BEHAVIOR OF SULFUR TRIOXIDE FORMATION IN 1.6MW PILOT PLANT FIRING HIGH SULFUR COALS INCLUDING PETROLEUM COKE BLENDS

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ABSTRACT To understand SO_2 oxidation mechanism in boiler furnaces and to examine its factors quantitatively, the effects of coal type and combustion stoichiometry on SO_3 formation have been investigated by conducting tests at 1.6MWth pilot plant having a test section simulating a horizontal tube bank. SO_3 concentration was high for coals containing high amounts of sulfur and vanadium oxides. SO_3 concentration decreased linearly with decreasing O_2 concentration. Reduction of combustion stoichiometry from 1.5 to 1.2 decreased SO_2 oxidation rate from 1.4 to 0.6% and from 2.4 to 1.0% for high sulfur coal and 40% petroleum coke blend, respectively. Our results are consistent with some field data and also significant for quantifying the effects of operating conditions on reducing SO_3 .

Keywords: SO_3 formation, High sulfur coals, Petroleum coke, Combustion stoichiometry, Pilot plant test

1. INTRODUCTION

Excessive level of SO_3 emission from high sulfur coal-fired boilers is problematic because of increasing corrosion rate of down stream surfaces and plume opacity at the stack. During coal combustion, sulfur in coal is converted to SO_2 in the furnace, and 1 to 3% of SO_2 further oxidizes to SO_3 at the convection pass and Selective catalytic reduction (SCR) system [1]. To mitigate SO_3 emission, factors essential for its formation and depletion should be understood quantitatively. Previous research has revealed that factors influencing the amount of SO_3 generated in furnaces are coal types, boiler types and operating conditions [2][3][4]. However, SO_2 oxidation data from actual combustion fields is still lacking to evaluate the degree of incidence among the factors.

The purpose of our work is to understand the SO_2 oxidation mechanism in actual combustion fields, and to evaluate the factors affecting SO_3 emission quantitatively. For this purpose, we have conducted tests at 1.6MWth pilot plant having a test section simulating a horizontal tube bank. This paper discusses the effect of coal type and combustion stoichiometry on SO_3 formation based on data obtained by the pilot plant tests.

2. EXPERIMENTAL

2.1 1.6MW Pilot Plant

Fig.1 shows the appearance and the schematics of the pilot plant operated for a series of tests. The combustor is a down flow furnace with a burner installed on the top. Furnace exhaust gas is cooled by an air heater and is introduced to an Air Quality Control System (AQCS) test facility, which consisted of an SCR, a gas-gas heater (GGH), a dry electrostatic precipitator (ESP), and FGD system. To investigate the effect of deposit ash on SO_3 formation, we installed a test section simulating a boiler tube bank upstream of the air heater. Gas temperature at the test section inlet was 923K and decreased to 823K at the test section outlet. Gas flow rate in the section was 13m/s, and

the residence time in the section was 0.1 second. In practical boilers, gas flow rate ranges from 10 to 30m/s. The residence time of 0.1 second in pilot plant corresponds to that of one bank installed in a 1000MW-class boiler.

SO_3 measurement ports with diameter of 40mm were located in position (a), (b), (c) and (d). Ports (c) and (d) were placed on the gas ducts upstream and downstream the test section to investigate the SO_3 formation at the simulating bank area.

Fig.1 Appearance and schematics of the pilot plant operated for a series of tests

Table1 lists the main test conditions of each test runs. We selected 2 types of U.S. eastern coals, which are Coals A and B, and prepared petroleum coke blends with the blend ratio of 20 and 40% by mixing petroleum coke and Coal B on a weight bases. For simplicity, in tables and figures in this paper, we represented 20 and 40% petroleum coke blends in pet coke 20% and pet coke 40%, respectively. Each test run has been performed for 4 or 5 days with the coal feed rate in range from 60 to 70kg/h. The effect of stoichiometry was evaluated with the tests using Coal B itself and a 40% petroleum coke blend.

