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Emissions of Sulfur Trioxide From Coal-Fired Power Plants

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ABSTRACT

Emissions of sulfur trioxide (SO_3) are a key component of plume opacity and acid deposition. Consequently, these emissions need to be low enough not to cause opacity violations and acid deposition. Generally, a small fraction of sulfur in coal is converted to SO_3 in coal-fired combustion devices such as electric utility boilers. The emissions of SO_3 from such a boiler depend on coal sulfur content, combustion conditions, flue gas characteristics, and air pollution devices being used. It is well known that the catalyst used in the selective catalytic reduction (SCR) technology for nitrogen oxides (NO_x) control oxidizes a small fraction of sulfur dioxide (SO_2) in the flue gas to SO_3. The extent of this oxidation depends on the catalyst formulation and SCR operating conditions. Gas-phase SO_3 and sulfuric acid (H_2SO_4), on being quenched in plant equipment (e.g., air preheater and wet scrubber), result in fine acidic mist, which can cause increased plume opacity and undesirable emissions. Recently, such effects have been observed at plants firing high-sulfur coal and equipped with SCR systems and wet scrubbers. This paper investigates the factors that affect acidic mist production in coal-fired electric utility boilers and discusses approaches for mitigating emission of this mist.

INTRODUCTION

As understanding of the adverse effects of air pollution has grown, so also has the complexity of coal fired power plant design and operation, especially with regard to air pollution control systems. Control of air pollutant emissions is not only a legal requirement, but is also becoming a financial necessity, as salability of effluents and trading of emissions permits increase the direct monetary value of emissions control. The days when one must only consider "the nuisance value of fly ash" are long past [Fryling, 1966].

As plant complexity has increased, so have unexpected consequences of changing segments of the total chemical process that occurs between fuel preparation and ultimate emissions. One of the more discernible adverse consequences is the formation and emission of SO3, as highlighted by the recent and well-publicized experiences of a power plant in Ohio [Hawthorne, 2001]. Although not directly subject to emission limits, SO3 is important to consider during the design and operation of coal-fired utility boilers for a number of environmental and plant performance reasons.

The formation of SO3 will occur during the combustion of sulfur-bearing fuels such as coal and heavy fuel oils. For reasons that will be discussed below, concentrations of SO3 in the boiler, stack, and/or plume can be high enough to cause adverse impacts to plant equipment and to the environment. Impacts on plant equipment can include corrosion, fouling, and plugging and may require additional hardware or changes in operation, including load limits, to minimize SO3 concentrations and the resulting adverse impacts.

Health and Environmental Effects

Formation of visible H2SO4 droplets depends upon the concentration and dew point of H2SO4 and the concentration of sub-micron particle upon which the acid can condense. As seen in Figure 1, the H2SO4 dew point is a function of water vapor and H2SO4 concentration, and increases as both these variables increase [Verhoff and Banchero, 1974]. The curves in Figure 1 determine the fraction of H2SO4 in the vapor and condensed phases for temperatures below the dew point. For example, a 250°F flue gas with 10% water vapor and 8 ppm H2SO4 will have a vapor phase acid gas concentration of approximately 2 ppm, with the remaining 6 ppm in the condensed phase.

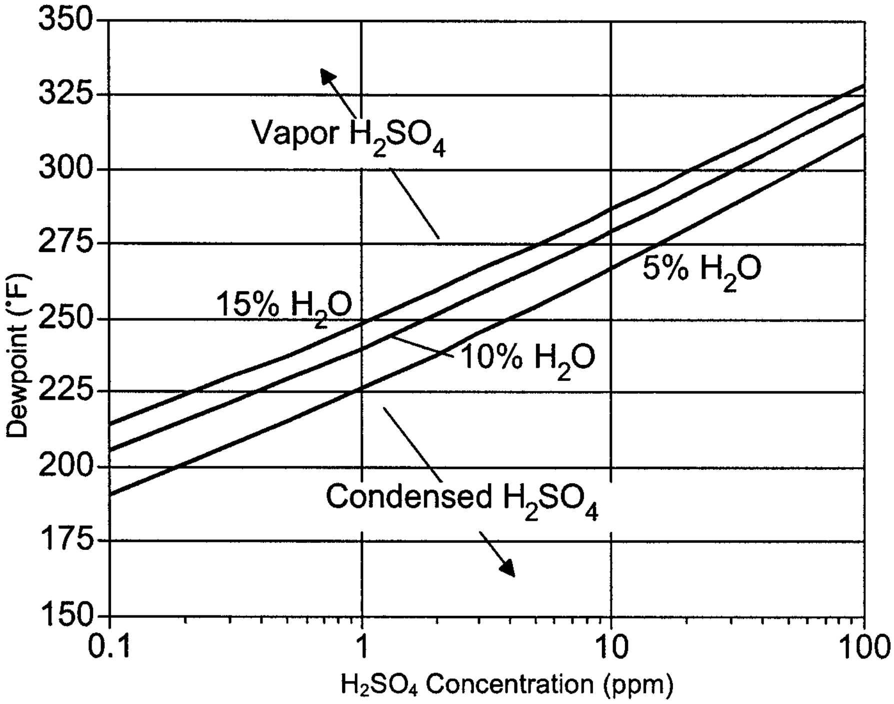

Figure 1 Dew point of H2SO4 as a function H2SO4 concentration for different water vapor concentrations (from Verhoff and Banchero 1974).

If temperatures at the stack are low enough and water vapor and H2SO4 concentrations are high enough, the condensed phase concentration of H2SO4 can be at a level that results in the formation of a visible plume attached to the stack. Once the gases leave the stack, the rate of cooling and subsequent H2SO4 condensation competes with the plume dilution by entrainment of ambient air into the plume. Even in cases where stack conditions are such that the H2SO4 is completely in the vapor phase at the stack exit, a detached plume may still form shortly downwind as temperatures drop below the dew point before concentrations fall below the point where H2SO4 condensation occurs.

In most cases, and particularly in the case where H2SO4, water, and sub-micron solid particles are present, condensation is the dominant formation mechanism. The opacity of these plumes is most strongly influenced by the concentrations of condensing species and sub-micron fly ash particles present in the stack gases. The size distribution of the sub-micron fly ash can also have a noticeable effect on plume opacity at low to moderate H2SO4 concentrations, as these particles act as condensation sites for the condensing vapor-phase H2SO4. The relationship between sub-micron particle concentration, H2SO4 concentration, and plume opacity is shown in Figure 2 for flue gas with a sub-micron particle mode at 0.15 µm diameter [Damle et al., 1984, 1987]. The gray area denotes a typical range of sub-micron particle concentrations downstream of an ESP [Markowski et al., 1980].

The curves in Figure 2 illustrate that H2SO4 concentration can have a strong impact on opacity when fine particle concentrations are present at realistic levels. Because the condensing acid particles can nucleate to form particles even at very low levels of pre-existing sub-micron particles, further reduction of sub-micron solid particles will not significantly reduce plume-opacity. As an example, a unit emitting 16 ppm of vapor phase H2SO4 and 5 mg/m^3 of sub-micron particles is predicted to result in a plume-opacity of about 35%. An

