Studies of the Fate of Sulfur Trioxide in Coal-Fired Utility Boilers Based on Modified Selected Condensation Methods

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The formation of sulfur trioxide (SO_3) in coal-fired utility boilers can have negative effects on boiler performance and operation, such as fouling and corrosion of equipment, efficiency loss in the air preheater (APH), increase in stack opacity, and the formation of $PM_{2.5}$. Sulfur trioxide can also compete with mercury when bonding with injected activated carbons. Tests in a lab-scale reactor confirmed there are major interferences between fly ash and SO_3 during SO_3 sampling. A modified SO_3 procedure to maximize the elimination of measurement biases, based on the inertial-filter-sampling and the selective-condensation-collecting of SO_3, was applied in SO_3 tests in three full-scale utility boilers. For the two units burning bituminous coal, SO_3 levels starting at 20 to 25 ppmv at the inlet to the selective catalytic reduction (SCR), increased slightly across the SCR, owing to catalytic conversion of SO_2 to SO_3, and then declined in other air pollutant control device (APCD) modules downstream to approximately 5 ppmv and 15 ppmv at the two sites, respectively. In the unit burning sub-bituminous coal, the much lower initial concentration of SO_3 estimated to be approximately 1.5 ppmv at the inlet to the SCR was reduced to about 0.8 ppmv across the SCR and to about 0.3 ppmv at the exit of the wet flue gas desulfurization (WFGD). The SO_3 removal efficiency across the WFGD scrubbers at the three sites was generally 35% or less. Reductions in SO_3 across either the APH or the dry electrostatic precipitator (ESP) in units burning high-sulfur bituminous coal were attributed to operating temperatures being below the dew point of SO_3.

1. Introduction

During combustion of sulfur-containing fuels, the majority of sulfur in these fuels is converted into sulfur dioxide (SO_2), with approximately 0.5–1.5% of the sulfur converted into sulfur trioxide (SO_3). Coals containing sulfur between 0.5–5 wt % can produce SO_3 concentrations of approximately ten parts per million by volume (ppmv) (*1, 2*). This is enough to create serious issues in coal-fired utility boilers (*1−4*). The SO_3 can increase opacity in the stack by forming sulfuric acid droplets and sulfate aerosols, which are fine particulate ($PM_{2.5}$) sources. Generally, the stack opacity can be seen as the color blue when the SO_3 concentration in the flue gas is greater than 5 ppmv. Sulfur trioxide can also react with ammonia or chloride in the flue gas to form submicrometer aerosols that create a white, opaque plume.

The potential corrosion of utility equipment (e.g., downstream ductwork, air preheater (APH), dry electrostatic precipitator (ESP), baghouse, and induced draft fan (I.D. fan)) is another important issue for boiler performance and operability. To avoid corrosion, the outlet temperature of the APH should be above the dew point of SO_3, which will decrease the electricity-generation efficiency of the boiler (the electricity generation efficiency of the boiler is decreased by 1% when the APH outlet temperature is increased by 20 °C (*3*)).

Recently, additional applications of SCR for NO_x emission control and mercury oxidation have begun to focus on the SO_3 issue since SCR catalysts may be responsible for additional SO_2 conversion to SO_3 in the flue gas (*5, 6*). The SCR temperature should be low enough to eliminate this potential SO_3 conversion. This would mean losing part of the capability of the SCR catalyst on NO_x removal efficiency. On the other hand, the more slipped NH_3 that leaves the SCR, the greater the likelihood that it will react with SO_3 to form ammonia bisulfate (ABS). It is a very sticky and heavy material, which could plug up downstream at the APH and baghouse. Activated-carbon injection (ACI) is currently the prevailing technology for mercury-emission control (*7*). Available SO_3 in the flue gas will deteriorate the adsorbent performance on mercury adsorption because of its competitive adsorption on the active sites of mercury adsorbents (*8−11*).

Thus, the many and varied issues caused by SO_3 in and out of the utility boiler have produced the need for the effective control of SO_3 in these boilers (*12−16*). The potential value of effective SO_3 control can exceed $2−3 million per year for a 500 MW unit (*3*). However, the benefits are likely to be deducted by the additional costs for the application of SO_3 abatement technologies, which depend on SO_3 concentrations in the flue gas. Thus, accurate, repeatable, and verifiable SO_3 sampling and analysis methods are very important. However, this is not the case for currently available SO_3 sampling methods because of the occurrence of potential interference from fly ash. This paper presents a detailed investigation of quality-control issues related to SO_3 measurements in coal-fired utility boilers with conventional air pollution control devices (APCDs) in three coal-fired power plants.

