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Dynamic Testing of Gasifier Refractory

Annual Progress Report for the Period September 28, 2003 to September 27, 2004

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December, 2004

U.S. Department of Energy Grant No.: DE-FG26-01-NT41279

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ABSTRACT

The University of North Dakota (UND) Chemical Engineering Department in conjunction with the UND Energy & Environmental Research Center (EERC) have initiated a program to thoroughly examine the combined chemical (reaction and phase change) and physical (erosion) effects experienced by a variety of refractory materials during both normal operation and thermal cycling under slagging coal gasification conditions. The goal of this work is to devise a mechanism of refractory loss under these conditions.

The controlled-atmospheric dynamic corrodent application furnace (CADCAF) is being utilized to simulate refractory/slag interactions under dynamic conditions that more realistically simulate the environment in a slagging coal gasifier than any of the static tests used previously by refractory manufacturers and researchers. Shakedown testing of the CADCAF has been comleted. Samples of slag and refractory from the Tampa Electric Polk Power Station have been obtained for testing in the CADCAF. The slag has been dried and sieved to the size needed for our flowing slag corrosion tests. Screening tests are in currently in progress. Detailed analysis of corrosion rates from the first tests is in progress.

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EXECUTIVE SUMMARY

As DOE continues to advance new power systems, materials issues are often pivotal in determining the ultimate efficiency that can be reached in the system. Refractory performance in slagging gasification represents one of these issues. The University of North Dakota (UND) Chemical Engineering Department in conjunction with the UND Energy & Environmental Research Center (EERC) have initiated a program to thoroughly examine the combined chemical (reaction and phase change) and physical (erosion) effects experienced by a variety of refractory materials during both normal operation and thermal cycling under slagging coal gasification conditions. The goal of this work is to devise a mechanism of refractory loss under these conditions.

The focus of the proposed work is to test the corrosion resistance of commercially available refractories to flowing coal slag, and propose the mechanisms of corrosion for the conditions studied. Corrosion is the degradation of material surfaces or grain boundaries by chemical reactions with melts, liquids, or gases, causing loss of material and consequently a decrease in strength of the structure. In order to develop methods of reducing corrosion, the microstructure that is attacked must be identified along with the mechanism and rates of attack. Once these are identified, methods for reducing corrosion rates can be developed.

The work will take advantage of equipment and experimental techniques developed at the EERC under funding from several DOE programs. The controlled-atmospheric dynamic corrodent application furnace (CADCAF) will be utilized to simulate refractory/slag interactions under dynamic conditions that more realistically simulate the environment in a slagging coal gasifier than any of the static tests used previously by refractory manufacturers and researchers.

The CADCAF was designed and construction was initiated under previous DOE funding. During the first two years of the current project, efforts focused on finalizing construction of the CADCAF. These final efforts focused primarily on issues related to sealing the CADCAF system, and dealing with a variety of safety related issues. Shakedown and screening testing verified operation of the system under reducing conditions.

Samples of slag and refractory from the Tampa Electric Polk Power Station have been obtained for testing in the CADCAF. Screening testing is in progress. Detailed analysis of the corrosion products will be performed during the next program year.

DYNAMIC TESTING OF GASIFIER REFRACTORY

INTRODUCTION

The recent events in California provide a strong impetus to the Vision 21 program being developed by DOE. While the rolling blackouts can be attributed primarily to shortsightedness in California's deregulation policy, evidence of the shrinking power reserves, and the need to build new electricity generation plants, is apparent. Coal gasification integrated into the energy cycle of a power plant is one of the more promising technologies that is capable of meeting the demand for new generating capacity while addressing the strong environmental concerns that have been delaying the construction of new power plants.

As DOE continues to advance new power systems, materials issues are often pivotal in determining the ultimate efficiency that can be reached in the system. A specific example is the need for refractories able to withstand both oxidizing and reducing environments, with high temperature strength, and the ability to resist corrosion by flowing slag and rapid thermal cycling. The University of North Dakota (UND) Chemical Engineering Department in conjunction with the UND Energy & Environmental Research Center (EERC) has undertaken a study to thoroughly examine the combined chemical (reaction and phase change) and physical (erosion) effects experienced by a variety of refractory materials during both normal operation and thermal cycling under slagging coal gasification conditions. The goal of this work is to devise a mechanism of refractory loss under these conditions.

The work takes advantage of equipment and experimental techniques developed at the EERC under funding from several DOE programs. The controlled-atmospheric dynamic corrodent application furnace (CADCAF) will be utilized to simulate refractory/slag interactions under dynamic conditions that more realistically simulate the environment in a slagging coal gasifier than any of the static tests used previously by refractory manufacturers and researchers. The CADCAF, along with advanced analytical techniques, provide the team with unique tools to evaluate the refractory problems facing the gasifier-based advanced power systems being developed under Vision 21.

Problem Definition

Corrosion is defined for this work as the degradation of material surfaces or grain boundaries by chemical reactions with melts, liquids, or gases, causing loss of material and consequently a decrease in strength of the structure. In order to develop methods of reducing corrosion, the microstructure that is attacked must be identified along with the mechanism and rates of attack. Once these are identified, methods for reducing corrosion rates can be developed.

