Reducing Ultra-Clean Transportation Fuel Costs with HyMelt$^{®}$ Hydrogen

Quarterly Report

July 1 – September 30, 2003

October 31, 2003

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For

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Catalytic burners for gas turbines using HyMelt carbon monoxide rich fuel gas may not require post combustion abatement controls. If this possibility comes to fruition, it will produce a significant economic benefit for power generation.

6.0 References

No references were cited in this document.

7.0 PLAN FOR THE NEXT QUARTER

Additional atmospheric testing is scheduled for the second week of December 2003. The testing will last 3 days. Illinois #6 coal and petroleum coke will be the feeds to be tested using bottom tuyeres. The tuyeres used in this testing will simulate commercial operation. We have delayed final design and procurement of the vessel for super-atmospheric testing until completion of the December testing.

Kvaerner will continue evaluating amine systems and complete the carbon monoxide shift study. Kvaerner will begin atmospheric test data evaluation for commercial design studies.

EnviRes and Siemens Westinghouse have finalized all input parameters for a combustion testing and Siemens Westinghouse will begin combustion simulations in the upcoming quarter.

DISCLAIMER

ABSTRACT

This report describes activities for the fourth quarter of work performed under this agreement. A second round of atmospheric testing was conducted as scheduled on September 2 through September 4, 2003. The test results demonstrated a much-improved rate of carbon dissolution with gas yields close to expectations. Additional atmospheric testing to demonstrate a commercially feasible feed and oxygen injection method is scheduled for the week of December 8, 2003.

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1.0 PROJECT OBJECTIVES, SCOPE AND DESCRIPTION OF TASKS

1. Introduction

EnviRes and DOE executed the cooperative agreement for this work on September 19, 2002. This document is the fourth quarterly progress report under this agreement. Kvaerner, MEFOS and Siemens Westinghouse will conduct most of the significant tasks in this project through subcontracts with EnviRes.

1.1 Scope of Work

Phase I of the work to be done under this agreement consists of conducting atmospheric gasification of coal using the HyMelt technology to produce separate hydrogen rich and carbon monoxide rich product streams. In addition smaller quantities of petroleum coke and a low value refinery stream will be gasified. DOE and EnviRes will evaluate the results of this work to determine the feasibility and desirability of proceeding to Phase II of the work to be done under this agreement, which is gasification of the above-mentioned feeds at a gasifer pressure of approximately 5 bar. The results of this work will be used to evaluate the technical and economic aspects of producing ultra-clean transportation fuels using the HyMelt technology in existing and proposed refinery configurations.

1.1 Phase I Task Description

Task 1.1 Project Management and Planning

This task includes all project planning; experimental test plans; risk analysis; implementation of a bridge loan, purchasing, contracting and accounting systems with requisite auditing; and execution of contracts with MEFOS, Kvaerner and Siemens Westinghouse. This task is being executed.

Task 1.2 Preparation and Shipment of Feedstock Materials

This task consists of procuring 25 tons of coal, 15 tons of petroleum coke and 48 – 55 gal drums of aromatic extract oil; transporting the coke and coal to a pulverizing facility; pulverizing, drying and loading the coke and coal into bags; and shipping the feedstocks to MEFOS in Lulea, Sweden. EnviRes completed this task

Task 1.3 Predictive Modeling of the HyMelt Process

This task consists of generating detailed reactor energy and material balances for each feedstock using the Fact Sage pyrometallurgical thermodynamic modeling program. Kvaerner will perform detailed process simulation using the Aspen Plus process simulator. Kvaerner, MEFOS and EnviRes will evaluate and analyze the results of predictive modeling. This task is being executed.

Task 1.4 Combustion Modeling and Analysis

Siemens Westinghouse will perform combustion turbine modeling using fuel gas conditions and compositions provided by task 1.3. This task is being executed.

