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

Fourth Quarterly Technical Progress Report

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1. 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 are being 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 September 30, 1996, three tests in this project were implemented, bringing the total tests to 5. In addition, a total of 10 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, including two that were performed in the previous quarter, were part of the first group of tests in which calcium sulfate were injected into the combustor. As reported in the previous Quarterly, the first test with gypsum was unsuccessful in achieving proper injection and slagging due to the high water content in the commercial gypsum used. Consequently, in the second test, plaster of Paris (p.o.p.), $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, with only 6.2% water content, was injected. 120 lb/hr of limestone for slag conditioning and additional 136 lb/hr of plaster of Paris was injected. Based on the stack SO_2 measurements, only 12% of the sulfur in the plaster of Paris was released into the gas phase in the combustor. However, 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. 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 SO_2 measurement. However, this ash sample was taken at the end of the test and it is not a real time ash sample. Efforts are planned to achieve real time ash samples

The first two, of the three tests in the present quarter, continued the test effort with plaster of Paris injection. In the first test, 150 lb/hr of p.o.p. was injected. In the second test, a mixture of silica powder, alumina powder, and p.o.p. was prepared in the ratio of 1/1/2.5 and injected into the combustor at the rate of 200 lb/hr. The coal feed rate ranged from 980 to 1160 lb/hr. The silica/alumina mixture was designed to simulate coal ash and its purpose was to increase the total slag flow rate.

In the first test in this quarter, the amount of sulfur retained in the slag was again small, 3.8% of the sulfur injected. Measurement of the stack gases showed that with limestone injection at a Ca/S mol ratio of 0.8 to 0.9, the coal sulfur emissions were reduced by 10 to 20%. With the additional injection of the p.o.p., the stack gas measurement indicated that all the coal sulfur and a small fraction of the sulfur in the p.o.p. evolved into the gas phase as SO₂. In addition, analysis of a grab sample of slag showed that almost none of the calcium oxide from the plaster of Paris reported to the slag. This agrees with particle retention analysis in the cyclone combustor which shows that the mean particle size of the p.o.p. of under 10 microns will blow out of the combustor.

To improve the probability of retention of the sulfur from the p.o.p. in slag, the slag mass flow rate was substantially increased by mixing the p.o.p. was mixed with alumina and silica. This was injected in the second test in this quarter. In this test, stack gas measurements showed that all the sulfur in both the coal and the p.o.p. was evolved as SO₂. One possible explanation for the dissociation of all the calcium sulfate in this test, compared to little dissociation in the previous test, is the longer residence time of the entrained particles in the second test. This was due to an off axis injection method used in the second test, compared to axial injection in the first test. Again, the analysis of the slag showed that essentially none of the p.o.p. was deposited in the slag.

In the third and final test of this period, the silica/alumina was mixed with calcium hydrate in the ratio of 1/1/2.5 in order to use the high sulfur capture capacity of the hydrate, compared to limestone, with a high slag mass flow rate. Again limestone was used for slag conditioning. The mixture injection rate was 200 lb/hr. Here higher reductions of SO₂ were measured, but not as high as in other tests without the added alumina and silica. Analyses of the slag showed that little of the calcium oxide from the calcium hydrate was reporting to the slag. Here again, the hydrate's particle size is in the 10 micron mean size range, compared to over 200 mesh (74 microns) for the limestone. where particle retention in the combustor is very small.

From tests in the previous 20 MMBtu/hr combustor, it was determined that a substantial part of sulfur capture with sorbent injection takes place inside the combustor. Therefore, one could conclude from these tests that since small calcium hydrate particles are most effective in sulfur capture, while retention of this particle size as calcium sulfate in the slag is small, it will not be possible to remove a substantial fraction of the coal sulfur with the slag. On the other hand, tests in the concurrent combustor test project, have shown that over 10% of the coal sulfur can be retained in the slag. This sulfur level is higher than measured previously in this combustor.

The focus of the tests in this project will now turn to the combined sulfur capture with sorbents and retention of the sulfur in slag. The objective will be to increase the calcium hydrate injection rate to levels at which the quantity of larger particles is sufficient to be retained in the combustor while at the same time increasing the slag mass flow rate. As of the date of this report, November 3, 1996, six additional tests using this approach have been implemented, and substantially higher sulfur reduction (in excess of 85%) in the stack gases have been measured. The slag sulfur results are as yet incomplete.