Refractory corrosion is of concern in gasification systems for several reasons. Gasifiers, especially those that remove the ash in the form of a molten slag, operate at high temperatures over 1400C. At these high temperatures, chemical equilibria can become favorable for the interaction/reaction of the ash material from the fuel with the refractory, and the liquid state of the slag assures rapid reaction. The reduced species that are typically present in gasifier slags are typically more corrosive than their oxidized forms, and cause the slag to become liquid at lower temperatures than typically seen in combustion systems. To complicate matters, a commercial gasification system can experience sudden changes in temperature, subjecting the refractory material to thermal shock, and can switch from reducing to oxidizing as a result of process upsets.

The fact that the slag is liquid not only causes high reaction rates with the refractory because of the rapid transport of slag corrodents to the refractory surface, but also leads to the penetration of the slag into the refractory, even those that are nonporous, setting up the potential for chemical reactions below the surface of the material. These reactions can result in the dissolution of the refractory material, in particular, the cement below the surface. Often of more importance though, is the crystallization of secondary species, often with higher specific volumes than the original material, which leads to expansion and bursting of the refractory.

The physical properties of the slag in a coal gasification system are functions of the characteristics of the fuel being utilized. One concern is the viscosity of the slag at operating temperatures in the gasifier. Slags of low viscosity will flow more easily and more readily penetrate the refractory material. In addition, a low viscosity material that readily flows will continually and rapidly remove any corrosion products formed at the surface of the refractory, and replace them with fresh slag. Therefore, rather than coming to an equilibrium, the continuously running slag continues to reestablish the chemical driving force required for rapid and severe corrosion. A second expectation with low viscosity slags is the formation of relatively thin layers of slag. While a thick slag may be able to "insulate"the refractory from the gas phase species, with a thin layer of slag the gaseous environment in the gasifier is able to participate in the chemical reactions between the refractory and the slag.

The reactivity of the ash with the refractory, and the proper selection of refractory material will also be impacted by the chemical composition of the ash. On a broad sense, differences in reactivity can be expected between a basic and an acidic ash. Other more subtle differences will manifest themselves as the both the elemental and mineral composition vary within these two broad classifications.

Experimental data for modeling refractory materials in coal gasification systems is scant. While some limited work has been performed at high temperature slagging combustion conditions, much of the limited research performed for slagging gasifiers is proprietary. Information obtained from the DOE programs such as Combustion 2000 can and should be utilized as a starting point for developing experimental methods and proposing mechanisms for refractory corrosion in gasification systems.

Fortunately, the high temperatures under investigation add some simplification to the understanding of ash/refractory interactions. While ash is typically a very nonhomogeneous material, the molten slag that is formed at the expected temperatures in the gasifier will be homogeneous. In addition, due to the high temperatures, it is expected that the system will be at thermodynamic equilibrium. This implies that existing thermochemical equilibrium models such as the Facility for Chemical Analysis of Thermodynamics, or FACT code, could be utilized to model behavior in the gasifier. While FACT and other models may be a part of the tools used to investigate the problem, they are often limited in their use because the current thermodynamic data bases do not include all of the species required to adequately model the complex system that exists in the gasifier. However, knowing that the system is homogenous and at equilibrium does allow the use of other analytical methods, such as heated stage x-ray diffraction to help define the system.

EXPERIMENTAL

The focus of the work is to test the corrosion resistance of commercially available refractories to flowing coal slag, and propose the mechanisms of corrosion for the conditions studied. The focus will then shift to improving the corrosion resistance of the near surface of the grains and bond phase between grains, since bonding phases normally have a lower melting point and lower corrosion resistance than does the bulk of the material. Other tests may focus on the use of slag additives to decrease the corrosivity of the slag itself.

Approach

The primary tool that will be used to simulate the interaction of the ash generated slag and refractory is the controlled-atmosphere dynamic corrodent application furnace (CADCAF). It was designed to simulate conditions of dynamic corrosion on the vertical wall of a refractory-lined coal gasifier or glass or steel industry furnace, under controlled atmospheric conditions. The CADCAF, shown schematically in Figure 1 has the capability of testing two refractory test blocks simultaneously, up to a maximum of 1600^{o}C. Two corrodent injector feed ports and a single view port are located on the removable portion of the top of the furnace. Corrodents may consist of any granular material such as coal or steel slag, or glass cullet. An exit port for the spent corrodent material is located at the bottom of the furnace. The molten spent corrodent material will exit the furnace through a heated ceramic tube into a removable refractory lined catch pot and be available for post-test analysis.