Table 1 Main test conditions for 1.6MW Pilot Plant tests

Item	Coal	Coal A	Coal B	Pet coke 20%	Pet coke 40%
Test time [h]		70	77	74	72
Coal feed rate [kg/h]		60	70	65	60
Total stoichiometry [-]		1.5	1.2-1.5	1.5	1.2-1.5
Gas temperature at the test section inlet [K]		823 - 923			
Temperature of cooling air of the bank [K]		Inlet:313, Outlet:623			

2.2 Test Section Simulating Horizontal Tube Bank

Fig.2 shows the schematics of the test section. An engineering drawing of the tube bank is shown in Fig.3. The bank size was reduced to 1/1000 scale of actual ones with satisfaction of geometric similarity. A bare tube having a diameter of 57mm constructed the bank, and was arranged 3 rows in width direction and 14rows in gas flow direction. Combustion gas was introduced from the topside to the bottom side of the test section. Cooling air was supplied from the bottom header of the bank at the temperature of 313K and discharged to the atmosphere through the upper header at the temperature of 623K. Temperature of cooling air was measured at 5 locations with the attached K-type thermocouples of 0.1mm diameter. The flow rate of cooling air was measured by an orifice flow meter mounted at the inlet of the airflow. Data from thermocouples and the flow meter were recorded with a data logger in the control room of the test plant.

Fig.2 schematics of the test section

Fig.3 Engineering drawing of the tube bank

2.3 Coal and Ash Analysis

The results of coal and ash analysis are listed in Table 2. Sulfur in coal varies from 1.6 to 3.5% and ash contents range from 6.1 to 10.3%. The amount of iron oxides in ash of tested coal was from 14 to 18% and this variation was not sufficient to distinguish each other. On the other hand, the amount of vanadium oxides was distinctive for each coal; it increased with increasing blend ratio of petroleum coke to Coal B. For example, the amounts of vanadium oxides were 0.09, 0.32, and 0.98% for the coals with Coal B itself, 20% and 40% petroleum coke blends, respectively.

As Graham et al have addressed in their study [5], iron oxides are well known catalysts for SO_2 oxidation. However, we do not use coals containing low iron oxides, such as Powder River Basin coals, because of low SO_3 emission. We decided that it is not appropriate to discuss the effect of test parameters with the small amount of SO_3 .

Table2 Properties of coal and ash used pilot test

Coal Analysis					
Item	Unit	Coal A	Coal B	Petcoke20%	Petcoke40%
HHV	kJ/kg	28180	27160	28330	30860
Total moisture	wt%	7.8	13.7	14.2	7.0
Ash	wt%	8.2	10.3	10.2	6.1
C	wt%	72.9	71.1	72.4	77.4
H	wt%	4.6	4.7	4.3	4.1
O	wt%	11.1	10.0	8.7	6.3
N	wt%	1.6	1.6	1.6	1.8
S	wt%	1.6	2.7	3.0	3.5
Fuel ratio	-	1.8	1.7	1.7	2.5
Ash Analysis					
Fe_2O_3	wt%	18.2	17.1	14.1	16.5
V_2O_5	wt%	0.09	0.09	0.32	0.98

2.4 Measurement of SO_3 Concentration

As illustrated in Fig.1, SO_3 concentrations were measured at (a) furnace hopper, (b) horizontal duct, (c) test section inlet, and (d) test section outlet. To quantify

reproducibility and errors in SO_3 values, measurements were repeated 2 or 3 times for each test condition. At each measurement, SO_3 sampling nozzle was inserted in the center of each duct or pipe to minimize the effect of distribution of SO_3 concentration in each flow passage plane. Sample gas was extracted through a quartz fiber filter inserted in the duct then passed through a spiral glass tube condenser. Temperature of the condenser was controlled at 373K. After each sampling, the filter and the condenser were rinsed with purified water separately. Then SO_4^{2-} concentration in each wash solution was analyzed by ion chromatography. The measurement limit of SO_3 was less than 0.1ppm.

SO_3 captured on the filter is assumed to be formed during combustion and originally existed in gaseous phase. Therefore, we added filtered and condensed SO_3 for data evaluation. Obtained SO_3 values were represented based on 6% of excess O_2 .

3. RESULTS

3.1 Effect of Coal Type

Table3 summarizes SO_3 concentrations measured at the test section outlet; hereinafter called $\text{SO}_{3\text{outlet}}$, for each tested coal with theoretical SO_2 concentrations and SO_2 oxidation rates. Theoretical SO_2 concentrations were calculated based on Sulfur in each coal. SO_2 oxidation rates were obtained by dividing $\text{SO}_{3\text{outlet}}$ by theoretical SO_2 .

