have been sufficiently cooled to maintain a solid layer of slag and this is exactly what was discovered in the post-test examinations: the last half inch or so had its original inner surface. The other location at the joint between the first and second cylinder is also shown in the figure, and on close examination it appears the joint is close to a natural dip in the temperature profile. In fact, the material loss graph, Figure 4.19, appears to parallel lines of constant temperature.

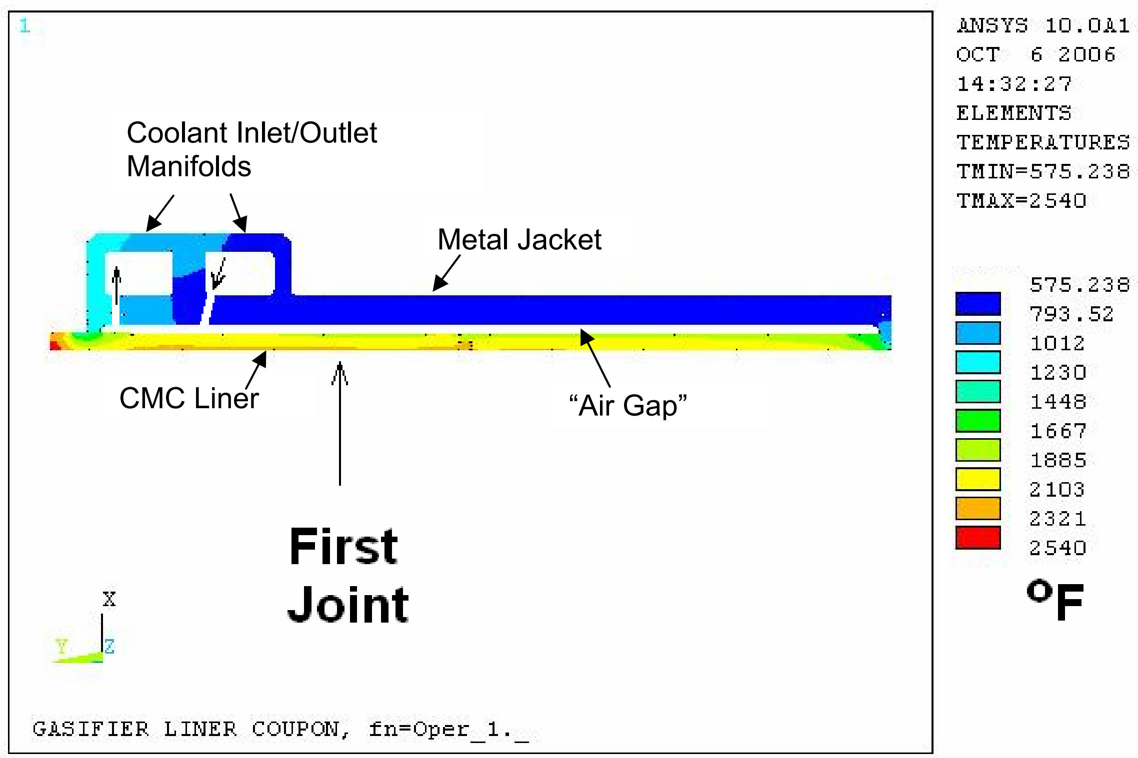


Figure 4.14 Thermal Map of Liner Cross Section, in ºF

Based on these analyses, the actual CMC surface temperatures were about 100ºC hotter than the measured CMC temperature until Test 20, and after Test 20 (when CMC thermocouples were no longer reliable), they were 200-300ºC higher than expected. When the analysis is performed on data any particular run, they turn out to be very close to the measured slag temperatures shown in Figure 4.7 as "TE-426A".

4.4.3 Post-Test CMC Examination and CMC-Slag Interaction

After disassembly of the gasifier test spool, the CMC liners were extensively photographed and section lines drawn in order to preserve locations of maximum and minimum slag deposition. In Figure 4.15 below, the largest remnants of slag are visible in sections C-D, F and G. It was immediately obvious in visual examination that there were areas where the CMC lost some material. Under low power magnification it is possible to count the layers of CMC weave, revealing that in many places there are one to three layers of fabric missing from the inner surface. Further examination with a scanning electron microscope (SEM) revealed several mechanisms for this, which will be described subsequently.

