CMC Bench Scale Material Test Plan

TOPICAL REPORT

Reporting Period
Start Date: February 1, 2006
End Date: May 30, 2006

Principal Authors
Mark Fitzsimmons Task Development Lead
Gerard Pelletier Ceramic Materials Scientist
Dave Grimmett Materials Corrosion Scientist

June 21, 2006

DOE Award Number
DE-FC26-04NT42237
Task 3.4 Bench-Scale Refractory Test Plan

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

DISCLAIMER

ABSTRACT

The test plan detailed in this topical report supports Task 3.5 of the project titled "Development of Technologies and Capabilities for Coal Energy Resources – Advanced Gasification Systems Development (AGSD)". The purpose of these tests is to verify that materials planned for use in an advanced gasifier pilot plant will withstand the environments in a commercial gasifier. Pratt & Whitney Rocketdyne (PWR) has developed this test plan with technical assistance from ceramic scientists at the Dept. of Energy Oak Ridge National Laboratory and Albany Research Center who will perform the environmental exposure tests.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

This test plan document describes the technical work to be performed at the Department of Energy (DOE) research laboratories at Oak Ridge National Laboratory (ORNL) in Oak Ridge, TN and the National Energy Technology Laboratory (NETC) materials research facility in Albany, OR. The work will be conducted in support of Pratt & Whitney Rocketdyne's Advanced Gasification Systems Development cooperative agreement DE-FC26-04NT42237 with the DOE.

The purpose of these tests is to verify that materials planned for use in an advanced gasifier pilot plant will withstand the environments in a commercial gasifier. Pratt & Whitney Rocketdyne (PWR) has developed this test plan with technical assistance from ceramic scientists at DOE-ORNL and DOE-NETC Albany who will perform 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.

This test plan document defines the objectives, scope, and success criteria for the test program. The plan also details the test hardware, the test requirements, and the post-test evaluation and analysis.

EXPERIMENTAL METHODS (TEST PLAN)

1.0 INTRODUCTION

This test plan supports Task 3 of the project titled “Development of Technologies and Capabilities for Coal Energy Resources – Advanced Gasification Systems Development (AGSD)”. The purpose of these tests is to verify that materials planned for use in an advanced gasifier pilot plant will withstand the environments in a commercial gasifier.

Materials intended for the gasifier liner have been tested in static slag adhesion and corrosion oven tests at the US DOE Albany Research Center, and have been subjected to the kinetic atmosphere of a gasifier reactor in tests at CANMET Energy Technology Centre—Ottawa, (CETC-O), however the design of the CETC-O Gasifier does not completely mimic the hottest portion of the environment near the advanced injector being proposed by Rocketdyne, specifically the higher temperatures and oxidizing environment that will exist in the region immediately downstream of the injector. The existing tests adequately reproduce environments for the bulk of the gasifier, but not the first quarter meter (10 inches) downstream of the injector face.

Although the existing conceptual design has these higher temperatures, some more difficult to fabricate designs may reduce the wall temperature, making the environment benign.

The environment in this test will bridge the gap between tests which have been performed for the downstream slagging environment and the hotter oxidizing region near the injector.

The tests planned will identify infant mortality issues, take measurements to assess approximate life in the worst case oxidizing environment and identify the best materials out of several candidates already downselected as being the most appropriate. (see section 5.1 for a description of the materials and their selection criteria)

Most importantly, the tests will identify the temperatures at which these various materials begin to have life reductions, providing firmer design goals for heat management through the wall of the gasifier.

2.0 OBJECTIVES

Test objectives are as follows:

- 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.
- Evaluate these same materials in slag adhesion tests similar to those performed in CY2005, but at higher temperatures in accordance with the steam/oxygen environment above.

3.0 SCOPE

There are several tests covered by this test plan, divided roughly into two major subcategories and to be performed at different locations:

- Slag adhesion/corrosion tests at ARC with subsequent destructive SEM analysis to evaluate surface degradation and crystal structures. The slag adhesion tests are to be similar to tests already performed in this facility for Rocketdyne in 2005.

