"NONEQUILIBRIUM SULFUR CAPTURE & RETENTION IN AN AIR COOLED SLAGGING COAL COMBUSTOR

Seventh Quarterly Technical Progress Report

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ABSTRACT

Calcium oxide injected in a slagging combustor react with the sulfur from coal combustion to form sulfur bearing particles, which are deposited on the liquid slag layer on the combustor wall. Due to the low solubility of sulfur in slag, it must be drained from the combustor to limit sulfur gas re-evolution. Analysis indicated that slag mass flow rates in excess of 400 lb/hr should limit sulfur re-evolution. The objective of this 36 month project was to perform a series of 16 one day tests to determine the factors that control the retention of the sulfur in the slag. In the present quarterly reporting period, 3 days of combustor tests were performed, bringing the total number of tests performed to 19. Two of the test were a repeat of two tests performed in the previous quarter with a high, 37% ash, Indian coal. The high slag flow rate with that coal resulted in the highest observed sulfur retention to-date, namely 20% of the injected sulfur. In the present quarter, this test was repeated with the same coal feed rate but with 75% longer period of 2.4 hours. The total mineral matter injected was 635 lb/hr, compared to only 19.7 lb/hr of sulfur, of which 75% was from injected gypsum. However, despite excellent slag flow from the previous Indian coal tests, only 5.8% of the sulfur from the gypsum reported to the slag. Since substantial amounts slag remained on the combustor walls, it is concluded that still longer duration tests are required to establish equilibrium conditions. Current efforts are focused on finding a U.S. source of high ash coal to implement additional tests.

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1. EXECUTIVE SUMMARY

The objective of this 36 month project is to determine the degree of sulfur retention in slag in a full scale cyclone coal combustor with sulfur capture by calcium oxide sorbent injection into the combustor. This sulfur capture process consists of two steps: Capture of sulfur with calcined calcium oxide followed by impact of the reacted sulfur-calcium particles on the liquid slag lining the combustor. The sulfur bearing slag must be removed within several minutes from the combustor to prevent re-evolution of the sulfur from the slag. To accomplish this requires slag mass flow rates in the range of several 100 lb/hr, and preferably over 400 lb/hr. To study this two step process in the combustor, two groups of tests were implemented. In the first group, calcium sulfate in the form of gypsum, or plaster of Paris, was injected in the combustor to determine sulfur evolution from slag. In the second group, the entire process was tested with limestone and/or calcium hydrate injected into the combustor.

This original planned effort was to consist of a series of up to 16 parametric tests in a 20 MMBtu/hr slagging, air cooled, cyclone combustor. These tests were completed in the previous quarter. However, due to the excellent results on sulfur retention obtained with a high (37%) ash Indian coal in the previous quarter, in which for the first time a record 20% of the injected sulfur was retained in the slag at slag flow rates above 400 lb/hr, it was decided to extend the test effort with high ash coals. During the present quarterly reporting period ending June 30, 1997, 3 tests in this project were implemented, bringing the total test days to 19. In addition, a total of 9 test days were completed during this quarter on the parallel project that utilizes the same 20 MMBtu/hr combustor. The results of that project, especially those related to improved slagging performance, have a direct bearing on this project in assuring proper operation at the high slag flow rates that may be necessary to achieve high sulfur retention in slag.

2 of the 3 tests in this period were performed with the high ash Indian coal.

In the first test with the Indian coal, difficulties were experienced with the coal feed lines shortly after startup, and in view of the limited quantity of Indian coal available, it was decided to terminate the test and correct the problem.

