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

Fifth Quarterly Technical Progress Report

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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. In the present quarterly reporting period, 10 days of combustor tests were performed, bringing the total number of tests performed to 15. A wide range of operating conditions were tested including injection of metal oxide powders to achieve total mineral injection rates in excess of 400 lb/hr at coal mass flow rates of around 1000 lb/hr. It was determined that efficient sulfur capture requires calcium oxide particle sizes that are too small to be effectively retained in the combustor. On the other hand, injection of coarse calcium sulfate particles into the combustor sharply increased the slag viscosity, thereby reducing the slag flow rate and causing substantial reevolution of the sulfur in the slag. It is tentatively concluded that conditions necessary for sulfur capture with sorbents and its retention in the slag cannot be efficiently achieved in one step in a cyclone combustor. It is further concluded that due to the increases in slag viscosity by calcium sulfate extremely high slag mass flow rates are required for sulfur retention in slag. Further tests in that direction are planned for the next quarterly reporting period.

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10. 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 parametric tests in a 20 MMBtu/hr slagging, air cooled, cyclone combustor. During the present quarterly reporting period ending December 31,1996, 10 tests in this project were implemented, bringing the total test days to 15. In addition, a total of 5 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.

7 of the 10 tests in this period were performed in October. The first group of tests continued the effort begun in the previous month in which an artificial ash consisting of a 50-50 mixture of silica and alumina coarse (100+ microns) powder was mixed with calcium hydrate (10 micron mean diameter) to achieve a high slag mass flow rate. The purpose of the test was to increase the slag mass flow rate in order to better retain sulfur in the slag.

In the 6th test on October 7th, calcium hydrate in a ratio of 1 to 1 was mixed with the above alumina-silica mixture. This mixture was mixed pneumatically with the coal and injected at a total rate of 300 lb/hr. The coal feed rate of 1080 lb/hr added 150 lb/hr of coal ash. Over 50% SO2 reduction was measured at the stack outlet from the boiler with the mixture injection. However, almost no sulfur reported to the slag. Analysis of the slag composition revealed that a substantial fraction of the injected calcium hydrate was blown out of the combustor. Therefore most of the reacted sorbent was collected in the baghouse. Ash samples from the baghouse were taken, and they showed elevated sulfur concentrations. However, these ash samples were grab samples and they cannot be correlated to the conditions in the combustor

The 7th tests on 10/14/96 was under similar conditions as the previous tests, except the coal feed rate was increased to 1180 lb/hr. Here for the first time over 95% SO2 reduction was measured with a gas sampling probe located near the far side wall of the boiler furnace. The SO2 measured at the stack outlet of the boiler was substantially higher. It was speculated at the time that this could have been due to uneven gas flow in the boiler furnace or possible blockage of the boiler gas probe. This test was terminated prematurely due to slag tap blockage.

The 8th test on 10/16/96 was partly a repeat of the previous test to validate the prior results. Feeding non-uniformity resulted in several flameouts due to blinding of the flame detectors. Here again the pattern of higher SO2 reduction at the boiler furnace gas probe compared to the boiler stack outlet was measured.

The 9th test on 10/17/96 focused on increasing the calcium hydrate injection rate above the 150 lb/hr in the previous two tests. This was accomplished by injecting calcium hydrate with the coal and injecting limestone separately. The hydrate feed procedure was modified to achieve a higher feed rate. At the higher feed rates, slagging in some cases became very poor and partial slag induced blockage of the exit nozzle developed. Nevertheless, calcium hydrate feed rates up to 350 lb/hr were achieved. Here again the SO2 sampled in the boiler furnace was 3 times lower than at the boiler stack outlet.

The 10th test on 10/30/96 was similar to the previous one, and calcium hydrate at 250 lb/hr were achieved. Here again the boiler probe SO2 was 3 times lower than at the stack. The oxygen level in the boiler was lower than at the stack boiler outlet. To eliminate combustion air leakage through cracks in the water tube wall separating the furnace box from the convective box, these cracks were patched with refractory material in early November. This test was significant in that good slag flow was obtained with calcium hydrate only, without the addition of limestone to condition the slag.

In view of the result that much of the hydrate is blown out of the combustor, the 11th test on 10/31/96 was planned with limestone only injection. Coal at 980 lb/hr was injected with 220 lb/hr of limestone. The objective was to take achieve a much higher particle retention in the combustor slag due to the larger limestone particle size. This was offset by the lower sulfur capture capability of limestone compared to calcium hydrate. Even with the limestone, good SO2 reductions were measured in the boiler and boiler stack outlet. Here again the former SO2 levels were substantially lower than the latter.

The 12th test on 11/13/97 was to determine the effectiveness of both sulfur capture in the combustor with retention of the reacted sorbent in the slag. Low ash, 6.14%, and low sulfur, 1.47%, coal at rates of 820, 980, and 1080 lb/hr was used. The limestone injection rates were 80, 90 and 100 lb/hr, the calcium hydrate rate was 150 lb/hr. The Ca/S ratios was 1.98 and 2.37 for limestone only, and 5.17 and 6.31 for the combined limestone and hydrate injection. The stoichiometric ratio, SR1, in the combustor averaged 1.09, i.e. fuel lean. The SO2 reduction at the stack probe ranged from 19% to 60%, while in the boiler it ranged from 77% to 97%. In terms of lb/MMBtu, the ranges are from 0.01 to 1.59 lb/MMBtu.

The purpose of the 13th test on 11/15/96 was also to determine the effectiveness of both sulfur capture in the combustor with retention of the reacted sorbent in the slag. In order to assure a higher percentage of sulfur retention in the slag, aluminum oxide powder was injected with the sorbent in order to increase the slag mass flow rate. Low ash, 6.26%, and low sulfur, 1.47%, coal at a rate of 980 lb/hr was used. The limestone injection rates were 70, 100, and 120 lb/hr, the calcium hydrate rate were 75 and 150 lb/hr, and the alumina rate was 110 lb/hr. The stoichiometric ratio in the combustor, SR1, was 1.06, i.e. fuel lean. The Ca/S ratios ranged from

1.62 and 2.33 for limestone only, to 4 and 7.54 for the combined limestone and hydrate injection. The SO2 reduction in the stack ranged from 27% to 58%, while in the boiler it ranged from 55% to 97%. In terms of lb/MMBtu, the range is from 0.06 to 1.37 lb/MMBtu. As reported for the other tests, the reason for the very high reduction in the boiler is not known.

