

MINIMIZING SO₃ EMISSIONS FROM COAL-FIRED POWER PLANTS

Emissions of particulate matter (PM), nitrogen oxides (NO_x), and sulfur dioxide (SO₂) have been substantially reduced over the past 35 years through the application of industrial control technologies and strategies. The installation of such control technologies has added to the complexity of coal-fired boilers and their operations. The side effects of changing the train of chemical processes that occur between fuel preparation and emissions increase the potential for unintentional and undesirable consequences. One of the more noteworthy adverse consequences is the formation and emission of sulfur trioxide (SO₃) and associated sulfuric acid (H₂SO₄) aerosol.

SO₃ is present in all emissions generated from the combustion of sulfur-containing fuels. Typically, approximately 1% of SO₂ is oxidized to SO₃ in a coal-fired boiler. Reaction with water in the flue gas quickly converts SO₃ to H₂SO₄. As the flue gas temperature falls, the H₂SO₄ vapor condenses to form droplets that are usually smaller than 1 µm in aerodynamic diameter. At concentrations typical of a near-stack plume, these droplets scatter light and can significantly increase the plume's opacity.

This near-stack opacity issue has not been a problem for most plants because the H₂SO₄ concentrations in the plume have remained low. Recently, however, more plants are experiencing or anticipating opacity problems associated with increased SO₃ and H₂SO₄. Such increases can be caused by the installation of selective catalytic reduction (SCR) systems, which reduce emissions of nitrogen oxides (NO_x) by up to 90%, but at the same time, increase the oxidation of SO₂ to SO₃, leading to increased H₂SO₄ emissions.

EPA's Air Pollution Prevention and Control Division is examining approaches to prevent and reduce excessive SO₃ formation and H₂SO₄ emissions (see Srivastava, R.K., et al. Emissions of Sulfur Trioxide from Coal-Fired Power Plants; *J. Air & Waste Manage. Assoc.* 2004, 54, 750-762). The

preferred approach is to minimize the formation of SO₃. Reducing excess oxygen and using low-sulfur coal are two methods that can be used to minimize the formation of SO₃ at the source, but many plants have limited ability to make such significant operational changes. Another approach is to select a catalyst with low guaranteed levels of SO₂-to-SO₃ oxidation. Manufacturers frequently guarantee SO₂-to-SO₃ conversion rates of 0.5% across the catalyst, which is often adequate to limit SO₃ emission rates to acceptable levels. For plants that use coals with sulfur contents greater than 2%, consideration of SO₃ formation rates may be a critical factor in the catalyst selection process.

Emission reduction approaches include injection of alkali sorbents into or downstream of the furnace, injection of ammonia (NH₃) downstream of the air preheater, and installation of a wet electrostatic precipitator (ESP). Use of alkali sorbents, such as hydrated lime, limestone, magnesium oxide, or sodium carbonate, can achieve SO₃ reductions of 40–80% with furnace injection, and 40–90% using post-furnace duct injection. Installations must consider additional particle loading on the ESP, the potential for SCR plugging, and other operational factors to ensure that no additional problems are introduced into the plant. Removal rates, and economic performance, will depend on sorbent type, injection location, and dry or slurry injection methods.

For units that have an SCR system in place, NH₃ injection downstream of the air preheater can be an attractive option because the same reagent is used for both NO_x and SO₃ emissions reduction. SO₃ removal rates of more than 90% have been reported in full-scale operation. Like alkali injection, NH₃ injection can increase ESP particle loading, but it can also reduce particle loading under certain conditions due to agglomeration. Excessive NH₃ can adversely impact the salability of the ash and significantly increase the net cost of the process.

Although gaseous SO₃ is highly water soluble, it is not effectively removed by wet flue gas desulfurization

(wet FGD) systems because it condenses into a submicron-sized aerosol at temperatures typical of FGD inlet conditions. Wet FGDs can remove some of these particles, but significantly greater acid mist removal is achieved by installation of a wet ESP immediately downstream of the scrubber. Wet ESPs can, in some cases, be installed at the outlet duct of the scrubber to form an integrated system, with reported removal rates of 70%.

Current EPA efforts are focused on supporting the development of a spreadsheet-based model of SO₃ formation and removal to enable plants to better predict their potential SO₃ emissions and evaluate prevention and mitigation options. Measurements from full-scale units form the basis of the model, which estimates formation in the furnace and across the SCR, and removal in the air preheater, the wet scrubber, and the ESP. The model considers absorption of SO₃ by fly ash and subsequent collection in the ESP, as well as removal by wet ESPs. This work is expected to be completed by early 2007.

Although not directly subject to regulation, SO₃ can be an important factor in the control of both PM and NO_x. Its formation across SCR systems and the formation of acid aerosol can impact a plant's efforts to achieve desired emissions levels. Consideration of SO₃ during SCR design and evaluation of the post-furnace systems as an interdependent system rather than a collection of independent devices can significantly reduce or eliminate the problems associated with SO₃.

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