2. Experimental Section

SO_3 Sampling Methods. There are three standard SO_3 sample-collection methods (EPA Method 17, Method 8A, and ASTM 3226-73T; details on these methods have been presented in the Supporting Information). These methods are based on either chemical absorption (EPA Method 17) using 80% isopropyl alcohol (IPA) as a trapping solution or the selective condensation of SO_3 from gas streams laden with SO_2 by controlling condensation temperatures (Method 8A and ASTM 3226-73T). Currently, the selective condensation method accurately separates SO_3 and SO_2 in coal-fired flue gas. However, this is not the case for EPA Method 17

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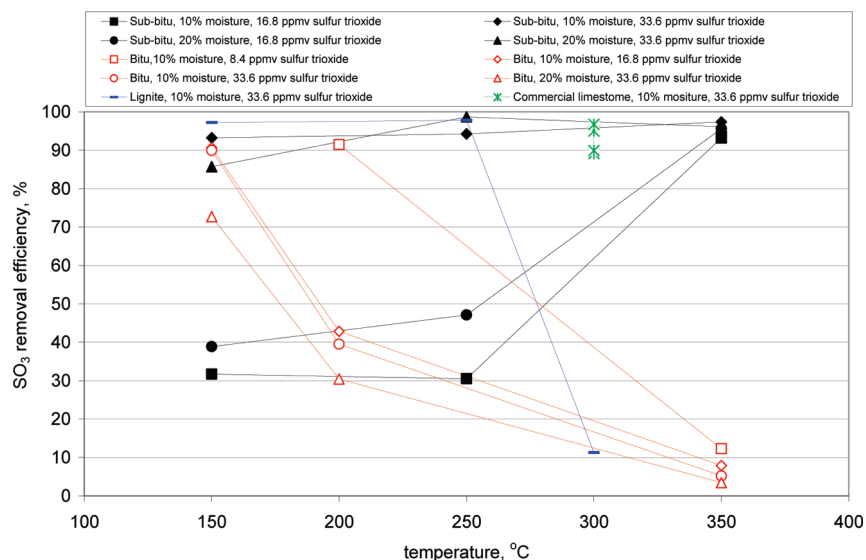§ Shanghai University of Electric Power.

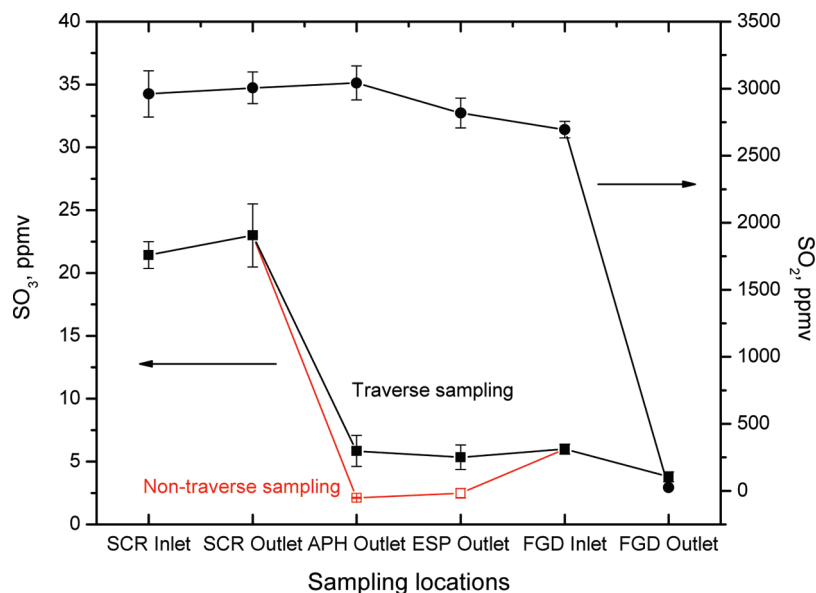FIGURE 1. Lab-scale tests of fly ash activity on SO_3 adsorption or reaction.

Legend:
- Sub-bitu, 10% moisture, 16.8 ppmv sulfur trioxide
- Sub-bitu, 20% moisture, 16.8 ppmv sulfur trioxide
- Bitu,10% moisture, 8.4 ppmv sulfur trioxide
- Bitu, 10% moisture, 33.6 ppmv sulfur trioxide
- Lignite, 10% moisture, 33.6 ppmv sulfur trioxide
- Sub-bitu, 10% moisture, 33.6 ppmv sulfur trioxide
- Sub-bitu, 20% moisture, 33.6 ppmv sulfur trioxide
- Bitu, 10% moisture, 16.8 ppmv sulfur trioxide
- Bitu, 20% moisture, 33.6 ppmv sulfur trioxide
- Commercial limestome, 10% moisture, 33.6 ppmv sulfur trioxide

FIGURE 2. Transformation of SO_3 and SO_2 in the flue gas at Site #1.

because of interference caused by partially dissolving SO_2 in an IPA solution, which has been confirmed in this study (see the Supporting Information and Table S1). The liquid SO_3 solution samples are subsequently subjected to determination of their SO_4^{2-} concentrations by two analytical methods, either using an Ion Chromatograph Analyzer (DX-120 IC in this study) or the standard titration method using a barium (Ba) salt solution. The accuracy of the titration method decreases when the SO_4^{2-} concentration in the sample solution is lower. Thus, in this study, all of our reported SO_2 or SO_3 data are based on the IC instrument analysis. A systematic study was conducted to investigate occurrences of interference by fly ash during SO_3 sampling. In field testing of different locations at three selected sites, three duplicate measurements under each test condition were conducted. The standard deviations of each test condition are presented in Figures 2, 3, and 4 for the three sites. In general the standard deviations were below 10%, except those approximately 40% when the average SO_3 concentrations in the flue gas were below 2 ppmv.