In the second test, the coal firing rate was 1180 lb/hr, the same as was used in the previous tests with this Indian coal. A major advantage of this high ash coal is that the relative concentration of the calcium sulfate, which was found in earlier combustor tests to sharply increase the slag viscosity, is now only a small fraction, 13%, of the total mineral matter flow rate. The present test period was extended by 75%, to over two hours, compared to the previous test. It was anticipated that this would allow equilibrium slag coverage of the combustor wall. In addition to the coal, 200 lb/hr of limestone was injected. Excellent slag flow was achieved. Toward the end of the test, gypsum at the rate of 100 lb/hr was also injected, resulting in about 15 lb/hr of sulfur injected from the gypsum. This equals about 2.6% of sulfur in the slag, if all the sulfur in the gypsum remained in the slag. The injected coal had a sulfur content of only 4.7 lb/hr. It was ignored in the sulfur balance because without fine calcium oxide particles very little sulfur from the coal reacts with the CaO. The injected mineral matter flow rate from the coal, calcined limestone, and dry gypsum was 635 lb/hr. Four slag samples were taken during the test. In the absence of gypsum, the sulfur content in the slag was below the detection limit of 0.01%. A sample taken 30 minutes after gypsum injection began had a sulfur content of only 0.02%, which is negligible. A second slag sample taken 50 minutes after injection started had a sulfur content of 0.15%, which represents only 5.8% of the sulfur content of the gypsum. This is almost a factor 4 lower than in the January 28 gypsum test.

In this test, the slagging was far better than in the earlier tests with the Indian. In the previous test, the slag was concentrated in large blocks, while in the present test, the slag flowed in about 1 inch size balls. This compares with small pebbles of several millimeters diameter resulting from low ash bituminous coal combustion. A mass balance revealed that only about one-half of the mineral matter injected was recovered from the slag tank in this test. This had also been observed in the earlier Indian coal test. It indicated that substantial quantities of slag remained on the combustor walls.

A subsequent test was performed with an 11% ash, bituminous coal. Very high slag flow was observed in the initial test period. The slag flow then decreased sharply. This confirmed that substantial quantities of slag had been coated on the combustor by the Indian coal ash. Post test slag analysis showed that no sulfur in the slag. It most probably had evolved during deposition in the combustor. The slag flow rate during this initial period was so high that slag froze in the lower water cooled section of the slag chute.

In conclusion, the conditions for high sulfur capture were present in the Indian coal tests, namely, the theoretical sulfur content was only a few percent of the slag flow rate, and the slag flow rate was in excess of 400 lb/hr. The sulfur content was higher than in the lower ash coal tests. It is also to be noted that early in the test effort last year, the slag sulfur content was relatively high, i.e. in the 10% range of the coal sulfur, using low ash bituminous coals. At that time, the thickness of the combustor refractory liner was greater than at present where part of the original refractory has been dissolved by the coal slag. Therefore, the earlier slag flow rate was higher, and the sulfur evolution was lower.

In view of the success with the Indian high ash coal, effort focused on obtaining a supply of very high ash U.S. coal in order to perform even longer duration tests with high ash coal. On source investigated was coal mine waste. A sample of this coal has been received from a coal washing plant in western PA. However, as delivered it was unsuitable for injection into the combustor. A 1 ton/hr coal mill at the Coal Tech Philadelphia test site has been partially refurbished by a sub-contractor. However, completion of this refurbishment effort is beyond current project resources. Therefore, an alternative search is in progress by the supplier of the pulverized coal for the test effort.

A no-cost 12 month extension to a total of 36 months was executed in the at the end of the present reporting period to allow further test and analytical efforts on the sulfur-slag process with high ash coals and high slag mass flow rates.

In conclusion, the record 20% sulfur retention in slag obtained in the initial high ash Indian coal tests partially validate the hypothesis that high slag mass flow rates will result in substantial sulfur retention in slag. Longer test periods are required to assure steady-state slag coverage and slag flow from the combustor to establish the maximum attainable slag retention. The balance of this project is being directed toward this effort.