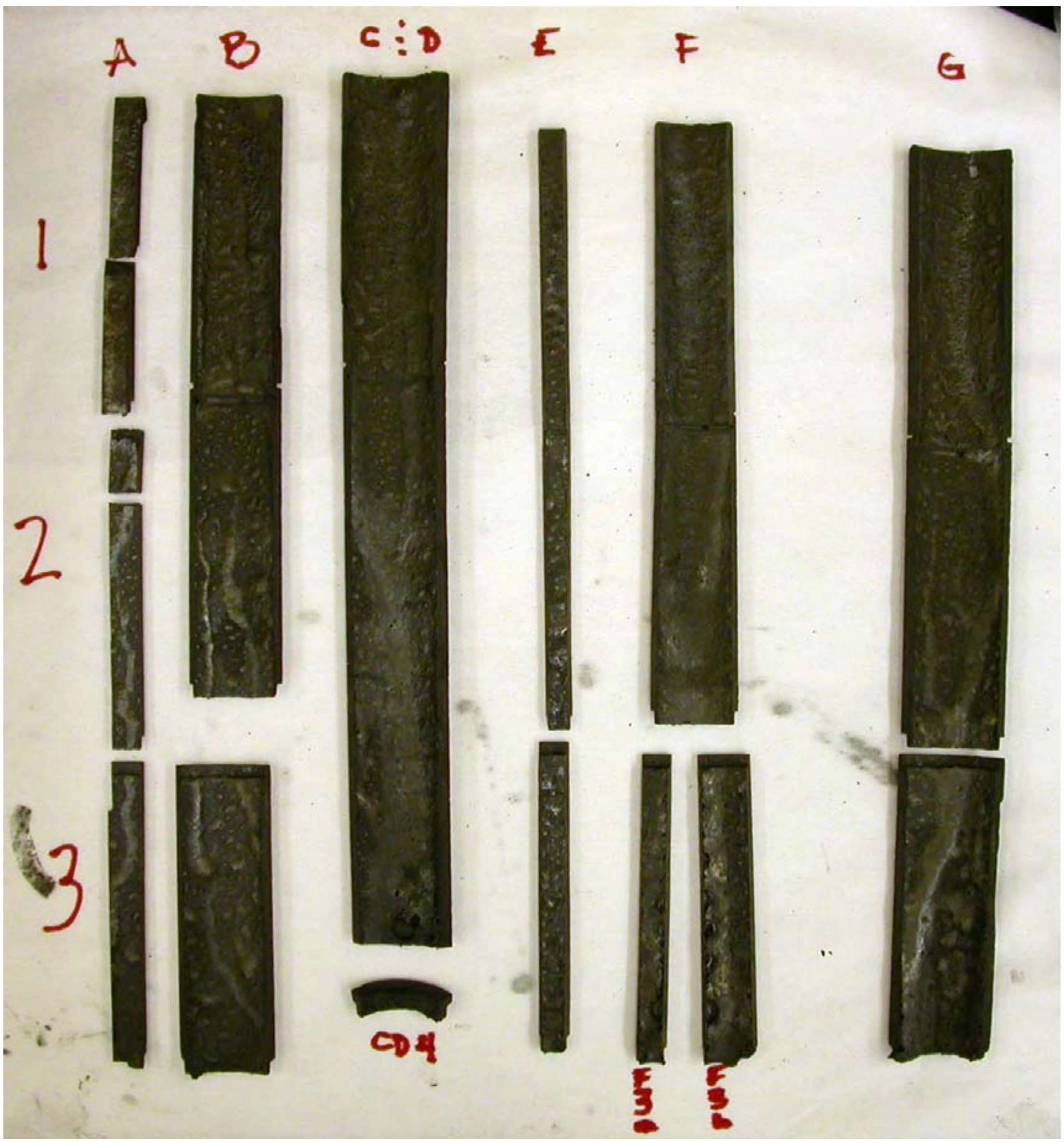


Figure 4.15 Sectioned CMC tubes

In addition to the sections shown above, pieces C+D and F were sectioned radially to see the change in thickness at different places around the cylinder. This was most illuminating, as the different layers of fabric can be seen and counted. Figure 4.16 is Tube #1 and Figure 4.17 is Tube #2. Both show the loss of the inner 1-3 layers of fabric.

Most interesting, however, is Tube #3 at the aft end (Figure 4.18) that is located in the last half inch of the tube which is resting on a metal lip at the bottom of the cooling jacket. Thermal analysis shows that this section of the tube was likely maintained at or below the softening temperature of the slag, as planned, for the entire duration of the test. This section of the CMC liner was appropriately cooled to allow the protective solid layer of slag to form and therefore did not lose any material from the inner surface.