The purpose of the 14th test on 11/19/96 was to operate the combustor under conditions of high sulfur capture with calcium hydrate injection and at high slag mass flow rates. This condition was achieved by mixing alumina and silica powder with calcium hydrate in the mass ratio of 1/1/2 of Al2O3/SiO2/Ca(OH)2. The coal feed rate was 980 lb/hr with 1.3% sulfur and 5.44% ash content. In addition, limestone at 100 lb/hr was injected. The total mineral matter injection mass flow rate for this condition was 285 lb/hr. As in the other tests in this series, the low ash content of the coal resulted in excessively high CaO concentrations in the mineral mixture, which resulted in high slag melting temperatures. Also due to the very low sulfur content of the coal, the Ca/S mol ratio from the hydrate was 3.4, while with the added limestone it was 5.9. The sulfur capture measured both in the boiler and in the boiler stack was very high. Sulfur reductions as high as 79% were measured in the stack and as high as 99% were measured in the boiler. This stack measurement corresponds to 0.19 lb/MMBtu. A brief minutes long test period was performed with injection of the mixture at 295 lb/hr, and here the SO2 reduction in the stack reached 89%.

The NOx emission at the boiler probe was reduced from 0.76 lb/MMBtu when the combustor stoichiometry was 1.1, i.e. fuel lean, to 0.34 lb/MMBtu with SR1 at 0.79, a fuel rich condition.

Analysis of one slag sample taken during this test showed that the bulk of the calcium hydrate particles were blown out of the combustor in that the CaO content of the slag was in better agreement with this assumption than with one in which all mineral matter reported to the slag in proportion to the ratios of injected materials.

The purpose of the 15th and final tests in this period on 11/21/96 was to determine sulfur in slag retention by injecting gypsum, $CaSO_4.2H_2O$, into the combustor. In the first test in this project in which gypsum was also injected the results showed that the calcium sulfate appeared to sharply increase the slag viscosity and very poor slagging was observed. Also it was deduced from the stack gas sampling that a substantial fraction, 70%, of the sulfur in the gypsum evolved in the gas phase as SO2. That coal in the first test in May 1996 was a high sulfur, 2.7%, coal, and the percentage of SO2 due to the gypsum was obtained by subtracting the contribution of the coal sulfur, assuming that it all had been converted to SO2.

In the present test a very low sulfur, 1./3%, coal was used, and the contribution of this sulfur to the total SO2 in the stack gases was a small fraction of the total sulfur injected with the gypsum. The coal feed rates were 820 lb/hr, 980 lb/hr and 1060 lb/hr. Limestone was injected at 75 lb/hr, this yielded an average Ca/S mol ratio of 1.89. Commercial garden gypsum, containing 12% free moisture was added at the rate of 200 lb/hr. As in the first gypsum test, slagging was very erratic. The sulfur in the gypsum was released into the gas phase at ranges from 36 to 48% for the boiler probe, and from 60% to 73% for the stack probe. This result was anticipated because the poor slag flow resulted in long residence times for the gypsum in the slag which allowed sulfur evolution.

In all the first 9 tests in this 10 test series, the sulfur content in the slag was negligible. In the gypsum injection tests, 14% of the injected sulfur remained in the slag drawn from the combustor. This level is more than adequate to retain all the coal sulfur at sufficiently high slag mass flow rates. However, the results of all the tests to date showed that operational issues such as the nature of the injected material, the mode of material injection, and the physical properties of the injected materials determine the slag mass flow rate. Since most of the present tests were performed with low ash coals, the mineral mass flow rate had to be augmented by injection of mineral additives. It is much more preferable to injected a very high ash (i.e. 30% to 50%) coal combined with a sulfur capture sorbent. Tests along this line are planned for the next quarter.

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 December 1996, a total of 57 days of tests, of which 15 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. 10 of the 15 tests to date on the present project were completed in the present reporting period, the fourth quarter of 1996.

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 consists of a series of up to 16 parametric tests in a 20 MMBtu/hr slagging, air cooled, cyclone combustor. During the present quarterly reporting period ending December 31,1996, ten tests in this project were implemented, bringing the total tests to 15. In addition, a total of 5 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 first four tests in this project that were performed in previous quarters, were part of the first group of tests in which calcium sulfate were injected into the combustor. As reported previously, the first test with gypsum was unsuccessful. This was attributed to the high water content in the commercial gypsum used. Consequently, in the second test, plaster of Paris (p.o.p.), $CaSO4. 0.5H20$, with only 6.2% water content, was injected. 120 lb/hr of limestone for slag conditioning and an additional 136 lb/hr of plaster of Paris was injected. Based on the stack $SO2$ measurements, only 12% of the sulfur in the plaster of Paris was released into the gas phase in the combustor. Slagging was very poor with the addition of p.o.p. and it was deduced that the calcium sulfate from the p.o.p. was depositing as slag on the combustor walls and remaining on the wall. However, only 6.7% of the combined coal and p.o.p. sulfur remained in the slag sampled from the flow out of the slag tap. Also, the grab samples of fly ash in the baghouse yielded only 4.5% sulfur concentration. This was much less than the anticipated concentration from the stack SO2 measurement. Note however, that the fly ash grab sample was taken at the end of the test and it is not a real time sample than can be time correlated with the slag sample.

The next series of tests with plaster of Paris (i.e. calcium sulfate) were designed to achieve higher slag mass flow rate in the combustor. In the first of these tests, the injection locations was changed to achieve a higher injection rate of plaster of Paris, and a 150 lb/hr rate was achieved. The results still showed very little sulfur in the slag.

Since the total injected ash mass flow rate in this test was 240 lb/hr, (assuming total evolution of the sulfur from the plaster of Paris), the next test was designed to increase the total ash mass flow rate by injecting an artificial "ash" consisting of a 50/50 (by weight) mixture of silica and alumina. This mixture was further mixed with an equal quantity of plaster of Paris. This resulted in a total injected ash flow rate of 328 lb/hr, again assuming total evolution of the SO2 in the p.o.p. Here again the sulfur in the slag was very low, which was attributed to the fine particle size (under 10 microns) of the p.o.p. blowing out of the combustor.

Consequently, it was decided to stop any further tests with calcium sulfate injection (i.e. p.o.p.) and implement further tests with calcium hydrate as a sorbent for sulfur capture. However, to retain the high slag mass flow rate, the hydrate was mixed with the artificial "ash" of alumina/silica. While better sulfur reductions were measured in the stack gases, the slag analysis showed that the fine particle size of calcium hydrate resulted in almost complete carryover of these particles into the combustor exhaust.

Since considerably higher sulfur concentrations were achieved in tests in the other project with only sorbent injection, the focus of the tests in the present (4th quarter of 1996) was on high sulfur capture with high rates of sorbent injection.

The following discussion elaborates on the tests in this quarter.

Project Tests No.6 to 12, October 1996:

The next seven tests were performed on October 7, 14, 16, 17, 23, 30 and 31. As reported in the previous Quarterly Report, the tests to date have not succeeded in producing high sulfur retention in the slag drained from the combustor. The results have clearly shown that the steps needed for capture of the sulfur gas emissions inside the combustor by a calcium based sorbent are apparently incompatible with the conditions needed to retain this reacted sorbent inside the slag. The best sulfur capture is obtained with very fine particles (under 10 microns in diameter) which are too small for efficient capture on the slag covered walls of the combustor

Despite this incompatibility between sulfur capture and slag retention, it should still be possible to retain a significant percentage of the sulfur in the slag if a sufficiently high slag mass flow rate can be developed inside the combustor. A substantial part of the effort on these seven tests was focused on this objective.