The powder feeder is a precise low-rate volumetric feeder with full hopper agitation made of 316 stainless steel material. The feeder needs to be gas tight to several inches of water to allow the system to be completely sealed to prevent the reactive gases to escape or oxygen to enter the system [current work is focused on sealing of the system]. For any given test, a preselected gas mixture will be introduced through a gas inlet valve located on the side of the

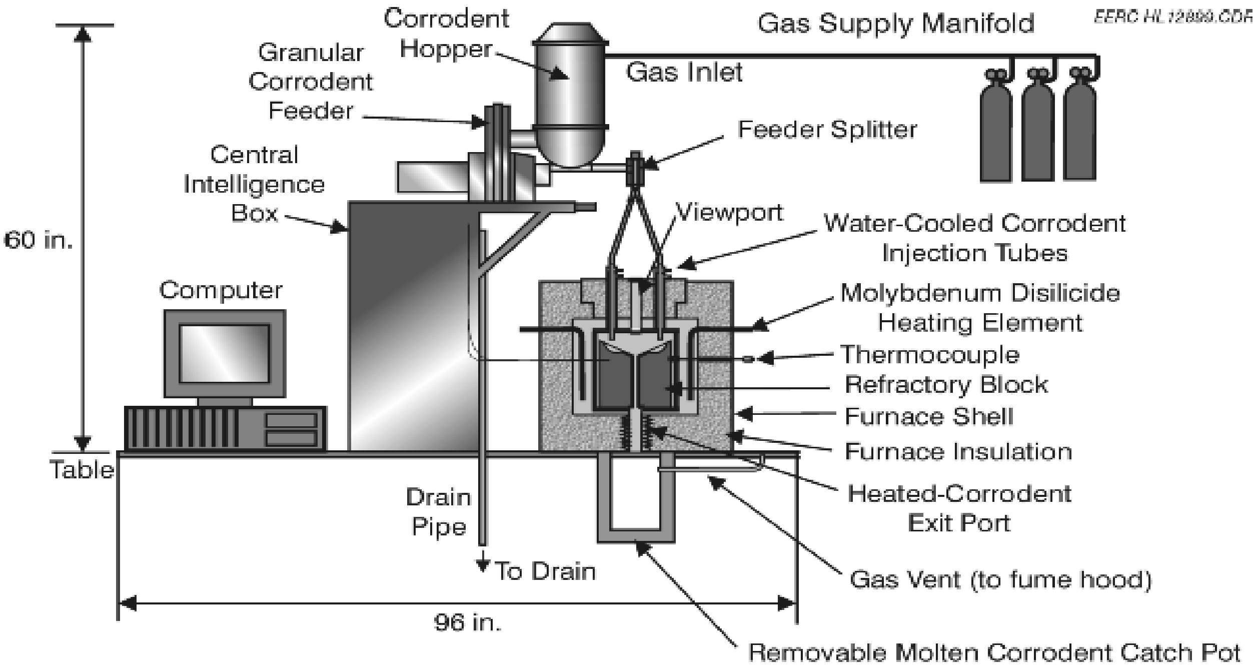

Figure 1. Schematic of the inside of the CADCAF with refractory blocks in place.

corrodent hopper. The gas will mix with the corrodent material, then enter the furnace through the feed injectors. It exits the system through a gas outlet vent located on one side of the slag catch pot, then exhausted through the fume hood.

Results from these dynamic experiments will be evaluated using several techniques to analyze the combined impacts of ash chemistry and refractory composition on refractory wear. Exposed refractory samples will be evaluated to determine the penetration depth and surface recession as a first estimate of the refractories resistance to attack. Scanning electron microscopy (SEM) will be used to determine if the primary attack was against the cement material or the aggregate. The SEM will be used to map the chemical composition of the exposed slag as a function of depth. These maps will help determine the penetration of various ash components into the refractory and/or the leaching of materials from the refractory. Selective penetration or leaching of specific elements will be important in understanding the mechanisms of refractory attack.

Another analytical tool that will be used in this study is heated-stage x-ray diffraction (XRD). Samples of slag prior to exposure to the refractory, and of the material after exposure (containing corrosion products), will be analyzed. The heated-stage XRD allows the user to identify the temperature at which various crystalline phases will form from the glass phase. Identification of the type of crystalline material that may be formed and under what conditions it forms will provide valuable insights into understanding methods by which additives to the slag or the refractory can help reduce corrosion rates.

The effect of process variables on surface recession of the refractories be investigated using the CADCAF. For example, small changes in temperature can significantly effect the viscosity of the flowing slag. These experiments will help evaluate the impact of slag viscosity on the mechanisms of refractory wear. Secondary effects of temperature that will also be considered is the crystallization of certain species from the slag as the temperature is reduced, and changes in the kinetics and chemical equilibrium with temperature variations.

CADCAF tests will be performed with both acidic and basic coal ashes. Under testing performed for Combustion 2000, basic slags were found to be more corrosive to certain refractories than acidic slags. With castable alumina refractories, the basic slags penetrated the refractory and formed secondary crystallization products that expanded and caused the refractory to burst. Therefore, the ash materials chosen for testing will include at least two bituminous and two low-rank (subbituminous or lignitic) coals. Selection of test materials(coals) will be made to compliment DOE’s existing data base.