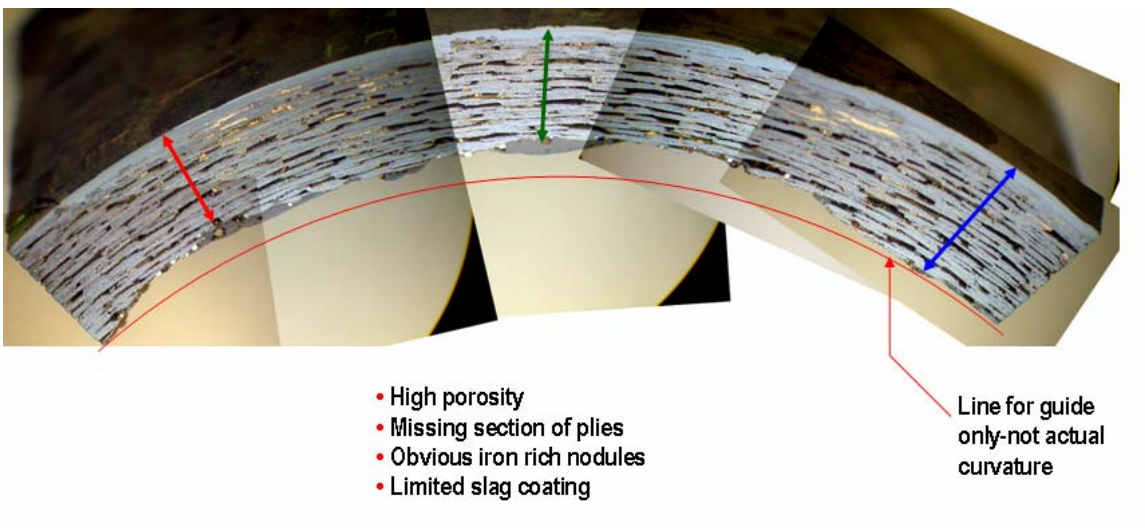


Figure 4.16 Horizontal section of CMC, Tube #1

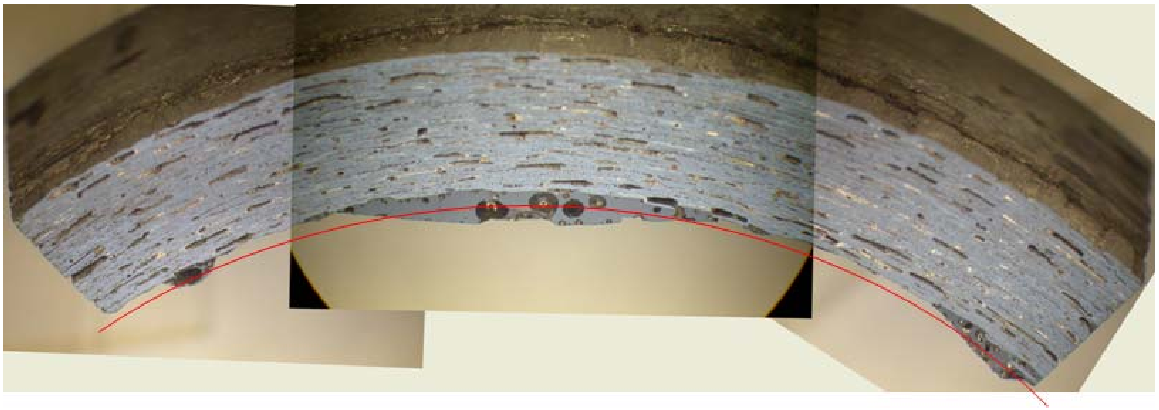


Figure 4.17 Radial section of CMC, Tube #2

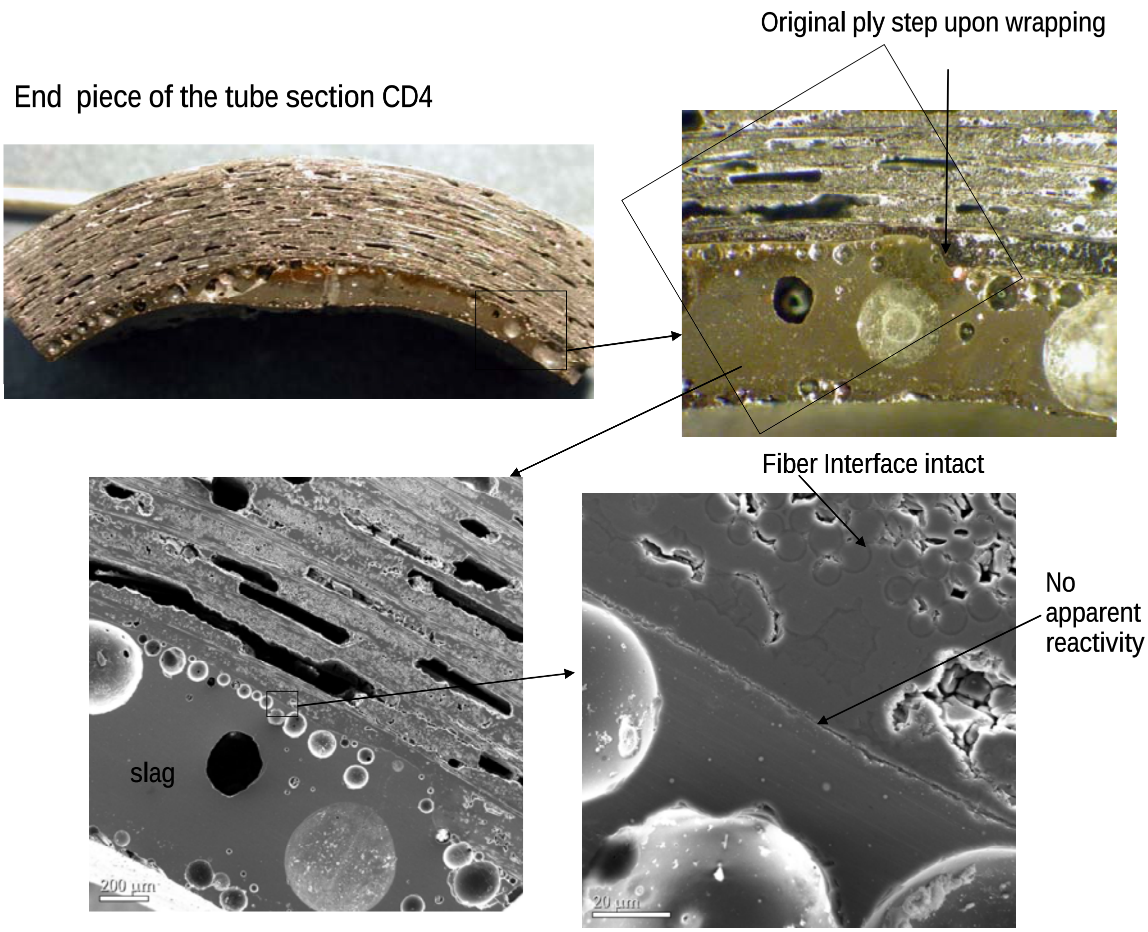


Figure 4.18 Full Thickness CMC, Tube #3, Showing that proper cooling can protect the surface.

After sectioning the liners as shown above, thicknesses of all of the pieces were measured. These measurements were made with optical devices using a fine scale, and were done independently at PWR and at Teledyne Scientific Company. The measurements are in close agreement. Figure 4.19 shows the results of all the thickness measurements combined in one graph. The initial O.D. is different for each part, as there is a diameter tolerance for the associated grinding operations during fabrication. The initial I.D. of all parts was the same, as they were all originally fabricated on the same mandrel. The very upstream edge of the first piece was not measured, as it was a fairly smooth radius along the entire corner. The very downstream ¼” was also not measured, since it consisted of a step.

Two locations can be seen where the cylinders did not lose material, one of which was shown above; the other is discussed below and shown in Figure 4.23.