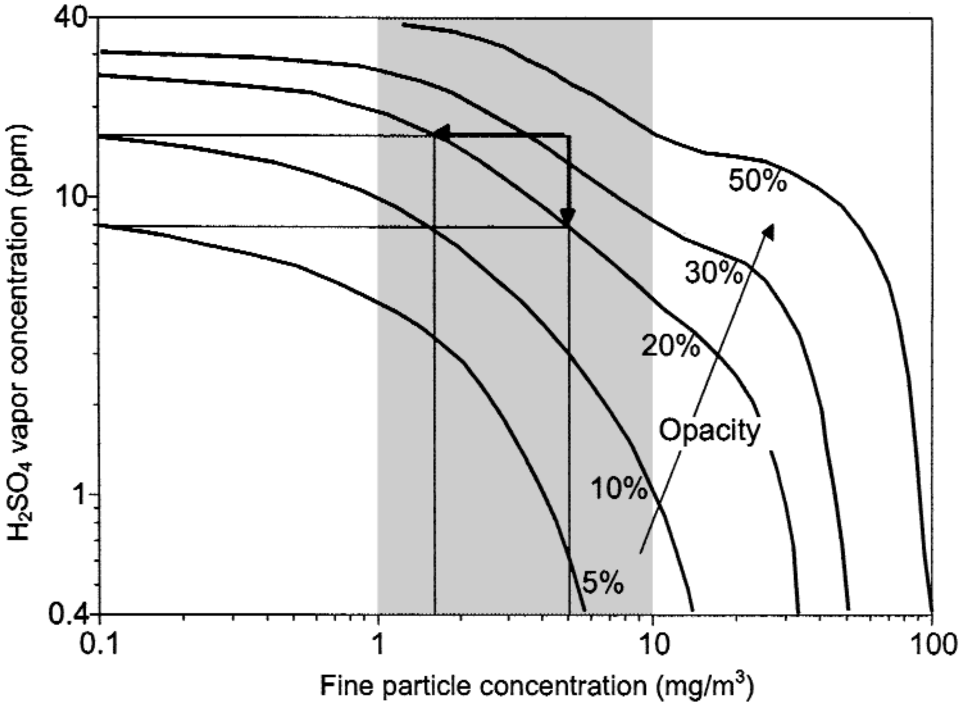

Figure 2 Iso-opacity plot calculated for a bimodal distribution of coarse and sub-micron particles. The sub-micron particle mode is at 0.15 µm diameter (from Damle et al., 1987). The gray area represents typical sub-micron mass concentrations in the stack of a coal-fired utility boiler (Markowski et al., 1980).

opacity of 20% can be achieved by a further reduction of sub-micron PM concentration to about 1.6 mg/m^3 (approximately 70%) or by a reduction of H_2SO_4 to about 8 ppm (a 50% reduction). For units with limited ability to further reduce PM emissions, control of SO_3 (and, subsequently, H_2SO_4) may be the only viable option for achieving plume-opacity requirements. Because essentially all the SO_3 is converted to H_2SO_4 at or below stack temperatures, Figure 2 also illustrates the impact of increases in SO_3 formation on plume-opacity. A unit with 1 mg/m^3 of sub-micron particles in the stack gases is predicted to experience doubling of plume-opacity from 5% to 10% when H_2SO_4 concentrations increase from 5 to 10 ppm.

Data on direct adverse effects on human health are inconsistent, but, in general, studies indicate that aqueous acidic aerosols at typical and even elevated ambient concentrations have minimal effects on symptoms and mechanical lung function in young healthy adults. However, there are studies that have shown changes in mucociliary clearance and modest bronchoconstriction in asthmatics exposed to elevated concentrations of 400 µg/m^3 or more. Of more concern than the effects of exposure to typical ambient levels of SO_3 or aqueous sulfuric acid (H_2SO_4) aerosols alone are exposures to these aerosols mixed with other ambient PM constituents, including elemental carbon and metals [EPA, 1996].

In situations where SO_3 and H_2SO_4 aerosols combine with a sinking plume, the ambient concentrations near the stack can reach significantly higher levels than those normally experienced. In such cases where meteorological and operating conditions combine to form a near-stack acidic fog, damage to property and vegetation can occur if the conditions are sustained for an extended period. Anecdotal evidence of adverse health impacts such as burning eyes, sore throats, and headaches has also been reported in such cases [Hawthorne, 2001].

Impacts on Plant Hardware

The most common problem associated with elevated concentrations of SO_3 is low temperature [< 300 °F (150 °C)] corrosion. Once formed, SO_3 reacts easily with the moisture in combustion flue gases to produce H_2SO_4. Below its dew point, H_2SO_4 condenses and will collect in relatively low temperature areas of the flue gas path, such as the air heater, and corrode the contacted metal components. The dew point varies with H_2SO_4 and water concentration in the flue gas, but is typically between 200 and 300°F (95 and 150°C, respectively). At higher temperatures [1100-1200°F (600-650°C)], catalytic reactions can occur with oxidized metal surfaces to form iron trisulfates or sulfite scale. These high temperature reactions are less common than the low temperature condensation and corrosion reactions. In addition to forming corrosive H_2SO_4, SO_3 reacts to form sulfate particles (see below), especially ammonium sulfate [$(NH_4)_2SO_4$] and ammonium bisulfate (NH_4HSO_4), which can lead to fouling and/or plugging of low temperature plant components, particularly the air heater. Formation of these sulfate particles also adds to the particle loading to particle control devices, especially the fine particle fraction [particulate matter (PM) smaller than 2.5 μm in aerodynamic diameter ($PM_{2.5}$)].

In some cases, modification or addition of hardware may be required to minimize corrosion or plugging. Particularly where plants have been retrofitted with wet flue gas desulfurization (FGD) systems, the reduction in flue gas temperature can result in increased H_2SO_4 condensation and subsequent corrosion. In such cases, the flue gas may require reheating to ensure it remains above the dew point. Reheating or increased fan power to overcome pressure drop across a plugged air heater both add to operating costs due to SO_3 formation [Zetlmeisl et al., 1983].

Regulatory Overview

There are currently no U.S. regulations that directly limit emissions of SO_3 and no regulations that directly limit emissions of H_2SO_4 aerosols from utility boilers. Other regulatory programs may, however, require SO_3 control as discussed below. German emission standards limit the combined SO_2 and SO_3 emission concentrations to a daily average of 50 mg/Nm^3 and a 30-minute average of 200 mg/Nm^3. There is no separate emission limit for SO_3 alone [Bock, 2002].

In the U.S., SO_3 emissions are included as part of limits on opacity and PM emissions, and H_2SO_4 is listed as a hazardous air pollutant (HAP) under Title III of the Clean Air Act (CAA) as amended in 1990 [CAAA, 1990]. Under Title III, electric utility generating stations are exempt from the mass emission limits of 10 tons (9.09 tonnes) per year of any single HAP or 25 tons (22.7 tonnes) per year of combined HAPs set for other industrial sources. Thus, although H_2SO_4 is a listed HAP and is emitted in significant quantities by coal-fired utility generating stations [EPA, 1998], there is no regulatory requirement to control these emissions as HAPs. They must, however, be reported to EPA under the Toxics Release Inventory (TRI) requirements. The H_2SO_4 is typically measured and reported as equivalent SO_3.

EPA has defined primary PM as particles that are either emitted directly as a solid or liquid or are emitted as a vapor but condense and/or react upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack. Secondary PM is composed of particles that form through chemical reactions in the ambient air well after dilution and condensation have occurred [EPA, 2002]. Under this definition, SO_3 or H_2SO_4 that is in vapor phase in the furnace or stack, but which either reacts to form sulfate particles or condenses to form liquid H_2SO_4 immediately after leaving the stack, is considered part of primary PM emissions and is therefore subject to PM emission limits.

In some states or localities, plants may be required to control SO_3 to maintain opacity standards. Even though opacity measurements in the stack may be within regulatory limits, the formation of a visible plume due to the presence of SO_3 may result in plume opacities higher than allowable levels and a need to control SO_3 emissions. Most states have a 20% opacity limit for stationary sources, including coal-fired utility boilers, and many also have provisions for higher opacity levels during unit start up. There are some exceptions to the 20% limit, with a few states having opacity limits of 40% and at least one (West Virginia) has a 10% opacity limit.

The formation of a detached plume occurs when in-stack opacity measurements are less than opacity measurements in the downwind plume. While in-stack opacity measurements are made using continuous emission monitors, measurements of the downwind plume opacity are covered under EPA Method 9 [40CFR60 Appendix A, 1996]. The increase in opacity from in stack measurements to downwind is often due to the condensation of vapors such as H_2SO_4 and can result in regulatory violations and good neighbor policy concerns.

FORMATION OF SO_3

Formation in the Boiler

The sulfur in coal has inorganic and organic components. The inorganic component is predominantly pyrite (FeS_2), which can exist both as distinct particles (excluded) and bound in the coal matrix (included). The organic component is part of the various organic structures present in coal. The fractions of included and excluded pyrite and organic component delivered to a furnace are known to be dependent on the fineness to which the coal is ground. During the combustion of coal, virtually all of the sulfur gets oxidized to gaseous species such as SO_2 and SO_3, with SO_2 being the principal oxide. Although detailed chemical mechanisms for oxidation of fuel sulfur are not understood well at present, it is believed that this oxidation proceeds through rapid formation of SO_2, occurring on a timescale comparable to that of fuel oxidation reactions. Since SO_2 formation is so rapid, its concentration can be estimated using equilibrium calculations.

