

## Formation of Sulfate Aerosol in an SO<sub>2</sub> Scrubbing System

By

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Southern Research Institute has participated in the U. S. Department of Energy project entitled "Comprehensive Assessment of Air Toxic Emissions from Coal-Fired Electric Generating Stations". This work included sampling, chemical analyses and mass balances on two large power stations with modern emission control systems for SO<sub>x</sub> and particulate matter (PM). Quantification of hazardous air pollutant emission rates was the primary focus of the measurement programs, and these results have been previously reported.<sup>1,2,3</sup> More recently, the results have been re-examined with an emphasis on the effectiveness of the control systems in reducing fine particle emissions.<sup>4</sup> In this paper, we will provide a further re-examination of the data from one of the sites at which sulfur trioxide as sulfuric acid aerosol was a significant component of the fine particle emissions.

The power station under study was the site of a Clean Coal Technology Project to demonstrate the Pure Air Advanced Desulfurization Process. The two units involved employ B&W cyclone boilers, each of which is equipped with an electrostatic precipitator. Flue gas from both units is combined to form a single stream that is treated by the wet scrubber. The fuel supply for both units is an Illinois/Indiana high sulfur bituminous coal with sulfur contents ranging from 2.5 to 4.5%.

Fine particle concentration measurements were performed at the inlet and outlet sampling locations of the Unit 8 electrostatic precipitator and the wet scrubber. Minimum collection efficiency of fine PM in the 1-2 micrometer aerodynamic diameter range across the precipitator was 96%, and overall mass collection efficiency was 99.82%. Penetration ratios across the inlet and outlet of the downstream scrubber in the 1-2 micron size range were greater than 1.0, which reflects the generation of fine particles across the scrubber.

An explanation of the cause of the scrubber particle generation is suggested by the following partial analysis of ash collected from the stack:

Aluminum	0.33%	Calcium	1.36%
Iron	0.70%	Magnesium	0.26%
Titanium	0.05%	Sulfate	73.9%

The values listed are averages from three determinations; they are given as weight percentages. Clearly, the analysis must represent a mixture of a small quantity of fly ash

with a large quantity of some sulfate compound. The 54:1 ratio of sulfate to calcium shows convincingly that the sulfate compound is not calcium sulfate (eliminating the possibility of the entrainment of gypsum-containing droplets in the scrubber). The similar high ratios of sulfate to each of the other measured metals eliminates sulfates for these metals. The most probable cation to be associated with sulfate is therefore hydrogen ion, arising from the condensation of sulfuric acid vapor as the gas was cooled in the scrubber. Although soluble in the scrubber liquor, the acid condensate would be expected to occur as such fine particles that they would elude capture in the scrubber.

Calculation from the stack concentration of particulate matter and the sulfate content therein shows that the sulfate in the solid is equivalent to a preexisting sulfuric acid concentration of 10 ppm. No actual measurements of sulfuric acid vapor were performed in the stack during this test series; however, wide experience with measurements of the acid in other plants indicates that 10 ppm is an entirely plausible emission in a plant burning a coal with 3.2% sulfur content at the time of testing.

As a result of plume visibility problems, the plant had installed an ammonia injection system with the objective of converting the sulfur trioxide vapor to ammonium sulfate and ammonium bisulfate PM that would be collected with relatively high efficiency in the ESP's. However, the ammonia supply was depleted during our test series and the available analytical data suggest that essentially no ammonia was present when the fine PM data were obtained.

In view of the lack of experimental data on ammonia injection, we have conducted a review of thermodynamic data to develop estimates of the effect of ammonia injection on the fine PM concentrations in the stack under the conditions of the test program.

A reaction product consisting of either the sulfate or the bisulfate or a mixture of the two is likely to occur as an aerosol of fine particle size, and as such is subject to collection in the ESP. An analysis of the thermodynamic data indicates that injection of 15 ppm of  $\text{NH}_3$  gas would reduce the equilibrium sulfuric acid vapor concentration at the temperatures measured to concentrations less than 0.1 ppm.<sup>5</sup> Any of the product slipping through the ESP may combine further with  $\text{NH}_3$  gas as the temperature falls, if the reaction is not already complete. The capture of any sulfate particulate emitted from the ESP by the downstream scrubber, however, is not likely.

If any  $\text{NH}_3$  still remains in the gas phase, on the other hand, it will be subject to absorption in the scrubber liquor or to possible chemical reaction with  $\text{SO}_2$  to produce a sulfite aerosol. Even a scrubber liquor relatively high in pH is likely to reduce the  $\text{NH}_3$  gas-phase concentration by a factor of 10 or so. The reaction with  $\text{SO}_2$ , on the other hand, is rather severely deterred by thermodynamic considerations. Let the conditions of potential reaction be given by an  $\text{NH}_3$  concentration of 15 ppm, an  $\text{SO}_2$  concentration of 300 ppm, and a water vapor concentration of 13% by volume.

The work of Scargill on the reactions to produce ammonium sulfite and ammonium pyrosulfite (analogous to ammonium bisulfate) permits the formation temperatures to be calculated.<sup>6</sup> At the reactant concentrations specified, the temperature for the incipient formation of the sulfite must be only 73°F, or the temperature for the pyrosulfite must be just 70°F. The actual temperature corresponding to adiabatic saturation of the gas stream in the scrubber, at 13% water vapor, is approximately 125°F. If Scargill's data are correct, reactions of NH<sub>3</sub> with SO<sub>2</sub> will not occur. Therefore, even if significant NH<sub>3</sub> concentrations were present at the scrubber inlet, it is highly improbable that any of the PM exiting the stack would have resulted from SO<sub>2</sub>-NH<sub>3</sub> reactions in the scrubber. A similar analysis of thermodynamic data concerning possible HCl-NH<sub>3</sub> reactions indicates that formation of NH<sub>4</sub>Cl aerosol is likewise improbable under the stated conditions.

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References:

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