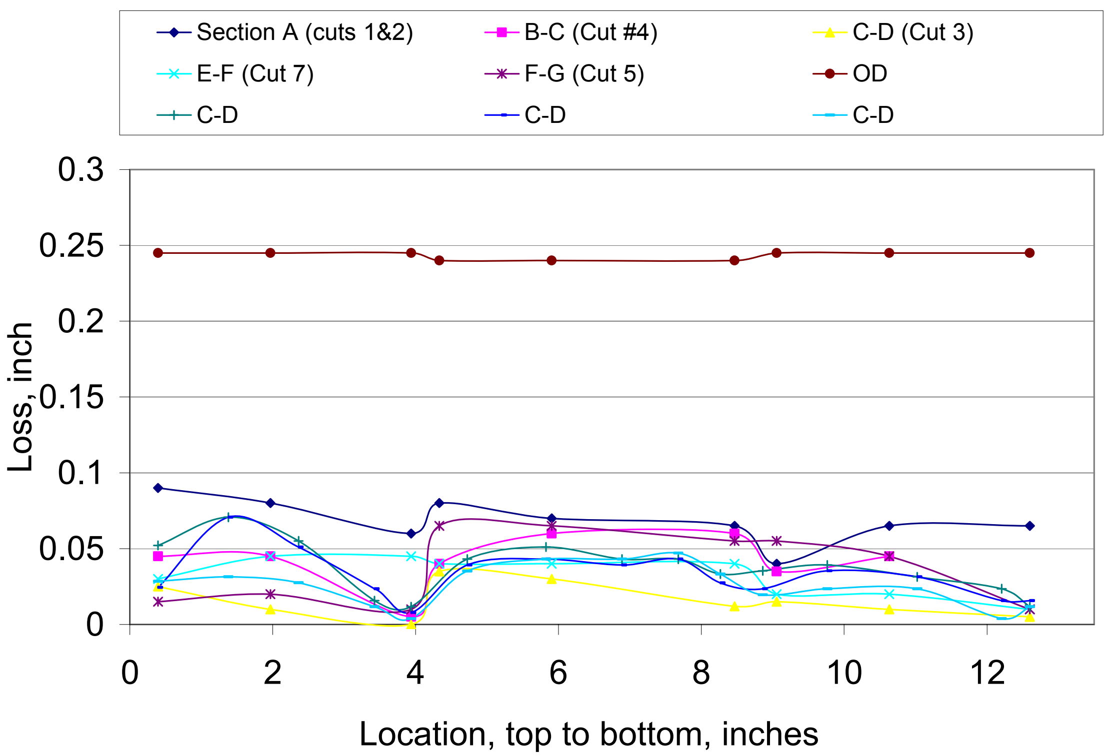


Figure 4.19 CMC Surface Recession (origin represents the initial I.D.)

Figure 4.20 is a section of the first CMC tube taken right at the leading edge (the radius on the lower left of the pictures). Slag is evident in between layers of the CMC fabric.

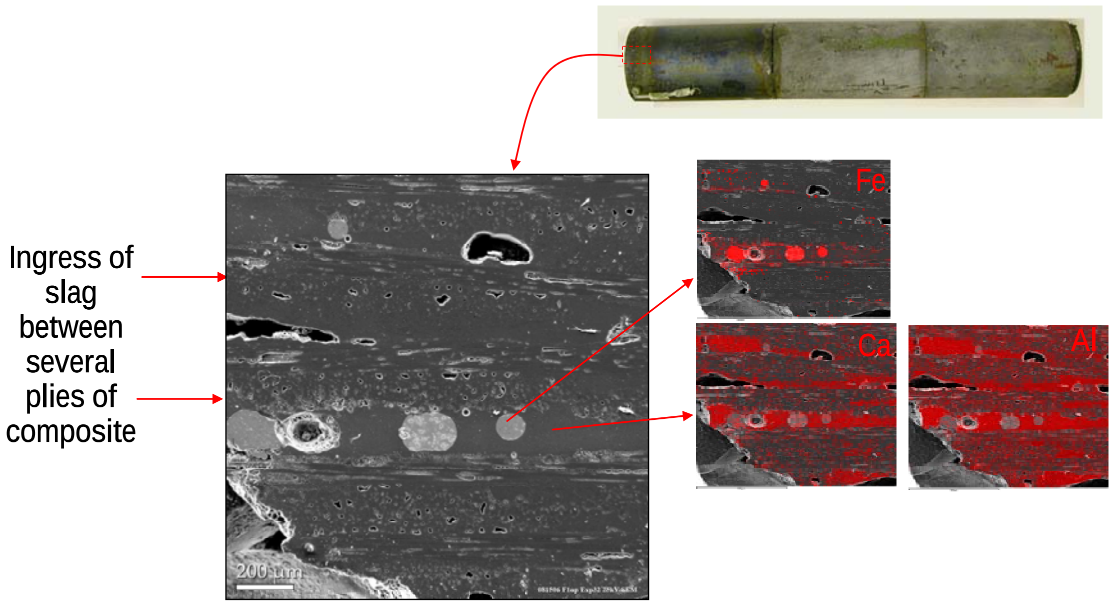


Figure 4.20 Leading edge of CMC Tube #1

Comparison of the previous figure with Figure 4.21 taken from the same section of (upstream) tube #1, but focusing on the OD, shows that temperature alone does not account for the loss of material, even in a highly reducing atmosphere, since there is no loss of material on the outer diameter. The material has been unaffected by the high temperatures, demonstrating that the loss of material requires either erosive (mechanical) or corrosive (chemical) attack from the environment. Further examination will prove that both were happening.