- Steam/Oxygen tests to be performed at ORNL with subsequent destructive stress testing and SEM analysis to evaluate surface degradation and crystal structures.

Four 500-hour duration Steam/Oxygen tests will be performed on a number of samples in a 5% oxygen, 95% steam atmosphere at partial pressures similar to those predicted near the flame front of a PWR advanced gasifier injector. Although the actual environment will not likely be as bad (due to the presence of instrumentation purges on the OD of the CMC in an operational gasifier) this will represent a conservative design approach.

The initial test is planned to be conducted at 900ºC. The temperatures for the three subsequent tests will be determined based on the outcome of the initial test and on further thermal analysis.

It is the intention of PWR to identify the best candidates for exposure to similar environments for long durations. To this end we would like to start with the most severe environment and if samples show little or no damage, this will inform later tests, indicating higher temperatures are acceptable and suggesting that later tests can remain hotter (eg: 900, 1000, 950, 850ºC). If damage is severe at 900ºC, this will indicate later tests must cover a lower temperature range to define approximate limits of the materials (eg: 900, 800, 700, 750ºC).

Section 7 provides more detail on the decision logic for these tests.

4.0 TEST SUCCESS CRITERIA

Overall success of the tests will be established by the following criteria:

- Measurements of: exposure temperature, exposure species concentrations, material weight loss, and material strength loss.
- Determine which of the seven materials is most likely to survive a slagging gasifier environment.
- Quantify degradation in the specified environments at various temperatures.
- Provide design guidance to the Pilot Plant design effort to do one or more of the following:
  1. Specify the one best material system for the pilot plant and commercial plant conceptual designs.
  2. Narrow the scope of materials down to the best two or three for the different environments in the gasifier to be tested in the Pilot Plant.

5.0 TEST HARDWARE

5.1 Material Downselection

PWR has reviewed the state of the art in ceramic matrix composites and discussed the application with a variety of the best CMC producers in the United States. The material properties of the materials that are known to be compatible with the various environments in a gasifier were then used to predict thermal and structural performance, leading to potential design solutions. From the list of basic material properties, a number of candidates could immediately be eliminated:

Low thermal conductivity ceramics are not strong enough to withstand the bare minimum thermal stresses in a gasifier, let alone provide margin for possible “hot spots” (usually this translates to ensuring high density composites and/or using high thermal conductivity parent materials).

Figure 5.1 is a list of materials considered for the gasifier liner.

Fiber	**Matrix**	**Process**	**Coating**	Conductivity	Slag Adherence	Resist H2O/O2	Resist Alkali Metals	Thermal Expansion like slag	Resist Spalling	Tensile strength
Ceramic	Ceramic	Process-1	No	**+**	**+**	**o?**	**+?**	**+**	**+**	**+**
Ceramic	Ceramic	Process-2	No	**+**	**+**	**–?**	**+?**	**+**	**+**	**+**
Ceramic	Ceramic-Oxide	Process-2	No	**+**	**+**	**o?**	**o+?**	**+**	**+**	**+**
Ceramic	Ceramic	Process-2	Yes	**+**	**+**	**+**	**+?**	**+**	**+**	**+**
Ceramic	Ceramic	Process-3	No	**+**	**+**	**o+?**	**o+?**	**+**	**+**	**+**
Ceramic	Ceramic	Process-3	No	**+**	**+**	**+?**	**o+?**	**+**	**+**	**+**
Oxide	Ceramic	Process-1	No	**o**	**+?**	**o?**	**o–**	**+**	**+**	**o**
Oxide	Oxide	Process-4	No	**o–**	**+?**	**+?**	**–**	**+**	**+**	**o**

+ = enhanced

0 = can be designed to accommodate

– = less than required

Table 5.1 Test Coupon Material Candidates

In general, silicon carbide ceramics appear to have the best overall performance, and for the majority of the gasifier they are ideal, however some oxidizing environment tests with non-oxide ceramics has shown they can be degraded in the presence of steam and oxygen, albeit at much higher temperatures and velocities, so the actual environment must be tested. Similarly the alumina (oxide-material reinforced) ceramics have superior oxidizing atmosphere properties, however their resistance to the slag has not been tested in the temperature range of interest, so they must be tested as well.