As reported previously, based on data on desulfurization of slags and theoretical slag flow analysis, the slag residence time in the combustor should be under 5 minutes. This requires a slag mass flow rate approaching 500 lb/hr for the present combustor. The coals used in the present tests had an ash content in the 5% to 14% range which resulted in a maximum ash flow rate of 168 lb/hr at the peak 1200 lb/hr coal rate used to date. Also, the sulfur content in the coal ranged from 1.3% to 3.6%. With the addition of calcium hydrate and limestone the mineral flow rate has been increased to the 400 lb/hr range. In prior tests in this combustor in Williamsport, coal fly ash had been mixed with these sorbents and which yielded total mineral flow rates above 600 lb/hr. However, fly ash particles are mostly less than 10 microns where particle retention in the combustor is very low.

The present 7 tests in October continued the effort begun in the previous month in which an artificial ash consisting of a 50-50 mixture of silica and alumina coarse (100+ microns) powder was mixed with calcium hydrate (10 micron mean diameter) to achieve a high slag mass flow rate.

In the 6th test on October 7th, calcium hydrate in a ratio of 1 to 1 was mixed with the above alumina-silica mixture. This mixture was mixed pneumatically with the coal and injected at a total rate of 300 lb/hr. On calcination in the combustor, the net mineral injection rate decreased to 264 lb/hr. The coal feed rate was 1080 lb/hr, which resulted in an additional 150 lb/hr mineral matter injection from the coal. This yielded a total mineral injection rate of 414 lb/hr. Attempts to increase the <u>mixture injection rate</u> to 400 lb/hr had to be rapidly terminated as it led to almost immediate flameouts resulting from blinding by the injected powder of the flame detectors.

Over 50% SO2 reduction was measured at the stack outlet from the boiler with the mixture injection. However, almost no sulfur reported to the slag. Analysis of the slag composition revealed that a substantial fraction of the injected calcium hydrate was blown out of the combustor. Therefore most of the reacted sorbent was collected in the baghouse. Ash samples from the baghouse were taken, and they showed elevated sulfur concentrations. However, these ash samples were grab samples and they cannot be correlated to the conditions in the combustor

The 7th tests on 10/14/96 was under similar conditions as the previous tests, except the coal feed rate was increased to 1180 lb/hr. Here for the first time over 95% SO2 reduction was measured with a gas sampling probe located near the far side wall of the boiler furnace. The SO2 measured at the stack outlet of the boiler was substantially higher. It was speculated at the time that this could have been due to uneven gas flow in the boiler furnace or possible blockage of the boiler gas probe. Due to the high slag mass flow rate <u>and</u> non-optimized slagging conditions, the slag tap blocked and the test had to be terminated before all test parameters could be measured.

The 8th test on 10/16/96 was partly a repeat of the previous test to validate the prior results. Feeding non-uniformity resulted in several flameouts due to blinding of the flame detectors. Here again the pattern of higher SO2 reduction at the boiler furnace gas probe compared to the boiler stack outlet was measured.

The 9th test on 10/17/96 focused on increasing the calcium hydrate injection rate above the 150 lb/hr in the previous two tests. This was accomplished by injecting calcium hydrate with the coal and injecting limestone separately. The hydrate feed procedure was modified to achieve a higher feed rate. At the higher feed rates, slagging in some cases became very poor and partial slag induced blockage of the exit nozzle developed. Nevertheless, calcium hydrate feed rates up to 350 lb/hr were achieved. Here again the SO2 sampled in the boiler furnace was 3 times lower than at the boiler stack outlet.

The 10th test on 10/30/96 was similar to the previous one, and calcium hydrate injection at 250 lb/hr was achieved. Here again , the boiler probe SO2 was 3 times lower than at the stack. The oxygen level in the boiler was lower than at the stack boiler outlet. It was suspected that combustion air might be leaking through possible cracks in the water tube wall separating the furnace box from the convective box. Internal inspection of the combustor subsequent to these tests confirmed the existence of cracks in this wall, and this was patched with refractory material in early November.

This test was significant in that good slag flow was obtained with calcium hydrate only, without the addition of limestone to condition the slag.

In view of the result that much of the hydrate is blown out of the combustor, the 11th test on 10/31/96 was planned with limestone only injection. Coal at 980 lb/hr was injected with 220 lb/hr of limestone. The objective was to take achieve a much higher particle retention in the combustor slag due to the larger limestone particle size. This was offset by the lower sulfur capture capability of limestone compared to calcium hydrate. Even with the limestone, good SO2 reductions were measured in the boiler and boiler stack outlet. Here again the former SO2 levels were substantially lower than the latter.

There are several possible explanations for the apparent higher sulfur capture in the boiler furnace. One is gas non-uniformity that result in a dead gas space where the boiler probe is located. Another is partial blockage of the probe gas passage by ash particles. Another is bypass of combustion gases from the upstream furnace section through leaks in the convective section wall to the stack. As noted this wall was patched at the beginning of November. However, as will be shown below no change in the previously observed difference in SO2 between boiler probe and stack probe was noted in the November tests.

As noted, as the mineral feed rates were increased, false flameouts were experienced due to blinding of the several flame detectors. As a result, modifications to the flame control circuits were implemented to reduce this problem.

Also, the fairly high mineral injection rates resulted in some problems with the slag tap operation which was aggravated by the high variability in the composition of the injected material. Nevertheless, in only one test was early termination of the test required due to a blocked slag tap.

Extensive combustor exit nozzle blockage with slag was experienced in several of the tests. In some cases it was possible to clear the blockage by changing operating conditions, and in two cases a water cooled pipe was inserted into the boiler to break the slag layer across the exit nozzle outlet. This blockage is attributed to the operating conditions, namely, the total thermal input and the magnitude and nature of the injected solid materials. Specifically, at higher thermal inputs the blockage cleared itself, while with higher metal oxide particle injection rates, the blockage rate increased.

The following tables summarize some of the results of the October 1996 tests.