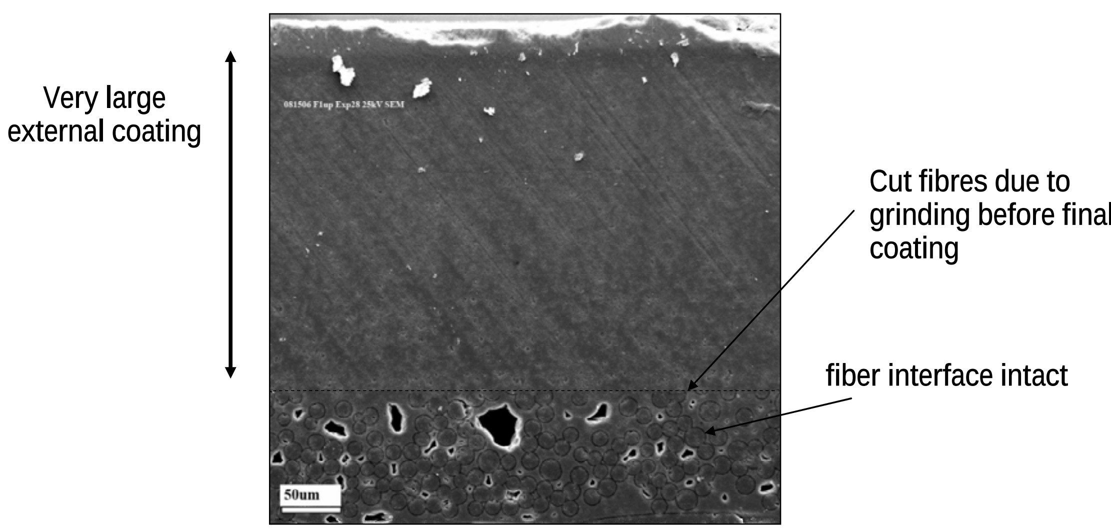


Figure 4.21 Cooled side (OD) of CMC Tube #1

Examining another slide taken downstream and on the ID of tube #1 provides an interesting clue as to how this erosion took place. In Figure 4.22 we can see that the slag has actually replaced the matrix and fiber interface coating in places, indicating that some damage occurs when liquid slag is allowed to attack the regions around fibers, and floats the fibers away as it flows down the surface; however this is not a complete picture.

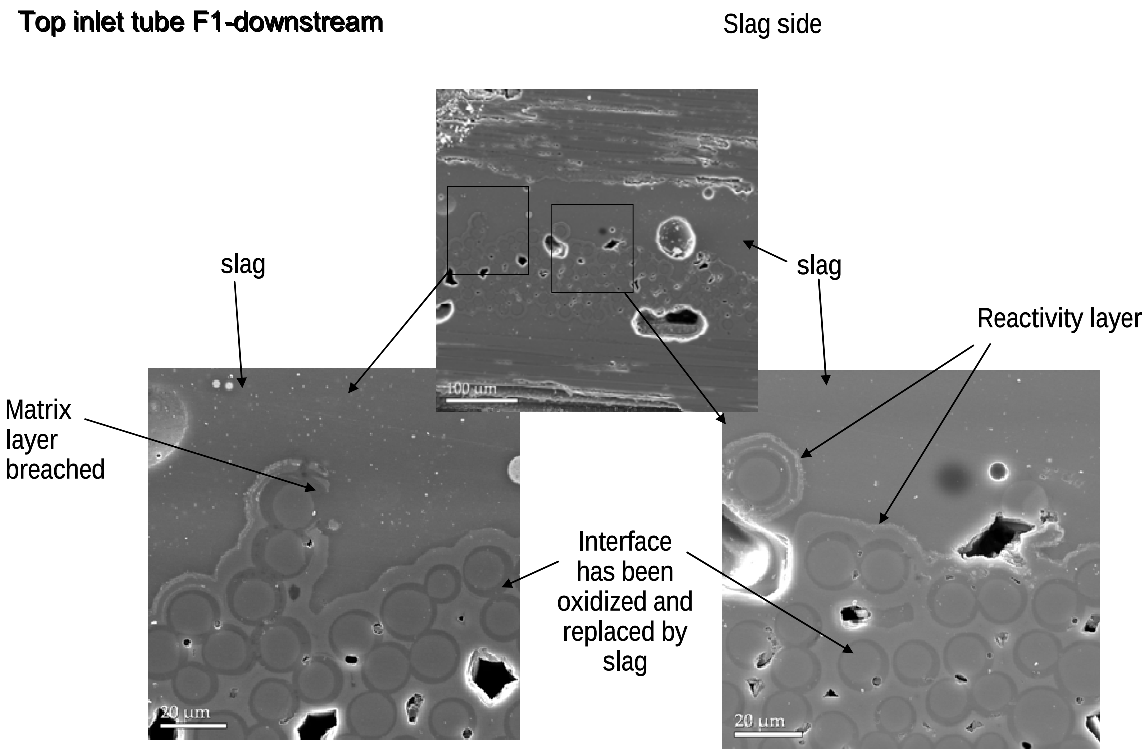


Figure 4.22 Fiber interface damage, CMC Tube #1 hot wall

Figure 4.23 shows an unusual zone, which is not typical, but may illustrate starkly the difference between a porous matrix and a well densified one. The cross section is from the joint between the first and second cylinders, and is the only location discovered in the first two cylinders that does not have any measurable material loss. There are a few special conditions at this location: the CMC liner cylinders are more dense at this than in the middle, the joint is close to the coolest portion of the cooling jacket, and the first cylinder contacts the metal of the cooling jacket, which may provide a more direct conductive path along the fibers from the joint to the metal contact zone.

As previously discussed, the extremely large voids shown in the figure below points to the root cause of the loss of liner material: significant void fraction is obvious in all of the CMC cylinders, which leads to a very low thermal conductivity, raising the internal temperature of the CMC and allowing the slag to erode the surface. The porosity also significantly increases the diffusion rate of oxygen, steam and other corrosive elements.

All of this suggests that properly densified ceramic should have enough conductivity to maintain a thicker layer of more viscous or frozen slag which would protect the surface.