Test Facilities. To investigate potential interferences of fly ash on SO_3, lab-scale tests were set up. A schematic of the fixed-bed reactor is shown in Figure S1 (see the Supporting
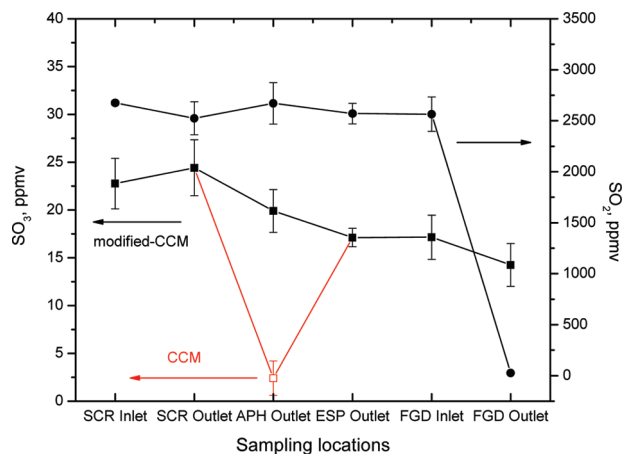

FIGURE 3. Transformation of SO_3 and SO_2 in the flue gas at Site #2.

Information), and a detailed description of the reactor setup and operation is also presented in the Supporting Information. Three full-scale utility boilers were selected to investigate
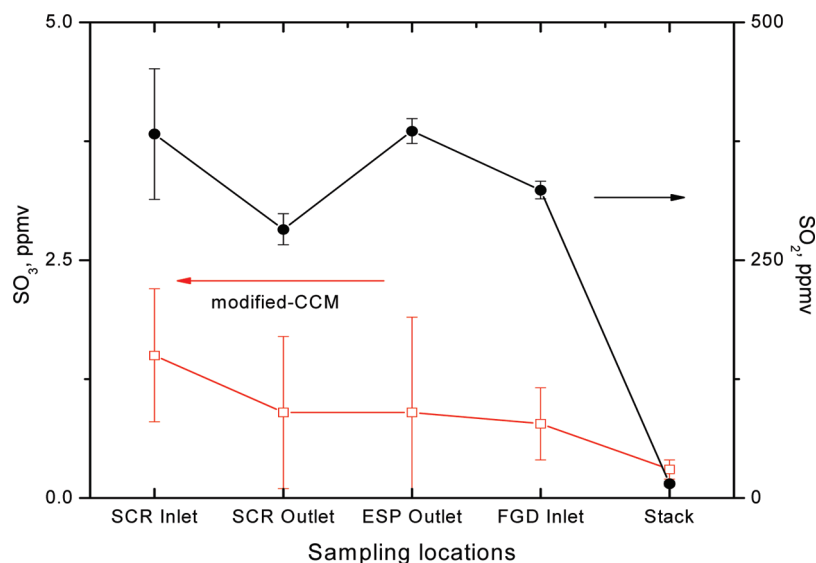
FIGURE 4. Transformation of SO₃ and SO₂ in the flue gas at Site #3.

the transformation of SO_3 inside their convective pass of boilers. In these boilers, a conventional APCD configuration was included, with the SCR, the APH, the ESP, and the WFGD. The wet-ESP is relatively new equipment for enhanced capture of SO_3 and particulate matter. However, we did not find an appropriate site with the wet-ESP equipped to perform SO_3 measurement tests. Thus, it was not included in this manuscript. A typical configuration of the testing unit is shown in Figure S2 (see the Supporting Information). The analysis results of coal and ash from these testing sites are shown in Table S2 (see the Supporting Information). In Sites 1 and 2, bituminous coals with similar sulfur content above 3.5% were burned. Low sulfur sub-bituminous coal was burned in Site 3. The most apparent difference in the three ash samples from the different sites was the amount of alkali earth metals. Sub-bituminous coal is known to be higher in its alkali earth metal content (Ca + Mg) than bituminous coal.

3. Results and Discussion

3.1. Interference of Fly Ash on SO₃ Collection (Lab-Scale Investigation).

There are two kinds of interactions between fly ash and SO_3, which are dependent on temperature. First, fly ash can be an SO_3 adsorbent under lower-temperature ranges, such as typical temperatures after the APH in coal-fired utility boilers. SO_3 most likely occurs as H_2SO_4 mist droplets and is condensed on the fly ash if the temperature is close to or below the dew point of SO_3. Fly ash with a developed pore structure, which most likely results from the carbon residue on fly ash, is responsible for condensation or enhanced adsorption of SO_3 on the fly ash.