2. PROJECT DESCRIPTION

2.1. 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 will be implemented through a series of up to 20 one day tests carried out in a 20 MMBtu/hr air cooled, slagging combustor-boiler installation located in Philadelphia, PA. The project will consist of two tasks. Task 1 consist of the experiments conducted in the 20 MMBtu/hr combustor, and task 2 will consist of analysis of this data. All the operating procedures for this effort have been developed in the 7 years of operation of this combustor.

2.2. Technical Approach

2.2.1. Overview of the Work

The work of this Phase 3 project will be implemented on Coal Tech's patented, 20 MMBtu/hr, air cooled cyclone coal combustor that is being 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 deposits 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 ammonia injection if 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 SO₂ reduction in the combustor. Prior to the start of the present project, the peak SO₂ 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 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) will be 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 will then be used to measure the combined sorbent-sulfur capture rate in the gas phase with the sulfur retention rate in the slag inside the combustor.

The 20 tests planned for this project will allow full parametric variation of these sulfur-sorbent capture and sulfur-slag re-evolution reactions.

2.2.2. 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 plan calls for a total of 20 one day tests. However, due to resource limitations, it is planned to accomplish the project objectives in as few as 15 one day tests. To meet all the parametric test variations, the duration of individual test conditions will be reduced.

In the first group of six tests, calcium sulfate as gypsum or plaster of Paris will 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 will 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 is 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 will 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 will be increased in discrete steps, with each step remaining fixed for a specific period.

These two groups of tests will 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 will focus 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.

In the third group of four tests, the entire sulfur capture process will 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 will 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 will 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 will be 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 will 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.

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.

3. PROJECT STATUS

3.1. Effort of the Present Quarter

3.1.1. Overview of the Effort of the Present Quarter.

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. Since that time a total of 41 days of tests, of which 5 were on the present project, were successfully implemented by the end of the third quarter of 1996. Following initial shakedown tests on gas, oil, and coal, coal fired operation under slagging combustor conditions have been solely implemented since the end of March 1996. Three of the 5 tests on the present project were completed in the present reporting period, the third 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 are being 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 is 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 September 30, 1996, three tests in this project were implemented, bringing the total tests to 5. In addition, a total of 10 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, including two that were performed in the previous quarter, were part of the first group of tests in which calcium sulfate were injected into the combustor. As reported in the previous Quarterly, the first test with gypsum was unsuccessful due to the high water content in the commercial gypsum used. Consequently, in the second test, plaster of Paris (p.o.p.), $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, 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 SO_2 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 purpose of the tests in the present quarter was to achieve, with plaster of Paris (i.e. calcium sulfate), conditions under which a high slag mass flow rate would result 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 150 lb/hr 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 next quarter will be on high sulfur capture with high rates of sorbent injection without the addition of artificial ash.

The following discussion elaborates on the tests.

3.1.2. Project Test No.3: The first test in this quarter was performed on August 2, 1996. Its objective was to determine the sulfur retention capability of sorbent bearing slag. Calcium sulfate in the form of plaster of Paris was injected into the combustor at a rate of 150 lb/hr through a central pintle into the combustor. Prior to the p.o.p. injection period, the coal feed rate was initially 980 lb/hr, equal to 11.8 MMBtu/hr, plus 0.9 MMBtu/hr of gas, followed by a 1050 lb/hr feed rate, equal to 12.7 MMBtu/hr plus 0.9 MMBtu/hr gas. The sulfur content of the coal was 3.44%, or 33.7 and 39.6 lb/hr, respectively. In addition 75 lb/hr of limestone was injected for slag conditioning.

The stack SO₂ measurement at the boiler outlet for the first coal flow rate was 1037 ppm at 8.6% oxygen by volume, 1125 ppm at 8.6% O₂ for the second coal feed rate. This number includes a correction factor for the SO₂ calibration gas in nitrogen and the combustion gas composition. At 100% conversion of coal sulfur to SO₂ would result in a SO₂ level of about

1950 ppm and 1970 ppm, respectively. These two values are 53% and 57% of the values at 100% coal sulfur conversion to SO₂. The Ca/S mol ratio is only 0.71 and 0.67, respectively. At this low value total of CaO injection, the SO₂ reduction should be very small, namely in the range of 10% to 20%.