Table 3 Comparison of $\text{SO}_{3\text{outlet}}$ for different types of coal

Item	Unit	Coal A	Coal B	Pet coke 20%	Pet coke 40%
S	wt%	1.6	2.7	3.0	3.5
V_2O_5	wt%	0.09	0.09	0.32	0.98
SO_3	ppm,6% O_2	8	23	58	64
SO_2	ppm,6% O_2	1131	1903	2080	2246
SO_2 oxidation rate	wt%	0.6	1.2	2.8	2.8

$\text{SO}_{3\text{outlet}}$ were 8, 23, 58, and 64ppm, which increased in the following order: Coal A, Coal B, 20% and 40% petroleum coke blends. The results in Fig.3 indicate that $\text{SO}_{3\text{outlet}}$ was higher for the coal containing higher amounts of sulfur and vanadium oxides.

In our tests, the SO_2 oxidation rate was 0.6 and 1.2% for high sulfur coals, and 2.8% for petroleum coke blends.

Referring to some field data in papers [1][2], SO_2 oxidation rates at the economizer of practical boilers are from 0.9 to 1.7% for high sulfur coals and 1.7 to 3.3% for petroleum coke blends. Our test data were in the reasonable range of those field data.

3.2 SO_3 Formation in Furnace

To understand the mechanism of SO_3 formation during the combustion process, the trends in SO_3 concentration as increased residence time were compared for Coal A, Coal B and 20% petroleum coke blend in Fig.4. For all coals, most SO_3 were formed at the area where the gas temperature above 1073K. At the area where the gas cooled below 1073K, the trend of SO_3 formation differed whether the tested coal contains petroleum coke or does not.

More specifically, the amount of SO_3 decreased for Coal A and Coal B, whereas it increased for 20% petroleum coke blend as increased residence time.

Fig.4 Trend of SO_3 formation as a function of residence time from burner exit

SO_3 formation in the test section was evaluated by plotting measured SO_3 at the section inlet; hereafter called $\text{SO}_{3\text{inlet}}$, versus $\text{SO}_{3\text{outlet}}$ (see Figs. 5 to 8). We measured SO_3 three times for each measurement condition to quantify reproducibility. Plots in figures represent values based on average SO_3 values of three measurements performed at the test section inlet and the outlet, and each plot area was illustrated as grey in all figures.

As a general trend, all plots in Figs.5 to 8 scattered along the reference lines showing one to one relation between $\text{SO}_{3\text{inlet}}$ and $\text{SO}_{3\text{outlet}}$. Thus the difference between them was relatively small.

However, when we focus on the exact positions of the plot areas (grey areas) against the reference lines, there can be seen some specific features derived from coal type. For example, the plots of Coal A tended to shift lower side against the reference line (in Fig. 5), on the other hands, the plots of Coal B and 20% petroleum coke blend (in Figs.6 and 7) tended to shift upper side against the line. The plots of 40% petroleum coke blend (in Fig. 8), distributed across the reference line.

According to these diagnostics, the following can be understood: (1) $\text{SO}_{3\text{outlet}}$ tends to be lower than the inlet SO_3 for Coal A and to be higher for Coal B and 20% petroleum coke blend, and (2) $\text{SO}_{3\text{inlet}}$ and $\text{SO}_{3\text{outlet}}$ are almost equal for 40% petroleum.

Fig. 5 Plots of SO_3 measured at the inlet and outlet of the test section at Coal A tests

Fig. 8 Plots of SO_3 measured at the inlet and outlet of the test section at 40% Petroleum coke blend tests

Fig. 6 Plots of SO_3 measured at the inlet and outlet of the test section at Coal B tests

Fig. 7 Plots of SO_3 measured at the inlet and outlet of the test section at 20% Petroleum coke blend tests

3.3 Effect of Combustion Stoichiometry

We investigated the effect of combustion stoichiometry on SO_3 formation at the tests of Coal B and 40% petroleum coke blend coals. For these tests, we varied stoichiometry from 1.2 to 1.5 based on the field data of economizer O_2 ($\approx 3\text{-}6\%$) of practical boilers in U.S. As is shown in Fig. 9, SO_3 concentration decreases almost linearly with decreasing O_2 concentration for both coals, and the difference between SO_3 concentrations at the same O_2 concentration became smaller at lower O_2 concentration.

The relationships between combustion stoichiometry and SO_2 oxidation of each coal are shown in Figs. 10 and 11. By reducing combustion stoichiometry from 1.5 to 1.2, SO_2 oxidation rates decreased from 1.4 to 0.6% for Coal B and from 2.4 to 1.0% for 40% petroleum coke blend. Maximum variations in data against the correlation lines were 30% for Coal B and 40% for 40% petroleum coke blend (grey areas shown in Figs. 10 and 11).