Second, SO_3 may react with multiple fly ash constituents, which are likely to be alkali earth metal oxides (such as CaO and MgO), alkali metal oxides (such as Na_2O and K_2O), and slipped NH_3 from the SCR. This scenario most likely occurs at temperatures above 150 °C, in which higher-reaction kinetics could be expected. Generally, alkali earth metal oxides may react with SO_3 in a larger temperature range, from above 800 °C at the superheater area and down to 300 °C before the APH. Alkali metal oxide will react with SO_3 to generate bisulfates of sodium (Na) and potassium (K) below 350 °C, which is a typical temperature at the SCR and the APH. Ammonia only reacts with SO_3 to generate $(NH_4)_2SO_4$ or $(NH_4)HSO_4$ at an even lower temperature range, such as typical temperatures within APH or ESP or the baghouse. Corrosion and fouling are easy to occur if the previously mentioned SO_3 adsorption and reaction with fly ash occurs

in the convective pass of the utility boiler. On the other hand, if the aforementioned SO_3 adsorption and reaction with fly ash occur inside the sampling train (mainly in the sampling probe and ash filtration system), both the negative and positive bias will be brought into the SO_3 measurement.

The setup temperatures of the sampling train (probe and fly ash filtration) must be higher than the dew point of SO_3 in the flue gas when sampling is conducted to prevent SO_3 mist droplets from condensing or adsorbing in the sampling train. If not, a negative bias is likely to be brought into the SO_3 measurement. The dew point of SO_3 varies according to the moisture content and SO_3 concentration in the flue gas (*17, 18*), which is shown in Figure S3 (see the Supporting Information). The dew point of SO_3 increases with the increase of the moisture content and SO_3 concentration in the flue gas. Generally, the moisture content is as low as 7% for bituminous-coal-derived flue gas and as high as 14% for sub-bituminous-coal or lignite-derived flue gas. The SO_3 concentration, based on field tests and knowledge of SO_3 formation during coal combustion, is generally below 50 ppmv. If 50 ppmv SO_3 is available in the flue gas with 20% moisture, the predicted dew point is about 160 °C based on calculations (*17, 18*). The EPA Method 8A and the controlled condensation method (CCM) both suggest temperatures of the sampling probe and fly ash filtration to be above 180 °C. This suggested temperature is high enough to avoid SO_3 condensation in the sampling probe and in fly ash filtration. An example of this occurs when the SO_3 sample collection is pursued at the ESP inlet, where the temperature of the ash-laden flue gas is close to the SO_3 dew point, as indicated in Figure S4 (see Supporting Information). When the fly ash filter is set up in front of the probe, the filtration temperature is close to the flue gas temperature in the sampling duct at around 150 °C. Sulfur trioxide concentration at the ESP inlet is much lower than at the ESP outlet, which is not logical. This is because the majority of SO_3 in the flue gas is lost in the filtration system. Therefore, a higher negative bias of SO_3 measurement is generally observed at the ESP inlet location if the filtration occurs in front of the probe. EPA Method 8 follows the regular stack sampling procedure to set temperatures of the sampling probes and fly ash filtration at about 125 °C during SO_3 sampling. Our field tests have found that even more SO_3 will be condensed in the sampling train.

The loss of SO_3 during sampling could be minimized if the fly ash filtration setup occurs after the sampling probe and its temperature is controlled above the dew point of flue gas, as indicated in EPA method 8A. Due to the application

of much higher temperatures than the dew point for both the sampling probe and filtration system, no SO_3 adsorption was observed in these two areas. Bias by SO_3 condensation could be eliminated by modifying the sampling methods. However, increasing temperatures of the sampling train may potentially bring about the transformation of some species of flue gas. Subsequently, these species would decompose under higher temperatures to emit SO_3 into the sampling train. For example, $(NH_4)_2SO_4$ or $(NH_4)HSO_4$, which is formed in the SCR at a lower temperature range, may decompose when it enters the sampling train operated at the higher temperature. In this case, additional SO_3 may be generated in the sampling probe and filtration system with an elevated temperature and finally captured in the SO_3 condenser to cause the positive bias in SO_3 measurements. Its impact is dependent on NH_3 slip concentration in the flue gas. Generally, $1-3$ ppmv of NH_3 is permitted to pass through the SCR; thus the maximum bias under sampling will be below 1.5 ppmv. This results in a larger relative bias when low-sulfur coals are burned since SO_3 concentrations are lower in the flue gas. Increasing the temperature of fly ash filtration also may cause another negative bias by alkali metal or alkali earth metal in the fly ash, which is dependent upon the actual content of these metal oxides. It is significant that sub-bituminous coal contains a great amount of alkali earth metals (5 times greater than that in fly ash). Consequently, higher bias is likely caused by the fly ash of sub-bituminous coal during SO_3 measurements.