The sulfur content of the coal was obtained from grab samples of coal that were taken on the previous test day, 7/31/96, and the one before that on 7/23/96. Both samples had 3.4 to 3.5% sulfur. The pulverized coal is purchased in lots of ten 1 ton supersacks. The previous lot had an average sulfur content of 2.5%. It had been used in the tests of June and July. It is possible that some of this coal adhered to the walls of the 4 ton bin and mixed with the newer higher sulfur coal during this August 2nd test.

In any case, for the purposes of the present test on slag desulfurization, the absolute value of SO₂ reduction from the sulfur in the coal is not important. What is important is that this reduction remains the same in the control experiments. This will allow measurement of the desulfurization of the injected calcium sulfate in the plaster of Paris.

The plaster of Paris was injected after an initial control period with coal at 1050 lb/hr and limestone at 75 lb/hr. The p.o.p. injection rate was 150 lb/hr, with the coal and limestone feed rate unchanged. After the injection of the plaster of Paris, a brief control test period at 1050 lb/hr of coal with limestone was performed. This was followed by another period of coal injection at 1160 lb/hr and limestone at 75 lb/hr.

Table 1 shows the theoretical SO₂ for 100% conversion of the coal sulfur and re-evolution of all the calcium sulfate in the plaster of Paris to SO₂ gas. This is compared with the measured values of SO₂ at the boiler outlet. In addition, gas samples were taken in the stack at the outlet of the induced draft fan. Both sets of measurements had infiltration air through cracks in the boiler case and the entire stack gas system. However, as can be seen from the O₂ levels in Table 1, the infiltration air is substantially greater in the stack. The gas sample analysis was performed at the oxygen level measured at the sampling point. In addition, humidification of the stack gases resulted in high moisture levels in the stack outlet samples. Several diffusion dryers and water condensers were used to condition the gas samples. However, due to these air and moisture dilution effects, the stack samples are considered less reliable than those in the boiler outlet.

Table 1: Boiler Outlet and Stack Gas Samples for the 8/2/96 Test

Time	13:50	14:00	14:36	15:05	1510	1515	1535	15:50	15:55
Location	Boiler	Boiler	Boiler	Boiler	Stack	Stack	Boiler	Boiler	Stack
Coal Rate, #/h	980	1050	1050	1050	1050	1050	1050	1160	1160
Limestone, #/h	75	75	75	75	75	75	75	75	75
CaSO ₄ *.5H ₂ O, #/h	0	0	150	150	150	0	0	0	0
O ₂ -Experiment-%	8.6	8.6	8.1	7.9	10.4	10.6	7.4	6.8	9.5
SO ₂ (Theory), ppm	1950	1970	3861	3918	3180	1654	2157	2270	1820
SO ₂ (Exper.), ppm	1037	1125	1625	1813	1687	839	1100	1250	1075
SO ₂ (Ex)/SO ₂ (Th), %	53	57	42	46	53	51	51	55	59
%S released from CaSO ₄ injected	N.A.	N.A.	25	34	49	N.A.	N.A.	N.A.	N.A.

Based on previous test experience, the SO₂ reductions measured in the absence of plaster of Paris injection are considered too high for the low Ca/S mol ratio of less than 1. The present result may be due variations in the sulfur content of the coal.

It is very clear from Table 1 that the injection of plaster of Paris (CaSO₄) significantly increases the SO₂ gas level, which indicates part of the CaSO₄ injected is dissociating. The amount of dissociation is estimated as follows:

In analyzing the SO₂ gas evolution from the injected p.o.p. it was assumed that the actual SO₂ levels due to the coal sulfur would not change due to the injection of the calcium sulfate. Consequently, in computing the degree of SO₂ evolution from the injected CaSO₄, the same percentage reduction in the measured SO₂ without the CaSO₄, namely 57% for the 1050 lb/hr coal condition, was used to compute the amount of evolution of SO₂ from the CaSO₄. This yielded re-evolution rates of 25% and 34% at the boiler outlet. The 49% value computed at the stack is considered less reliable due to the various air infiltrations noted above.

The analysis of the slag sample taken during the injection of the plaster of Paris is shown in Table 2.