Task 1.5 Design and Fabrication of Pilot Plant Specific Molten Iron Bath Apparatus

MEFOS will design and fabricate all solid feeding systems and oxygen injection systems required by the testing. EnviRes will assist MEFOS in designing the petroleum liquid feed system. MEFOS will design the shell of the high-pressure reactor. MEFOS and EnviRes completed the originally planned injection system for this task. MEFOS and EnviRes designed and fabricated a tuyere for submerged injection. MEFOS and EnviRes are currently designing and fabricating a commercially feasible tuyere for testing in December.

Task 2.0 Project Testing

Task 2.1 HyMelt Atmospheric Pressure Testing in a Molten Iron Bath

MEFOS designed and fabricated the petroleum liquid feed system. This injection system was tested in a cold flow environment. The injection systems were hot commissioned. Any equipment revisions indicated by cold flow testing and hot commissioning were made. Process performance testing was performed for each feed. Execution of this task continues.

2.0 EXECUTIVE SUMMARY OF WORK DONE DURING THIS REPORTING PERIOD

Experimental testing of coal, petroleum coke and a heavy oil began on June 5 and continued through June 13. We believe that these tests represent the first instance of injection of these feeds into molten iron without the concurrent injection of substantial quantities of oxygen and other materials. The tests in June resulted in unacceptably low rates of carbon dissolution in the molten iron. Preliminary results from tests conducted in September indicate that much better carbon dissolution rates result from submerged injection. We have scheduled additional atmospheric testing using tuyeres for both oxygen injection and coal or coke injection to begin December 8, 2003. The December testing will operate in a commercially practical mode.

An economic evaluation by Kvaerner indicated that water gas shifting of carbon monoxide is prohibitively expensive at $2.86 per kscf of incremental hydrogen produced over the fuel value of the feed carbon monoxide. HyMelt, unlike most other coal gasification processes, does not require water gas shifting to produce high purity hydrogen. Detailed flow sheets, equipment sizing, equipment cost, and preliminary operating cost estimates are presented in this report. Kvaerner obtained cost estimates from UOP for Polybed PSA hydrogen purification.

EnviRes and Siemens Westinghouse Power Corporation decided to evaluate catalytic burners for gas turbines using the carbon monoxide rich fuel gas from the HyMelt process. If performance similar to that already demonstrated with natural gas can be achieved with HyMelt fuel gas, we believe that post combustion abatement controls will not be required to meet currently envisioned new source performance standards for NO_x and CO emissions.

Brad Quinlan, auditor for the Defense Contract Audit Agency [DCCA] under contract by the U.S. Department of Energy, conducted a follow-up audit of the financial reporting and accounting system of EnviRes on July 9 & 10. An exit conference with Daniel French, EnviRes Controller, was conducted on July 10. On July 25 we received an electronic copy of the audit report concluding, "EnviRes' accounting system is adequate for accumulating costs under Government contracts".

3.0 Experimental

MEFOS Activities

As described in the previous quarterly report, testing using coal, coke and liquid petroleum injection were conducted from June 5 through June 13. Appendix I contains a detailed description of this work reported by MEFOS. MEFOS generated a large amount of data in this work. The data presented represent a summary of the data generated and still the data presentation takes tens of pages. The raw data from which MEFOS generated this summary can only be managed electronically.

The MEFOS report in Appendix I points out that some problems in sampling and analyzing streams occurred during the test program. Some of these problems included air infiltration into the process gas sample lines between the sample probe and the analytical equipment, calibration drift for the mass spectrometer, feed misidentification and other problems that were not clearly identified. Most of these problems can be corrected by standard data reconciliation techniques. Since the volume of data is great, data reconciliation represents a long and arduous task that would consume substantial resources and money. As we will describe later, the rate of carbon dissolution into the metal for the June test program was unacceptably low. Initial data analysis of work performed in early September indicate that we achieved acceptable carbon dissolution rates for at least some of the injection periods and that the quality of the gas analysis was better than that generated in June. We will, therefore, focus attention and resources on test periods that represent commercially attractive operating conditions. Our analysis of the June data will review the useful data generated with greater effort reserved for later work.

The MEFOS report in Appendix I describes the equipment, the materials used, the testing procedure and the heat notes in sufficient detail so that no further comment regarding them will be made. Additional comments on the results will be made in section 4.0 Discussion.