The specific materials chosen represent a cross section of fabricators and matrix infiltration methods, and in one case a state of the art environmental barrier coating proven to retard oxygen and steam from degrading the ceramic material.

The rationale for the overall list is as follows: detailed analysis of the environment and duty cycle of the proposed gasifier indicates that non-oxide ceramic systems have the best chance of long term durability in all the environments in the gasifier, but the range of ceramic crystal structures possible and the variety of manufacturers and coatings available forces the conclusion that there may be large variation in the performance of different ceramic fiber/ceramic matrix products. Even though the ceramic material may have problems with steam and oxygen, the existing data are at considerably higher temperatures and greater porosity.

Nevertheless, the possibility that steam may pose a problem for the non-oxide ceramic systems also forces the conclusion that oxide materials must be tested even though it may cause a significant design change to accommodate the low thermal conductivity and lower strength.

Finally, analysis of the oxide materials based on published properties shows that its low conductivity forces the overall gasifier design to be altered rather drastically. Thus, an oxide fiber/ceramic matrix option is listed as a material that will likely provide the desired thermal conductivity and allow a similar design if this material is selected.

5.2 Albany Research Center Test Coupons

Samples are approximately 38-76mm (1.5-3 inches) rectangular or square, but can be any size. At least two of each material will be required for these tests in order to support the testing, in case more than one temperature is desired so the results can be differentiated.

Figure 5.1 CMC Test Samples being exposed at ARC

5.3 ORNL Steam and Oxygen Furnace Exposure Test Bars

The samples to be tested at ORNL will consist of three types: Tensile Bars, Bend Bars and existing cylinders taken from the CANMET test rig (coated with slag).

The bend bars will be used for primary evaluation of the degradation from chemical exposure, including mass loss and material regression. Tensile bars will consist of only three of the major material combinations in order to extrapolate the exposed bend bar data into high temperature zones and to provide similar firm data on the change (if any) of materials properties due to exposure. Tensile bar mass will be tracked as well, but their complex shape makes the life estimate less precise.

Bend bars will be rectangular, approximately 3.2x9.7mm (.125x.38 inches) cross section and varying in length from 63-94mm (2.5-3.7 inch). The length will be used to positively identify each different material, as many of them will resemble each other. Thus, even if other identification methods fail, there will be non-intrusive ways of identifying materials without damaging or altering them.

Tensile bars will similarly have different lengths. The lengths of tensile bars and bend bars are shown in Table 5.2. A typical bend bar (drawing supplied by ORNL for use in their laboratory) is shown in Figure 5.2.

Material				BB length		Tensile Length	
Fiber	**Matrix**	**Process**	**Coating**	inch	mm	inch	mm
Ceramic	Ceramic	Process-3	No	2.5	63.5		
Ceramic	Ceramic	Process-2	Yes	2.7	68.58		
Ceramic	Ceramic-Oxide	Process-2	No	2.9	73.66		
Oxide	Ceramic	Process-1	No	3.1	78.74	4	101.6
Ceramic	Ceramic	Process-1	No	3.3	83.82	4.2	106.68
Ceramic	Ceramic	Process-2	No	3.5	88.9		
Oxide	Oxide	Process-4	No	3.7	93.98	4.4	111.76