Table 2: Analysis of the Slag From the Combustor with Injection of Plaster of Paris

Slag Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Sulfur in Slag
Coal Ash +CaO from CaCO ₃ & w/o CaSO ₄ - Theory-%	29	17	14	23	19
Coal Ash +CaO from CaCO ₃ and CaSO ₄ -Theory-%	22	13	11	42	25
Slag Sample Analyzed-%	27	19	22	20	1.3

It is clear from this Table that the best agreement between the theory, which is based on the actual chemical composition by weight of the injected materials, agrees best with the analysis

of the slag that assumes that all the injected plaster of Paris is blown out of the combustor and does not report to the slag. The last column shows the percent of sulfur in the slag. The theoretical value assumes that the sulfur partitions in the slag and fly ash according to the relative slag and fly ash distribution in the system. Since essentially none of the injected CaSO₄ reported to the slag, the measured sulfur content of 1.3% represents about 7% of the coal sulfur. This is at the low end of the range of sulfur concentrations in slag measured in the slag in the other tests in the related DOE project.

The result is consistent with the fact that the retention capacity of the cyclone combustor is very low to particles less than 10 microns in diameter, which is the mean size of the plaster of Paris particles. However, it is also significant that despite passage through a 3000°F gas stream, the bulk of the CaSO₄ particles did not dissociate in this test. This was not the case in the next test, where all the calcium sulfate dissociated. The latter may be due to a longer gas transit time resulting from off axis injection versus axial injection in the present test. The present tests does suggest that if sulfur capture is achieved in the colder injection zone of the combustor, then the reacted calcium-sulfur particles can retain a significant fraction of the sulfur despite passage through the hot zone of the combustor.

In comparing the results of this test with the previous one on June 28, 1996, in which plaster of Paris was injected into the combustor, it is noted that in the previous test it had been concluded that the calcium from the plaster of Paris had preferentially reported to the slag while in the present test of August 2nd the calcium oxide from the plaster of Paris appeared to have blown out almost completely out of the combustor. In the previous test injection of the plaster of Paris was off-axis while in the present test it was axial through a pintle. In the latter case, one would expect less retention of particles, especially fine ones. Consequently in the next test in this Quarter, injection was again off axis.

3.1.3. Project Test No. 4: This test also involved injection of CaSO₄ in the form of plaster of Paris. However, two major changes were made. One change was to use off axis injection as had been done in test No.2. However a different injection procedure was used. In test no 2 the plaster of Paris was pneumatically mixed with the coal and injected through the coal ports. In the present Test No.4, a new flow splitter was installed that enabled injection nearer to the wall of the combustor at four orthogonal locations. These ports were closer to the wall than the coal injection ports .

The second major change was to mix the plaster of Paris with an artificial ash consisting of a 50%-50% mixture of alumina and silica powder of about 100 mesh size to simulate bituminous coal ash. This was done to increase the slag mass flow rate in the combustor which according to the kinetics of slag desulfurization would result in greater sulfur retention in the slag. In the previous 20 MMBtu/hr combustor tested in Williamsport, coal fly ash had been injected at rates as high as 500 lb/hr. However, the mean particle size of fly ash is less than 10 microns and a substantial amount of this ash blew out of the combustor. The experience with the fine plaster of Paris in test No.3 indicated that the same result would occur in the present combustor. Therefore, the coarser artificial ash mixture was selected. This 50/50 mixture was in turn mixed with plaster of Paris in the ratio of 100/100/250 , alumina, silica, plaster of Paris.

The above mixture was injected into the combustor at the rate of 200 lb/hr. The coal feed rate was 980 lb/hr, sulfur content of 3.6%, and limestone at 75 lb/hr were injected. This yielded a total mineral mass flow of 360 lb/hr. The combustor was operated very fuel rich, SR1=0.76, and final combustion in the boiler yielded an SR2=1.47. Table 3 summarizes the stack gas sampling results.

Table 3: Boiler Outlet and Stack Gas Samples for the 9/19/96 Test

Time	14:08	14:15	14:40	14:59	1504	1540	1540	1610	1615
Location	Boiler	Stack	Stack	Boiler	Boiler	Boiler	Stack	Stack	Boiler
Coal Rate, #/h	980	980	980	980	980	980	980	980	980
Limestone, #/h	75	75	75	75	75	75	75	75	75
SiO,Al ₂ O ₃ , CaSO ₄ * .5H ₂ O, mix, #/h	0	0	200	200	200	200	200	200	200
O ₂ -Experiment-%	8.4	12.3	12.6	9.0	9.0	8.6	12.6	12.2	9.0
SO ₂ (Theory), ppm	1951	1319	2146	3080	3080	3173	2146	2265	2865
SO ₂ (Exper.),ppm	1980	1375	2090	2200	2970	2530	2310	2410	3355
SO ₂ (Ex)/SO ₂ (Th),%	101	104	97	71	96	80	108	107	117
%S released from CaSO ₄ injected	N.A.	N.A.	93	26	91	47	100	100	100