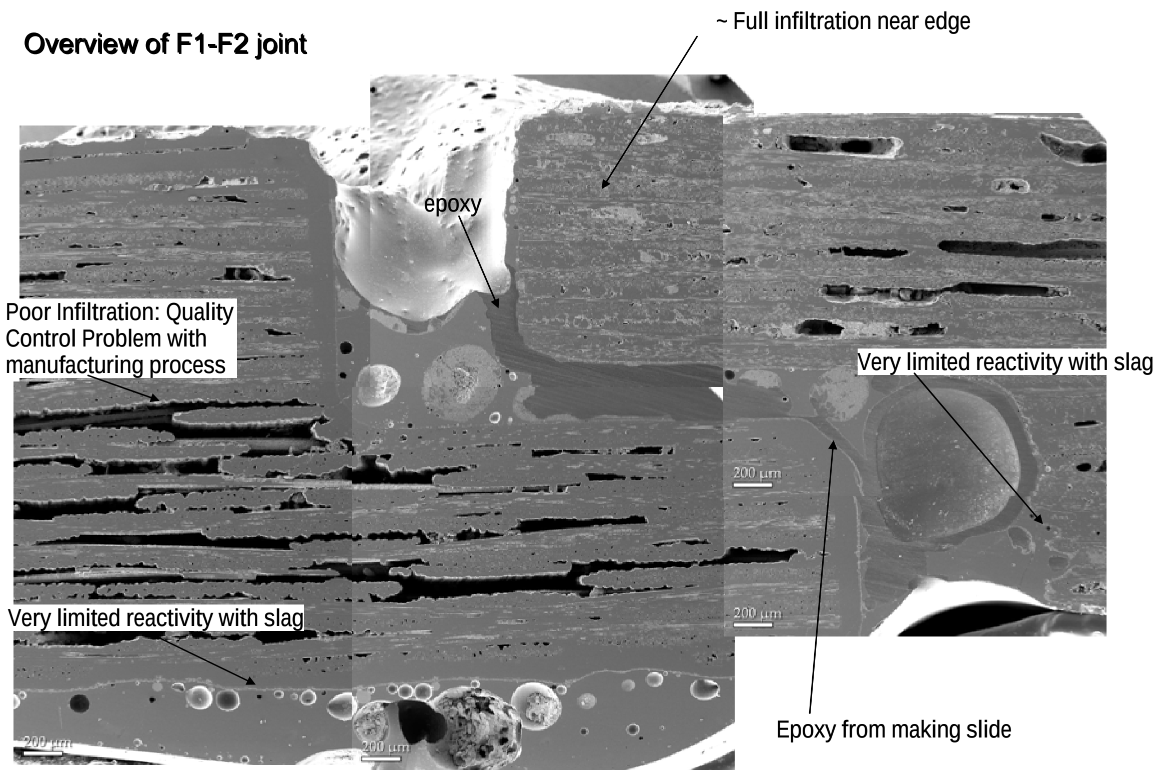


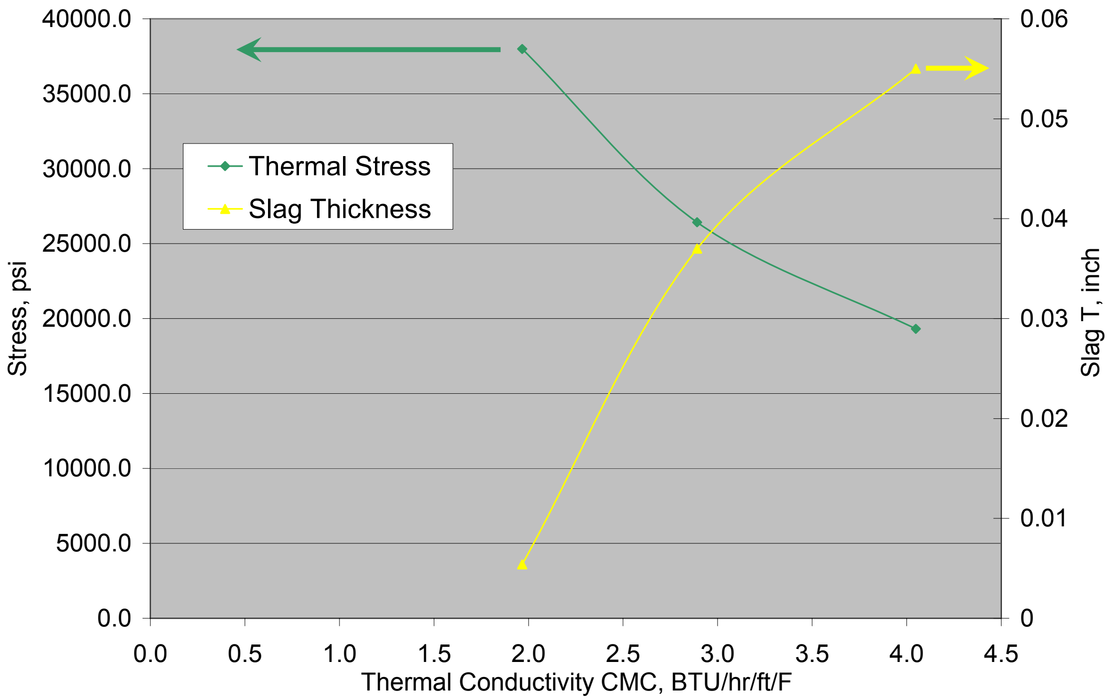
Figure 4.23 Full Thickness CMC, Tube #1&2 interface

4.4.4 CMC Liner Design Evaluation and Recommendations

Some significant issues with porosity in the ceramic liners manufacturing have been brought to light. This is a critical element in proper gasifier liner design, since the strength and thermal conductivity are directly related to material porosity, and losses in thermal conductivity adversely affect thermal gradient, increasing internal stress of a liner whose strength is reduced by the same porosity.

