

# LEHIGH ENERGY UPDATE



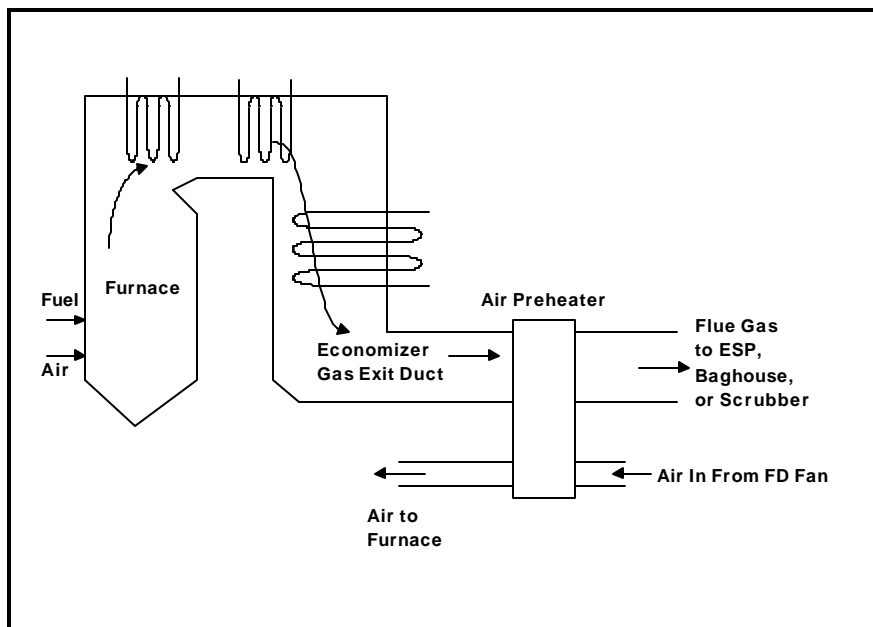
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## PREDICTING SULFURIC ACID EMISSIONS FROM POWER PLANTS

Due to concern over the release of potentially harmful toxic metals and chemical compounds to the environment, beginning in 1998, utilities with coal- or oil-fired generating plants will be required to submit an annual Toxics Release Inventory to EPA. The inventory will list amounts of each toxic substance emitted annually from each site; and the database containing this information will be maintained by EPA and made publically available. Sulfuric acid is one of the chemicals on the list of those which must be inventoried. Although, up to now, most utilities have given little thought to the amounts of  $H_2SO_4$  emitted from their stacks, this substance may become a headache for utilities in the future, according to speakers at a recent DOE workshop<sup>(1)</sup>.

Research, performed by the Energy Research Center over the last two decades, shows emissions of  $H_2SO_4$  from the stacks of coal and oil-fired boilers are highly dependent on fuel characteristics and boiler design and operating conditions. To understand how these fit together, it is helpful to examine the processes by which  $SO_3$  and sulfuric acid are formed.

In a typical pulverized coal boiler, combustion gases flow from the furnace to a series of heat exchangers in the convective pass. The gas temperature ranges from 2000 to 2500°F at the furnace exit to 600 to 700°F at the economizer gas exit. The gas temperature then decreases through the air preheater to about 300°F at the air preheater



Sketch of Typical Pulverized Coal Boiler

exit. In the case of units with cold side electrostatic precipitators, flue gas flows from there to the ESP inlet before going up the stack.

Sulfur trioxide ( $SO_3$ ) is formed at high temperatures in the furnace and convective pass by the reaction of sulfur dioxide ( $SO_2$ ) with oxygen, and there are numerous design and operating parameters which influence the extent of  $SO_3$  formation. Among these are fuel sulfur content, coal fineness, ash content and composition, convective pass surface area, tube metal surface temperature distributions and excess air level. Thus, the same fuel burned in two different boilers, or in the same boiler at two different operating conditions, can produce substantially different levels of  $SO_3$ . This is illustrated in the table which shows the

concentrations of  $SO_3$  measured in the economizer exit gas ducts at three different pulverized coal boilers. All burn eastern bituminous coals with sulfur contents of 2 to 3 percent. The  $SO_3$  concentrations are markedly different for the three boilers and also vary with load level and economizer  $O_2$ .

The  $SO_3$  formation process is complete once the flue gas reaches the air preheater. The  $SO_3$  then leaves a typical coal-fired boiler as a liquid deposit trapped in the air preheater, as vapor adsorbed onto fly ash, and as  $H_2SO_4$  vapor and mist carried out the stack.