Another approach that will be used to both help elucidate mechanisms and to assist in the development of more corrosion resistant refractories is to investigate a variety of refractory compositions. Phase diagrams will be utilized to identify stable high-melting material that could modify the bonding phase of the refractory. Mechanisms of reducing corrosion to be investigated include the formation of corrosion-resistant surface layers and increased sintering to raise strength and seal pores to reduce slag penetration.

Slag additives will be investigated as methods of altering the chemical and/or physical properties of the slag. Results of experiments under combustion conditions indicate that the flowing slag becomes significantly less corrosive as the slag dissolves some of the refractory. This may be due to changes in the slag viscosity or by changing the chemical composition of the slag so that it becomes saturated with the chemical species found in the refractory. As the saturation point is approached, dissolution rates would be expected to decrease markedly.

Thermal shock is can also play a critical role in refractory wear. The potential impact of thermal cycling will be evaluated using two different approaches. The first makes use of the penetration and compositional data obtain during CADCAF tests performed at a constant temperature. The intent is to determine the type and amount of slag penetration and reaction that has occurred with a given slag/refractory composition. Using this information and data generated from the heated XRD experiments, the potential to form crystallization products on cooling that will expand and cause the refractory to burst will be evaluated. A second technique will be to cycle the temperature of the CADCAF, allowing the refractory to freeze and remelt over several cycles and comparing these results to those obtained from the standard tests performed under constant temperature.

Scope Of Work

The primary objective of this work is to perform well defined experiments that provide insight and understanding into the performance of refractory materials under slagging gasification conditions that will lead to the development of mechanisms of refractory loss under gasification conditions. This objective will be met by simulating ash/refractory interactions using a bench-scale test apparatus, followed by analysis of the corroded refractory and slag using advanced analytical techniques.

Task 1 - Selection of Materials for Initial Screening

Initial tests will be performed using two coal ashes and five different refractory materials. Ash from a bituminous and a low-rank coal will be selected to allow a comparison between an acidic and basic ash. These test coals will be selected in conjunction with DOE to compliment existing information from Combustion 2000 and other programs. Refractories will be chosen in conjunction with refractory companies to represent the best commercially available materials.

Task 2 - Broad Brush Screening CADCAF Tests

Ten tests will be performed using the CADCAF - 2 ashes with 5 different refractories. Test durations are expected to be between 50 and 100 hours. Following each test, the refractory blocks will be analyzed macroscopically and microscopically using the SEM to measure ash penetration and refractory wear. Elemental mapping will be performed of the refractory material to determine which elements penetrated into the refractory and to what depth. The slag collected during the tests will be analyzed for bulk composition and with heated-stage XRD to evaluate the glass and crystalline phases present in the slag. In addition, the heated-stage XRD will be used to determine the crystallization behavior of the slag and indicate possible additives that can be used to reduce the corrosivity of the slag. Viscosity versus temperature measurements will also be employed to suggest appropriate additives and critical slag temperatures that affect the corrosivity of the slag. These analytical techniques will be used to analyze samples generated from some or all experimental work performed during this program (Tasks 1-5).

Task 3 - Directed CADCAF Testing

Results from Task 2 are expected to give an indication of slag/refractory combinations that exhibit different levels of refractory wear, penetration, and crystallization. Some preliminary hypotheses will be made based on Task 2 results. Starting from these hypotheses, additional tests (up to 10) will be planned to help prove, disprove, and/or expand on the preliminary findings. These tests are likely to include different ash and refractory types and/or additives which will be carefully selected to help pinpoint corrosion mechanisms.

The same analytical techniques outlined in Task 2 will be used to analyze the samples generated in Task 3. Based on Task 3 results, revised hypotheses of corrosion mechanisms and ways of reducing or preventing corrosion will be developed.

Task 4 - Thermal Shock

Testing during Task 4 will investigate the effect of temperature cycling on refractory materials. The first series of corrosion tests to be performed will be isothermal at two or three different temperatures to investigate the indirect impacts of temperature on refractory wear. These will include impacts of slag viscosity, crystallization, and possibly reaction kinetics.

The CADCAF will also be operated in a non isothermal mode to investigate thermal shock. In this mode, the CADCAF will be operated at a high temperature for a preset period of time and allowed to cool to the point where the slag freezes. The CADCAF will be reheated to the point of a flowing slag, held at that temperature for a preset period of time, and again cooled. This will be repeated for 5 cycles. Two experiments will be performed with a basic and acidic coal ash. The analysis of these samples will focus on differences between these samples and those generated from the standard isothermal tests.

This type of thermal shock experimentation has not been previously performed, so it is expected that some development work will be required. Ash and refractory types will be selected based on results from the previous tasks.

Task 5 - Development of Mechanisms

The primary objective of the work is to develop an understanding of ash/refractory interactions that will lead to the development of mechanisms that describe the interactions of slag (coal-ash) and refractory. Although listed as the last task, the development of mechanisms will be a consistent theme throughout this project. Mechanisms will be hypothesized early in the program, and will be utilized to direct the testing during the program. The proposed mechanism will be constantly updated as new data is generated. Likewise, the latest hypothesis will be used to determine the next series of tests. At the end of the Task 5, final mechanisms that describe the behavior noted during the program will be proposed. Additional experimental work will be performed as required to verify assumptions.