The following graph (Figure 4.24) illustrates these trends. The CMC inner wall temperature increases for lower thermal conductivity values. Therefore, the slag layer will be thinner and less viscous, allowing liquid and gas components of the combustion process access to the ceramic. The increased stress due to the thermal gradient goes up rapidly as well. Halving the conductivity approximately doubles the thermal gradient and the stress. If the conductivity loss is due to porosity, the ultimate failure stress limit of the material will be lower as well.

Figure 4.24 Conductivity Effect on Stress and Slag Protective Layer



To avoid these risks, the ceramic must be made with a reliable process that produces very dense and highly conductive material. In addition, there must be a good thermal conduction path from the ceramic to the coolant. In the previous test, an attempt to “finesse” the thermal conductivity by inserting layers of gas and alumina felt produced a condition that was not as controllable as it might have been, and introduced the possibility of “racetracking” or increased heat transfer and simultaneously increased availability of oxygen to attack the material.

In a material test such as the one described, all attempts to control the test environment must be made, so as not to produce ambiguous results. On the other hand, this test, with its widely varying conditions between warm up, slagging operation, and thermal gradients along the length and through the wall, was a good test of the proposed gasifier liner concept, as it illustrated many of the things that can happen in a real world system requiring complex operating system and many operators.

The most important aspect of the PWR gasifier CMC liner design is constant cooling of the ceramic liner. Any deviations significantly below the design cooling rate can have damaging effects on the liner, thus the system must be controlled with positive limits on the liner temperature.

The tests performed at CANMET underscored some key failure modes that can happen even with these safeguards (and assuming the quality control issues of porosity and conductivity have been managed):

1. Instrumentation that changes during the test can provide false justification to believe the temperature is under control.
2. Test articles which have sustained damage internally (eg: gasification of ceramic components) can become porous and brittle, leading to elevated temperatures and/or lower structural limits for the assembly.

The latter of these two is perhaps less obvious. Damage can happen for any number of reasons, but one important cause is transients from startup/ignition or from turbulent flows that increase local heat transfer to the wall. Other causes of internal damage to the ceramic component could be local chipping from rough handling in installation, repeated thermal cycling, especially if slag has infiltrated into joints between dissimilar materials, inducing high stress on cool down.

In summary, the evidence strongly indicates that, given proper thermal protection (active cooling), the silicon carbide ceramic can survive unchanged. However, oxygen diffusion barriers will be required. Since there were also zones where the CMC was damaged, specific issues to the design have been discovered which make it susceptible to damage. These issues that must be managed for future bench-scale test and demonstration programs to provide a robust design include:

- Low conductivity ceramic (specifically: porosity in fabrication)
- Excess oxygen for extended periods in the pristine condition (prior to initial slag deposition)
- Insufficient cooling
- Unknown temperatures from corroding thermocouples (leading to insufficient cooling)
- Low melt temperature slag (design operation temperature must have margin below the softening temperature of the coal being gasified)
- Pressure and flow fluctuations which can increase the hot flame zone
- Low carbon conversion, which can aggravate the previous effect
- “Racetrack” leaks behind the hot wall (leading to insufficient cooling and active erosion)

4.5 Metal Coupon Samples

Eight potential gasifier liner alloys were placed near the outer diameter of the cylindrical silicon carbide liner as shown in section 3 above. The exact locations are shown in Figure 3.4, and it can be seen that there was ¼" of alumina felt insulation between the CMC and the metal samples. The final application of ceramic cement completely covered the top of the insulation and coupons. The configuration was such that no slag would come in contact with these metal coupons during the test. The coupons were exposed to 26 hot tests in the CANMET gasifier, including approximately 103 hours of slagging operation and 450 hours of natural gas warm up time. Figure 4.4 above shows the typical temperature of the samples (TE-423C, TE-428 and TE-429) which ranged from 550°C to 750°C at the end of each test day.

Post-test examination of these coupons was by visual observation, optical microscopy and SEM/EDS imaging and analysis. None of the exposed alloys had a large amount of corrosion or pitting. A thin protective chromium oxide enhanced layer was formed that inhibited oxidation and sulfidation of the underlying alloys. The protective oxide layer could fail in isolated locations allowing for sulfidation and formation of a chromium depleted external scale. Although corrosion rates could not be estimated, recommendations were made that may help in making judgments in alloy selection. Based on SEM observations in isolated areas of the specimens, Hastelloy C22 and Alloy 20 may receive a lower level of confidence due to grain boundary attack and lack of an enhanced chromium oxide protective layer respectively.

Table 4.4 below shows the list of samples, location and identifying marks, as well as pre and post test mass. There was no appreciable material loss.

Table 4.4 Metal Corrosion Samples

Sample Number	1/2x3/4xthickness other description:	Alloy	Thickness inch	Before Mass grams	Location	Post Test Ma grams	loss grams
1	no cuts	Alloy 20	0.26	11.2	Between 424C and 422A	11.2	0
2	3 corners cut	RA-333	0.27	12.7	clockwise in numerical order	12.7	0
3	2 corners	RA-600	0.265	12.6	clockwise in numerical order	12.6	0
4	4 corners	G-3	0.247	11.5	clockwise in numerical order	11.5	0
5	1 corner	C-2000	0.127	5.9	clockwise in numerical order	5.9	0
6	2 corners adjacent	G-35	0.135	6.3	clockwise in numerical order	6.3	0
7	2 corners opposite	C-22	0.134	6.4	clockwise in numerical order	6.4	0
8	3 corners cut	C-276	0.132	6.3	clockwise in numerical order	6.3	0

No pitting was seen in any specimens. The specimens did not exhibit any significant change in grain size during high temperature exposure. For most of the materials, some areas of the coupon surface had some adhering scale. This scale was not widespread, but present in only a few areas. Corrosion and surface irregularities were seen for all specimens in isolated areas and not over the entire surface of the specimens.