Preliminary analysis of the data generated June 5 to 13 indicated that carbon dissolution rates into the metal were unsatisfactory. MEFOS and EnviRes concluded that the problem was caused by problems associated with top entry lances. We further concluded that although significant improvements could be made to top entry lances and the way they are utilized, most of these improvements were not achievable within the financial and time constraints of this project. MEFOS suggested that we test tuyeres for coal and petroleum coke injection. The quickest, most cost effective, most likely to succeed approach was to use a side entry lance 10 cm from the bottom of the refractory lining. The initial tuyere to be tested was a single lanyard (one tube) design. Argon would transport the solid feed from the feed hopper to the tuyere. Figure 1 is a view of the universal converter with the lance installed. The single rubber hose conveys the pneumatically transported particulate to the tuyere near the center of the figure. The stainless steel tubing connects a pressure gauge (to the top) allowing the inlet pressure to the tuyere to be monitored. The universal converter is tilted to the charging or tapping position in Figure 1. The hood that collects product gases and air for combustion appears at the very top of the figure. A connection for bottom stirring (not connected) appears at the lower left.

On Tuesday, September 2, 2003 we made several injection attempts with coal and petroleum coke. All attempts resulted in an occluded tuyere (the pressure drop across the tuyere was high and there was almost no flow). We observed that a solid accretion had formed on the inside wall of the universal converter at or near the location of the tuyere outlet. Figure 2 shows a dark formation near the tuyere outlet that appears to be a metal accretion.

We decided to use a slit tuyere in place of the single lanyard tuyere. Figure 3 shows an end view of the slit tuyere. A slit tuyere consists of two concentric pipes with the OD of the inner pipe only slightly smaller than the ID of the outer pipe. Such a design is much more resistant to metal intrusion into the annular space. We decided to inject air in the annular space and coal in the center pipe. The center pipe ID was 8.0 mm. We felt that the slightly exothermic effect of the small amount of injection air would retard or prevent accretion formation. MEFOS worked into the night to install the new tuyere. Figure 4 shows the installation of the slit tuyere in the universal converter. This view is similar to Figure 1. Note that there are two hoses. The original rubber hose still transports the solid feed. The second hose transports the air for the slit tuyere. We resumed testing on the morning of September 3. Little difficulty was encountered with coal or coke injections after installing the slit tuyere.

Figure 5 shows the temperature probe just after its removal from the universal converter. The outer wall of the temperature probe is approximately 8 mm of rolled cardboard. In the absence of oxygen, which is the case in the universal converter, the cardboard lasts for more than 30 seconds even when immersed in molten iron. This is longer than the insertion time of the probe. The temperature probe measures the temperature one time before it is discarded. MEFOS measured the metal temperature approximately once every 2 minutes during feed injection or oxygen injection and at least once, with a different probe, every time the universal converter was tilted.

Figure 6 shows the metal sample probe just after its removal from the universal converter. The sample probe also has a cardboard outer wall. The tip of the sample probe has a hollow ceramic cavity that allows metal to enter and freeze. The Tip is covered with a metal shroud that prevents slag from entering the cavity as the probe passes through the slag layer. The shroud melts in the molten iron. The probe can sample metal from 10 to 20 cm below the metal surface. MEFOS took metal samples using this method approximately once every 10 minutes. MEFOS also took metal samples with a different probe when the converter was tilted. The hopper and chute in the right center of both Figures 5 and 6 allows lime, scrap and fluxing agents to be added to the universal converter during operation.