Throughout the test program, the project team will maintain constant communication with refractory vendors to ensure refractory materials being investigated represent commercial and experimental formulations that are realistic for commercial application. This direct communication will also promote timely dissemination of results. Results from the program will also be presented at the annual DOE Contractor's Review Meeting.

Deliverables

This program was originally designed for a doctoral student or two master's students, with additional work for an undergraduate student. It was assumed that the doctoral/master's student would spend a significant portion of the first year becoming familiar with the project and performing a detailed review of the literature. It was also expected that the final construction and shakedown activities would be completed prior to the start of this project. Therefore, the first year's experimental work was planned accordingly. However, since the CADCAF was not operational at the start of the current project, considerable time has been spent addressing the sealing and safety issues discussed previously. This has set the project approximately one year behind schedule.

Current plans are to complete the screening test and begin the directed CADCAF testing early in the third year and focus on thermal shock testing, mechanism development and thesis/dissertation preparation during the remainder of the third year. Limited experimentation will occur during the third year when required to substantiate assumptions. Revised project milestones are listed in Table 1.

RESULTS AND DISCUSSION

Task 1 - Selection of Materials for Initial Screening [on-going]

The objectives of the current project were discussed with plant personnel at the Tampa Electric Polk Power Station. Samples of slag and refractory were requested for testing in the CADCAF. A 55 gallon drum of gasifier slag along with several refractory bricks of the type that they use in the gasifier have been received. The slag has been dried and sieved to the size needed for our flowing slag corrosion tests. As will be discussed later, preliminary testing with

Table 1. Project Milestones

Activity	Months from Contract Award
Selection of Materials for Testing	6
Literature Review and Screening Tests	(12)* 38
Contractor's Review Meeting	12
Directed CADCAF Testing	(21) 40
Thermal Shock Tests	(24) 42
Contractor's Review Meeting	24
Mechanism Development	44
Peer Review Meeting	44
Final Project Report	48

* Original schedule

this sample showed the slag was made up of two distinct phases, one melting at around 1400°C and the second phase at a much higher temperature. This caused difficulties in performing the tests. Therefore, a second sample received from TECO as a part of a different project is being utilized for the program.

Tampa Electric personnel have also requested that we test bricks of refractory made by Salazar and Sons which they are contemplating using in the gasifier. Paul Salazar visited UND to discuss the testing and provided a sample brick, sized to our specifications, of a vibratable

SiC/Al_2O_3 material that Salazar and Sons is proposing for the Polk gasifier.

Refractory block analysis

Commercial refractory bricks are being used for testing. Since these bricks were already formed, they required machining to form flow channels and slag wells to represent the actual flow along the walls of a gasifier. Figure 2 presents one of the samples used for testing.

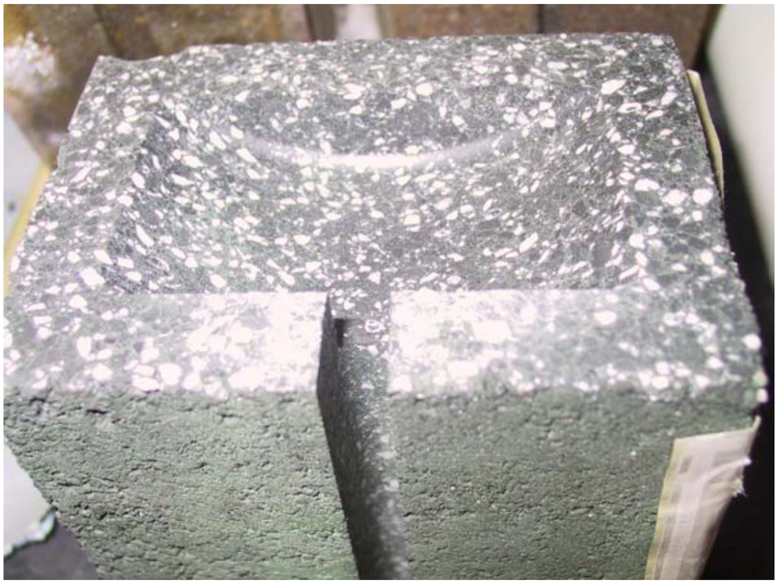

Figure 2. Refractory sample showing slag well and flow channel

The porosity of refractory samples is one of the core factors in their degradation. Slag can penetrate by capillary action and lead to formation of the spinel phase. A fully dense refractory would have very high corrosion resistance. However, porosity cannot be eliminated due to the thermal gradient and differential thermal expansion encountered. Refractories are also designed to provide thermal insulation which requires a certain porosity for the bricks. Most commercial refractory bricks are produced by sintering chrome particles resulting in approximately 80-85% dense material. Refractory samples were analyzed using a modified ASTM C20 standard for measuring apparent porosity. Values are reported in Table 2.