Table 1: Boiler Outlet and Stack Gas Samples for the 7th test on 10/14/96t

Time	11:45	12:15	12:20	13:00	13:15	13:20	13:20
Location	Stack	Stack	Boiler	Stack	Boiler	Stack	Boiler
Coal Rate, #/h	1180	1180	1180	980	980	980	980
Limestone, #/h	75	0	0	0	0	0	0
Ca(OH)2,#/h	0	150	150	150	150	150	150
SiO2/Al2O3,#/hr	0	150	150	150	150	150	150
O2-Experiment-%	8.4	6.9	7.5	7.7	6.3	7.4	5.7
SO2 (Theory), ppm	1712	1889	1802	1644	1799	1638	1846
SO2 (Exper.),ppm	1550	1078	667	594	198	660	360
SO2(Ex)/SO2(Th),%	**91**	**57**	**37**	**36**	**11**	**40**	**20**
Ca/S mol ratio	**0.7**	**1.8**	**1.8**	**2.1**	**2.1**	**2.1**	**2.1**

The results in table 1 were obtained with 3.1% sulfur coal, and with injection of calcium hydrate and a mixture of alumina and silica. The latter simulated an artificial ash. As noted in this test, the calcium hydrate produced high SO2 reduction even at low Ca/S mol ratios. Also as noted, the boiler probe yielded substantially higher SO2 reductions.

The analysis of the slag sample taken during this test is shown in Table 2.

Table 2: Analysis of the Slag From the Combustor in Test No.7 on 10/14/97

Slag Composition	Time	SiO2	Al2O3	CaO	Sulfur in Slag	Injected minerals ,#/h
Coal Ash +CaO from Ca(OH)2& AL2O3/SiO2- Theory-%	12:30	31	27	**27**	**8.7**	**417**
Slag Sample Analyzed-%	12:30	30.5	29.6	**8.9**	**0.16**	
Coal Ash +CaO from CaCO3 and CaSO4-Theory-%	13:00	30.5	27.6	29	**8.65**	**355**
Slag Sample Analyzed-%	13:00	34.8	37.1	**12**	**0.06**	

The slag samples in table 2 show clearly that most of the CaO from the calcium hydrate particles are blown out of the combustor and do not report to the slag. This explains the low sulfur content of the slag, despite the very high injected mineral materials rate of about 400 lb/hr. The sulfur content of the fly ash drawn from the barrel that collected this ash from the baghouse was only about 13% of the coal sulfur, assuming that one-third of the fly ash and two-thirds of the CaO reported to the baghouse. Thus a sulfur balance in the entire combustion flow train has not been obtained.

A similar result was obtained in the slag samples taken in the other tests in October, and they will not be shown here.

Figures 1 and 2 show the SO2 reduction obtained in tests No. 10 (10/30/96) and No.11 (10/31/96). As noted above, the first test was with calcium hydrate injection only at a high rate of 250 lb/hr and coal at 1080 lb/hr in a nominal 2.3% sulfur coal. In the second test, the limestone injection rate was 220 lb/hr with the coal rate at 820, 980, and 1180 lb/hr. The coal sulfur was about 1.8%.

As noted above, the SO2 reduction in the boiler is substantially greater than at the stack. Possible explanations were given above, but no conclusive explanation has as yet been obtained. Figure 1 also shows that relatively little additional reduction is obtained in the stack as the Ca/S mol ratio increases above 3. Comparing figures 1 and 2 one notes that the limestone is less effective than the hydrate and as in the case of the hydrate, additional limestone has no effect above a Ca/S of 4. Finally, in both tests, the amount of sulfur in the slag measured was in the range of a few tenth's of one percent.

Figure 1: % SO2 Reduction vs Ca/S Mol Ratio-10/30/96 Test

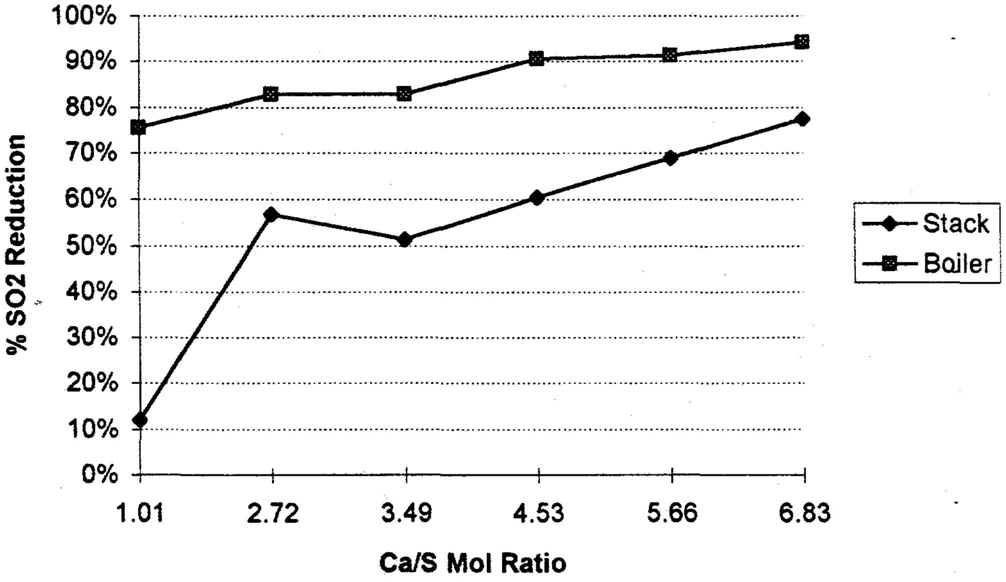
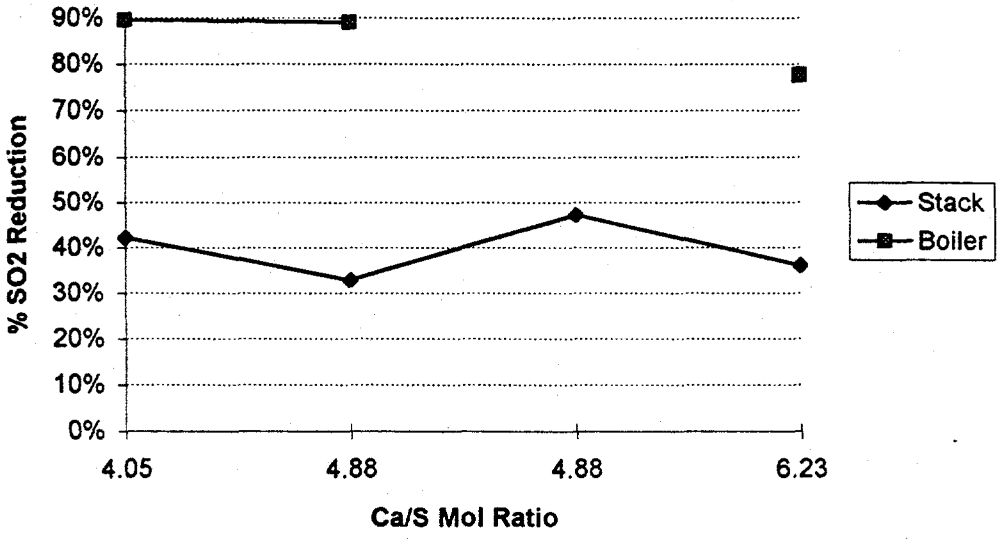