Unlike the results of the previous test on August 2nd, Table 3 shows that in the present test all the sulfur evolved as SO₂ with and without the injection of the alumina/silica/plaster of Paris (CASO₄) mixture. The difference between the two tests was that in the previous one, the p.o.p. was injected axially through a pintle, while in the present tests it was mixed with the alumina and silica and injected separately off axis near the combustor inner wall. The SO₂ stack/boiler measurement show that all the sulfur in the CASO₄ particles evolved into the gas phase as SO₂. The three materials were mixed in a cement mixer and it is quite probable that the mixing was not uniform, which would account for the deviation in two of the samples from 100% SO₂ gas evolution. A probable explanation for the high release of SO₂ from the injected plaster of Paris is that in the present test, the off axis injection resulted in a longer residence time of the particles than in the previous tests where injection was by axial pintle.

The complete evolution of SO₂ from the coal is not surprising considering the low limestone injection rate. This resulted in a Ca/S mol ratio of only 0.7 and little capture of sulfur was anticipated. It is possible that the large SO₂ reduction of 50% measured in the 8/2/96 test and in the 9/26/96 test under the first test condition at identical Ca/S mol ratios was due to the lower sulfur coal in that test. Grab samples of coal were analyzed in the two tests prior to the 8/2 test, but not on the 8/2 test. As a result of this experience, grab samples of coal are now being taken during the sampling of slag and gas.

Table 4 shows the concentration of major species in several slag samples from this test. As noted 980 lb/hr of coal, 75 lb/hr of limestone, and 200 lb/hr of the 1/1/2 alumina/silica/plaster of Paris mix was injected. The total mineral matter injection rate was 328 lb/hr, assuming all the SO₂ evolved from the plaster of Paris.

Table 4: Analysis of the Slag From the Combustor with Injection of Plaster of Paris, Alumina, and Silica, Limestone and Coal

Slag Composition	SiO ₂	Al ₂ O ₃	CaO	Sulfur in Slag
Coal Ash +CaO from CaCO ₃ w/o Al ₂ O ₃ /SiO ₂ /CaSO ₄ mix-Theory-%	37	29	15	25
Coal Ash +CaO from CaCO ₃ and CaSO ₄ in mix-Theory-%	32	25	25	17
Slag Sample Analyzed-% 14:55 hr	29	29	18	.08
Slag Sample Analyzed-% 15:42 hr	26	32	16	.05

The last column shows the theoretical concentration of sulfur in the slag if all the coal sulfur and sulfur from the injected plaster of Paris had reported to the slag in a concentration proportional to the relative concentrations of slag and fly ash, namely 67% slag/33% fly ash. It is clear that essentially no sulfur reported to the slag. These measured concentrations were very much less than values of several percent that were measured in the 8/2/96 test and in the parallel project with coal and sorbent injection only. This could be due to the apparent complete conversion of all sulfur from the coal and the plaster of Paris to SO₂. It is not clear why this occurred with injection of this mixture, unless it was due to very poor mixing during the preparation of this material.

It is also clear from Table 4 that almost none of the injected CaSO₄ particles from the plaster of Paris reported to the slag, in agreement with the previous test of 8/2/96. This is very strong evidence that when the reacted sulfur bearing calcium particles are less than 10 microns in size, as was the case with the plaster of Paris, and as was the case with calcium hydrate injection, little capture of these particles in the slag takes place. This means that the single step approach of using calcium hydrate injection in the combustor to capture sulfur and to remove the reacted sorbent in the slag will not be effective. An alternative approach would be to capture the reacted sorbent in the stack baghouse and inject it near the combustor wall to achieve better capture in the slag. Alternatively, a special slagging combustor could be used to accomplish this task in larger installation having multiple combustors.