The primary reaction that results in SO_3 formation in flames is:

$$SO_2 + O + M \rightarrow SO_3 + M \qquad \text{(R1)}$$

This recombination reaction proceeds rapidly near the combustion zone in the presence of super-equilibrium concentrations of oxygen atoms (O). The consumption of SO_3 near flames occurs primarily via:

$$SO_3 + HO_2 \rightarrow HOSO_2 + O_2 \qquad \text{(R2)}$$

and

$$SO_3 + O \rightarrow SO_2 + O_2 \qquad \text{(R3)}$$

A few other reactions are considered to result in formation and destruction of SO_3 near the flame zone, but the effect of these on SO_3 concentrations is relatively minor. Table 1 summarizes the reactions involving SO_3 in the combustion zone [Alzueta et al., 2001].

Table 1 The reactions involving SO_3 in the combustion zone. The rate constants are listed in the form $k=AT^{\beta}\exp(-E_A/RT)$ with units in mol-cm-s

Reaction	**A**	β	E_A/R
$SO_3 + H = HOSO + O$	2.5e05	2.92	25300
$SO_3 + O = SO_2 + O_2$	2.0e12	0.00	10000
$SO_3 + SO = SO_2 + SO_2$	1.0e12	0.00	5000
$SO_2 + O + M = SO_3 + M$	9.2e10	0.00	1200
$SO_2 + OH = SO_3 + H$	4.9e02	2.69	12000
$HOSO_2 = SO_3 + H$	1.4e18	-2.91	27600
$HOSO_2 + O = SO_3 + OH$	5.0e12	0.00	0
$HOSO_2 + OH = SO_3 + H_2O$	1.0e12	0.00	0
$HOSO_2 + O_2 = SO_3 + HO_2$	7.8e11	0.00	330

To understand SO_3 formation, calculations were made using the sulfur chemistry described above with gas compositions and temperature-time history characteristic of a coal-fired boiler. This history is shown in Figure 3. Initial gas phase compositions are assumed to result from complete combustion (with 10 and 30% excess air) of a Montana sub-bituminous and a Western Kentucky bituminous coal. The sub-bituminous coal is composed of 53.26% (by weight) carbon, 3.35% hydrogen, 0.87% nitrogen, 0.78% sulfur, 9.34% ash, 21.23% water, and 11.16% oxygen. The bituminous coal contains 69.79% carbon, 4.79% hydrogen, 1.34% nitrogen, 2.95% sulfur, 7.47% ash, 5.0% water, and 8.65% oxygen. The initial compositions resulting from complete combustion of above coals are then equilibrated at 1647°C (1900 K) to provide the input composition for the chemical kinetic calculations based on the above sulfur chemistry. Note that the H_2-O_2-CO subset of the hydrocarbon mechanism given in Warnatz et al. (1996) is used in these calculations. This subset includes 25 reactions involving 11 species.

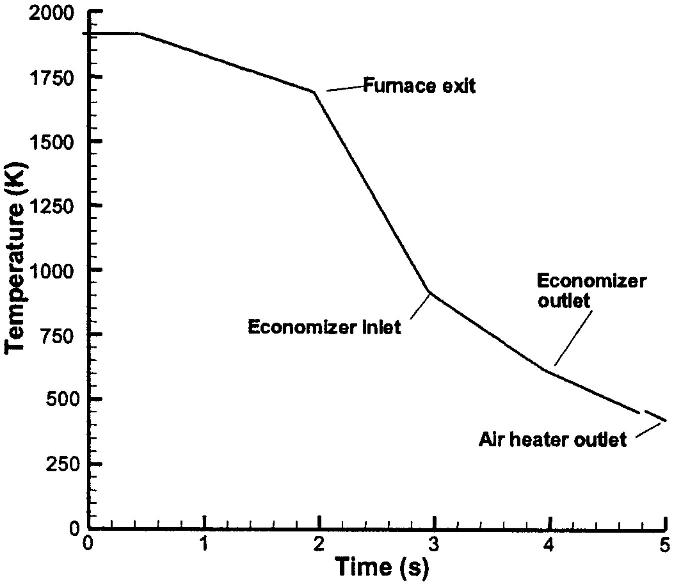

Figure 3 Temperature-time history for a coal-fired power plant (from Senior et al., 1999)

Figures 4a and 4b plot SO_3 mole fraction and the ratio SO_3 mole fraction/SO_2 mole fraction versus time, respectively. Since Reaction R1 is exothermic, little SO_3 is formed initially at high temperatures in the furnace. As the flue gas cools, SO_3 is produced, and the rate of production is high in the convective region of the boiler (see Figures 3 and 4a). SO_3 production via gas-phase sulfur kinetics is complete before the flue gas enters the economizer. The results also reflect that SO_3 production increases with coal sulfur content and furnace excess air level. This is because an increase in sulfur content of coal and/or furnace excess air level results in a corresponding increase in the concentration of SO_2 and/or oxygen atom (O), which, in turn, results in greater production of SO_3 via reaction R1. Finally, Figure 4b reflects that SO_2 conversion rate (i.e., SO_3/SO_2 molar ratio) for the modeled coals ranges between 0.1 and 0.65%, approximately, and is relatively independent of coal type at a specific excess air level. Since boilers are operated with between 10 and 30% excess air, a 0.65% conversion of coal sulfur to SO_3 should provide a conservative estimate of SO_3 production in the furnace.

In addition to the SO_3 formation in the furnace discussed above, additional formation takes place in the temperature range of 1100-800°F (593-427°C) found in the economizer region of the boiler. This formation results from oxidation of SO_2 via molecular oxygen (O_2) [Hardman et al., 1998] catalyzed by iron oxides present in both ash and tube surfaces. This oxidation mechanism depends on several operating and design parameters including SO_2 concentration, ash content and composition, convective pass surface area, gas and tube surface temperature distributions, and excess air level. Since the impact of these parameters depends on site-specific factors (e.g., cleanliness of tube surfaces), it is difficult to characterize the extent of SO_3 formation due to catalytic oxidation of SO_2. A laboratory study found

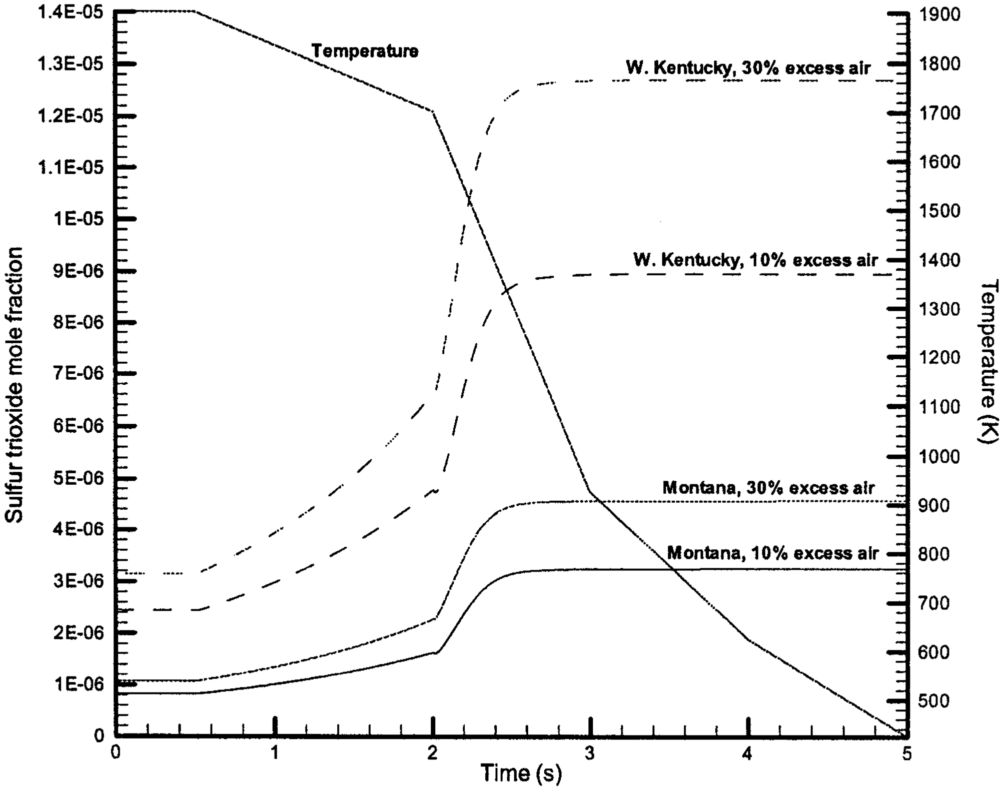

Figure 4a SO3 produced during coal combustion.