Figure 2: % SO2 Reduction vs Ca/S Mol Ratio-10/31/96 Test

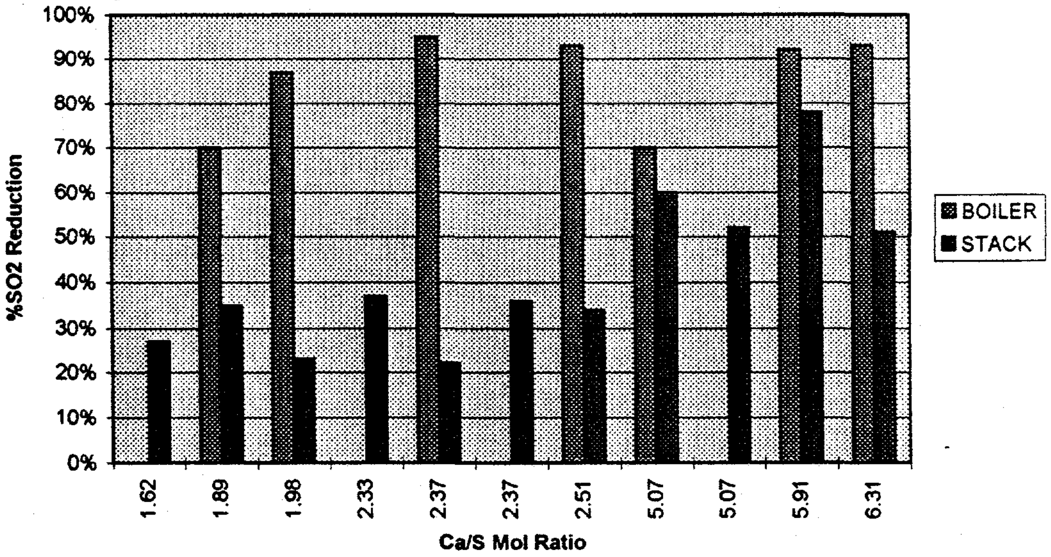


Project Test No. 12, Nov.13, 1996

The purpose of this test was to determine the effectiveness of both sulfur capture in the combustor with retention of the reacted sorbent in the slag. The test was performed with low ash, 6.14%, and low sulfur, 1.47%, coal at rates of 820, 980, and 1080 lb/hr. The coal HHV was 13,830 Btu/lb. Due to the low ash content of the coal , the injection of limestone and calcium hydrate increased the theoretical content of the CaO to 50% where the slag melting temperature is high. The limestone injection rates were 80, 90 and 100 lb/hr, the calcium hydrate rate was 150 lb/hr. Table 3 summarizes some of the test conditions and results. Combustion gas samples were measured in the furnace section of the boiler and in the stack outlet of the boiler. The stoichiometric ratio, SR1, in the combustor averaged 1.09, i.e. fuel lean, with a range from 1 to 1.16, and one brief condition at 0.91, fuel rich. The total SR2 in the furnace ranged from 1.46 to 1.71. The Ca/S ratios was 1.98 and 2.37 for limestone only, and 5.17 and 6.31 for the combined limestone and hydrate injection. However, since limestone has been found to be about 1/3 as effective as hydrate as a sorbent, the effective Ca/S mol ratio was for the latter two cases was 3.49 and 5.12. Figure 3 shows a summary of the SO2 reduction versus Ca/S for limestone and the Ca/S for the combined sorbents averaged for each tests performed in November 1996, namely tests No.12 to No.15. Note that the Ca/S mol ratios are the actual values, i.e. the limestone Ca/S ratio has not been reduced by a factor of 3 to account for its lower sulfur capture capability. The SO2 reduction at the stack probe for Test No.12 ranged from 19% to 60%, while in the boiler it ranged from 77% to 97%. In terms of lb/MMBtu, the ranges are from 0.01 to 1.59 lb/MMBtu.

In addition to the probe inserted through the rear boiler wall on the far side from the convective section to a distance of about 4 feet from the rear boiler wall, a second water cooled sampling probe was inserted through the rear boiler wall to a location about 4 feet from the exhaust from the combustor. The internal boiler furnace is about 10 feet long. Both these probes were in general agreement with each other, especially with respect to the SO2 data. However, late in the test , one of the three particulate filters in the gas sampling line was removed from the boiler sampling line and the SO2 reduction at that time 3:35 PM, was only 70%, compared to 60% for the same condition in the stack. This compares with a 96% reduction in the previous sample at 2:52 PM. It is thus possible that the filter was blocked with particulates from the combustion gases. However, the NOx emissions was also lower in the boiler, 0.47 lb/MMBtu versus 0.69 lb/MMBtu at the stack. Also the oxygen concentration in the stack is higher 8.1% versus 7.4%. The last item can be explained by air infiltration into the boiler which is under negative draft of several inches water gage. However, the higher NOx level can only be due to infiltration of gases directly from the combustor to the stack through cracks in the convective - furnace section refractory wall or through a bleed line in the combustor. The latter has been found to increase SO2 emissions in the stack by 20% when a valve in a bleed line from the combustor to the stack was opened. Therefore it appears that the lower SO2 and NOx levels in the furnace probe location are real effects, whose explanation at present is not clear.

Figure 3: % SO2 Reduction versus Ca/S Mol Ratio-November 1996



The results in figure 3 will be discussed further during the presentation of the results of the other three November tests. At this time it is to be noted that the average SO2 reduction in the November tests, as measured at the stack, was somewhat lower than in the late October tests, as shown in figure 1 and 2. Both test groups were performed with low sulfur coal (1.5%<S<2.4%). However, there was some differences such as the mix of limestone and calcium hydrate, which is much more effective in capturing sulfur, and the coal feed rate, and the use of 10 gal/hr of oil in the October tests. The data were not analyzed to find the impact, if any, of these differences. Also, the fluid mechanical effects of mixing of the coal, sorbent and air are most probably important in explaining the differences in the results. As noted, different injection locations were used in several of the tests. All these parameters need to be evaluated before final conclusions can be drawn. However, it can be stated with some certainty that to achieve the shown SO2 reductions does not require the very high Ca/S ratios shown in these figures.

Table 3: Analysis of the Slag From the Combustor in Test No.12, Nov. 13,1996

Slag Composition	Time	SiO2	Al2O3	Fe2O3	CaO	Sulfur in Slag	Injected minerals,#/h
Coal Ash +CaO from CaCO3 Theory-%	14:50	18	11	5	50	12	102
Slag Sample Analyzed-%	14:50	24	20	9	35	0.01	
Coal Ash +CaO from CaCO3 and Ca(OH)2-Theory-(w.hyd)%	13:25	10	7	3	71	7	**232**
Coal Ash +CaO from CaCO3 and Ca(OH)2-Theory-(w/o hydrate in slag)%	13:25	20	13	6	44	13	118 (assume w/o hyd in slag
Slag Sample Analyzed-%	13:25	22			39	0.12	

Table 3 shows the slag analysis for this test. The sample at 14:50 where only limestone was injected is consistent with other tests which show that aluminum oxide leached from the combustor wall enhances this material in the slag.