Figure 1 presents test results of SO_3 adsorption and reaction by selected fly ashes in a lab-scale fixed-bed reactor. Data points under varied test conditions show much more scatter on SO_3 capture efficiency by sub-bituminous-coal-derived fly ash than those by bituminous-coal-derived fly ash and Texas-lignite-derived fly ash. Bituminous-coal-derived and Texas-lignite-derived fly ashes presented higher SO_3 adsorption efficiency only under a low-temperature range (about 150 °C), which decreased gradually when the temperature increased to 350 °C. At about 150 °C, both bituminous-derived and Texas-lignite-derived fly ashes demonstrated greater than 75% SO_3 capture efficiency. The variation of their actual SO_3 capture efficiency depended more on SO_3 concentration in the gas stream and less on fly ash properties, because variations of SO_3 concentration have a more obvious impact on the SO_3 dew point. Therefore, sulfuric acid mist is most likely formed to enhance SO_3 condensation on tested fly ash at this low temperature range. As temperatures increased to around 200 °C, the SO_3 capture capability decreased by 50 to 60%. At temperatures as high as 350 °C, their SO_3 capture efficiency dropped below 10%. This behavior should correlate to the low alkali earth-metal content in the fly ash, which caused less active bituminous-coal-derived and Texas-lignite-derived fly ashes to react with SO_3 even at a higher temperature range. The transition temperature of SO_3 adsorption and SO_3 reaction with active constituents in fly ash can occur above 150 °C and below 350 °C. Unlike bituminous-coal-derived and Texas lignite-derived ashes, sub-bituminous-coal-derived fly ash showed more than 90% of SO_3 capture efficiency at 350 °C. This is coincident with the performance of some commercial CaO-based adsorbents above 300 °C. Higher alkali earth-metal oxides (CaO+ MgO) in sub-bituminous-coal-derived fly ash may be responsible for its active performance under higher temperature ranges. At lower temperature ranges (150 °C), sub-bituminous coal-derived fly ash with low carbon content performed poorly in capturing SO_3. The increase of SO_3 concentrations in the gas stream, relative to the decrease of its dew points, will increase SO_3 capture efficiencies of sub-bituminous coal-derived fly ash. This confirmed that the effect of SO_3 condensation is a dominant factor for SO_3 capture by sub-bituminous coal-derived fly ash in lower-temperature ranges.

Based on this study, it is likely that the higher temperature filtration in the sampling train could help to eliminate the bias by SO_3 condensation or adsorption only when bituminous coal or Texas lignite is burned. Increasing the filtration temperature in the sampling train would increase the bias when sub-bituminous coal is burned because the transition of SO_3 condensation or adsorption to react with alkali earth-metal oxides occurs during increased temperature. Thus, the effectiveness of temperature increases of the sampling train on accuracy improvement of SO_3 sampling only works with bituminous coal or Texas lignite but not in cases of sub-bituminous coal. To thoroughly eliminate bias brought about by fly ash during SO_3 sampling, an inertial sampling probe was used. This SO_3 sampling method was called the modified CCM in this study. The applied temperature of the inertial probe should be controlled to be the same temperature as the flue gas at the sampling site before the APH and to be at higher temperatures than the SO_3 dew points after the APH.

3.2. Validation Results from Three Full-Scale Sites. *Site #1.* This test site burned high-sulfur bituminous coal. Figure 2 summarizes the results obtained from the measurements of SO_2 and SO_3 at six locations in Site #1. It indicates that concentrations of SO_2 remained relatively constant throughout the convective pass through the Site #1 unit, which started at the SCR inlet location prior to the WFGD unit location. There was only a slight decrease of SO_2 concentration after the flue gas passed through the ESP unit from 3042 ppmv at the ESP inlet to 2817 ppmv at the ESP outlet. Another slight decrease of SO_2 concentration occurred between the ESP outlet and the WFGD inlet, where SO_2 was about 2700 ppmv. This indicated that very little SO_2 could be removed by the ESP unit under the lower temperature of 150 °C in Site #1. A dramatic drop of SO_2 concentration occurred after flue gas passed through the WFGD unit, where the SO_2 concentration dropped to a level of 24 ppmv with 99.1% achievable SO_2 removal efficiency.

The SO_3 concentration at the SCR inlet was about 21 ppmv and increased slightly to 23 ppmv at the SCR outlet across the SCR unit. However, the SO_3 concentration decreased sharply after flue gas passed through the APH facility. At the first sampling location after the APH, which was the ESP inlet, the SO_3 concentration was only about 2.11 ppmv, and it stayed relatively constant throughout the ESP. At the ESP outlet the SO_3 concentration was still as low as 2.48 ppmv. The observed change between concentrations of SO_3 at the SCR inlet and the ESP outlet may be due to the condensation of H_2SO_4 mist inside the APH. According to the operation record during the flue gas sampling, the average temperature at APH was about 138 °C. It was very close to the approximate estimation of the dew point of SO_3 at this location (134 °C) (*17, 18*). It is possible that some sulfuric acid droplets might have formed on the heat exchanger surface. Formation of those condensed droplets on the APH would greatly decrease the concentration of SO_3 in the flue gas. On the other hand, it was unexpected that SO_3 concentrations at the ESP inlet and outlet were lower than those at the WFGD inlet and stack, where SO_3 concentrations are about 5.99 ppmv and 3.79 ppmv, respectively. A follow-up traverse sampling test on SO_3 measurements at the ESP inlet and outlet confirmed the occurrence of flue gas stratification inside the APH or the ESP. Measured average SO_3 concentrations were about 5.85 ppmv and 5.34 ppmv at the inlet and the outlet of the ESP, respectively. These were consistence with SO_3 concentrations at the WFGD inlet. The validation SO_3 measurement in Site #1 indicated that lower operational temperatures of the APH outlet was responsible for a major drop of gaseous SO_3 concentration of about 74% or less in the APH. An additional