Table 2: Data from refractory sample porosity testing

Dimensions	Volume	Dry wt.	Wet wt.	Porosity
mm	**cc**	**g**	**G**	**%**
20.7x15.83x14.8	4.9	16.15	16.54	8.1
20.55x19x18.1	7.1	27.76	28.43	9.6
18.8x16.6x15.75	4.9	17.45	17.78	6.8
21.13x18.59x14.25	5.6	21.66	22.23	10.1
19.53x17.8x16.7	5.8	22.78	23.48	12.0
22.7x13.5x13.3	4.1	15.33	15.66	8.6

The porosity of the samples was found to increase with chrome content (Figure 3). Increased chrome content leads to better resistance to corrosion while increased porosity leads to poorer corrosion resistance. It will be interesting to observe the combined effect of increasing porosity and chrome on the corrosion resistance of the samples. Detailed XRF analysis and SEM analysis of the refractory samples are available.

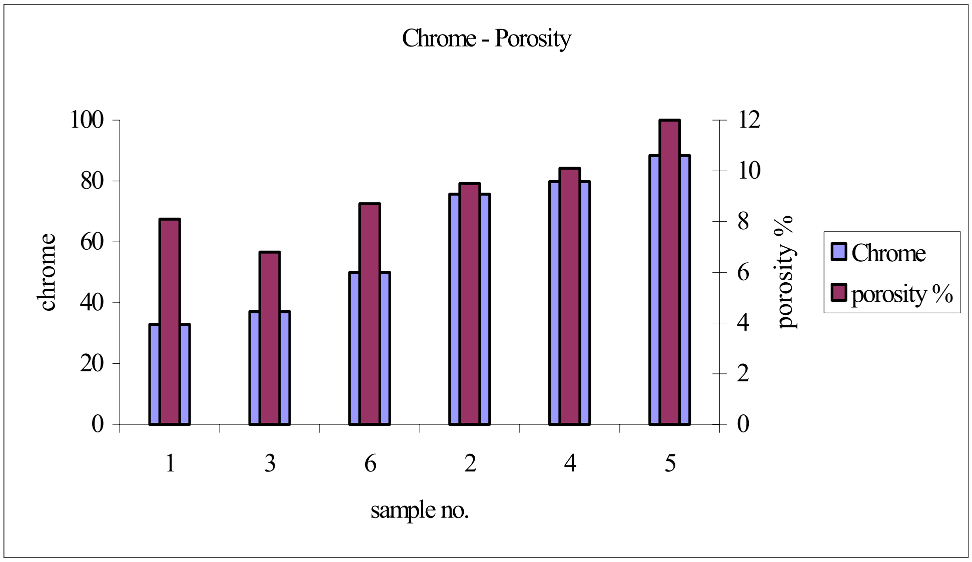

Figure 3: Relation between chrome content and porosity of samples

Task 2 - Broad Brush Screening CADCAF Tests [on-going]

Design Changes

The CADCAF was designed and construction was initiated under previous DOE funding. All of the major components had been purchased, manufactured, and installed under the previous program. Since the start of the current project, efforts have focused on finalizing construction of the CADCAF. These final efforts focused primarily on issues related to sealing the CADCAF system, and dealing with a variety of safety related issues. The sealing problem turned out to be more difficult than originally envisioned. Initially, it was thought that the primary leakage was through the lid of the crucible in the test chamber. As testing continued, it was determined that although leakage through the lid may have been a major source of leakage, leakage through the porous refractory material (crucible walls) was also a problem. Efforts undertaken to correct these problems were summarized in the previous annual report to provide guidance to others who may encounter similar problems.

The original purpose of developing the CADCAF was to study slag-refractory interaction under reducing conditions. Thus, a reducing gas flow system is the core of the project. Ideally, to simulate the environment in slagging gasifiers, the exact composition of flue gas should be used for testing. However, due to safety, health hazard concerns, cost, and complexity, hydrogen is being used to simulate the reducing environment. Iron is present in coal in substantial amounts and is affected by the reducing conditions. Hence, it is considered as a reference point in defining the oxygen concentrations within the furnace crucible. The reducing gas is a mixture of 2% hydrogen and balance nitrogen. Whether an atmosphere is reducing to iron or not, depends on the ratio of water vapor pressure to hydrogen pressure in that atmosphere. At atmospheric pressures, this ratio is simply the ratio of volume fractions of the component gases in the mixture.

Let us consider a typical reduction reaction occurring in the furnace atmosphere.

$$FeO + H_2 \rightarrow Fe + H_2O.$$

For this reaction, the equilibrium constant is the ratio $K = \frac{p_{H_2O}}{p_{H_2}}$

This constant is a function of temperature. The variation is represented graphically in Figure 4.