The sample at 13:25 in which 150 lb/hr of calcium hydrate was injected with 80 lb/hr of limestone agrees well if one assumes that almost all the hydrate was blown out of the combustor. This has been reported previously in that the small hydrate particles whose mean size is under 10 microns are blown out of the combustor. The implication of this result is that sulfur capture and retention in the slag cannot be implemented in one step because the hydrate will not be retained in the combustor. The same result was obtained in the samples taken at 12:30 and 12:09. In both cases no evidence of the 150 lb/hr of calcium hydrate is found in the slag.

During this tests substantial deposits of slag occurred during periods of high injection rates which nearly closed the exit nozzle of the combustor. It was therefore necessary to break these deposits loose on several occasions during the tests to allow continued operation.

Project Tests No. 13, Nov.15, 1996

The purpose of this test was also to determine the effectiveness of both sulfur capture in the combustor with retention of the reacted sorbent in the slag. In order to assure a higher percentage of sulfur retention in the slag, aluminum oxide powder was injected with the sorbent in order to increase the slag mass flow rate. The test was performed with low ash, 6.26%, and low sulfur, 1.47%, coal at a rate of 980 lb/hr, whose HHV was 13,900 Btu/lb. Due to the low ash content of the coal , the injection of limestone and calcium hydrate increased the theoretical content of the CaO to 50% where the slag melting temperature is high. The limestone injection rates were 70, 100, and 120 lb/hr, the calcium hydrate rate were 75 and 150 lb/hr, and the alumina rate was 110 lb/hr. Combustion gas samples were measured in the furnace section of the boiler and in the stack outlet of the boiler.

The stoichiometric ratio in the combustor, SR1, was 1.06, i.e. fuel lean, and the total SR2 in the furnace was 1.53. The Ca/S ratios ranged from 1.62 and 2.33 for limestone only, to 4 and 7.54 for the combined limestone and hydrate injection. However, since limestone has been found to be about 1/3 as effective as hydrate as a sorbent, the effective Ca/S mol ratio for the latter two cases was 2.92 and 5.68. These SO2 results are included in the data shown in figure 3 for November, 1996. The SO2 reduction in the stack ranged from 27% to 58%, while in the boiler it ranged from 55% to 97%. In terms of lb/MMBtu, the SO2 emmision range is from 0.06 to 1.37 lb/MMBtu. As reported for the other tests, the reason for the very high reduction in the boiler is not known. It has been noted that the readings initially shoot up to a high value and then gradually decrease to a very low value. For example, in the boiler gas sample at 12:45 AM, the initial reduction is 71% and the final reduction is 85%. This overshoot phenomena is not observed with the stack samples. Blockage of the gas sampling train in one of the particle filters, which could have been a factor in the previous test on 11/13/96 was eliminated by removing one of the three filters in the gas line.

Table 4: Analysis of the Slag From the Combustor in Test No.13, Nov. 15,1996

Slag Composition	Time	SiO2	Al2O3	Fe2O3	CaO	Sulfur in Slag	Injected minerals,#/h
Coal Ash +CaO from CaCO3 Theory-%	13:37	19	12	6	49	12	117
Slag Sample Analyzed-%	13:37	21	15	8	32	0.03	
Coal Ash +CaO from CaCO3 and Al2O3-Theory-%	13:07	10	54	3	25	6	227
Slag Sample Analyzed-%	13:07	17	24	6	33	0.05	

Table 4 shows the slag sample analysis at two conditions. With limestone injection only at 13:37 hours, the sample agrees reasonably well with the composition of injected material. The sample at 13:07 was taken when alumina powder was injected into the combustor, and the analysis clearly shows that most of this alumina remained in the combustor wall. This is not surprising in view of the high melting temperature of the alumina. In both slag samples the amount of sulfur in the slag is negligible, as would be expected from the low slag mass flow rates.

Project Test No 14. Nov.19, 1996

The purpose of this tests was to operate the combustor under conditions of high sulfur capture with calcium hydrate injection and at high slag mass flow rates. This condition was achieved by mixing alumina and silica powder with calcium hydrate in the mass ratio of 1/1/2 of Al2O3/SiO2/Ca(OH)2. Coal feed rate was 980 lb/hr with HHV of 13580 Btu/lb, 1.3% sulfur and 5.44% ash. In addition, limestone at 100 lb/hr was injected. The total mineral matter injection mass flow rate for this condition was 285 lb/hr. As in the other tests in this series, the low ash content of the coal resulted in excessively high CaO concentrations in the mineral mixture, which resulted in high slag melting temperatures. Also due to the very low sulfur content of the coal, the Ca/S mol ratio from the hydrate was 3.4, while with the added limestone it was 5.9. However, as the limestone is about 1/3 as effective as limestone, the maximum effective Ca/S was 4.2. The sulfur capture measured both in the boiler and in the boiler stack was very high. Sulfur reductions as high as 79% were measured in the stack and as high as 99% were measured in the boiler. This stack measurement corresponds to 0.19 lb/MMBtu, which is below the SO2 emission goal of 0.2 lb/MMBtu set for the parallel DOE sponsored project. As in the other tests, no conclusive explanation for the better performance of the boiler gas sampling location has been found. The data from this run is also incorporated in the results of figure 3, specifically it is the data at a Ca/S of 5.91, which shows very high SO2 reduction in both the boiler (79%) and the stack (92%).

A brief minutes long test period was performed with injection of the mixture at 295 lb/hr, and here the SO2 reduction in the stack reached 89%. In the absence of the mixture, the SO2 reduction in the stack was only 34% with only limestone at Ca/S mol ratio of 2.5, while in the boiler it was 94%.

The NOx emission at the boiler probe was reduced from 0.76 lb/MMBtu when the combustor stoichiometry was 1.1, i.e. fuel lean, to 0.34 lb/MMBtu with SR1 at 0.79, a fuel rich condition. The latter value is almost at the 0.3 lb/MMBtu that is set for the Philadelphia emission limit, and it is near the 0.2 lb/MMBtu set as a goal for the parallel DOE project. (Since NOx testing was not part of this project, the NOx data is reported in the parallel project's reports. NOx data was taken in all the tests in this project.)

Analyses of one slag sample taken during this test when the 200 lb/hr mixture was injected, at 11:45 AM, shows that the bulk of the calcium hydrate particles were blown out of the combustor in that the CaO content of the slag was in better agreement with this assumption than with one in which all mineral matter reported to the slag in proportion to the ratios of injected materials. The agreement with the injected silica concentration is not as good. However, this may have been due to non-uniform mixing of the three materials. As these results are similar to those shown for the previous two slag test analyses, they will not be shown here.