Virtually all utility boilers use air preheaters to transfer energy from the hot gases leaving the economizer to the air flowing into the boiler. Two types of air preheaters, the rotary regenerative type and the

tubular type are in common use, with the regenerative design capturing the largest share of the utility market. Usually, the gas temperature is reduced within the air preheater from an inlet level of 600 to 700°F to an exit level of about 300°F. During this process, the SO<sub>3</sub> undergoes some important changes. Gas phase SO<sub>3</sub> reacts with vapor phase H<sub>2</sub>O to form vapor phase H<sub>2</sub>SO<sub>4</sub>. The extent of this reaction depends on temperature and the reaction is essentially complete by the time the flue gas has reached the cold end of the air preheater.

Condensation of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O subsequently occur if the local metal temperatures in the air preheater flow passages drop below the acid dewpoint. Dewpoint is a function of both H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> concentrations in the flue gas, generally ranging from 250 to 285°F. Some units are operated with the air preheater metal surface temperatures below the dewpoint and others are operated with sufficiently high stack temperatures so no acid condensation occurs.

The ERC has conducted exhaustive studies of acid condensation in air preheaters, using a combination of computer

simulations, laboratory experiments and field investigations. The results show at metal temperatures below the acid dewpoint, the rate of condensation of sulfuric acid on the surface is strongly dependent on the acid concentration of the flue gas and wall temperature. In addition, in a rotary regenerative air preheater, where the flow passages are alternately exposed to combustion air and flue gas, evaporation of condensed acid occurs from the surface of the flow passage to the incoming air stream. The degree to which this evaporation process occurs is primarily a function of the moisture content of the inlet air and the surface temperature of the flow passage.

According to Nenad Sarunac, a Research Engineer with the Center, "Due to the design of the air preheater and its mode of operation, there are strong transverse variations in flue gas temperature and H<sub>2</sub>SO<sub>4</sub> vapor concentration leaving the air preheater. Due to condensation within the air preheater, the average SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> concentration of the gas flowing through the air preheater can easily be decreased by a factor of 2. At the same time, it is not unusual to see extremely large variations in

SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> vapor concentration from one side of the gas exit duct to the other."

*"We believe the tools we've created will be very helpful in developing accurate estimates of annual sulfuric acid emissions from power plants . . . these same techniques can be used to develop . . . strategies for minimizing acid emissions."*

In addition to condensing onto cold metal surfaces in the air preheater and at the duct walls, H<sub>2</sub>O, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> become adsorbed onto the surfaces of the fly ash particles entrained with the flue gas. The rate of adsorption increases rapidly as the flue gas reaches the cold end of the air preheater, and this process continues as the flue gas flows through the duct connecting the air preheater to the electrostatic precipitator. Recent studies at the ERC show the rate of adsorption to depend strongly on temperature, gas phase SO<sub>3</sub> and H<sub>2</sub>O concentrations and ash surface properties. The adsorbed acid and water have a large effect on fly ash resistivity and thus control ESP performance. In some units, additional SO<sub>3</sub> is injected into the flue gas to condition the fly ash and improve ESP collection efficiency.

Sarunac notes, "As a consequence of the factors affecting the formation of SO<sub>3</sub> and condensation, evaporation and adsorption of H<sub>2</sub>SO<sub>4</sub>, sulfuric acid emissions from a boiler are highly variable. Fuel quality has an obvious influence. But variations also occur with unit load and with boiler and air preheater control settings. In addition, with seasonal changes in inlet air temperature and

Pulverized Coal Fired; 2 - 3% Sulfur Coal			
Unit	SO <sub>3</sub> (ppm)	Unit Load (MW)	O <sub>2</sub> (%) at Economizer Gas Exit
A	1 to 2.5	585	2 to 4
A	2.5 to 5	425 & 300	4 to 7
B	20	640	--
C	21 to 24	700	4 to 5
C	27	180	10

Table 1: Measured SO<sub>3</sub> Concentrations in Economizer Gas Exit Ducts of Three Coal-Fired Boilers

ambient humidity, the  $H_2SO_4$  in the stack varies from Winter to Summer in many units.”

“In past years, most of the concern with  $SO_3$  dealt with its effect on fouling and corrosion of air preheaters and cold end ductwork and on its role in promoting high ESP collection efficiency. Much of

the work we've done for utilities has focused on optimizing air preheater design and operations and boiler operating conditions to avoid opacity excursions, minimize heat rate and limit expenditures associated with air preheater maintenance. We believe the tools we've created to do this will be very helpful in developing

accurate estimates of annual sulfuric acid emissions from power plants. At the same time, if it becomes desirable to do so, these same techniques can be used to develop boiler operating and component design strategies for minimizing acid emissions.” •