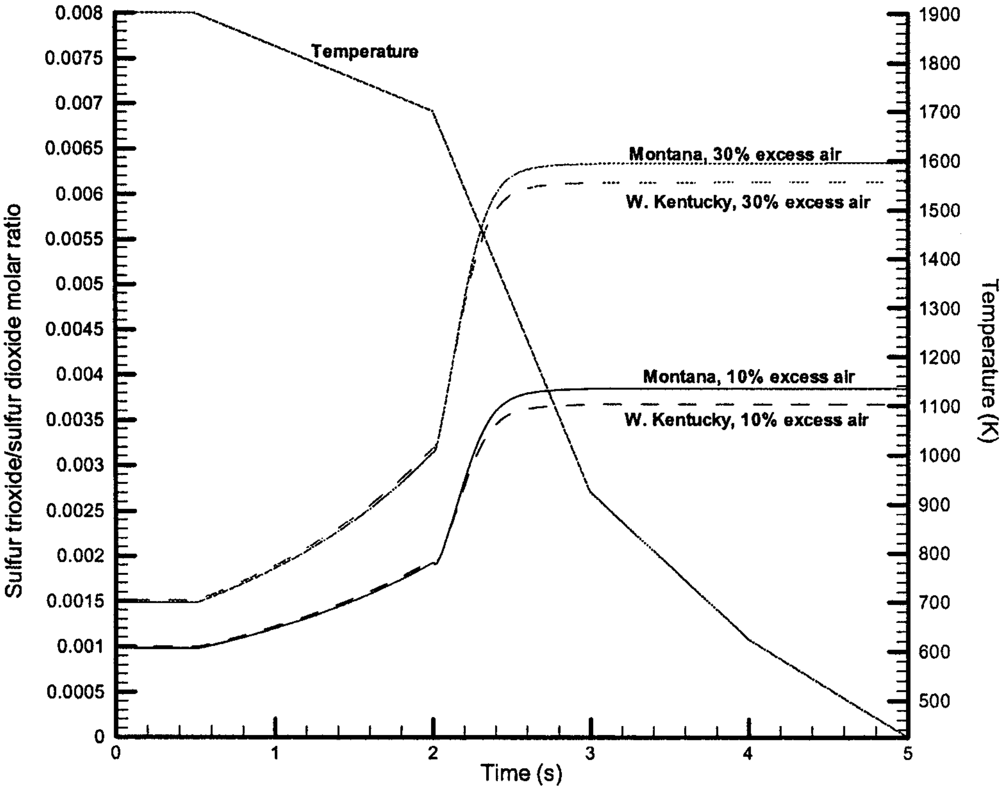

Figure 4b SO2 conversion during coal combustion.

that the oxidation rate of SO_2 in the presence of fly ash was between 10 and 30% [Marier et al., 1974] and increased essentially linearly with the iron oxide content of the ash. These oxidation rates are substantial higher than those found in coal fired boilers, for which data suggests furnace/economizer conversion to be approximately 0.8 to 1.6% for bituminous and 0.05 to 0.1% for sub-bituminous coals [Monroe, 2001]. The above laboratory study results indicate that temperatures and residence times greater than, and carbon ash contents lower than, those typically found in coal-fired utility boilers are required to achieve high oxidation rates.

Formation of SO_3 in SCR Reactors

The SCR technology is increasingly being used at power plants to control emissions of NO_x. In the SCR process, ammonia (NH_3) is injected into the flue gas within a temperature range of about 600 to 750°F (315 to 400°C), upstream of a catalyst. Subsequently, as the flue gas contacts the SCR catalyst, NO_x, which predominantly is NO in combustion devices, is chemically reduced to molecular nitrogen (N_2). In the most commonly used SCR process layout, known as hot-side SCR, the catalyst is located between the economizer and the air preheater (APH).

It is well known that the catalyst used in the SCR technology oxidizes a small fraction of SO_2 in the flue gas to SO_3:

$$SO_2 + \tfrac{1}{2} O_2 \rightarrow SO_3 \qquad \text{(R4)}$$

The extent of this oxidation depends on the catalyst formulation and SCR operating conditions. Generally, this oxidation can range from 0.25% to 0.5% of SO_2 per layer of catalyst in bituminous and 0.75 to 1.25% per layer in low-sulfur sub-bituminous coal applications. Also, in general, 2-3 layers of catalyst are used in SCR applications. To examine what this oxidation means, consider an SCR application using two layers of catalyst, each with an SO_2 oxidation guarantee of 0.25%. Also assume that the concentrations of SO_2 and SO_3 in the flue gas at the inlet of the SCR reactor are 2000 ppm and 20 ppm, respectively. Then based on oxidation across the first catalyst layer, the concentrations of SO_2 and SO_3 at the beginning of the second layer will be 0.9975x2000 = 1995 ppm and 2000-1995 + 20 = 25 ppm, respectively. Similarly, the concentrations of SO_2 and SO_3 at the end of the second layer will be 0.9975x1995 = 1990 ppm and 1995-1990 + 25 = 30 ppm, respectively. Thus, the SO_3 loading in the flue gas at the exit of the SCR reactor will be 50% more than that at the inlet. This example illustrates that level of oxidation across the catalyst can have a large impact on SO_3 concentration.

In general, for a given catalyst material experiencing same flue gas conditions, the oxidation rate of SO_2 to SO_3 (or conversion rate) is inversely proportional to area velocity (AV), which is simply the ratio of flue gas volumetric flow rate to geometric catalyst surface area. This implies that the conversion rate is proportional to catalyst volume (and hence geometric surface area) and gas residence time in the catalyst. Thus, the conversion rate, k, can be expressed as:

$$k = K/AV \qquad (1)$$

where the constant of proportionality, K, is a function of catalyst material and design as well as flue gas properties [Gutberlet et al., 1999], i.e.,

$$K = f(\text{catalyst material, catalyst design, flue gas properties}) \qquad (2)$$

Svachula et al. (1993) have conducted a systematic study of oxidation of SO_2 to SO_3 over honeycomb SCR catalysts. Their findings are as follows:

(1) the conversion rate depends primarily on the vanadium content of the catalyst and, therefore, can be controlled by adjusting this content;

(2) the oxidation reaction is considerably slower than diffusion of SO_2 within the pores of the catalyst. Therefore, the entire volume of the catalyst is active in oxidation of SO_2 to SO_3 in contrast to reduction of NO_x to N_2, which, being diffusion-limited, occurs mainly at the catalyst surface. The rate of oxidation is linearly proportional to catalyst wall thickness. Accordingly, reducing the wall thickness should not affect NO_x reduction, but should reduce SO_2 to SO_3 conversion;

(3) the reaction rate is of variable order in SO_2 concentration, increases with temperature, is independent of concentrations of oxygen and water in practical applications, is strongly inhibited by NH_3, and is slightly enhanced by NO_x.

SO_3 DEPLETION OR CONVERSION TO H_2SO_4

Processes in Air Preheaters

Utility boilers use APHs to transfer heat from hot flue gas exiting the economizer to combustion air flowing into the boiler. These APHs are available in rotary regenerative and tubular designs, with the former used more widely. Typically the flue gas temperature at the APH inlet is between 600 and 700°F (316 and 371°C) and about 300°F (149°C) at the exit. SO_3 is hygroscopic and, therefore, absorbs vapor-phase moisture at temperatures above its dew point to form H_2SO_4 vapor [Hardman et al., 1998]. This process occurs in the APH. The extent of conversion of SO_3 to H_2SO_4 depends on the temperature distribution in the APH and flue gas moisture content. However, virtually all SO_3 converts to H_2SO_4 at temperatures of 400°F or less. If local metal temperatures in the APH flow passages drop below the acid dew point (ADP), some H_2SO_4 condenses on these surfaces as liquid droplets (aerosol). This rate of condensation is dependent on the wall temperature and H_2SO_4 concentration in the flue gas.