None of the alloys exposed to gasifier conditions for 103 hours at 500°C to 700°C (932°F to 1292°F) had a large amount of corrosion or pitting. A thin protective chromium oxide enhanced layer was formed that inhibited oxidation and sulfidation of the underlying alloys. The thickness of this layer was variable from alloy to alloy and for a single alloy from one area of the surface to another. For all alloys tested, the protective oxide layer could fail in isolated locations allowing for sulfidation and formation of a chromium depleted external scale. This external scale could have been removed during the testing, during cooling while the gasifier was off line, during cooling at the end of the test or after completion of the test when the coupons were removed and the adjacent ceramic cement was chipped away. For this reason, examination of SEM images alone could not be reliably used to measure penetration and corrosion rates.

Longer scale exposure tests of thousands of hours are often used to make comparisons between alloys in the gasification and energy production industries. With the relatively short exposure time of 103 hours and irretrievable scale removal, measurement of a corrosion rate was not possible.

5.0 CONCLUSION

The test program consisted of 103 hours of slagging gasifier operation, exposing the CMC liner sections to a highly reducing slag environment to evaluate material survivability in specific gasifier regions. The test program met the objectives to obtain information enabling predictions of useful life in an advanced gasifier, to identify infant mortality design issues, cooling schemes and limits of operation in the reducing environment, and to demonstrate that CMC liners can be protected from this slagging gasifier environment with a combination of active cooling and thermal and chemical barriers.

The tests have shown that the dense (low porosity) CMC liners will provide the best protection, and the results indicate that adequate cooling (maintaining the surface temperature below the slag softening temperature) will enable the CMC liner to survive intact for an extensive duration. There were several areas where the original CMC liner surface was completely intact at the end of the test program. The indication is that, in zones where the cooling was able to maintain the CMC liner within the planned temperature range, a solid layer of slag was formed on the CMC liner inner surface and protected the liner from erosion and corrosion. The test results indicate that silicon carbide material can survive a slag environment (perhaps even a viscous, partially melted slag environment) without chemical attack. However, the presence of porosity can result in high internal stresses that will cause spalling and material erosion. In a woven composite, interlaminar strength is lower than the in-plane strength, and a high temperature gradient will cause surface layers to peel apart, and the interface material which provides toughness can be damaged. The fact that material can be lost under these conditions provides clear direction for a design solution and criteria for acceptance in fabrication that will be utilized in subsequent PWR gasifier programs.

The quality control issue for liner design is a primary finding of the test program. Wide variation in ceramic porosity was found from sample to sample and in various locations in the liners. Reasonable process control will be critical to fabricating a successful gasifier liner.

Additional CMC bench-scale testing at DOE Oak Ridge National Laboratory and DOE-NETL Albany on a wider range of CMC formulations is currently underway and will guide the design of a suitable ceramic for this application. PWR developed the test plan with technical assistance from ceramic scientists at DOE-ORNL and DOE-NETC Albany who will be performing the environmental exposure tests. The test program will evaluate seven of the best commercially available ceramic matrix composite (CMC) material systems in a steam/oxygen environment at temperature ranges likely to be encountered based on PWR pilot plant and commercial gasifier design trade studies at ORNL. Four 500-hour steam/oxygen tests will be conducted at partial pressures and temperatures similar to those predicted near the flame front of a PWR advanced gasifier injector. Subsequent destructive stress testing and SEM analysis to evaluate surface degradation and crystal structures will also be performed. Tests will also be conducted to evaluate these same materials in slag adhesion tests at NETC-Albany with subsequent destructive SEM analysis to evaluate surface degradation and crystal structures. Results of this additional bench-scale CMC test activity will be documented in a Topical Report later in 2007 under subtask 3.5 Bench-Scale Refractory Test.

Tests of liners near the injector end of a gasifier will also show the sensitivity of the liner and slag layer to turbulent flow, but these tests have shown it is likely that eddy currents will require the liner to be overcooled near the head end of a gasifier in order to avoid hot spots where erosion can take place.

The metal jacket appeared unchanged from the original pre-test condition and no evidence of corrosion was observed.

The test program provided a significant amount of information in the areas of thermal control, CMC materials and processing for improved capability in a gasifier environment, and CMC liner fabrication that will be used extensively for upcoming advanced gasifier projects.

LIST OF FIGURES

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ACRONYMS AND ABBREVIATIONS

A Amperes
AGSD Advanced Gasification Systems Development
ANSI American National Standards Institute
ASME American Society of Mechanical Engineers

B&PV Boiler and Pressure Vessel Code controlled by ASME
BTU British Thermal Unit

°C degrees Centigrade/Celsius
CANMET Canada Materials and Energy Technologies branch of NRCan
CETC-O CANMET Energy Technology Centre - Ottawa
CMC Ceramic Matrix Composite
CS Carbonaceous Solids
CVD Chemical Vapor Deposition

DDACS Digital Data Acquisition and Control System
DI de-ionized
DOE Department of Energy

°F degrees Fahrenheit
FS Factors of Safety
ft feet

g grams
G gravitational force constant multiple
GN_2 Gaseous Nitrogen
GND Ground

HEX Heat Exchanger
HIP High Interface Pressure braze
Hz Hertz

KPa kiloPascal

lbf Pounds Force
lbm Pounds Mass

MHz Megahertz
MPa Mega Pascal
ms milliseconds

N Newton
NIST National Institute of Standards and Technology (Gaithersburg, MD)

NPT National Pipe Thread standard

NRCan Natural Resources, Canada
P/N Part Number
PIP Polymer Infiltration and Pyrolysis
psia Pounds per Square Inch Absolute
psid Pounds per Square Inch Difference
psig Pounds per Square Inch Gage

PWR Pratt & Whitney Rocketdyne

SCH Schedule: piping standard
scfm Standard Cubic Foot per Minute
scm Standard Cubic Meters

TC Thermocouple