2. RESULTS AND DISCUSSION

2.1. PROJECT DESCRIPTION

2.1.1. Objectives

The primary project objective is to determine the degree of sulfur retention in slag in a full scale cyclone coal combustor. This non-equilibrium process is a key step in the capture and retention of sulfur released during coal combustion by the interaction with calcium based sorbent particles. By encapsulating the sulfur bearing calcium particles in slag, the need for landfilling of this waste is eliminated. This objective is being implemented through a series of 16 one day tests carried out in a 20 MMBtu/hr air cooled, slagging combustor-boiler installation located in Philadelphia, PA. The project consists of two tasks. Task 1 consists of the experiments conducted in the 20 MMBtu/hr combustor, and task 2 consists of analysis of this data. All the operating procedures for this effort have been developed in the 9 years of operation of two designs of this combustor.

2.1.2. Technical Approach

2.1.2.1. Overview of the Work

The work of this project is being implemented on Coal Tech's patented, 20 MMBtu/hr, air cooled cyclone coal combustor that is installed on an oil designed, package boiler at a new facility at the Arsenal Business Center in Philadelphia, PA. This new facility consists of a refurbished and upgraded 20 MMBtu/hr combustor that had been tested at a manufacturing plant in Williamsport, PA from 1987 through 1993. The primary fuel has been, and will remain, coal. Other tests, including combustion of refuse derived fuels and vitrification of fly ash, have been successfully performed. Additional ash injection may be required to achieve high sulfur retention in the slag in the present combustor tests.

The combustor's novel features are air cooling and internal control of SO_2, NO_x, and particulates. Air cooling, which regenerates the heat losses in the combustor, results in a higher efficiency and more compact combustor than similar water cooled combustors. Internal control of pollutants is accomplished by creating a high swirl in the combustor which traps most of the mineral matter injected in the combustor and converts it to a liquid slag that is removed from the floor of the combustor.

SO_2 is controlled by injecting calcium oxide based sorbents into the combustor to react with sulfur emitted during combustion. The spent sorbent is dissolved in the slag and removed with it, thereby encapsulating the sulfur in slag. Part of the sorbent exits the combustor with the combustion products into the boiler where it can react with the sulfur. The primary objective of the present tests is to maximize the degree of sulfur retention in the slag. All spent sorbent not reporting to the slag is either deposited in the boiler or it is removed in the stack particle scrubber.

NO_x is controlled by staged, fuel rich combustion inside the combustor. Additional reductions are achievable by reburning in the boiler or by sorbent injection in the stack gases.

Excellent progress had been made prior to the start of the present project in meeting several of these combustor performance objectives. One of the most important objectives of this technology development effort is to demonstrate very high SO_2 reduction in the combustor. Prior to the start of the present project, the peak SO_2 reduction achieved with sorbent injection in the combustor had been 90%. Of this amount a maximum of 11% of the total coal sulfur was trapped in the slag. Evaluation of this prior data indicated that the low sulfur retention in the slag was due to excessive slag residence time in the combustor. Since the solubility of sulfur in slag is low, long slag residence times (in excess of 5 minutes) can result in substantial sulfur gas re-evolution into the gas phase.

To reduce the slag residence time in the combustor in the present project tests, the slag mass flow rate must be increased to over 400 lb/hr by either using very high ash coals or by injection coal ash with the coal. High ash mass flow rates increase the slag flow rate.

In order to determine the non-equilibrium sulfur-slag chemistry, calcium sulfate (anhydrite) was injected into the combustor to vary the slag flow rate inside the combustor and to measure the sulfur gas evolution rate independently of the calcium-sulfur heterogeneous capture reaction. This information was used in subsequent tests to measure the combined sorbent-sulfur capture rate in the gas phase with the sulfur retention rate in the slag inside the combustor.

The 16 tests planned for this project should allow full parametric variation of these sulfur-sorbent capture and sulfur-slag re-evolution reactions.

2.1.2.2. Task Description

Task 1: Sulfur Chemistry Tests in the Slag of a Cyclone Combustor.