Table 5.2 CMC Bar Lengths for simplifying ORNL Lab Tracking

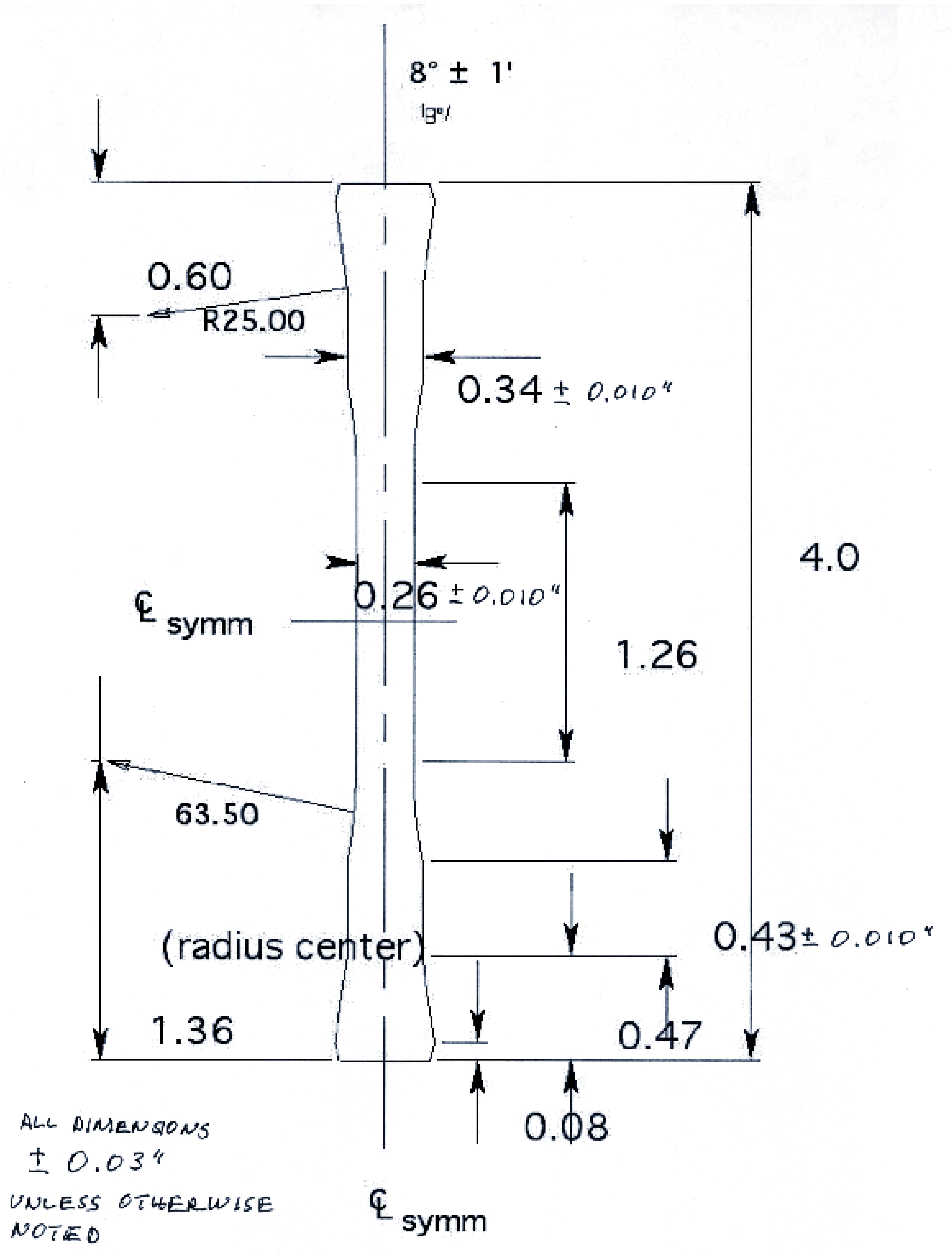

Figure 5.2 Tensile Bar Design from ORNL Lab

6.0 ARC Test Requirements

6.1 General

The tests performed in 2005 on ceramic fiber/ceramic matrix CMC coupons consisted of melting slag onto a flat panel, exposing the coupons to 815ºC (1500ºF) in argon for one week, one month and three month durations. This exposure was followed by sectioning and SEM analysis of the samples, revealing that there was no corrosive activity on the coupons (beyond the initial melt and surface adhesion) over these periods.