SO$_3$ drop inside the WFGD was found to be about 10%. Thus, a total of almost 85% of SO$_3$ was removed in Site #1. Some corrosion problems reported in the APH of this unit may confirm the possibility of SO$_3$ deposition in the APH. No blue plume was found at the stack of Site #1 because of its lower occurrence of SO$_3$ in the stack's flue gas (3.79 ppmv), as shown in Figure S5 (see the Supporting Information).

Site #2. The test unit of Site #2 burned similar bituminous coal as that used in the unit of Site #1. Its APCD configuration was also similar but differed in the applied SCR catalyst. The flue gas stratification was not found at the convective pass after the APCD. The outlet temperature of the APH, which averaged 155 °C, was above the dew point of SO$_3$ in the flue gas (140 °C). Figure 3 presents the measurement results of SO$_2$ and SO$_3$ at six locations before and after each APCD component. As can be seen in this figure, the SO$_2$ concentration remained relatively constant at about 2600 ppmv throughout the flue gas path until the inlet of the WFGD facility. After the flue gas passed through the WFGD, the SO$_2$ concentration decreased dramatically to 27 ppmv. By comparing the change of SO$_2$ concentrations across the WFGD unit, the SO$_2$ removal efficiency was calculated to be 99.0%.

The SO$_3$ concentration was about 23 ppmv at the SCR inlet and increased a small amount to 24.5 ppmv after the flue gas passed through the SCR catalyst bed. This smaller increase of SO$_3$ was the SO$_2$ conversion effect of the SCR catalyst in Site #2, which is similar to that occurring on the SCR catalyst in Site #1. Starting from the SCR outlet, the SO$_3$ in the flue gas gradually decreased to 19.5 ppmv, reaching the ESP inlet through the APH, and continued its drop to 17 ppmv, reaching the ESP outlet through the ESP facility. In Site #2, maintaining a higher temperature at its APH outlet than that in Site #1 may be the major reason of SO$_3$ adsorption on fly ash in Site #2. There were no reports of equipment corrosion occurring in Site #2. At the stack, the SO$_3$ concentration was about 14 ppmv. As indicated in Figure S5 (see the Supporting Information), blue plume was clearly seen at this site's stack. The total removal efficiency of SO$_3$ was calculated to be about 41%, including an 18.5% drop in the APH and a 5% drop through the ESP inlet and 16.8% drop across the WFGD.

Site #3. In Site #3, sub-bituminous coal was burned. Its sulfur content was as low as 0.4 wt %. However, its fly ash was rich in alkali earth metals (Ca + Mg). The test results on the transformation of SO$_3$ and SO$_2$ in flue gas are presented in Figure 4. Similar to the two previous sites, the SO$_2$ concentrations in Site #3 remained relatively constant at about 350 ppmv starting at the SCR inlet and continuing to the WFGD inlet. It was found that increased alkali metals in its fly ash did not impact on SO$_2$ capture. The SO$_2$ concentration, at the WFGD outlet, decreased dramatically to about 15 ppmv with a 96.1% SO$_2$ removal efficiency. The SO$_3$ concentration decreased from approximately 1.0 ppmv to 0.3 ppmv after the WFGD. The total removal efficiency of SO$_3$ was 81.5%. A 45% decrease of SO$_3$ was found after flue gas passed through the SCR, and another 35% SO$_3$ decrease was found in the WFGD. The fly ash deposit in the SCR may have been responsible for the SO$_3$ drop because of higher reactivity of alkali earth metal on SO$_3$. Due to very low SO$_3$ concentrations in its stack flue gas, no blue plume was found in its stack, as indicated in Figure S5 (see the Supporting Information).

Tests of sulfur trioxide (SO$_3$) at selected, full-scale utilities confirmed the interference of fly ash on SO$_3$ measurement based on an available standard method and successful applications of a modified procedure using the inertial sampling in both bituminous and sub-bituminous coal flue gas. On-site practices also indicated that increasing the filtration temperature would help to eliminate sampling bias

for bituminous coals or Texas-lignite but not for sub-bituminous coals due to reactions between SO$_3$ and the alkali and alkaline earth oxides in fly ashes derived from these coals. Tests with this modified ASTM method, incorporating inertial sampling, indicated that SCRs slightly increase the occurrences of SO$_3$ in the flue gas because of its SO$_2$ oxidation effects, which are generally within 10%. The efficient control of SO$_2$ emissions using the WFGDs seems not to extend to their SO$_3$ capture capability, which is generally below 35%. Behavior of SO$_3$ across the APH is dependent on operational temperatures at the APH outlet. Higher operational temperatures than the SO$_3$ dew points would maintain SO$_3$ in the gas phase, while lower temperatures than the SO$_3$ dew point cause SO$_3$ either to react with fly ash constituents or adsorb on fly ash.