This task will consist of four groups of tests designed to validate the sulfur chemistry in slag under non-equilibrium conditions. The tests are designed to validate the chemical and fluid mechanical processes occurring in the capture and retention of sulfur in slag. These reactions are based on prior analytical and experimental work in coal slags and coal like slags, such as steel blast furnace slags. The original plan called for a total of 20 one day tests. However, due to resource limitations, the plan was modified to accomplish the project objectives in as few as 16 one day tests. To meet all the parametric test variations, the duration of individual test conditions was reduced. As of the date of this report, 8/13/97, 19 tests, 3 more than the 16 tests planned, have been completed and all the technical issues related to this project have been identified.

According the original project plan, which was modified as the test effort proceeded, it was planned to perform a first group of six tests, in which calcium sulfate as gypsum or plaster of Paris was to be injected into the 20 MMBtu/hr combustor at a rate that duplicates the complete reaction of sulfur from a **2% sulfur** coal with calcined calcium oxide particles. While maintaining this sulfur concentration fixed, the total slag mass flow rate was to be increased in discrete steps, with each step remaining fixed for a specific period. The purpose of these tests and the second group of tests was to measure sulfur re-evolution from a sulfur based calcium compound at concentrations that duplicate the maximum amount of sulfur that can be captured in the combustor with calcium oxide sorbents.

In the second group of six tests, calcium sulfate was to be injected into the 20 MMBtu/hr combustor at a rate that duplicates the complete reaction of sulfur from a **4% sulfur** coal with calcined calcium oxide particles. While maintaining this sulfur concentration fixed, the total slag mass flow rate was to be increased in discrete steps, with each step remaining fixed for a specific period.

These two groups of tests were to determine the sulfur retention capability of slag as a function of slag residence time in a commercial scale combustor, namely the unit rated at 20 MMBtu/hr. In other words these tests focused only on the sulfur retention in slag. This type of test was performed briefly in the 20 MMBtu/hr combustor facility and the results indicated that this is an effective method for studying sulfur retention in slagging cyclone combustors.

As these tests were implemented, it was determined that high calcium sulfate levels in the slag sharply increased the slag viscosity to the point of severely inhibiting slag flow. The nature and number of these tests was modified, as is explained in Project Status Section of these Quarterly Progress reports.

In the third group of four tests, the entire sulfur capture process was to be implemented from the injection of the uncalcined sorbent to its reaction in the combustor and impact and removal with the slag. The slag mass flow rate was to be adjusted to duplicate the optimum slag flow rate determined from the group one tests. These fuel rich and fuel lean tests will serve to validate the entire sulfur capture and retention process in the combustor.

In the final group of four one day tests, reacted sorbent collected in the boiler and stack baghouse was to be injected into the combustor at the optimum slag mass flow rate determined from the first two groups of tests. The objective of this test series was to determine the degree of sulfur encapsulation in slag in cases where the magnitude of sulfur capture with injection of sorbent in the combustor is insufficient to meet environmental emission standards.

All the experiments were to be conducted in accordance with the procedures developed in the seven years of testing in Williamsport and in the current tests in Philadelphia on the 20 MMBtu/hr combustor.

As the test effort proceeded the test plan was modified to account for the results of prior tests. The overall project objectives had been met as of the end of the 12/31/96 reporting period. Subsequent efforts were focused on operation with very high (over 20%) ash coal where the high slag flow rate favors sulfur retention in slag. This was verified in the previous quarterly reporting period with a 37% ash Indian coal. Further tests with this coal were implemented in the present reporting period., as will be discussed in the Project Status Section 2.2 of this Report.

Task 2: Analysis

The results of the tests in task 2 will be analyzed using two and three dimensional combustion codes for the conditions existing in this combustor, and a code for analyzing slag flow on the walls of the combustor. The results will be compared with prior tests in the present combustor and with laboratory scale data on the sulfur chemistry process in coal and steel slags.

The analytical procedures and bench scale tests on sulfur-slag reactions developed in prior decades will be used for this purpose.