One difficulty in implementing this and all the tests during November, was the deposition of slag at the combustor exit nozzle outlet. This blocked the outlet to over 50% and it necessitated stopping injection while the slag was cleared with a ram from the rear of the boiler. This problem was most probably due to the slow melting rate of the relatively coarse (over 150 microns) of the injected silica and alumina powder. The original plan to injected fly ash was not implemented because the fly ash is under 10 microns in mean size and the bulk of this fly ash would blow out of the combustor, as was experienced in prior tests in Williamsport with the previous version of this combustor.

Project Test No.15: November 21, 1996

The purpose of this test was to determine sulfur in slag retention only by injecting gypsum, $CaSO_4.2H_2O$, into the combustor. In the first test in this project in which gypsum was also injected, the results showed that the calcium sulfate appeared to sharply increase the slag viscosity and very poor slagging was observed. Also it was deduced from the stack gas sampling that a substantial fraction, 70%, of the sulfur in the gypsum evolved in the gas phase as SO2. That coal in the first test in May 1996 was a high sulfur, 2.7%, coal, and the percentage of SO2 due to the gypsum was obtained by subtracting the contribution of the coal sulfur, assuming that it all had been converted to SO2.

In the present test a very low sulfur, 1.3%, coal was used, and the contribution of its sulfur to the total SO2 in the stack gases was a small fraction of the total sulfur injected with the gypsum. Stack samples were taken with a probe inserted in the rear corner of the boiler on the wall opposite to the convective tube bank. As already noted, this probe location was a "dead zone" as the gas flow turns toward the convective tubes at the rear of the boiler.

The other gas sampling probe was in the stack outlet from the boiler at a location near the top of the boiler. As discussed in connection with all other tests, the SO2 concentration from the boiler probe was substantially lower than from the stack probe. No conclusive explanation for this discrepancy has been found. One possible explanation is the placement of the probe in a dead gas zone, which allows additional reaction time between suspended sorbent particles and the sulfur gas. However, this conclusion is contradicted by the observation in one test where a 10 foot long water cooled sampling probe was inserted from the rear of the boiler to a location several feet downstream of the combustor gas exit nozzle. Here also a substantially lower SO2 concentration than in the stack was measured. Another explanation is that combustion gases infiltrate through a substantial number of cracks in the refractory placed between the boiler water wall tubes to separate the convective bank from the furnace in this D type design boiler.

That even small amounts of gas bypassing the furnace section can impact the stack SO2 concentration was observed when a small pipe that connects the combustor directly to the stack was opened to allow gas bleed into the stack. This bypass represents only 9% of the combustor exit nozzle cross-section. In several tests, the SO2 concentration in the stack rose by about 20% when this small bypass was opened. To limit this bypass effect, the cracks in the boiler furnace wall were sealed with refractory cement prior to the November 1996 tests. However, no substantial change in the difference between the boiler and stack gas sampling was observed. It is thus possible that other sources of infiltration such as cracks in the boiler enclosure which allow atmospheric air infiltration to the negative draft boiler to take place. That this takes place was observed by the consistently higher O2 content of the stack gas compared to the boiler sampling location.

In the present tests, the coal feed rates were 820 lb/hr, 980 lb/hr and 1060 lb/hr. At the two low coal rates, 20 gal/hr of oil was injected. In all the tests, 0.7 MMBtu/hr of propane pilot flame was used. The coal's HHV was 13,580, the ash content was extremely low, 5.44%, and the sulfur content was also very low, 1.3%. The thermal input was augmented by the addition of oil at 20 gal/hr with the addition of minute amounts of propane pilot gas, the resultant thermal input ranged from 14.64 to 16.81 MMBtu/hr. Limestone was injected at 75 lb/hr, this yielded a Ca/S mol ratio of 2.25, 1.88, and 1.74, respectively at the 3 coal feed rates. After establishing a baseline, gypsum, containing 12% additional free moisture was added at the rate of 200 lb/hr. As in the first gypsum test, slagging was very erratic. In fact near the end of the gypsum injection period, after 1-1/2 hours, particles of gypsum began to appear in the slag removal conveyor belt, and the injection of gypsum was terminated.

Table 5 shows the SO2 concentration measured in the boiler and stack, with and without the injection of gypsum. This is compared with the theoretical value based on full conversion of all sulfur to SO2. Note that the Ca/S mol ratio from limestone injection was low, averaging only 1.89 for the three test conditions, where historically the amount of sulfur capture by the limestone has been very low. This is confirmed for the stack sample in the absence of gypsum. (Note: The experimental data shows the amount of SO2 released into the gas phase.) However, for the boiler sample under the same condition, the reduction is 91%, and as noted, we have no clear explanation for this. Using these two data points as base lines, the next set of data show the percent of sulfur released from the injected gypsum. One notes that the sulfur in the gypsum release ranges from 36 to 48% for the boiler probe, and from 60% to 73% for the stack probe. The combustor was operated fuel rich with a stoichiometric ratio ranging from 0.71 to 0.85. Substantial sulfur evolution was anticipated because the poor slag flow resulted in long residence times for the gypsum in the slag which allows sulfur evolution.

Table 5: Boiler Outlet and Stack Gas Samples for Test No.15, 11/21/96 Test

Time	10:55	10:55	11:25	11:30	11:35	12:08	12:08	12:20	12:32
Location	Boiler	Stack	Stack	Boiler	Stack	Stack	Boiler	Boiler	Stack
Coal Rate, #/h	820	820	980	1060	1060	980	980	980	980
Limestone, #/h	75	75	75	75	75	75	75	75	75
CaSO4* 2H2O, #/h	0	0	176	176	176	176	176	176	176
O2-Experiment-%	7.7	6.9	8.1	5.50	7.7	4.7	2.6	6.5	7.1
SO2 (Theory), ppm	658	619	2516	2573	2191	2475	2787	2528	2692
SO2 (Exper.),ppm	62	414	1558	991	1558	1532	9310	1116	1558
SO2(Ex)/SO2(Th),%	9	67	62	38	71	62	30	44	58
Ca/S(limestone only)	2.25	2.25	1.88	1.74	1.74	1.88	1.88	1.88	1.88
%S released from CaSO4 injected	N.A.	N.A.	**60**	**48**	**73**	**60**	**36**	**56**	**55**

Table 6 shows the slag analysis of the samples taken from the combustor during this test. It is compared to the theoretical value based on the chemical composition of the injected material. There is some variation in the coal properties and for this reason some representative properties, such as HHV, sulfur, and ash content , were sampled periodically during the test. Detailed analysis of the coal and slag for all data conditions is too costly. The coal and ash samples for table 6 were taken at 11:58 AM, and they were assumed to represent the input conditions for this entire test. However, due to interaction of the slag with the resident refractory and slag from prior tests on the combustor wall, variations in the analyzed slag composition is expected.