Figure 1. Initial Tuyere Installation in the Universal Converter

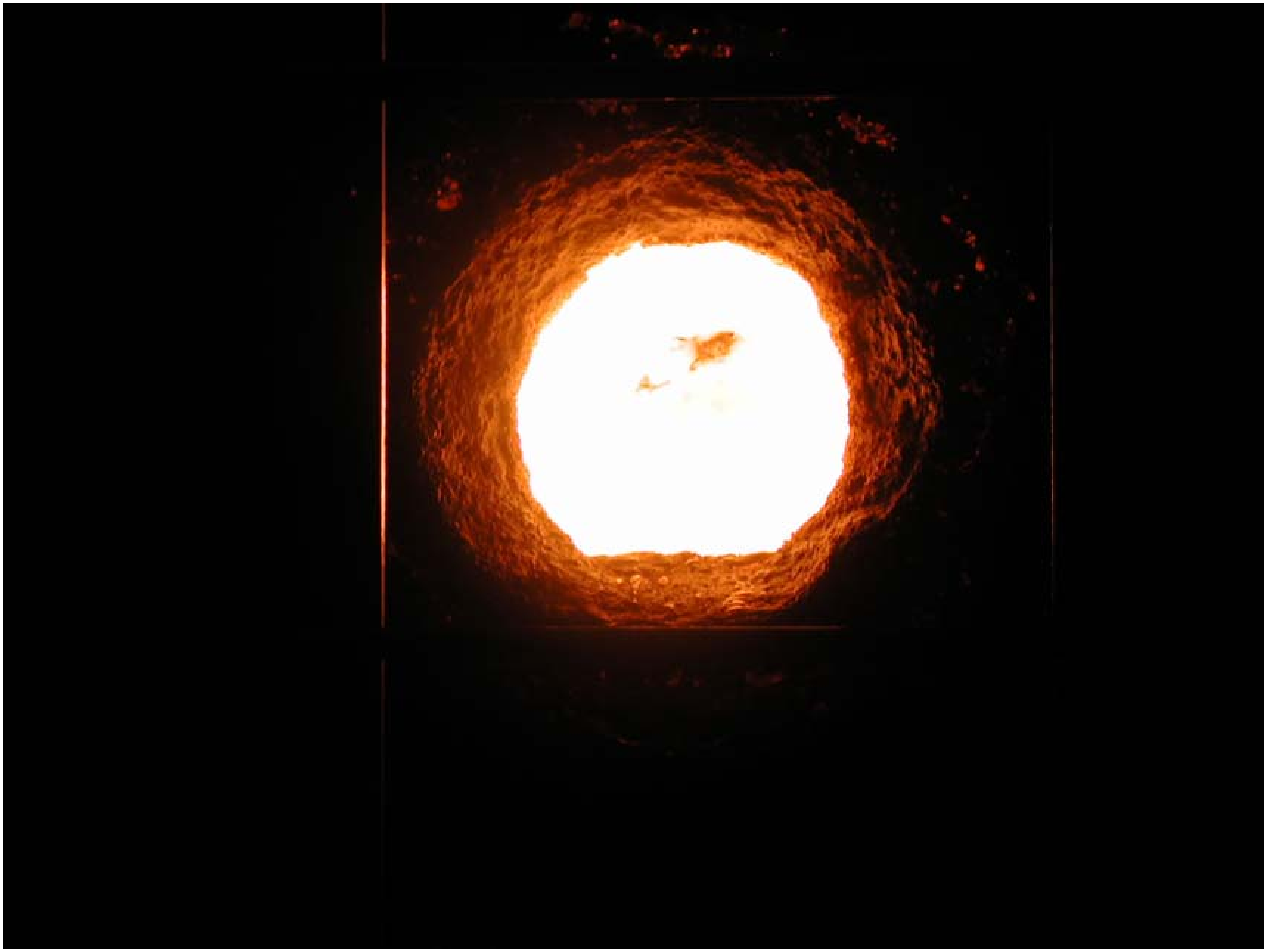

Figure 2 Metal Accretion or Mushroom on Refractory at or near Tuyere outlet

Figure 3 Discharge End View of Slit Tuyere Before installation

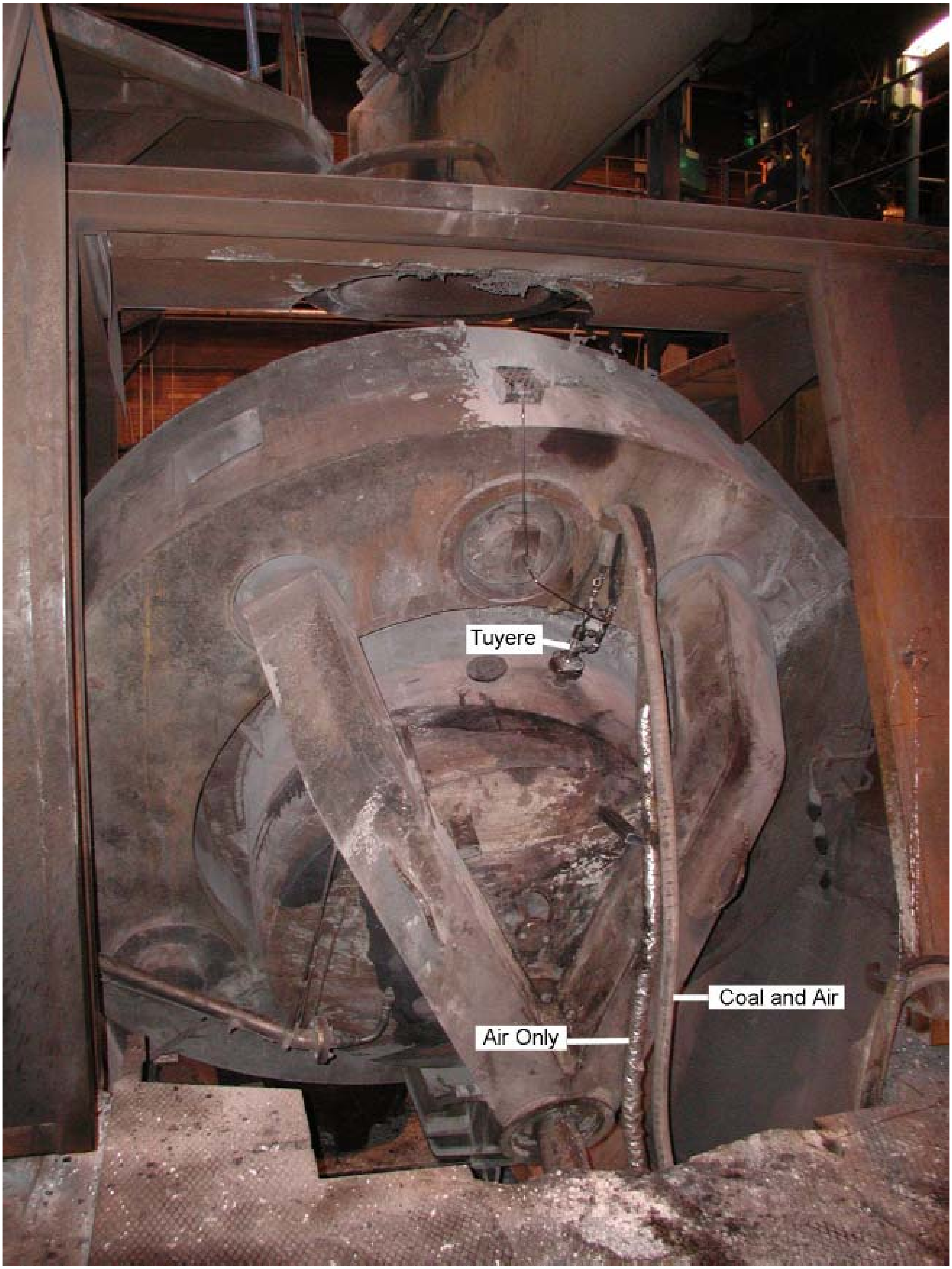

Figure 4. Slit Tuyere Installed on the Universal Converter

Figure 5. Temperature Probe Removal During Decarburization for Universal Converter

Figure 6 Metal Sample Probe Removal During Decarburization

Kvaerner Activities

Kvaerner initiated simulation activities using Aspen Plus. The HyMelt reactor section process flow sheet appears in Appendix II page 2, the flow sheet for the amine system appears in Appendix II on AII page 15 stream flows for this flow sheet appear on AII page 14 and the flow sheet for the water gas shift appears in Appendix II on AII page16 stream flows for this flow sheet appear on AII page 17 to 19. Kvaerner obtained cost estimates from Dow for the amine system and UOP for the PSA hydrogen purification system. This information is also given in Appendix II. Kvaerner estimated the differential cost for shifting nearly all of the carbon monoxide produced in a 450 t/d demonstration plant.

