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

Sixth Quarterly Technical Progress Report

DOE Contract No:: DE-AC22-95PC95102

Contract Period of Performance: 9/14/95 to 9/13/97

Period Covered by Report: January 1,1997 to March 31,1997

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Date Submitted: April 14, 1997

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ABSTRACT

Calcium oxide sorbents injected in a slagging combustor react with the sulfur released during coal combustion to form sulfur bearing particles, some of which are deposited on the liquid slag layer on the combustor wall. Since the solubility of sulfur in liquid slag is low, the slag must be drained from the combustor to limit sulfur re-evolution into the gas phase. The objective of this 24 month project is to perform a series of 16 one day tests to determine the factors that control the retention of the sulfur in the slag that is drained from the combustor. The last of the 16 tests planned for this project was completed in the present reporting period. This was the first test in this project that validated one of the primary hypothesis of this project, namely to retain substantial quantities of sulfur in slag requires high slag mass flow rate. Previous attempts to achieve high sulfur retention with artificial slag met limited success. In this, the 16th test, a high, 37%, ash Indian coal was injected into Coal Tech's 20 MMBtu/hr air cooled, slagging combustor with gypsum, $CaSO_4$ ($2H_2O$). The slag analysis showed that 20% of the sulfur in the gypsum remained in the slag. This is double the highest sulfur concentration in slag measured in numerous test operationn with this combustor. While the test results to date have met the objectives of this project, further high slag mass flow rate tests are planned with the Indian coal to optimize sulfur retention in slag.

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1. EXECUTIVE SUMMARY

The objective of this 24 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. 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 entire effort consists of a series of up to 16 one day parametric tests in a 20 MMBtu/hr slagging, air cooled, cyclone combustor. During the present quarterly reporting period ending March 31,1997, the final test planned for this project was implemented. In addition, a total of 16 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.

In the prior tests in this project, the sulfur content in the slag was generally negligible. In the tests with combined sulfur capture and slag retention through the injection of fine particle calcium hydrate, the very low sulfur content in the slag was due to the minimal retention of the reacted calcium hydrate particles in the combustor. In the tests were the only the sulfur retention capability of the slag was studied, the sulfur retention ranged from negligible to under 10%. Gypsum having a coarse particle size distribution or plaster of Paris having a very fine particle distribution was injected into the combustor. The latter particles were mostly blown out of the combustor. While the former reported to the slag, their presence in the slag substantially increased the slag viscosity, resulting in poor slag flow. To correct this problem by reducing the concentration of the gypsum relative to slag, artificial ash was co-injected with the coal and gypsum in order to increase the total slag mass flow rate. This somewhat improved the slag flow to the extent that as much as 8% of the sulfur reported to the slag. Also, a number of tests in the parallel 20 MMBtu/hr combustor project earlier last year yielded sulfur concentrations up to 10%. It is believed that the latter result may have been due to excellent slag flow in those tests which allowed rapid slag draingae before the sulfur re-evolved.

In early January 1997, Coal Tech obtained several tons of extremely high ash (37%) Indian coal from DOE-FETC in Pittsburgh. This coal was used in the 16th test in this project in late January. Gypsum was injected with the coal. Excellent combustion and slag flow was obtained. In addition, the high ash levels reduced the thermal load on the combustor wall. **Of greater significance was the observation that of 20% of the sulfur content of the gypsum reported to the slag**.

With this test, the required and planned 16 tests in this project have been completed. However, in view of the excellent results with the Indian coal, further tests are planned with this coal in the next quarter. The test objective will be to further increase the sulfur content of the slag with gypsum injection and to attempt to increase the sulfur capture in the combustor and its retention in slag.

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 up to 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 will be increased 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 will 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, 2/2/97, all 16 tests have been completed and almost all 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 have been met as of the end of the present reporting period. This 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 March 1997, a total of 74 days of tests, of which 16 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. The 16th and final required test for the present project was completed in the present reporting period, the first quarter of 1997.

It will be recalled that the objective of this 24 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, preferably 500 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 entire effort consisted of a series of 16 parametric tests in a 20 MMBtu/hr slagging, air cooled, cyclone combustor. During the present quarterly reporting period ending March 31,1997, the final originally planned test in this project was implemented. This brings the total tests to the 16 planned for this project. In addition, a total of 16 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.

The following discussion elaborates the one test in this quarter.

Project Tests No.16, January 28,1996:

In early January, Coal Tech obtained almost 4 tons of extremely high ash (37%) Indian coal from DOE-FETC storage in Pittsburgh. Part of the coal was tested on the 20 MMBtu/hr combustor on January 23, and slagging was excellent with large pieces interspersed with the more usual small pieces of slag. The coal feed rate was 1180 lb/hr, resulting in an ash injection rate of 440 lb/hr of coal ash plus fluxing materials. Consequently, it was decided to inject gypsum with the coal in the next test as part of the present project. This test was performed on the 28th. During the first part of the test the same high rate of slag flow as obtained in the previous test was

observed. As the gypsum was injected, the slag flow rate slowed until it stopped completely. Nearly one ton of coal was burned. Subsequent to the test, the slag quench tank was drained and the entire slag removal duct was filled with about 100 lbs of slag. Furthermore, in the next test on January 31st on the parallel project using a low ash US coal, a substantial amount of slag was released early during the test which came from deposits of slag from the Indian coal test of the 28th.