In a regenerative APH, where flow passages are periodically exposed to hot flue gas and relatively cold incoming combustion air, evaporation of condensed H_2SO_4 occurs on exposure to air. The rate of this evaporation is dependent on moisture content of air and metal surface temperature of the APH flow passage [Levy, 1998; Sarunac and Levy, 1999].

Devito and Oda [1998] have reported that, based on the results of an extensive field test program, approximately 40% of the flue gas SO_3 present at the regenerative APH inlet is removed in the APH by the condensation-evaporation mechanism discussed above. The tubular APH design does not have surfaces that are periodically exposed to combustion air; except for small leakages in welds and seal, no mixing of the flue gas and combustion occurs. Therefore, the resultant H_2SO_4 formed is not removed by evaporation into the combustion air and passes directly out of the APH. Yilmaz et al. (1995) have modeled the acid condensation phenomenon in tubular APHs.

In addition to the condensation-evaporation of SO_3 discussed above, an additional conversion process takes place in boilers equipped with SCR. In such a case, NH_3 is injected as a reagent in the SCR process. A minor fraction, 2 to 5 ppmv, of injected ammonia slips past the SCR catalyst and does not react with NO_x. This fraction of NH_3, known as NH_3 slip, reacts with SO_3 downstream of the SCR reactor and forms ammonium sulfate and ammonium bisulfate salts and, thereby, results in removal of SO_3 from the flue gas. This salt formation can be detrimental to the APH performance if APH passages become plugged and pressure loss across the APH results in forcing off-line washing. The amount and type of ammonia salt formed will depend on the amount of NH_3 slip; based on typical concentrations of SO_3 and H_2O in flue gas, the amount of NH_3 slip is the limiting factor in salt-formation reactions.

Localized Condensation of H_2SO_4 in the Duct Between APH and PM Control

Condensation of H_2SO_4 can also take place in the duct between the APH and the PM control device. For example, due to the rotating heat transfer element employed in the regenerative APH, gas flow stratification across the flow cross-section downstream of the boiler is enhanced in the APH. As a result, strong transverse variations in gas temperature and H_2SO_4 vapor concentration can exist in the gas leaving the APH. These variations can lead to localized condensation of H_2SO_4. Based on operating conditions, localized condensation can also occur in units using tubular APHs. For a given combination of flue gas H_2SO_4 concentration, dew point and, moisture content, Figure 1 can be used to determine if condensation is occurring.

Flyash Adsorption and Removal of H_2SO_4 in PM Control Equipment

In addition to the processes described above, some H_2SO_4 gets adsorbed on fly ash in the APH and downstream equipment. The rate of this adsorption depends on the temperature of the flue gas; concentration of H_2SO_4; and fly ash properties, in particular, alkalinity. The adsorption may increase rapidly as the flue gas reaches the cold end of the APH and may continue in the duct between the APH and the PM control equipment. The adsorbed H_2SO_4 gets removed with the fly ash in the PM control device [electrostatic precipitator (ESP) or baghouse.

The firing of sub-bituminous coals, which generally have sulfur contents on the order of 0.5%, results in fly ash with a relatively high amount of alkali (20-30% by weight). Such alkaline ash adsorbs virtually all H_2SO_4 in the flue gas. In such cases, SO_3 injection is required for improving electrostatic precipitator (ESP) performance. In contrast, based on fly ash properties and temperature, the majority of SO_3 in flue gas of a bituminous coal-fired boiler may, or may not, be adsorbed in flyash [Gutberlet et al., 1999]. Finally, hot-side ESPs operate at high enough temperatures where little adsorption of H_2SO_4 occurs.

As mentioned above, adsorption of H_2SO_4 on fly ash depends on alkalinity of fly ash and concentration of H_2SO_4. Figure 5 illustrates the general adsorption characteristics of fly ash as a function of the molar ratio of alkali content of fly ash and SO_3 concentration at the inlet of the APH. The alkali content of fly ash is defined as the molar sum of magnesium oxide (MgO) and calcium oxide (CaO) in the ash. This figure represents a correlation of data from RPI field-testing programs concerning SO_3 production and capture in flue gas systems.

Aerosol Formation in Wet Flue Gas Desulfurization Systems

As the H_2SO_4 vapor containing flue gas passes through a wet flue gas desulfurization (FGD) system, it is rapidly cooled below the acid dew point. Since the rate of this cooling is greater than the rate of absorption of H_2SO_4 vapor in the scrubber solution, the dew point crossover results in H_2SO_4 mist with sub-micron droplets [Gutberlet et al., 1999; Blythe et al., 2001b]. Generally, larger droplets in the mist can be removed in the scrubber, but the sub-micron droplets are not removed and are emitted from the stack. This explains why wet FGD systems are relatively inefficient in removing SO_3/H_2SO_4. In general, about 50% of the H_2SO_4 entering the scrubber may be removed in the scrubber.

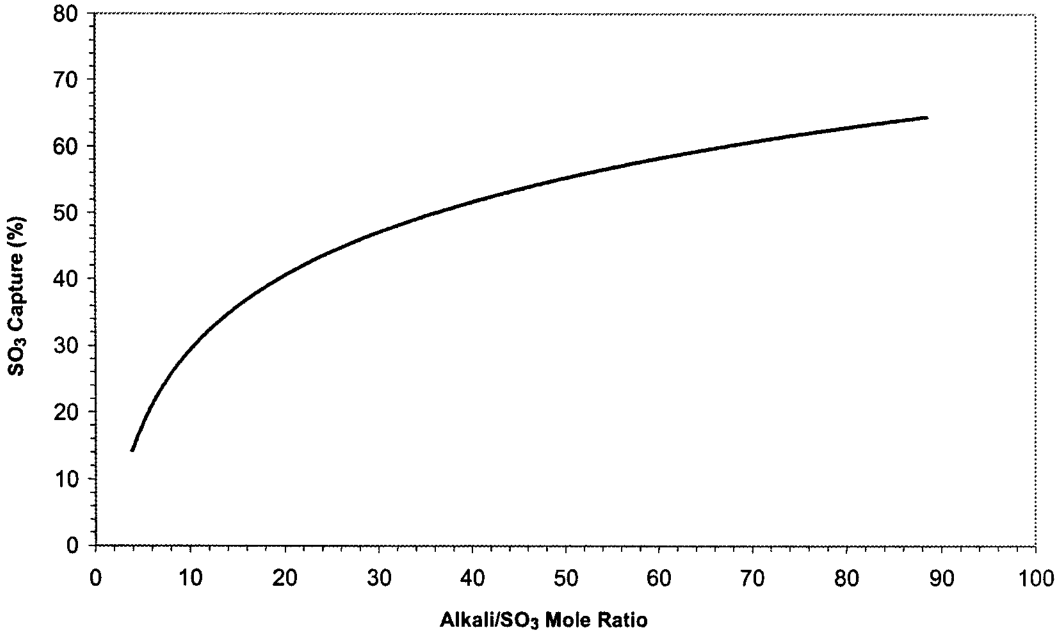

Figure 5 Fly ash SO3 capture rate downstream of furnace.

MEASUREMENT OF SO3

The measurement techniques for SO3 and H2SO4 have recently been under review for accuracy and improvement for Toxic Release Inventory (TRI) reporting. The Controlled Condensation System (CCS) has been used since the 1960's for the measurement of SO3 and H2SO4 in flue gas streams [Lisle and Sensenbaugh, 1965; Dismukes, 1975]. Recently a review and verification project has been undertaken by Electric Power Research Institute (EPRI) to qualify the CCS method and compare field data to available prediction methods used to estimate SO3 emissions for TRI reporting [Blythe et al., 2001a]. The EPRI project compared laboratory data to field test data for a variety of coals with a range of sulfur and fly ash chemical compositions. The study further investigated the SO3 removal rates and efficiencies of the plant equipment used for field verification.