Fig. 9 Variation of SO_3 at the test section outlet with O_2 at the furnace exit for different types of coal

Fig.10 Variation of SO_2 oxidation rate with stoichiometry at the Coal B test

Fig. 11 Variation of SO_2 oxidation rate with stoichiometry at the 40% Petroleum coke blend tests

4. DISCUSSION

To understand the formation mechanism of SO_3 in boiler furnaces and to examine the factors quantitatively, a series of tests have been conducted at 1.6MWth pilot plant having a test section simulating a horizontal tube bank. The effects of coal type and combustion stoichiometry on SO_3 formation are discussed below.

SO_3 concentration was higher for the coal containing higher amounts of sulfur and vanadium oxides. When sulfur in coal burns in furnace, most of them are converted to SO_2 , and then further oxidized to SO_3 with a certain oxidation rate. Hence, under the same oxidation rate, coals containing higher amount of sulfur inevitably produces higher SO_3 . Also, vanadium oxides in petroleum coke are well-known catalyst of SO_2 oxidation and accelerate the oxidation reaction. In addition, SO_2 oxidation rates of our test results were found to be in reasonable range of field data from U.S. power plants (see, for example, [2]). This consistency helps to ensure the validity of our pilot plant tests on examining SO_2 oxidation characteristics in boiler furnaces.

The trend of SO_3 formation at the area where gas temperature below 1073K differed whether the tested coal

contains petroleum coke or does not. For Coals A and B, the amount of SO_3 decreased with increasing residence time. As the reason for this, it assumed that the accumulated ash in the horizontal duct captured SO_3 . In this case, SO_3 stays in the furnace and are not to be measured. In contrast, the amount of SO_3 increased for 20% petroleum coke blend. This believed to be due to catalytic effect of vanadium oxides in petroleum coke. From these effects, ash deposition behavior is also supposed to affect the difference in SO_3 concentration for each coal. However, the difference between ash deposition behaviors of tested coals, specifically the amount of accumulated ash in the horizontal duct and deposited ash on tubes in the test section, was not pronounced.

SO_3 formation in the test section simulating a boiler tube bank was difficult to evaluate because the difference between SO_3 measured at the test section inlet and that at the outlet was relatively small. The reason for this is probably due to the short residence time; 0.1 second, in the test section. As shown in Fig.1, the residence time from the burner exit to the test section inlet was 10 seconds and most SO_3 were formed before the test section inlet. In experiments, there is a limitation of increasing residence time because of their facility scale.

Some small specific features derived from coal type can be explained by the balance between the adsorption effect of unburned carbon in ash (UBC) and the catalytic effect of iron and vanadium oxides. UBC of Coal A, in which test $\text{SO}_{3\text{outlet}}$ was lower than $\text{SO}_{3\text{inlet}}$, was 8.1%, and was the highest amount among those of other coals (Coal B; 3.3%, 20% petroleum coal blend; 4.5%, 40% petroleum coke blend; 5.7%). From this result, SO_3 was assumed to adsorb to UBC rich ash in the test section and decrease at the section outlet for Coal A; this means the adsorption effect appears to be greater than the catalytic effect. When we consider the other cases similarly, the following can be understood. In case of Coal B and 20% petroleum blend, the catalytic effect was greater than the absorption effect, and then SO_3 tended to increase in the test section. In case of 40% petroleum blend, both effects are competitive (remember that UBC in ash 40% petroleum coke was 5.7%, this was higher than those of Coal B and 20% petroleum blend), and then SO_3 did not change before and after the test section.

SO_3 concentration decreases almost linearly with decreasing O_2 concentration for both coals. Fernando et al [2] have reported that SO_3 concentration at economizer declines almost linearly at a 585MW boiler field test. Our results are consistent with their findings and also significant for quantifying the effect of combustion stoichiometry on reducing SO_3 .

5. CONCLUSION

The effects of coal type and combustion stoichiometry on SO_3 formation have been investigated quantitatively by conducting tests at 1.6MWth pilot plant having a test section simulating horizontal tube bank.

Our study led to the following conclusions:

- SO_3 formation was high for coals containing high amounts of sulfur and vanadium oxide.
- SO_3 concentration decreased linearly with decreasing O_2 concentration. Reduction of combustion stoichiometry from 1.5 to 1.2 decreased SO_2 oxidation rate from 1.4 to 0.6%

and from 2.4 to 1.0% for Coal B and 40% of petroleum coke blending, respectively.

(c) The amount of SO_3 formed at the simulating a tube bank was relatively small compared with that at the area before the bank. There seems to be some difference in results between coals, however it is not enough to discuss the effect of coal types.

6. REFERENCES

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