2.2. PROJECT STATUS

2.2.1. Effort of the Present Quarter

Overview: The implementation of the work on this project involves testing on Coal Tech's 20 MMBtu/hr slagging coal combustor-boiler test facility. A second generation combustor was installed at a new facility in Philadelphia in 1995 and it became operational at the end of 1995. By the end of June 1997, a total of 83 days of tests, of which 19 were on the present project, were successfully implemented. 12 days of shakedown tests on gas, oil, and coal were completed in March 1996. Since then all tests involved coal fired operation under slagging combustor conditions. 3 of the 19 tests to date on the present project were completed in the present reporting period, the second quarter of 1997.

It will be recalled that the objective of this project is to determine the degree of sulfur retention in slag in a full scale cyclone coal combustor with sulfur capture by calcium oxide sorbent injection into the combustor. This sulfur capture process consists of two steps: Capture of sulfur with calcined calcium oxide followed by impact of the reacted sulfur-calcium particles on the liquid slag lining the combustor. The sulfur bearing slag must be removed within several minutes from the combustor to prevent re-evolution of the sulfur from the slag. To accomplish this requires slag mass flow rates in the range of at least several 100 lb/hr, preferably over 400 lb/hr, or greater. To study this two step process in the combustor, two groups of tests have been implemented. In the first group, calcium sulfate in the form of gypsum or plaster of Paris was injected in the combustor to determine sulfur evolution from slag. In the second group, the entire process is tested with limestone and/or calcium hydrate injected into the combustor.

This original planned effort of up to 16 parametric tests in a 20 MMBtu/hr slagging, air cooled, cyclone combustor was completed in the previous quarter, ending March 31,1997. During the present quarterly reporting period ending June 30,1997, three tests beyond the original plan for this project were implemented, bringing the total tests to 19. In addition, a total of 9 test days were completed during this quarter on the parallel project that utilizes the same 20 MMBtu/hr combustor.

The reason for the extension of the test effort was that a limited supply of several tons of very high (37%) Indian ash was obtained through DOE's Pittsburgh Operations in January 1997. In a pair of tests with this coal in January 1997 excellent results on sulfur retention were obtained with this coal. For the first time in the decade long operation of this combustor, a record 20% of the injected sulfur was retained in the slag at slag flow rates above 400 lb/hr. It was, therefore, decided to extend the test effort with high ash coals. During the present quarterly reporting period ending June 30, 1997, 2 additional tests with this Indian coal were completed.

Tests in the Present Quarter:

In the first test with the Indian coal, difficulties were experienced with the coal feed lines shortly after startup, and in view of the limited quantity of Indian coal available, it was decided to terminate the test and correct the problem.

In the second test, the coal firing rate was 1180 lb/hr, the same as was used in the previous tests with this Indian coal. A major advantage of this high ash coal is that the relative concentration of the calcium sulfate, which was found in earlier combustor tests to sharply increase the slag viscosity, is now only a small fraction, 13%, of the total mineral matter flow rate. The present test period was extended by 75%, to over two hours, compared to the previous test. It was anticipated that this would allow equilibrium slag coverage of the combustor wall. In addition to the coal, 200 lb/hr of limestone was injected. Excellent slag flow was achieved. Toward the end of the test, gypsum at the rate of 100 lb/hr was also injected, resulting in about 15 lb/hr of sulfur injected from the gypsum. This equals about 2.6% of sulfur in the slag, if all the sulfur in the gypsum remained in the slag. The injected coal had a sulfur content of only 4.7 lb/hr. This coal sulfur was ignored in the sulfur balance because without fine calcium oxide particles very little sulfur from the coal reacts with the CaO. The injected mineral matter flow rate from the coal, calcined limestone, and dry gypsum was 635 lb/hr. Four slag samples were taken during the test. In the absence of gypsum, the sulfur content in the slag was below the detection limit of 0.01%. A sample taken 30 minutes after gypsum injection began had a sulfur content of only 0.02%, which is negligible. A second slag sample taken 50 minutes after injection started had a sulfur content of 0.15%, which represents only 5.8% of the sulfur content of the gypsum. This is almost a factor 4 lower than in the January 28 gypsum test.