The general arrangement of the CCS and thimble holder is shown in Figures 6 and 7, respectively. The measurement system consists of quartz lined heated probe which draws gas through a quartz thimble for the removal of particulate matter. The probe and thimble are heated to avoid condensation of SO3 vapor in the gas sample. The gases enter a temperature-controlled condenser where the SO3 is condensed on the wall and collected and measured after the sample run via a deionized water rinse. The EPRI project has concluded that alkaline ash will produce a bias in the SO3 measurement. The bias is a result of SO3 removal in the thimble holder by the alkaline ash collected on the quartz thimble. This bias is seen as significant for low sulfur, high alkaline ash fuels (PRB coals). The CCS was found to have a bias of 20 to 25% low readings for high sulfur, acidic ash fuels and greater than 40% for PRB coals. A possible solution to the bias is utilized in Europe [Gutberlet 2002]. The test method uses a system similar to the CCS; however, the quartz thimble is replaced with a small tubular ESP. The tubular ESP removes the ash to the sidewalls away from the gas stream; in contrast the quartz thimble filters the flue gas through the collected ash. Furthermore, the European system can distinguish between gaseous and aerosol SO3 using deionized water procedures of various collection plates. The European SO3 method system has been used extensively in the U.S. on a variety of coals with repeatable and reliable results.

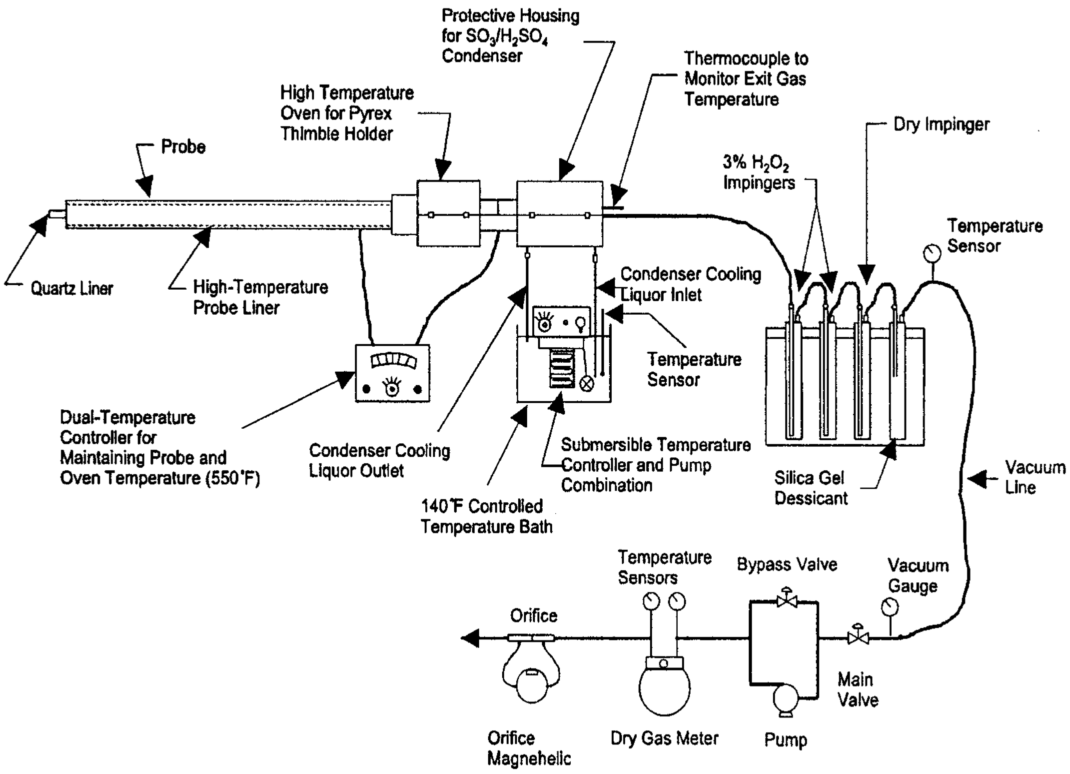

Figure 6 Controlled condensation system (CCS) sampling train.

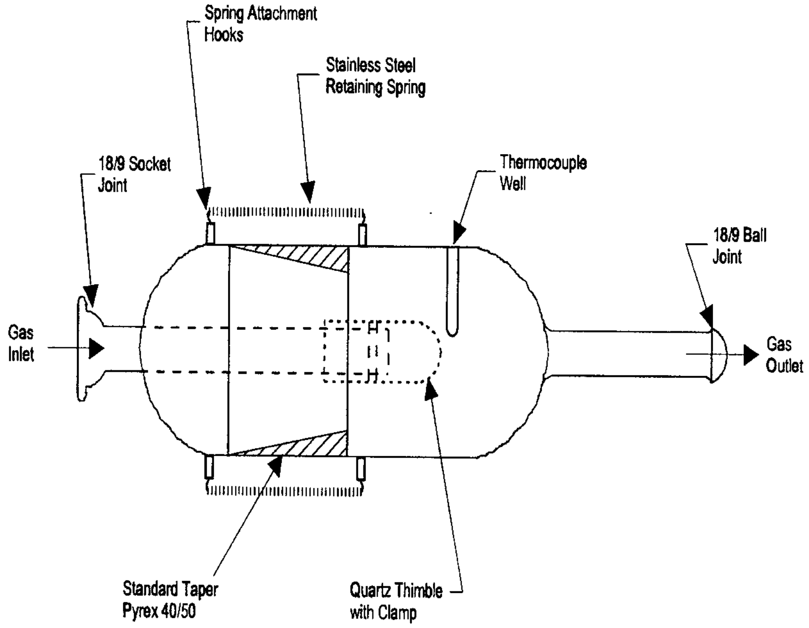

Figure 7 CCS thimble holder.

MITIGATION OF SO3 EMISSIONS

The mitigation of SO3 has been an active area of research for many years [Reese et al., 1965]. This research has resulted in the development, refinement, and implementation of different techniques and methods for the successful mitigation of SO3 in the flue gases of fossil fuel fired boilers. Recently, a guide that summarizes SO3 mitigation options and their respective success in either full scale or pilot testing has been written [Peterson et al., 1994]. Since the guide was issued, the installation of full-scale SCR units has made the need for mitigation greater. Consequently, the number of full-scale tests and operating installations of SO3 mitigation equipment has increased.

Alkali Addition into Furnace

The injection of alkali in the flue gas stream has been a method of SO3 mitigation for almost 30 years [Reese et al., 1965]. The location in the flue gas stream and delivery method of the alkali has been studied and tested depending on operating and site conditions.

The addition of alkali into the furnace has recently been proven effective at the full scale [Gutberlet et al., 1999; and Blythe et al., 2001b]. However, the method of delivery and effectiveness of the alkali used varies from site to site depending on specific conditions. The addition of limestone to coal prior to pulverization for the control of SCR catalyst arsenic poisoning has been shown to be an effective method of furnace SO3 control. Recent commissioning data [Hutcheson et al., 2002] has shown at least a 50% reduction in furnace SO3 from limestone addition. The injection of alkaline sorbents (calcium and magnesium based slurries) has been shown to be effective at controlling SO3 emissions of the furnace [Blythe et al., 2001b]. The slurry injection method has successfully obtained SO3 furnace conversion reductions of 40 to 80% but has been found to be sensitive to injection location and elevation. The effects of the MgO sorbent slurries on SCR catalyst activity are currently under investigation. To date, no studies have measured the potential benefit of SCR catalyst arsenic poisoning control by MgO sorbent injection. The addition or injection of alkaline in the furnace does not influence the conversion rate of the SCR catalyst.