Siemens Westinghouse Power Corporation Activities

EnviRes, Siemens Westinghouse Power Corporation and some consultants of Siemens Westinghouse discussed the merits of diffusion and catalytic burners for gas turbines. We decided to evaluate a catalytic burner because it offers the potential of meeting future NO_x emission requirements without a selective catalytic reduction (SCR). Appendix III contains most of the information developed for this issue.

4.0 Results and Discussion

MEFOS Activities

For all injections performed in June, the methane content of the product gas was in the range of 5 to 10%. In some tests coke could be seen floating on the slag when the universal converter was tilted after injection. Dust samples contained as much as 90% carbon. Pages 49 to 51 of the MEFOS report show the carbon yield to metal for coal, petroleum coke and aromatic extract oil. Carbon yield to metal is calculated as the quotient of the change in the total mass of carbon dissolved in the metal divided by the total mass of carbon contained in the injectant for that period. The change in the total mass of carbon in the metal is calculated as the product of the mass of metal in the bath and the change in the weight fraction of carbon in the metal from the beginning to the end of the injection period. Since the yield is expressed as a percentage, the above quotient should be multiplied by 100%.

The maximum value for carbon yield to metal must always be less than 100% for several reasons. First, any oxygen contained in the feed will convert in near quantitative fashion to carbon monoxide. With Illinois #6 coal having 8.26% oxygen, the amount of carbon in the feed not reporting to the metal by this mechanism should be 7 to 10% of the feed carbon. If the coal moisture content increased during storage, this number will be higher. Similarly any methane formed will reduce the amount of carbon reporting to the metal from the feed although the thermodynamic amount of methane should always be less than 1% at these conditions. Second, any FeO present in either the metal or slag from decarburization will react with feed carbon to form carbon monoxide. In this case the value of carbon monoxide produced will have a maximum value near the beginning of the injection period and decrease as oxygen is consumed. Third, any slag reactions such as $CaO + C + S \rightarrow CaS + CO$ will consume carbon that would otherwise report to the metal. Slag reactions should consume very little carbon since the ratio of slag to metal is always small.

Top entry oxygen blowing typically created substantially more FeO in the slag than does tuyere injection of oxygen. Values of FeO in the slag are given in the MEFOS report in Appendix I. FeO in the slag after oxygen blowing typically ranged from 5 to 15%.

The carbon yield to metal for coal ranged from 59.6% to 13.7%, for petroleum coke the values ranged from 72.4 to 22.4% and for oil the values ranged from 33.4% to 11.4%. The oil injection differed significantly from the method of injection for coal and petroleum coke. The carbon yield to metal for petroleum coke and coal become nearly equal when the effect of oxygen contained in the coal is considered. For both petroleum coke and coal the carbon yield to metal decreased with increasing feed rate. The decrease in transport gas flow rate with increasing solid flow and thus the velocity of the gas particulate stream impinging on the slag/metal surface may explain at least in part the decrease of carbon to metal with feed rate.

MEFOS discusses many of the trends in product gas compositions. Several problems with sampling and analysis combined with injection problems, described earlier make detailed analysis of the gas compositions questionable without significant effort to correct for these problems. It is unclear whether the high COS values result from the high FeO levels in the slag. It is unclear whether oxygen in air leakage into the sample lines to various analyzers reacted with hydrogen and/or CO.

The results of mercury sampling and analysis show a wide range of mercury levels if the data are correct. We only sampled and analyzed the product gas for mercury three times during June testing.