Subsequent analysis of the pilot plant and commercial gasifiers indicate that near the injector there may be locations where higher temperatures dictate more difficult to fabricate designs and/or require more heat loss to the cooling circuit. Thus, tests to be performed in these bench scale evaluations will begin with 900ºC (1650ºF) exposures for one month.

If samples do not show additional losses compared to the 2005 samples, the furnace temperature will be increased to 1000ºC (1830ºF) for an additional month of exposure.

If material loss is unacceptable (i.e. showing advancement over the initial application corrosion depth) the furnace temperature will be reduced to 850ºC (1560ºF) and new samples will be tested for one month.

6.2 Exposure Method

Test coupons will first be exposed to slag at 1450ºC: 3+2 min. with scraping followed by 1250ºC: 2 min. twice in order to get the slag adhered into a hard layer on the CMC.

6.3 Post Test Analysis

Test coupons will be cross-sectioned and analyzed at the initial exposure and after one month and two month exposures. SEM analysis will include composite morphology and chemical analysis of the slag/CMC interaction zone.

7.0 ORNL Test Requirements

The major objective of this test is to determine the approximate temperature below which at least one of the candidates will be unaffected by the atmosphere in question.

7.1 General

Make 7 different materials into similar bend and tensile bars. (all materials made into bend bars, three materials of major material subcategories will be tensile bars for detailed evaluation to compare room temp and high temp properties. See Section 5.3)

Submit bend and tensile bars to 500 hour exposure of 95% steam + 5% oxygen environment at various temperatures. The make-up gas of steam and oxygen must be sufficient to overwhelm the anticipated vaporization rate of the samples (use ceramic material loss rate at 1200ºC as the conservative estimate).

ORNL will track part weight loss (to the nearest 0.1 mg) and identity through exposures.

ORNL will perform bend tests at RT and Tensile tests at RT and 900ºC.

ORNL will perform SEM work to evaluate material loss nature, corrosion and grain changes of the different materials.

7.2 Test Exposure Matrix and Logic

Four 500-hour tests will be conducted. Enough bend bar samples have been made to expose one set (of 3) to each of four different temperatures and one set (of 3) to all four 500-hour exposures. Although one 500 hour test at a specific temperature is good, subsequent measurements at longer durations is more useful for extrapolation for very long exposures.

The first set of samples will be exposed to 900ºC, as this represents a reasonably cost effective design point to accommodate in the thermal management scheme, and appears to be close to (just under) the high temperature limit of long life for ceramic material in this atmosphere. If all (or a majority) of the samples are fine after 500 hours, a subsequent test will be performed at 1000ºC, and the remaining two tests will be done at 950, 900 or 1000ºC (the highest temperature at which the results were benign).

If a majority are damaged at 1000ºC, subsequent tests will be done at 950ºC, and so on, until the temperature where negligible material loss and strength reduction is identified for a majority of the samples.

This logic is shown graphically in Figure 7.1, illustrating that the intent is to maximize test time at the highest temperature that is “benign” to the samples.