3.3. Discussion. Tests either in the lab-scale fixed-bed reactor or in three full-scale utilities revealed a clear picture of the fates of SO$_3$ under the quenching process of flue gas (the temperatures of interest range from 350 °C of the SCR to 60 °C of the WFGD). Variations of SO$_3$ concentrations are more dependent on coal sulfur content, operational conditions of SCR catalysts, SO$_3$ dew points, and interactions between SO$_3$ and fly ash. For the two units burning bituminous coal, SO$_3$ levels starting at 20 to 25 ppmv at the inlet to the SCR increased slightly across the SCR. In the unit burning low-sulfur sub-bituminous coal, the SO$_3$ concentration was even reduced from 1.5 ppmv to about 0.8 ppmv across the SCR, because of the capture capability of alkali earth metals in its fly ash under typical SCR temperatures. Thus, commercial SCR catalysts did not significantly convert SO$_2$ to SO$_3$ (generally less than 0.5%) (*19*).

As for interactions between SO$_3$ and fly ash, carbon residue and alkali earth metal in fly ash presented different trends as temperatures changed. Under higher temperature ranges, typically at locations prior to the APH, alkali earth-metal constituents than carbon residues in fly ash were active on SO$_3$ capture through chemical reactions to form sulfate salt. Under lower temperature ranges, typically at locations after the APH, the fly ash functioned as major adsorption sites for SO$_3$ condensation or carbon residues. Thus, factors controlling the SO$_3$ dew point, including SO$_3$ concentrations, moisture content, and flue gas temperatures, dominated SO$_3$ capture efficiencies and further determined the available SO$_3$ in the gas phase. Higher SO$_3$ concentrations, higher moisture content, and lower temperatures in the flue gas resulted in more SO$_3$ condensation or adsorption on fly ash and removal by ESP. Sub-bituminous coal generally had higher alkali earth metals in their fly ash, which allowed the SO$_3$ in their flue gas to be captured effectively after flue gas in the higher temperature zone prior to the APH. Bituminous coals generally had high carbon-residue content in fly ash but a lower occurrence of alkali earth metal constituents, which allowed the SO$_3$ in the flue gas to be captured effectively after APH. As for accurate SO$_3$ measurements, special attention should be paid to SO$_3$ sampling at locations prior to the APH when burning sub-bituminous coal and at locations after the APH when burning bituminous coal. In both cases, the inertial probe, which could significantly eliminate interference of fly ash, should be applied.

The fates of SO$_3$ in the coal-fired flue gas raise two other points of interest. The first is the relevance of SO$_3$ in the flue gas to its impact on mercury-capture efficiencies by activated-carbon injection (ACI) (*8, 11, 20*). The SO$_3$ and mercury preferentially shared the same active sites on the activated carbon, even those with halogen doped activated carbon, because of the formation of sulfuryl chloride or sulfuryl bromide (*11*). When considering concentrations of SO$_3$ in flue gas in ppmv contrasting with concentrations of mercury in ppbv, this impact is significant. The mechanism of this interference should be similar to the interaction between

SO$_3$ and carbon residue on fly ash. Solutions for eliminating this interference could include the development of high-temperature mercury adsorbents, such as those adsorbents working effectively under temperatures higher than 300 °C, where carbon-based mercury adsorbents would not simultaneously capture SO$_3$. Thus, competition of mercury and SO$_3$ on active sites of carbon-based adsorbents could be largely eliminated. Second, the problems of blue plume and PM$_{2.5}$ particulate matters, caused by SO$_3$ emissions into the environment, are another area focused on by power plants and the U.S. EPA (21). In all three cases of this study, SO$_3$ removal by the WFGD was found to be low (35%) and not efficient. This finding was supported by previous studies, which confirmed that the quick quenching of flue gas inside the WFGD resulted in the formation of fine SO$_3$ condensed droplets and, thus, could easily escape the capture of WFGD (2). Therefore, potential options for overcoming the impacts of SO$_3$ on ACI and stack emissions of SO$_3$ will ultimately remove SO$_3$ in the flue gas prior to the locations of activated carbon injection. This could be achieved by co-injecting mercury adsorbents (activated carbon) and SO$_3$ adsorbents (8−11), such as sodium bicarbonate (NaHCO$_3$) and hydrated lime (Ca(OH)$_2$). There are indeed merits to applying this co-injection method.

Rough engineering estimates show that lower concentrations of SO$_3$ in the flue gas (a few or tens of ppmv) and higher reactivity of injected adsorbents, lower injection rates of adsorbents. Therefore, significant abrasion of devices and pressure drop caused by injected adsorbents may not be expected. Because injection could be conducted before the fly ash collection devices, the majority of injected adsorbents will be captured with the fly ash. It is crucial to use adsorbents with higher reactivity (such as sodium bicarbonate and hydrated lime) to minimize injection rates of these adsorbents. However, the merits of future studies on the aforementioned questions in a long-term evaluation period are still clear and worth pursuing.