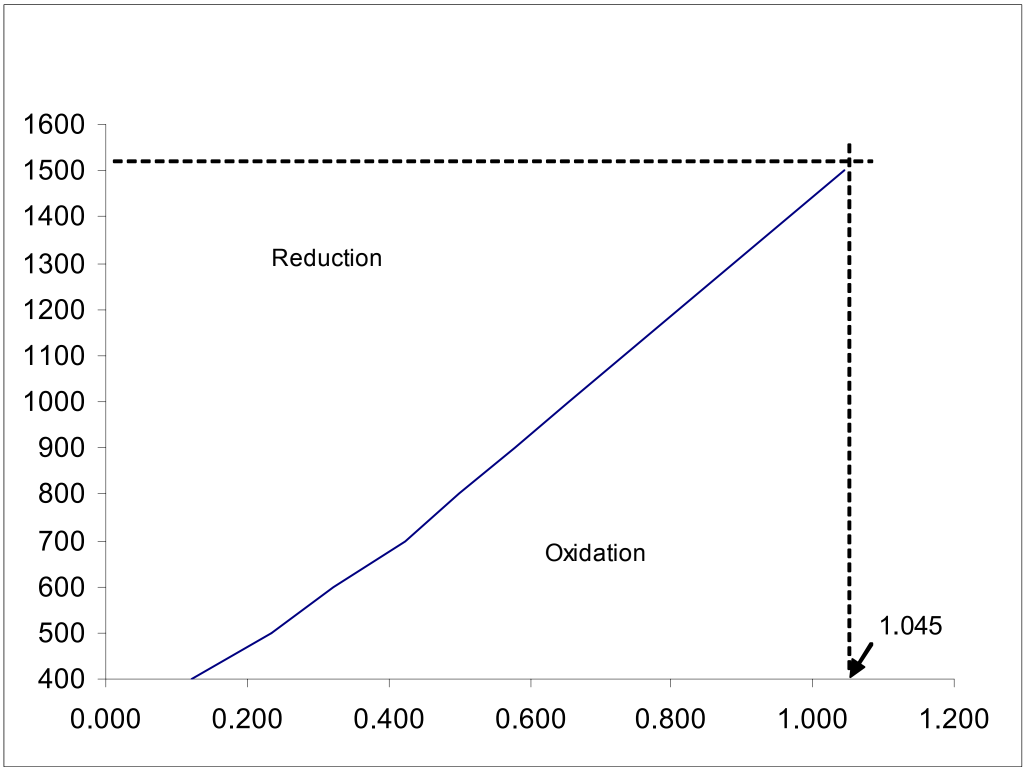

Figure 4. Ratio of H_2O/H_2 partial pressures to temperature

At a temperature of 1500°C, the ratio is 1.045. This means that atmospheres with H_2O/H_2 ratios up to 1.045 are reducing. An important point worth noting is that the water formed is entirely due to the reaction between hydrogen and oxygen that may be present in the gas. Hence, the water-to-hydrogen ratio is in effect oxygen-to-hydrogen ratio. This has been the logic behind maintaining the reducing atmosphere in the CADCAF.

A classical feedback control system which ensures that 2% hydrogen in nitrogen gas mixture enters the CADCAF was added to the system. To ensure that the crucible is filled with this reducing gas mixture, the crucible is sealed using high temperature alumina based sealants. A major hurdle in creating a positive pressure within the alumina crucible is its porosity. Extensive pressure drop across the chamber required a glaze material that will seal the pores and retain the gas mixture within the crucible. A limiting factor in material selection for this purpose is the high operating temperature (1500+°C). The glaze coating used on the crucible is a commercially available refractory coating grade RX-36. It has a glazing temperature of 1480°C and a maximum operating temperature of 1950°C. An SEM analysis of the sample revealed that the major contents were calcium aluminosilicates. At temperatures above 1500°C; however, the glaze coating does not form as desired. Hence, the CADCAF operating range is kept under that value. This was possible as it is still above the fluid temperature of the ash (1400°C).

With this information in mind, the furnace temperature was set to 1490°C. However, during a trial run it was found that the slag did not melt at that temperature. Further investigation showed that the temperature at the actual slag –refractory interaction point was approximately 170°C lower than the set point. After better insulating the crucible, the temperature drop of 170°C was reduced to approximately 75°C . Although some loss can be attributed to the insulating properties of the crucible and cooling effect of fresh gas flowing into the system, it was seen that most of the heat was lost through the water-cooled slag injectors. There was a huge temperature drop in the short distance between the exit tip of the slag (380°C) injector and the surface of the refractory sample (1380°C). Two options were available as a remedy. Firstly, the distance between these two points was increased by pulling up the slag injection port by a couple of inches. After running a 20 hour test under these conditions, it was seen that the gradient was still to high to melt the slag that was in contact with the sample, but not the one that was collected above this molten layer. It was concluded that further insulation and modification in design would be required to reduce the heat sink effect caused by the injector ports. To reduce the heat sink effect caused by the water-cooled injectors, a donut shaped piece of insulation was used at the bottom of the slag injector assembly and the injector tubes were pulled upwards away from the crucible. The modified design allowed slag to flow through the orifice while simultaneously providing good thermal insulation. A rough schematic of the modification is shown below in Figure 5. This modification reduced the heat loss from the injector port cooling system to an acceptable level.