(Note: 1000ºC is the practical limit for the ORNL furnace in this atmosphere)

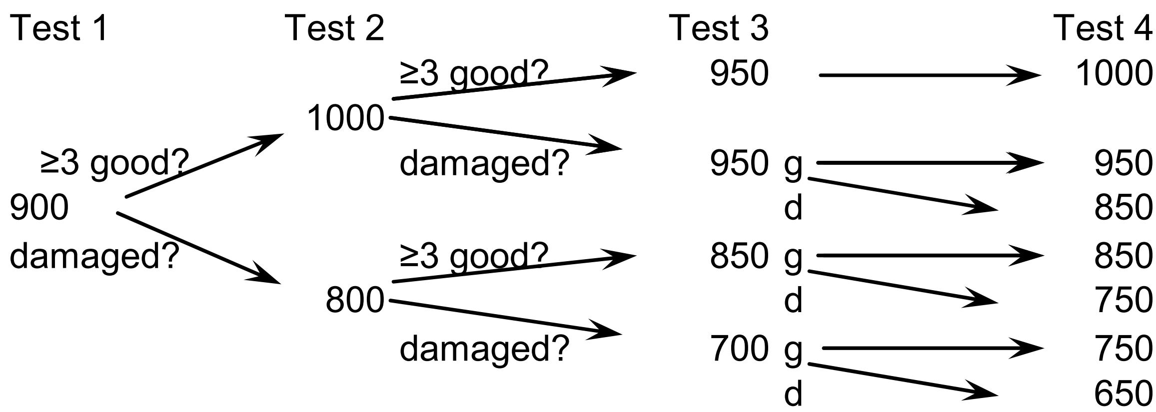

Figure 7.1 ORNL Exposure Logic

"Good" in the figure and "benign" are defined as material loss rate that is acceptable to support a 3-10 year life (see section 7.5 for an example). Since there are many sample materials and only one furnace, the question remains how many of the samples must be considered "good" in order to increase (or maintain) the temperature of the next test? If we say 1 of 7, this would mean one sample at least is acceptable, but if it is the most expensive, or relies on technology that has only one supply stream (no viable competitor), this is poor planning for future commercial use. If we say 3 of 7 good are necessary, this ensures there are at least three materials left in the mix which are holding their own and the planned experiment should ensure data which covers a number of viable alternatives and defines a temperature limit for half (or more) of the samples.

Figure 7.2 on the following page illustrates when samples will be inserted and removed from the furnace.

7.3 Instrumentation

Pressure transducers, thermocouples, mass flow meters. The make up gas flow rate must be adequate to ensure an oxygen flow rate of approximately 3-60 ml/min @ STP and a water flow rate of 13-260 ml/hour water, a blend of 5% oxygen and 95% steam at the temperature and pressure desired (300 psia). This will ensure the diluent gas will be 1,000 to 50,000 times the volume of silicon which may outgas from the samples, but will not be high enough to make a high-velocity flow stream past the samples.