In this test, slag flow was far better than in the earlier tests with the Indian coal. In the previous test, the slag was concentrated in large blocks, while in the present test, the slag flowed in about 1 inch size balls. This compares with small pebbles of several millimeters diameter resulting from low ash bituminous coal combustion. A mass balance revealed that only about one-half of the mineral matter injected was recovered from the slag tank in this test. This had also been observed in the earlier Indian coal test. It indicated that substantial quantities of slag remained on the combustor walls after combustor shutdown.

A subsequent test was performed several days later with an 11% ash, bituminous coal. Very high slag flow was observed in the initial test period. The slag flow then decreased sharply. This confirmed that substantial quantities of slag had been coated on the combustor by the Indian coal ash. Post test slag analysis showed that no sulfur in the slag. It almost certainly evolved during deposition in the combustor. The slag flow rate during this initial period was so high that slag froze in the lower water cooled section of the slag chute.

The conditions needed for high sulfur capture were present in the Indian coal tests, namely, the theoretical sulfur content was only a few percent of the slag flow rate, and the slag flow rate was in excess of 400 lb/hr. The sulfur content in the slag was higher than in the lower ash coal tests. It is also to be noted that early in the present combustor's test effort last year, the slag sulfur content in the slag was relatively high, i.e. in the 10% range of the coal sulfur, using low ash bituminous coals. At that time, the thickness of the combustor refractory liner was greater than at present where part of the original refractory has been dissolved by the coal slag. Therefore, the earlier slag flow rate was higher, and the sulfur evolution was lower.

In view of the success with the Indian high ash coal, effort focused on obtaining a supply of very high ash U.S. coal in order to perform even longer duration tests with high ash coal. On source investigated was coal mine waste. A sample of this coal was received from a coal washing plant in western PA. However, as delivered, it was unsuitable for injection into the combustor due to substantial content of rocks. A 1 ton/hr coal mill at the Coal Tech Philadelphia test site has been partially refurbished by a sub-contractor. However, completion of this refurbishment effort is beyond current project resources. Therefore, a search is in progress by the supplier of the pulverized coal for the test effort to find high ash coal.

In conclusion, the record 20% sulfur retention in slag obtained in the initial high ash Indian coal tests partially validate the hypothesis that high slag mass flow rates will result in substantial sulfur retention in slag. Longer test periods are required to assure steady-state slag coverage and slag flow from the combustor to establish the maximum attainable slag retention. The balance of this project is being directed toward this effort.

2.3. EFFORT OF THE NEXT QUARTER

The results to date show that sulfur retention in slag, which requires a high mass flow rate due to the low sulfur solubility in slag, is primarily a combustor operational problem. High slag mass flow rates are difficult to achieve in low ash coal with the addition of metal oxide powders, due uneven melting, exit nozzle slag blockage, etc. In addition, it was discovered from the gypsum and plaster of Paris injection tests that substantial calcium sulfate concentration in slag greatly increase the slag viscosity. Therefore, sulfur retention in slag requires even higher slag mass flow rates than previously assumed because it is necessary to limit the calcium sulfate content of the slag. In the tests in this reporting period the theoretical maximum slag mass flow was 635 lb/hr.

3. CONCLUSIONS:

These tests during the present quarterly reporting period confirm previous conclusions that slag flow operational conditions are the primary determinant in sulfur retention in the combustor. The high ash Indian coal tests have shown that the air cooled combustor operates very well with such high ash coals, and the resultant high slag flow rates are compatible with high sulfur retention in the slag. Efforts are underway to find domestic sources of high ash coal for further tests.