Acknowledgments

Supporting Information Available

Statements on standard methods of SO$_3$ sampling and the lab-scale reactor, five figures and two tables. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Bionda, J. *Flue gas SO$_3$ determination - Importance of Accurate Measurements in Light of Recent SCR Market Growth*, 2002 DOE/NETL Conference on SCR and SNCR Reduction NO$_x$ Control, Pittsburgh, PA, 2002.

(2) Srivastava, R. K.; Miller, C. A. Emissions of sulfur trioxide from coal-fired power plants. *J. Air Waste Assoc.* **2004**, *54*, 750–762.

(3) Moser, R. *Benefits of Effective SO$_3$ Removal in Coal-fired Power Plants: Beyond Opacity Control, Mega Symposium*, Baltimore, MD, 2006.

(4) Buckley, W. P.; Altshuler, B. Sulfuric acid mist generation in utility boiler flue gas. *Power Eng.* **2002**, *11*, 132–136.

(5) Forzatti, P.; Nova, I.; Bertta, A. Catalytic properties in deNO$_x$ and SO$_2$-SO$_3$ reactions. *Catal. Today* **2000**, *56* (4), 431–441.

(6) Dunn, J.; Stenger, H. G.; Wachs, I. Oxidation of sulfur dioxide to sulfur trioxide over supported vanadium catalyst. *Appl. Catal. B: Environ.* **1998**, *19* (2), 103–117.

(7) Ravi, K.; Srivastava, N.; Hutson, B.; Martin, F.; Staudt, P. J. Control of mercury emissions from coal-fired electric utility boil. *Environ. Sci. Technol.* **2006**, *40* (5), 1385–1393.

(8) Sjostrom, S.; Wilson, C.; Bustard, J.; Spitznogle, G.; Toole, A.; O'Palko, A.; Chang, R. *Full-scale Evaluation of Carbon Injection for Mercury Control At A Unit Firing High Sulfur Coal* The MEGA Symposium; U.S. EPA - DOE - EPRI: Washington, DC, 2006.

(9) Nelson, S. *Brominated sorbents for small cold-side ESPs, hot Side ESPs, and fly ash use in concrete*; Report to U.S. DOE/NETL, Cooperative Agreement No. DE-FC26-05NT42308; Sorbent Technologies Corporation: 2006.

(10) Kang, S. *Field demonstration of enhanced sorbent injection for mercury control*; Report to U.S. DOE/NETL, Cooperative Agreement No. DE-FC26-04NT42306; Alstom Power, Inc.: 2006.

(11) Presto, A. A.; Granite, E. J. Impact of sulfur oxides on mercury capture by activated carbon. *Environ. Sci. Technol.* **2007**, *41* (18), 6579–6584.

(12) Altman, R.; Buckley, W.; Ray, I. Wet electrostatic precipitation demonstrating promise for fine particle control. *Power Eng.* **2001**, *1*, 37–39.

(13) Control of Sulfuric Acid Mist Emissions from Existing Sulfuric Acid Production Units. EPA Report 450/2-77-019 (OAQPS N0. 1.2-078).

(14) Brandes, S. D.; Rosenhoover, W. A.; Devito, M. S. *The Development and Evaluation of A Cost-effective Method for Reducing SO$_3$ From Coal-fired Boiler Flue Gas*, 17th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, 2000.

(15) Adams, B.; Cremer, M.; Ma, J.; Valentine, *Improving Effectiveness of SO$_3$ Mitigation Systems With CFD Modeling*, DOE Environmental Controls Conference, Pittsburgh, PA, 2006.

(16) Peterson, J.; Jones, A. F. *SO$_3$ mitigation guide*; EPRI Report Number TR-104424; EPRI: Palo Alto, CA, 1994.

(17) Verhoff, F. H.; Banchero, J. T. Predicting dew points of flue gases. *Chem. Eng. Prog.* **1974**, *70* (8), 71–72.

(18) Okkes, A. G. Eliminating a sulfuric acid mist plume from a wet caustic scrubber. *Hydrocarbon Process. J.* **1997**, *66* (7), 53–55.

(19) Tronconi, E.; Cavanna, A.; Orsenigo, C.; Forzatti, P. Transient kinetics of SO$_2$ oxidation over SCR-DeNO$_x$ monolith catalysts. *Ind. Eng. Chem. Res.* **1999**, *38* (7), 2593–2598.

(20) Pavlish, J. H. Preface to the AQVI special issue of fuel processing technologies entitled: Air Quality VI: mercury, trace elements, SO$_3$, particulate matters, and greenhouse gases. *Fuel Process. Technol.* **2009**, *90* (11), 1327–1332.

(21) Final Rule to Add PM$_{2.5}$ Precursors to the Transportation Conformity Rule. EPA420-F-05-005; U.S. Environmental Protection Agency: May 2005. Available at http://www.epa.gov/otaq/stateresources/transconf/rule_to_add_pm2-5.htm (accessed month day, year).

ES903661B