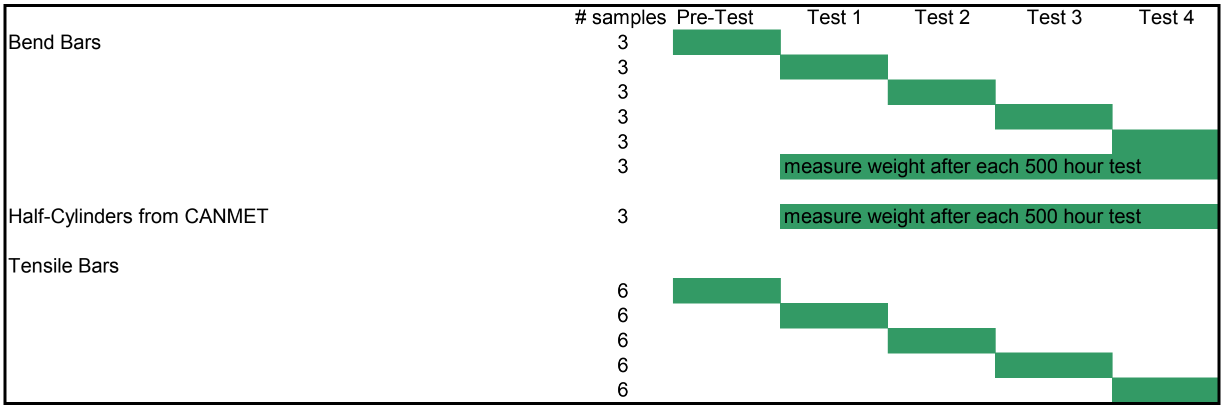

Figure 7.2 Sample Insert/Removal Schedule

7.4 Post Test Evaluations

7.4.1 Bend Bars

Three bars of each material (Table 5.2) and steam exposure will be subjected to destructive 4 point bend tests. Weight to the nearest 0.1 mg will be tracked before and after each exposure. Entire flexural stress (in mega Pascals or pounds) versus deflection (in mm or inches) curve. The flexural stress will be calculated per C1431 using elastic beam theory and it is a function of the specimen dimensions and the magnitude of the support and loading spans. Three bars of each material will also be tested without any exposure.

7.4.2 Tensile Bars

Weight to the nearest 0.1 mg will be measured before and after exposure. For each of the three tensile bar materials listed in table 5.2 and steam exposure, there will be three samples tested at room temperature and three tested at 900ºC. Entire stress-strain curve to be taken. Stress in (mega Pascals or psi) and strain (in %). Proportional stress limit (in MPa) per ASTM C1275. Ultimate tensile strength (in MPa) and tensile strain (in %).

7.4.3 SEM Analysis

SEM examination to determine change in surface chemistry, grain size, etc.

7.4.4 Cylinders

Cylinders will be cut into bend bars (5-10 are possible from each cylinder) and tested as in 7.4.1. Cylinder bend bars must be tested in such a way that the slag surface is in compression and the OD (clean surface) is in tension. Material will also be mounted and examined as in 7.4.3.

7.5 Life Calculations

This example calculates the material loss from a CMC bend bar after exposure based on total mass of the sample. CMC samples will be of various lengths (Length) to identify each material, but all will have the same cross section (Wd,Ht)

$Wd := .125 \cdot in$ $\qquad$ $Ht := .375 \cdot in$

$i := 0..6$

$Length_0 := 2.5 \cdot in$

$Length_i := Length_0 + i \cdot .2 \cdot in$ $\qquad$ $Length = \begin{pmatrix} 2.5 \\ 2.7 \\ 2.9 \\ 3.1 \\ 3.3 \\ 3.5 \\ 3.7 \end{pmatrix} in$

Initial Volume V1 = Length * Wd * Ht

$$V1 = \begin{pmatrix} 1.92 \\ 2.074 \\ 2.228 \\ 2.381 \\ 2.535 \\ 2.689 \\ 2.842 \end{pmatrix} mL$$

Mass of each sample is an input variable: Mbefore and Mafter. (For this example we will generate masses assuming ρ is the theoretical density of the ceramic, but for the actual calculation, ρ will be calculated as follows for every sample, as each sample may differ in density.)

$$Mbefore := \begin{pmatrix} 6.145 \\ 6.637 \\ 7.128 \\ 7.62 \\ 8.112 \\ 8.603 \\ 9.095 \end{pmatrix} \cdot gm$$

$$\rho_i := \frac{Mbefore_i}{Length_i \cdot Wd \cdot Ht}$$

=Mbefore/V1

$\rho_i =$

3.2	$\frac{gm}{cm^3}$
3.2	
3.2	
3.2	
3.2	
3.2	
3.2	

After measuring weight Post-Test, the density before testing will be used to calculate the new volume. Mass measurements will be taken to the nearest milligram, which is more than sufficient to show life of 3 years or more, as the example will show.

$$Mafter := \begin{pmatrix} 6 \\ 6.5 \\ 6.9 \\ 6.7 \\ 7.3 \\ 8.6 \\ 9 \end{pmatrix} \cdot gm$$

These numbers are made up for the example.

$$V2_i := \frac{Mafter_i}{\rho_i}$$ Resulting in: $$V2 = \begin{pmatrix} 1.875 \\ 2.031 \\ 2.156 \\ 2.094 \\ 2.281 \\ 2.688 \\ 2.812 \end{pmatrix} mI$$