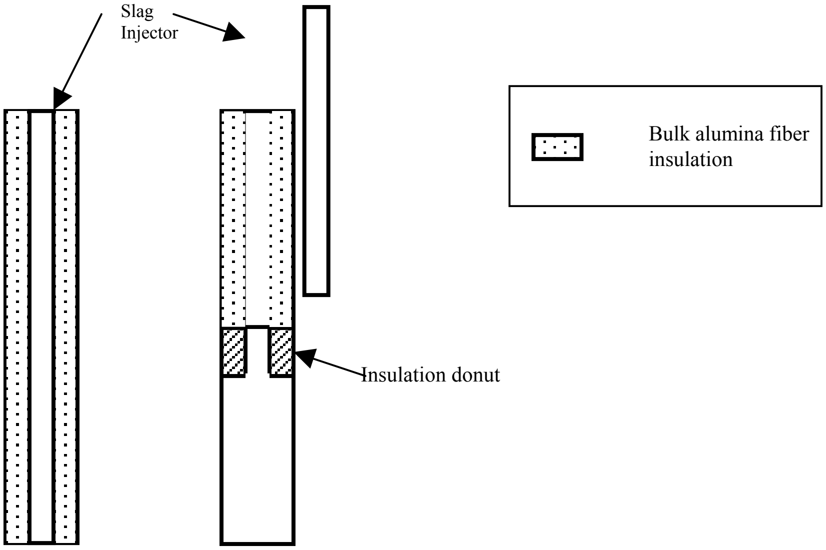

Figure 5. Schematic showing modifications in the slag injector assembly

Slag composition analysis

The slag (Slag A) to be used for testing refractory samples in the CADCAF was sized and screened to –20+60 mesh. An XRF analysis of slag A is shown in Table 3. Preliminary tests conducted with this slag showed that the slag did not melt completely at the specified test temperature of 1500°C. Initially it was assumed that this was due to the cooling effect of the water-cooled slag injectors. Design modifications were made to nullify their heat sink effect as is discussed in the previous section. Although this increased the temperature at the slag-refractory interaction point, the slag still did not melt completely. A fusion test was repeated on slag A. During the test, it was observed that the sample swelled to almost three times its initial size before softening and melting. This information, coupled with the presence of a trickle of liquid on the refractory sample suggests the presence of a two-phase system of the slag at 1450°C.

Table 3. XRF analysis of slag samples A and B

Oxides	Weight %	
	Slag A	Slag B
SiO_2	50.0	50.2
Al_2O_3	17.6	17.5
Fe_2O_3	16.0	12.3
TiO_2	0.9	0.9
P_2O_5	0.7	0.3
CaO	2.6	5.2
MgO	1.8	1.6
Na_2O	1.9	5.2
K_2O	2.5	2.1
NiO	1.2	0.5
V_2O_5	4.7	4.4
SO_3	-	-

The two phases as present on the refractory sample are shown in Figure 6. The bright orange spots are iron oxide and green patches are that of chrome oxide surfaces exposed to slag. Most of the solid retained in the slag well was in the form of sintered powder particles. The second phase of the slag, which had a melting temperature below 1490°C trickled down the sample as expectecd. This can be seen in the Figure 7. An SEM analysis of the deposit along this flow line revealed that the composition is same as that of the refractory brick. The liquid medium that carried the refractory particles is not found in the analysis, indicating no slag/refractory interaction for this short test.

Figure 6. Slag well after 20 hour test with Slag A showing presence of two distinct phases

A new slag, one with a single amorphous phase was selected for further testing. Slag B was available and had composition almost similar to Slag A. The composition of Slag B as indicated by XRF analysis is also given in Table 3. From Table 3 we can see that Slag B has higher amounts of fluxing agent oxides such as calcium and sodium oxide. It was expected that this slag would form a free flowing viscous liquid phase at the test temperature of 1400°C. A simple melting test under oxidizing conditions confirmed this. Equal amounts of Slag B (1gram) were melted in a furnace at 1500°C and it was seen that Slag B formed a homogenous glass as expected. A detailed ash fusion test was then conducted on the slag samples to get accurate temperature values that may be used to set the test temperature. The results from the tests are given in Table 4.

Figure 7. Picture of slag well after 20 hours of testing with Slag A showing little interaction between the slag and refractory.

Table 4: Ash Fusion Test Data for Slag Samples under Reducing & Oxidizing Conditions

	Slag A		Slag B	
	Oxidizing	Reducing	Oxidizing	Reducing
Initial	2323	2249	2228	2173
Softening	2341	2375	2269	2210
Hemispherical	2568	2649	2511	2245
Fluid	2653	2701	2613	2497

*All values in degree F

Current Status

- The porosity in the crucible has been eliminated allowing reducing conditions at gasifier operating temperatures.
- Refractory samples have been machined to desired specifications and relevant chemical and physical properties characterized.
- Final design modifications on the CADCAF have been completed and flowing slag has been achieved at temperatures and gas compositions that allow evaluation of refractory corrosion under gasification conditions.
- The first tests have been successfully completed. Analysis of the material is currently underway.

CONCLUSIONS

Corrosion tests are currently in progress. There are no firm conclusions at this time.

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