3.1.4. Project Test No. 5: In view of the poor results with the injected calcium sulfate particles, it was decided to focus on the next phase of the test effort, namely to inject calcium hydrate for sulfur capture combined with a high slag mass flow rate. This was implemented in the next test on September 26, 1996. To achieve a high slag mass flow rate, the alumina/silica powder was mixed with the calcium hydrate in the ratio of 1/1/2.5 respectively. The injection rate of this mixture was 200 lb/hr. Attempts to inject 300 lb/hr were not successful due to pneumatic feed limitations and blinding of the flame safety system. In addition, in some of the test conditions 75 lb/hr limestone were injected.

Table 5 summarizes the results of this test. Grab samples of coal were taken near the periods when slag samples and stack gas samples were taken. The Table shows the coal sulfur

level used during the gas sample. Grab samples of coal were taken at 12:30 PM, 14:27 PM, and 15:30 PM. The sulfur concentration was 3.51%, 2.97%, and 2.52 % respectively. This decrease in sulfur content was due to the introduction of 1 ton of low sulfur coal in the previously used 3.5% sulfur coal in the 4 ton bin. There is, however, the possibility, that some of the stack gas analysis may have been taken during periods when the coal sulfur level may have been different, and this may account for some variability in the data.

Table 5: Boiler Outlet and Stack Gas Samples for the 9/26/96 Test

Time	12:10	12:15	13:10	13:20	13:38	13:40	14:10	14:15
Location	Boiler	Stack	Boiler	Stack	Boiler	Stack	Boiler	Stack
Coal Rate, #/h	1060	1060	1060	1060	1060	1060	1060	1060
Coal sulfur, %	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6
Limestone, #/h	75	75	0	0	0	0	75	75
Al ₂ O ₃ , SiO ₂ , Ca(OH) ₂ , mix #/h	0	0	200	200	200	200	0	0
O ₂ -Experiment-%	10.2	12.5	10.8	13.4	10.8	13.2	8.6	11.4
SO ₂ (Theory), ppm	1718	1336	1627	1197	1627	1215	1974	1520
SO ₂ (Exper.), ppm	979	792	847	605	627	506	1760	1705
SO ₂ (Ex)/SO ₂ (Th), %	57	59	52	51	41	42	89	112
Ca/S mol %	0.63	0.63	1.26	1.26	1.26	1.26	.63	.63

Table 5: Continued

Time	14:50	14:52	15:20	15:30
Location	Boiler	Stack	Boiler	Stack
Coal Rate, #/h	1060	1060	1200	1200
Coal sulfur, %	3.0	3.0	2.52	2.52
Limestone, #/h	0	0	75	75
Al ₂ O ₃ , SiO ₂ , Ca(OH) ₂ , mix #/h	200	200	200	200
O ₂ -Experiment-%	8.7	12.1	8.8	11.4
SO ₂ (Theory), ppm	1720	1232	1597	1252
SO ₂ (Exper.), ppm	1353	946	1056	941
SO ₂ (Ex)/SO ₂ (Th), %	79	77	66	69
Ca/S mol %	1.26	1.26	2.36	2.36

The first two columns show the results with coal and limestone which served as the base case. The large reduction of SO₂ at such low Ca/S of only 0.63 with limestone suggests that the sulfur content in this sample may have been lower than assumed based on the 12:30 PM grab sample. The addition of the Al₂O₃/SiO₂/Ca(OH)₂ mixture resulted in only a slight increase in the Ca/S mol ratio in the first two gas samples. This improved with time and in 20 minutes, the SO₂ reduction increased by an additional ten percentage points.

An attempt to increase the injection rate of the mixture to 300 lb/hr at 14:50 PM had to be terminated within 15 minutes due to blockage of the pneumatic feed lines. The limestone then

was turned on at a rate of 75 lb/hr. The SO₂ levels increased sharply to full conversion of the coal sulfur to SO₂. This SO₂ level is substantially higher than the values measured in the base case, which as noted may be due to the variability in the coal sulfur level. The mixture was then turned on again at 200 lb/hr and the limestone was turned off. Again a modest reduction comparable to the earlier reduction with this mixture was observed.

Finally, the coal feed rate was increased to 1200 lb/hr from 1060 lb/hr and the mixture and limestone was injected. This yielded a Ca/S mol ratio of 2.36. A further modest reduction in SO₂ emissions was measured.