The hydrogen-purging test for sulfur removal described on page 49 of the MEFOS report shows that much more sulfur disappeared from the metal and slag than could be accounted for by the amount of H_2S appearing in the product gas. Similar unexplained sulfur disappearance from the metal was always experienced in the early bench scale tests.

The vanadium tests show that vanadium has a partition coefficient that is highly dependent on the oxygen potential. These tests (page 35 and 43 of the MEFOS report) also show that vanadium in the slag can be reduced causing the vanadium to report back to the metal after it has been oxidized from the metal into the slag for vanadium levels of 0.6 to 0.8% in the metal.

Kvaerner Activities

Kvaerner completed an economic comparission of using the carbon monoxide rich stream for fuel vs. shifting the carbon monoxide rich stream to hydrogen. Results of this work are given in Appendix II. UOP estimated a cost of $1.7 MM for a Polybed PSA system capable of producing 15.31 MMSCFD of product hydrogen UOP estimated a cost of $2.5 MM for a unit capable of producing 28.39 MMSCFD. Kvaerner obtained or determined detailed flow sheets, material balances, energy balances, equipment sizing and operating costs. Kvaerner obtained or determined similar information from Dow for an amine system to remove H_2S from the product hydrogen. As presented in Appendix II Kvaerner determined that the incremental cost over fuel value for upgrading the carbon monoxide rich HyMelt stream was $2.86 per kSCF of hydrogen produced.

Siemens Westinghouse Power Corporation Activities

EnviRes and Siemens Westinghouse decided to model and test a catalytic burner instead of a diffusion burner for proposed gas turbines using the carbon monoxide rich stream as fuel. Most if not all combustion systems for IGCC turbines use diffusion burners to combust carbon monoxide rich fuel. These burners simply provide residence time and mixing for combustion to take place. Diffusion burners tend to produce NO_x levels of 25 ppmv when the flue gas is adjusted to a standard value for excess oxygen. Diffusion burners usually produce CO emissions in excess of 5 ppmv. It is likely that new source performance standards will require both NOx and CO emissions to be below 3 ppmv for power plants by the time a commercial HyMelt plant is built. If both of these hypotheses are correct, combustion turbines (including those firing natural gas) will be required to have post combustion abatement controls for both NO_x and CO. While diffusion burners have not been specifically tested with a fuel that is representative of the carbon monoxide rich stream from HyMelt, we believe that the results would be very similar.

Siemens Westinghouse had a catalytic burner program under development before this project began. They have tested a prototype of their catalytic burner with natural gas at commercial conditions. In these test they found that NOx and CO emissions could be kept under 2 ppmv under optimal operating conditions. If similar results can be obtained for the HyMelt carbon monoxide rich stream, gas turbines using catalytic burners may not require post combustion abatement controls for a HyMelt gasifier. This appears to us to be a strong incentive to pursue catalytic burners. If catalytic burners are not feasible for HyMelt carbon monoxide rich gas we can switch to diffusion burners with very little uncertainty.

5.0 Conclusions

All testing conducted from June 5 to 13 gave unacceptable carbon dissolution rates. At low feed rates both petroleum coke and coal resulted in approximately 70% of theoretical. At higher feed rates the rate of carbon dissolution dropped rapidly to near 20% of theoretical. Carbon dissolution rates for oil were even worse. Carbon dissolution rates could be improved with better injection lance design, but we feel that the probability of obtaining 98% of theoretical is unlikely with top entry lances.

Preliminary results based on visual observation and preliminary operating data indicate that submerged injection of coal and petroleum coke results in a much better carbon dissolution rate. The carbon dissolution rate also appears to be less dependent on coal or coke feed rate.

Hydrogen purging to remove sulfur does not appear to be attractive, however, during the testing much more sulfur disappeared than could be accounted for by H_2S appearing in the product gas. Further investigation of this phenomenon appears warranted.

Based on the economic analysis by Kvaerner, we believe that shifting carbon monoxide to hydrogen is not economically attractive at an incremental cost of \$2.86/kSCF above fuel value. We further conclude that gasification processes that must use water gas shift to produce hydrogen are at a disadvantage to processes that directly produce hydrogen.