Assuming the material loss from all surfaces is equal and approximately linear with time (supported by previous ceramic steam exposures), we can calculate a thickness of loss, t, for each sample.

$$V2 = \left(Length_i - t_i\right)\cdot\left(Wd - t_i\right)\cdot\left(Ht - t_i\right)$$

Which can be rewritten as follows to find the root of the equation f(t,i):

$$f(t,i) := V2_i - \left(Length_i - t\right)\cdot(Wd - t)\cdot(Ht - t)$$

$t := 0\cdot in$ (Initial guess for solving)

root (f (t , i) , t)	root (f (t , i) ,
$2.14382\cdot10^{-3}$	$5.44529\cdot10^{-3}$
$1.87907\cdot10^{-3}$	$4.77283\cdot10^{-3}$
$2.92599\cdot10^{-3}$	$7.43201\cdot10^{-3}$
0.01127	0.02863
$9.31899\cdot10^{-3}$	0.02367
$3.48648\cdot10^{-5}$	$8.85565\cdot10^{-5}$
$9.57263\cdot10^{-4}$	$2.43145\cdot10^{-3}$

Now assuming since the material loss will only be from the OD of the commercial liner (slag is deposited and frozen on the ID) and the acceptable loss of material is half the thickness of the liner (test samples exposed to all four 500 hour tests and material loss from the cylindrical slag covered samples will confirm or refute these assumptions and the calculation will be altered as required). The mass delta is shown to demonstrate that measuring to the nearest milligram is sufficient.

$$Life(t) := \frac{0.125\,in}{t}\cdot 500\,hr$$

Life(root (f(t,i),t))

3.326	yr
3.794	
2.437	
0.633	
0.765	
204.504	
7.448	

Loss:

$$Delta = \begin{pmatrix} 145 \\ 137 \\ 228 \\ 920 \\ 812 \\ 3 \\ 95 \end{pmatrix} mg$$

CONCLUSION

This test plan represents a risk mitigation activity which will provide guidance in designing gasifier liners resistant to the various chemical attack environments in the advanced compact PWR gasifier. The results of the testing will be reported in the second quarter of 2007 at the conclusion of the test program. This test plan represents only the test methodology and logic for chemical bench tests on CMC liners with alternate materials and material processing methods. This test approach represents a low cost low risk method of determining the readiness of this technology, as it includes only materials readily scaleable to a larger size gasifier, materials which are known to be chemically resistant to the environments, and the test conditions are reproducing as closely as possible the actual conditions in a larger gasifier.

LIST OF FIGURES

LIST OF TABLES

ACRONYMS AND ABBREVIATIONS

AGSD	Advanced Gasification Systems Development
ANSI	American National Standards Institute
ARC	Albany Research Center
ASME	American Society of Mechanical Engineers
°C	degrees Centigrade/Celsius
C/O	Checkout
CMC	Ceramic Matrix Composite
DOE	Department of Energy
°F	degrees Fahrenheit
FS	Factors of Safety
ft	feet
g	grams
I.D.	internal diameter
IPT	Integrated Product Team
KPa	kiloPascal
lbf	Pounds Force
lbm	Pounds Mass
MI	Melt Infiltration
MPa	Mega Pascal
N	Newton
NIST	National Institute of Standards and Technology (Gaithersburg, MD)
NPT	National Pipe Thread standard
OD	Outer Diameter
ORNL	Oak Ridge National Laboratory
P/N	Part Number
psia	Pounds per Square Inch Absolute
PWR	Pratt & Whitney Rocketdyne
SCH	Schedule: piping standard
scfm	Standard Cubic Foot per Minute

sci Standard Cubic Inch
scm Standard Cubic Meters
SEM Scanning Electron Microscope/Microscopy

TC Thermocouple