In the final case of 1200 lb/hr coal, 75 lb/hr limestone, and 200 lb/hr mixture, the mineral injection rate was 371 lb/hr. This value includes the calcination of the calcium hydrate and limestone. Due to the modest reduction in stack SO₂, compared to higher reductions previously observed with calcium hydrate injection alone, it may be concluded that the high slag flow rates do not by itself lead to high sulfur capture.

The next item of interest in connection with this test is the composition of the slag samples from the combustor. Three slag grab samples were analyzed. The results are shown in Table 6.

Table 6: Analysis of the Slag From the Combustor with Injection of Calcium Hydrate, Alumina, and Silica, Limestone and Coal

Sample Time	Slag Composition	SiO ₂	Al ₂ O ₃	CaO	Sulfur in Slag
12:30	Coal Ash +CaO from CaCO ₃ Theory-%	30	18	<u>21</u>	20
12:30	Slag Sample Analyzed-%	29	22	<u>20</u>	.04
14:13	Coal Ash +CaO from CaCO ₃ -Theory-%	30	17	23	20
14:13	Slag Sample Analyzed-%	37	29	15	.03
15:08	Coal Ash +CaO from CaCO ₃ & from Al ₂ O ₃ /SiO ₂ /Ca(OH) ₂ mix-Theory-%	28	21	34	8
15:08	Same, except assume all CaO from Ca(OH) ₂ escapes combustor-%-Theory	36	28	<u>15</u>	10
15:08	Slag Sample Analyzed-% 15:42 hr	34	31	<u>18</u>	.06

The first slag sample was taken during the Base Case when only limestone was injected. The second sample was taken during the short period when the artificial slag mixture was briefly turned off. Since this followed the aborted attempt to increase the feed rate of the artificial ash to 300 lb/hr, some of the material from that interval may have drained during the sample period. Therefore, the correlation between measurement and theory is not as good. The third sample was taken when both limestone and the alumina, silica, and calcium hydrate mixture was injected. As in the case with the mixture with plaster of Paris, the third case with the calcium hydrate shows that it was also blown out of the combustor and did not report to the slag. This is seen by the agreement of the measured CaO concentration 18% with the computed value without the hydrate 15%. As with the plaster of Paris, the reason is that the average particle size of the hydrate is in the 10 micron range.

Since the best sulfur capture takes place with the small calcium hydrate particles, it appears that it will be difficult to retain these small particles in the slag in the combustor.

Another point of interest for this third case is that at high slag mass flow rates the amount of sulfur in the slag needed to retain all the coal sulfur is only about one-third of that necessary at low slag mass flow rates. However, this test series had substantially lower sulfur levels in the slag than had been obtained previously. This is consistent with the observation that the captured sulfur from the small hydrate particles is blown out of the combustor. This conclusion is consistent with the measurement of a grab sample from one of the barrels that collected fly ash from the baghouse in this run. Here the measured sulfur content was 4.4 % of the mineral matter in the ash. This patterns of higher sulfur content in the fly ash has been observed in all the tests conducted to date in both projects. Considerable effort has been expended to obtain real time samples of this fly ash which is quite difficult. Additional work in this area is planned.

3.1.5. Conclusions:

The results of these three tests show that the particle size that is most effective in capturing sulfur (less than 10 microns) is the size that is generally blown out of the combustor and does not report to the slag.

Similarly, the small particle size of the plaster of Paris , i.e. calcium sulfate, prevented its use as a material to measure slag desulfurization. Another attempt will be made to find a source of larger calcium sulfate particles.

The use of the artificial ash of alumina-silica did not appear to enhance the sulfur capture or retention process. On the contrary, it appeared to lower the sulfur concentration in the slag. However, it did help in relining the combustor wall with refractory material.

It appears that most of the capture sulfur reported to the fly ash, and effort will continue to obtain real time samples of the ash.

Finally, these were substantial differences in the performance and slag deposition and slag tap operation depending on the mineral matter composition, the method of injection, and the total mineral mass flow rate. Further work is planned on quantitatively determining these relationships.

4. EFFORT OF THE NEXT QUARTER

In the next quarter, the primary focus will be on the sulfur capture process with calcium hydrate injection in the combustor. In addition, further improvements in the gas, slag, and fly ash sampling and analysis will be made to obtain a quantitative sulfur balance in the entire system. These tests will then be followed with the first tests in the two step sulfur capture process in which fly ash taken from the baghouse will be injected into the combustor. Here the method and location of injection will be very important due to the very fine particle size of the fly ash.