Alkali Injection After Furnace

The injection of other alkaline materials after the furnace/economizer exit has been used for the control of SO3 for both APH corrosion and stack emissions [Peterson, et al. 1994]. The primary sorbents used are compounds such as hydrated lime [$Ca(OH)_2$], limestone ($CaCO_3$), MgO, and sodium carbonate ($NaHCO_3$). The selection of a sorbent for a given site will depend on economic factor such as availability and required SO3 removal rates. Alkali injection has successfully removed between 40 and 90% of the SO3 in the flue as various plants depending on the injected material and injection rate [Peterson, et al. 1994]. The sorbents are introduced into the flue as either a dry powder or mixed with water to form slurry prior to injection. The location in the flue gas stream varies. Plants with APH cold-end corrosion problems may elect to inject the sorbent before the APH; however, adequate APH cleaning equipment is required with this configuration. In general, for SO3 control the common injection location is between the APH and the ESP. The injection of sorbent before the ESP must consider the effect on particulate control. The ESP will have higher inlet mass loading, and the fly ash will have different resistivity characteristics. It has been reported that dry injection of hydrated lime has resulted in strong sparking and lower operating currents in the ESP during pilot scale testing [Peterson, et al. 1994]. The injection of sodium materials can result in landfill problems due to the leaching of the water soluble sodium salts.

Ammonia Injection Before ESP

The injection of ammonia after the APH and before the ESP has been shown to be <90% effective in the removal on SO_3 in full-scale application [Peterson et al., 1994]. This method of mitigation results in the formation of ammonium sulfate and ammonium bisulfate salts in the ESP, depending on the NH_3 and SO_3 concentration ratios. The formation of ammonium bisulfate is expected when NH_3 to SO_3 molar ratios are less than 1.0; this formation tends to decrease the ESP particle loading due to fly ash agglomeration. Ammonia injection prior to the ESP is used for fly ash conditioning to increase ESP performance due to the agglomeration effects. With NH_3 to SO_3 molar ratios between 1.0 and 2.0, increased formation of ammonium sulfate is expected, with an increase in the particle loading of the ESP. The injection of ammonia results in the adsorption of ammonia by the fly ash. Since the fly ash will contain most of the injected ammonia, the concentration may exceed acceptance limits for ash salability or disposal. Additional treatment of fly ash holding ponds and basins may be required if large amounts (~30 ppmv) of SO_3 are being removed. High concentrations of atmospheric ammonia vapor can result when the fly ash is wetted. Generally, these concentrations are not a health concern, but may be irritating to operators. The use of ammonia for SO_3 mitigation is practical on units equipped with SCRs, since ammonia is used as the reagent and is readily available on site.

Fuel Switching and Blending

The firing of sub-bituminous coals typically results in low SO_3 formation and emission rates. However, equipment and fuel cost factors often make such a change impossible. Many boiler systems do not have the capacity and the equipment to accommodate the firing of sub-bituminous coal without major modifications that make fuel switch economically unacceptable. Coal availability and costs can also constrain fuel switching. One possible solution is the blending of bituminous and sub-bituminous coals to create a blend that has fuel and ash characteristics favorable for SO_3 emissions. This strategy is currently used for the control of SO_2 emissions. When sub-bituminous coals are blended with bituminous coals, the overall sulfur content of the fuel is reduced, resulting in a reduction of the SO_2 concentration in the flue gas as well as the conversion of SO_2 to SO_3 in the furnace and SCR and, thereby, resulting in an overall reduction in SO_3. Also, the sub-bituminous coal ash contains large percentages of alkaline materials that further assist in the capture of SO_3 in the APH and ESP.

Wet Electrostatic Precipitators

Similar to dry electrostatic precipitators (ESPs), wet electrostatic precipitators (WESPs) operate in a three-step process involving: (1) charging of the entering particles; (2) collection of the particles on the surface of an oppositely charged surface; and (3) cleaning the collection surface. Both technologies employ separate charging and collection systems. However, the collecting surface in WESPs is cleaned with a liquid, in contrast to mechanically in dry ESPs. Consequently, the two technologies differ in the nature of particles that can be removed, the overall efficiency of removal, and the design and maintenance parameters [Altman et al., 2001a]. While dry ESPs are typically limited to power levels of 100-500 watts per 1,000 cfm of flue gas, WESPs can operate with power levels as high as 2,000 watts per 1,000 cfm. Due to wet cleansing of the collection system, particulate matter does not accumulate in the collection electrodes; this mitigates particle re-entrainment. Based on these factors, WESPs can collect sub-micron particles and acid mist very efficiently. WESPs can be configured for vertical or horizontal gas flows in tubular or plate designs. Tubular designs offer smaller footprint and, in general, are more efficient than the plate type.

WESPs can be easily integrated with a wet scrubber. In fact, integration of the WESP within the wet scrubber is a design option with many attractive features including [Bielawski, 2001] a compact footprint; the ability to integrate the handling of the wash water and solids from the WESP with scrubber slurry, avoiding the need for separate tank and blowdown system; and the ability to collect the fine sulfuric acid mist, which typically escapes the scrubber due to its very small droplet size.

In 1986, the first commercial WESP application on a U.S. power plant took place when AES Deepwater, a 155 MW cogeneration plant firing petroleum coke as the primary fuel, was equipped with a WESP. With the WESP in operation, the plume opacity at the plant is generally 10% or less [Kumar and Mansour, 2002].

Recently, an up-flow tubular design WESP has been retrofit Northern States Power Company's Sherco Station in a wet scrubber/WESP configuration. Two more power plant applications are underway presently: 1) 5,000 cfm slipstream at Bruce Mansfield Station; and 2) a plate type WESP for integration with Powerspan's ECO technology to be demonstrated at First Energy's R.E. Burger plant.

Tests at the Sherco Station (WESP retrofit to the outlet section of the wet scrubber) allowed the scrubber to maintain a 70 % SO_2 reduction while keeping particulate emissions at 0.01 lb/106 Btu and opacity under 10%. Full conversion of all scrubber modules at the plant with WESPs is now underway [Altman et al., 2001a]. The WESP at the Mansfield Station is achieving greater than 95% removal of SO_3 and PM2.5 and stack flow with near-zero opacity [Reynolds, 2002].

Changing the operation of APH

Increasing the heat transfer (or the cooling of the flue gas) in the APH would appear to be a potentially viable strategy for removing some of the SO_3/H_2SO_4 in the APH. This, in turn, would lead to increased condensation of H_2SO_4 in the APH and also to improved plant efficiency. However, the dew point at the APH outlet is around 230°F (110°C), thereby limiting the SO_3 removal to about 90% [Gutberlet et al., 1999]. On the other hand, potential for corrosion in the APH and downstream duct would increase with increased H_2SO_4 condensation. Consequently, more frequent soot blowing may be required to control this corrosion. These factors would need to be considered while deciding to change the APH operation to mitigate SO_3 emissions. Data reflects that about 25% increase in H_2SO_4 condensation may be possible by lowering the flue gas temperature at the APH exit by about 40°F (22°C).

SUMMARY

Formation and emissions of SO_3 can lead to serious problems for plant operation and for achieving environmental compliance. The formation of SO_3 is complex, depending upon fuel, operating parameters, and plant configuration, and understanding the parameters leading to excessive generation of SO_3 and subsequent formation of H_2SO_4 can minimize their presence and adverse impacts. Elevated SO_3 concentrations can lead to corrosion, the formation of sulfite scale, fouling and plugging of low temperature plant components, and can add to the particle loading to control equipment. In some cases, elevated SO_3 concentrations can lead to the formation of visible plumes at the stack exit or shortly downstream of the stack, resulting in noncompliance with local regulations. SO_3 can be formed in the boiler during the combustion of sulfur-bearing fuels, or downstream, particularly in SCR reactors. SO_3 that forms H_2SO_4 can condense on low temperature components or, in some cases be absorbed by fly ash. Absorption by fly ash is much greater for the high alkaline ashes present in sub-bituminous coals, and, in some cases, injection of SO_3 may be needed to improve ESP performance. SO3 has traditionally been measured using extractive controlled condensation methods, but, more recently, methods are being developed and applied that provide semi-continuous measurements or predictions.

SO3 formation can be mitigated using a variety of methods. Injection of alkali materials into the furnace, either with the fuel or in slurry form, have resulted in reductions of up to 80%. Post-furnace injection of alkali materials can achieve up to 90% reductions, but can increase particle loadings and ash resistivity characteristics, and potentially result in landfill problems due to leaching of water soluble salts. Ammonia injection can also reduce SO3 by roughly 90%, again with the disadvantage of increasing particle loading to the downstream collection systems. In plants with adequate operational and equipment flexibility, fuel switching can be used to reduce formation and emissions of SO3, although coal costs and availability and plant design may limit the use of this approach. Wet ESPs are also an option for control of SO3 and subsequent visible plumes, and a variety of designs have been successfully demonstrated for collection of acid mists and opacity control.