The following Table shows the partitioning of mineral matter in the slag in the combustor during the test of the 28th.. For all three test conditions, the Indian coal feed rate was 1180 lb/hr. Condition #1 was the base line condition during which 200 lb/hr of limestone was injected. The CaO from the limestone is shown in the second column. The 2nd and 3rd test condition, involved the injection of limestone at 150 lb/hr and gypsum at 100 lb/hr. Note that the gypsum also contained 18% free water. The CaO contribution from the gypsum is shown in the third column. The next three columns show the percentages by weight of silica, alumina (from the coal ash) and the calcia (from the limestone and gypsum) that would have reported to the slag, if all the mineral mater partitioned to the slag as injected. The next lower row, shows that actual percentages measured in the slag samples. Considering that random samples were taken, the agreement between the various metal oxides is reasonably good. Note that the analytical method used by the outside slag analysis laboratory to measure CaO generally under-reports the actual CaO content.

The next columns show the expected sulfur percentages in the slag if all the sulfur reported to the slag as injected. Since test condition #1 clearly shows that none of the sulfur in the Indian coal reported to the slag, another column has been added showing the amount of sulfur in the slag from the gypsum only, excluding the coal sulfur.

Test Cond.	CaO fr. limestone, #/h	CaO fr. gypsum #/h	Ash Total #/h	SiO2, %	Al2O3, %	CaO, %	Sulfur, inc.coal,%	Sulfur w/o Coal S, %	
#1	112	0	540	31%	14%	22%	1%		Theory
#1				45%	19%	14%	0.01%		Measure
#1							0%		%S in slag
#2	84	27	539	31%	14%	22%	4.49%	3.55%	Theory
#2				37%	17%	15%	0.71%	0.71%	Measure
#2							16%	20%	%S in slag
#3	84	27	539	31%	14%	22%	4.49%	3.55%	Theory
#3				42%	18%	19%	0.33%	0.33%	Measure
#3							7%	9%	%S in slag

The second test condition was drawn from a slag sample taken in the course of the test as the slag flowed out of the slag tap onto the slag conveyor belt located in the water filled slag tank.

The third test condition was from a sample of slag that remained stuck in the slag chute and was removed after the test was completed. This last slag sample remained at higher

temperature in the slag chute and it was not immediately quenched in the water, as was the case with the second sample. Therefore as anticipated, some of the sulfur evolved from this slag.

The key result from this analysis is that 20% of the sulfur in the injected gypsum remained in the slag. This is the highest number recorded in this project, and it is far higher that in all previous tests with injection of either gypsum or plaster of Paris, where the quantity of sulfur retained in the slag was at best a few percent. It is also by a factor of two, the highest level of sulfur in slag measured in several 1000 hours of operation of this combustor beginning in 1997.

Measurement of the stack SO2 gas sampled in the stack outlet of the boiler yielded about 60% of the coal and gypsum sulfur in the gas Phase. A random sample of fly ash taken after this test shows that its sulfur content was about 0.8%. Based on overall mass balances for this combustor, an average of about 1/3 of the mineral matter reports to the baghouse. On this basis only about 27% of the coal sulfur reported to the fly ash. Thus the sulfur mass balance for this tests is 60% to the gas phase, 16% to the slag, and about 9% to the fly ash. Since the test was of limited duration of several hours, a completely quantitative sulfur mass balance cannot be obtained. However, the present result clearly shows that sufficiently high slag mass flow rate results in significant sulfur retention in slag. It is interesting that the slag mass flow rate that resulted in this sulfur retention was in the range of 400+ lb/hr predicted at the start of this project.

2.3. EFFORT OF THE NEXT QUARTER

Since there remains a little over 1 ton of Indian coal, it is planned to perform at least one additional test with gypsum injection to further optimize the sulfur retention in slag. A request has been made to the DOE representative in New Delhi, India, for additional coal for further tests. Also, the feasibility of obtaining fine, high ash coal mine waste from Western PA will be explored. It is now clear that the procedure for high sulfur retention in slag has been demonstrated. However, further work is needed on the possibility of combining the sulfur capture process with the slag retention process.

3. CONCLUSIONS:

The 16th test performed during the present quarterly reporting period has demonstrated that a very high ash coal can retain a substantial quantity of sulfur in the slag. Further tests are planned to increase the degree of sulfur retention by another gypsum injection test in the Indian coal. Also, the data obtained to date will be evaluated to determine is conditions can be achieved in which both sulfur capture and retention can be combined inside the combustor