Table 6: Analysis of the Slag From the Combustor in Test No.15, Nov. 21,1996

Slag Composition	Time	SiO2	Al2O3	Fe2O3	CaO	Sulfur in Slag	Injected minerals,#/h
Coal Ash +CaO from CaCO3 & w/o gypsum Theory-%	10:53	18	12	5	50	12	86
Slag Sample Analyzed-%	10:53	25	27	5	22	0.04	
Coal Ash +CaO from CaCO3 & w/o gypsum Theory-%	11:21	20	12	6	45	12	95
Slag Sample Analyzed-%	11:21	23	23	5	31	0.04	
Coal Ash +CaO from CaCO3 & w. gypsum-Theory-%	12:00	12	8	4	66	12	152
Slag Sample Analyzed-%	12:00	15		3	37	0.91	
Coal Ash +CaO from CaCO3 & Fe2O3 powder-Theory-%	14:18	20	12	6	45	13	95
Slag Sample Analyzed-%	14:18	15		3	37	1.86	

In general the samples taken agree reasonably well with the composition of the injected material, and the differences can be readily explained. Due to the low ash concentration in the coal, even the small amount of limestone injected resulted in a CaO concentration well in excess of the optimum value of 25% to 40% at which the slag mixture viscosity is at a minimum. The iron content in this coal ash is very low, and this substantially increases the slag melting temperature. Prior to 11:15 AM, only coal and limestone was injected. Gypsum injection began at 11:15 AM and continued for 1-1/2 hour. Prior tests have shown that it takes at least 10 minutes for the slag composition to reflect the injection of a new material. Therefore, the samples at 10:53 AM and 11:21 AM reflect the conditions in the absence of the injected gypsum. The measured value of silica and iron agrees well with the theoretical value. The aluminum oxide concentration is substantially higher than the value based on the coal ash due to enrichment of the slag by alumina in the ceramic liner of the combustor. The CaO concentration is substantially below the theoretical values. This is due to the analytical technique used to measure the CaO content in slag. At very high levels of CaO, the technique substantially under reports the CaO content.

Gypsum injection began at 11:16 AM, and the slag composition with gypsum injection at 11:21 AM shows no sulfur while at 12:00 noon enhanced sulfur represented 8% of the injected amount is measured. The latter sample clearly shows the presence of some gypsum. Note that slagging was very poor and intermittent. Therefore, much of the gypsum's sulfur remained either on the combustor wall or was released as SO2 gas. The key result is that very little of the sulfur remained in the slag.

In an attempt to lower the slag melting temperature, iron oxide powder was injected briefly into the combustor with coal and limestone. The resultant slag sample, taken at 2:18 AM, shows no evidence of iron oxide enhancement in the slag. However, the CaO content agrees reasonably well with the anticipated value, while the silica is substantially below the value based on the coal ash composition. This suggests that much of the slag drawn from the combustor at this time was due to accumulated slag on the combustor wall from materials injected earlier in the test. It also shows that the iron oxide did not melt to any significant amount in the combustor. This was also confirmed from observation of red iron dust coatings on several portions of the combustor wall. The other result of interest is that 14% of the injected sulfur remained in the slag.

In this test gradual buildup of slag at the outlet of the combustor exit nozzle occurred with time. This blockage became severe enough to cover over 50% of the outlet, which resulted in combustion gas escape through the slag tap chute in the slag water filled removal tank. This blockage is caused by the incomplete melting of some of the injected minerals inside the combustor. It was caused in part by the large particle size of the injected material, including the gypsum particles which averaged over 100 microns in mean size. As noted this problem had been encountered in the previous tests in this project. A mechanical ram had been used to clear the slag at the combustor outlet during operation. This clearing procedure was used during the present test twice, but it proved too awkward to implement.

Conclusion from the gypsum injection test, (No.15).

The test results show that proper slag flow is the critical parameter needed to retain significant amounts of sulfur in the slag. The measured concentrations of up to 14% of the coal sulfur in the slag are sufficient to remove all the sulfur in any coal containing several percent sulfur provided the slag mass flow rate is sufficiently high. In the present combustor this requires a slag mass flow rate of 400-500 lb/hr. Injection level approaching this range, namely over 400 lb/hr of metal oxides, were used. However, due to factors such as injection location, injected particle sizes, and combustor operating conditions, the desired high slag mass flow rate was not achieved. This is, however, an operational issue, not a fundamental physical or chemical issue. Therefore, based on the present tests results sufficient sulfur can be retained in the slag to remove a substantial portion of the sulfur, provided the proper slag mass flow rate conditions are achieved in the combustor.

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 for the first time 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.

There is one condition that has not yet been tested, namely sulfur retention in a coal with an extremely high ash content, namely 30% to 50%. This coal will allow injection of gypsum with coal without the need of any additional additive metal oxide powders. In the next quarter a test with such a coal is planned. Based on the results of such a test, a decision of what further tests are required will be made.

3. CONCLUSIONS:

These tests during the present quarterly reporting period show that :

1. There is clearly greater reduction of SO2 and NOx in the furnace of the boiler compared to the stack. This was verified in one test with two sampling probes placed at different locations inside the furnace. After eliminating such factors as probe line blockage such as would occur in a particle filter, the most probable explanation is that combustor exhaust gases leak directly into the stack. However, there are most probably other, presently unknown, factors which influence this result.

2. Achievement of high slag mass flow rates, which are required for sulfur retention in slag, is a operational problem not a physical or chemical barrier problem. The factors that impact the slag mass flow rates are particle size, melting point of the mineral matter, injection location, slag melting temperature, and slag accumulation in the combustor slag tap and exhaust nozzle. This conclusion was validated in the one test in which large diameter gypsum particles were injected in the combustor. While a poor slag flow rate was observed in the gypsum test, it was nevertheless possible to retain 14% of its sulfur content in the slag. This compares with less than 1 percent in the tests with direct sorbent injection. Also as reported previously, in some of the tests in the parallel project over 10% of the coal sulfur reported to the slag.

3. The one unanticipated result at the start of this project, the impact of calcium sulfate on increasing the slag viscosity was not previously known. No evidence of this effect had been previously found in the extensive literature on coal and steel slags. This means that even higher slag mass flow rates than the 400-500 lb/hr for the present scale 20 MMBtu/hr combustor are required if substantial quantities of sulfur are to be retained in slag.

4. It is, therefore, concluded at this time that sulfur capture by sorbent injection and its retention in the slag in the combustor cannot be implemented in one step. Meeting the requirement of high slag mass flow rates in the combustor appears to be primarily a combustor operational problem, it can almost certainly be achieved by more extensive combustor tests. However, it is uncertain whether these conditions will be compatible with a commercially viable combustor.

5. Finally, with the completion of the four tests in November, a total of 15 of the 16 tests planned for this project have been completed. The focus of current tests in the related DOE project on the 20 MMBtu/hr combustor is on further optimization of the slag tap operation and eliminating exit nozzle slag blockage. On the completion of these tests, it is planned to perform several additional tests at high slag mass flow rates using very high (over 30%) ash coals to determine if over 10% sulfur can be retained in the slag.