REFERENCES

Altman, R., Offen, G., Buckley, W., and Ray, I. (2001a). “Wet electrostatic precipitation demonstrating promise for fine particulate control – part I,” Power Engineering, pp. 37-39, January 2001.

Altman, R. (2001b). “Wet electrostatic precipitation demonstrating multiple pollutant control in industrial applications holds promise for coal-fired utility emission reduction of acid mist, PM2.5, and mercury,” presented at the U.S. EPA/DOE/EPRI Combined Power Plant Air Pollution Control Symposium: “The Mega Symposium,” Chicago, IL, August 20-23, 2001.

Alzueta, M.U., Bilbao, R., and Glarborg, P. (2001). “Inhibition and sensitization of fuel oxidation by SO_2,” Combustion and Flame, Vol. 127, pp. 2234-2251.

Bielawski, G.T. (2001). “How low can we go?” presented at the U.S. EPA/DOE/EPRI Combined Power Plant Air Pollution Control Symposium: “The Mega Symposium,” Chicago, IL, August 20-23, 2001.

Blythe, G., Galloway, C., and Rhudy, R. (2001a). “Flue gas sulfuric acid measurement method improvements,” presented at the U.S. EPA/DOE/EPRI Combined Power Plant Air Pollution Control Symposium: “The Mega Symposium,” Chicago, IL, August 20-23, 2001.

Blythe, G., McMillan, R., Davis, J., Lamison, M., Beeghly, J., Benson, L., Goetz, E., and Rhudy, R. (2001b). “Furnace injection of alkaline sorbents for sulfuric acid control,” presented at the U.S. EPA/DOE/EPRI Combined Power Plant Air Pollution Control Symposium: “The Mega Symposium,” Chicago, IL, August 20-23, 2001.

Bock, J. (2002). Personal communication with J. Bock of Siemens AG, Redwitz, Germany, June 18, 2002.

Clean Air Act (1990). Public Law 101-549, Clean Air Act Amendments of 1990, November 15, 1990.

Damle, A.S., Ensor, D.S., and Sparks, L.E. (1984). “Prediction of the opacity of detached plumes formed by condensation of vapors,” Atmospheric Environment, Vol. 18, pp. 435-444.

Damle, A.S., Ensor, D.S., and Sparks, L.E. (1987). "Options for controlling condensation aerosols to meet opacity standards," Journal of the Air Pollution Control Association, Vol. 37, pp. 925-933.

Devito, MS., and Oda, R.L. (1998). "Flue gas SO3 stratification at ESP inlets," presented at the DOE-FETC Conference on Formation, Distribution, Impact, and Fate of Sulfur Trioxide in Utility Flue Gas Streams, Pittsburgh, PA, March 1998.

Dismukes, E.B. (1975). "Conditioning of fly ash with sulfur trioxide and ammonia," U.S. Environmental Protection Agency, EPA-600/2-75-015 (NTIS PB-247231), Office of Energy, Minerals, and Industry, Research Triangle Park, NC, 1975.

EPA Method 9 (1996). "Visual Determination of the Opacity of Emissions from Stationary Sources," 40CFR60, Appendix A.

EPA (1998). "Study of hazardous air pollutant emissions from electric utility steam generating units — Final report, Volume 1," U.S. Environmental Protection Agency, EPA-453/R-98-049, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1998.

EPA (1996). "Air quality criteria for particulate matter," U.S. Environmental Protection Agency, EPA-600/P-95/001 (NTIS PB96-168224), National Center for Environmental Assessment, Research Triangle Park, NC, April 1996.

EPA (2002). "Consolidated emissions reporting," Federal Register, Vol. 67, pp. 39602-39616, June 10, 2002.

Fryling, G.R., ed. (1966). Combustion Engineering, Combustion Engineering, Inc., New York.

Gutberlet, H. (2002). Personal communication with H. Gutberlet of E.On Engineering, Gelsenkrichen, Germany, July 7, 2002.

Gutberlet, H., Hartenstein, H., and Licata, A. (1999). "SO_2 conversion rate of $deNO_x$ catalysts – effects on downstream plant components and remedial measures," presented at the PowerGen 1999, New Orleans, LA, 1999.

Hardman, R., Stacy, R., and Dismukes, E. (1998). "Estimating sulfuric acid aerosol emissions from coal-fired power plants," presented at the DOE-FETC Conference on Formation, Distribution, Impact, and Fate of Sulfur Trioxide in Utility Flue Gas Streams, Pittsburgh, PA, March 1998.

Hawthorne, M. (2001). "Plant spewing acid clouds," Columbus Dispatch, August 3, 2001.

Hutcheson, L., Martin, M., Ake, T., Erickson, C.A., Nystedt, P., McFarland, E., Favor, C. (2002). "Selective catalytic reduction system performance at Duke Energy's Cliffside Unit 5 power station," to be presented at the EPRI 2002 Workshop on Selective Catalytic Reduction, Atlanta, GA, October 22-23, 2002

Kumar, K.S., Mansour, A. (2002). "Wet ESP for controlling sulfuric acid plume following an SCR system," presented at the ICAC Forum 2002, Houston, TX, February 12-13, 2002.

Levy, E.K. (1998). "Effect of boiler operations on sulfuric acid emissions," presented at the DOE-FETC Conference on Formation, Distribution, Impact, and Fate of Sulfur Trioxide in Utility Flue Gas Streams, Pittsburgh, PA, March 1998.

Lisle, E.S., and Sensenbaugh, J.D. (1965). "The determination of sulfur trioxide and acid dew point in flue gases," Combustion, Vol. 36, pp. 12-16.

Marier, P., and Dibbs, H. P. (1974). "The catalytic conversion of SO_2 to SO_3 by fly ash and the capture of SO_2 and SO_3 by CaO and MgO," Thermochimica Acta, Vol. 8, pp. 155-165.

Monroe, L. (2001). "An updated method for estimating total sulfuric acid emissions from stationary power plants," Research and Environmental Affairs Department, Southern Company Generation and Electricity Marketing, P.O. Box 2641, Birmingham, AL.

Peterson, J., and Jones, A.F. (1994). "SO_3 mitigation guide," EPRI Report Number TR-104424, October 1994.

Reese, J.T., Jonakin, J., and Caracristi, V.Z. (1965). "Prevention of residual oil combustion problems by use of low excess air and magnesium additive," Journal of Engineering for Power, Transactions of ASME, Series A, Vol. 87, pp. 229-236.

Reynolds, J. (2002). Personal communication with J. Reynolds of Croll-Reynolds Co. Inc., Westfield, NJ, August 8, 2002.

Sarunac, N., and Levy, E. (1999). "Factors affecting sulfuric acid emissions from boilers," presented at the EPRI/DOE/EPA Air Pollution Control Symposium: "The Mega Symposium," Atlanta, GA, August 16-20, 1999.

Senior, C.L., Sarofim, A.F., Zeng, T., Helble, J.J., and Mamani-Paco, R. (2000). Fuel Processing Technology,Vol. 63, pp. 197-213.

Svachula, J., Alemany, L.J., Ferlazzo, N., Forzatti, P., Tronconi, E., and Bregani, F. (1993). "Oxidation of SO_2 to SO_3 over honeycomb deNOxing catalysts," Ind. Eng. Chem. Res., Vol. 32, pp. 826-834.

Warnatz, J., Maas, U., and Dibble, R.W. (1996). Combustion, Springer-Verlag, New York, pp. 67-71.

Yilmaz, A., Pechulis, M., D'Agostini, M.D., Levy, E., Sarunac, N., and Maust, P. (1995). "Cold end acid condensation in tubular air preheaters," American Society of Mechanical Engineers, PWR-Vol. 28, 1995 Joint Power Generation Conference, Vol. 3, pp. 473-480.

Zetlmeisl, M.J., McCarthy, K.J., and Laurence, D.F. (1983). "Investigation of some factors affecting nonflame generation and suppression of SO_3," Industrial Engineering and Chemistry Product Research and Development, Vol. 22, pp. 710-716.