U.S. Department of Energy • Office of Fossil Energy National Energy Technology Laboratory



# Successes

## SO<sub>3</sub> Emission Control Technology for Coal-Fired Power Plants

#### **A**DVANCED **R**ESEARCH

To support coal and power systems development, NETL's Advanced Research Program conducts a range of pre-competitive research focused on breakthroughs in materials and processes, coal utilization science, sensors and controls, computational energy science, and bioprocessing—opening new avenues to gains in power plant efficiency, reliability, and environmental quality. NETL also sponsors cooperative educational initiatives in University Coal Research, Historically Black Colleges and Universities, and Other Minority Institutions.

#### ACCOMPLISHMENTS

- ✓ **Process innovation**
- ✓ Cost reduction
- ✓ Greater efficiency
- Environmental benefits



#### Introduction

With support from the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL), the Energy & Environmental Research Center (EERC), along with Marsulex Environmental Technologies and the ALSTOM Power Inc. Air Preheater Company, has been working to develop solutions to sulfur trioxide (SO<sub>3</sub>) emission problems in coal-fired boilers. A significant pollutant in its gaseous form, SO<sub>3</sub> is the primary agent in acid rain and a precursor to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).

To meet the specific reductions in sulfur dioxide (SO<sub>2</sub>) and nitrogen oxide (NO<sub>x</sub>) emissions required by the 1990 Clean Air Act Amendments, coal-fired electric utility emission reduction strategies have included installation of flue gas desulfurization (FGD) systems for SO<sub>2</sub> control and selective catalytic reduction (SCR) technology for NO<sub>x</sub> control. However, while reducing SO<sub>2</sub> and NO<sub>x</sub>, these technologies have increased the potential for emission of SO<sub>3</sub> and sulfuric acid aerosols and, in turn, increased stack opacity (a measure of particulate emissions). The reasons are clear: 1) FGD systems allow power plant operators to fire cheaper high-sulfur coals, which generate more SO<sub>3</sub> than do more expensive low-sulfur coals. While effective for SO<sub>2</sub> capture, wet FGD has been shown to have a minimal effect on removal of SO<sub>3</sub>; and 2) SCR for NO<sub>x</sub> control results in increased SO<sub>3</sub> concentrations in the flue gas as a result of catalytic oxidation of SO<sub>2</sub> by the SCR. The problem may be aggravated by fine particles formed by the reaction of SO<sub>3</sub> with excess ammonia present from the FGD or SCR process, resulting in a highly visible "blue plume" emitted from the stack.

## **Technical Approach**

The basis of the  $SO_3$  reduction technology being demonstrated by the EERC and its partners is to provide controlled condensation of  $SO_3$  by injection of fine particles immediately upstream of the air preheater (APH). The particles provide nucleation sites for heterogeneous condensation in preference to homogeneous condensation and condensation on metal APH surfaces. The condensation process does not depend on the composition of the particles, but only on the particle-size distribution and particle concentration. Limestone was chosen for its low cost and its ability to provide a degree of acid neutralization after condensation has occurred.

A computer model developed by the EERC determines the amount of  $SO_3$  transformations and interactions across an APH to assist in developing strategies to minimize the level of  $SO_3$ released to the environment. The predictive model developed by the EERC utilizes 1) an ash

## **PROJECT I:**

Evaluation of SO<sub>3</sub> Emission Control by Flue Gas Humidification at the R. Paul Smith Station

#### DURATION

Start Date: 04/01/2001

End Date: 06/30/2002

#### Соѕт

Total Project Value \$244,000

**DOE/Non-DOE Share** \$97,500 / \$146,500

## **PROJECT 2:**

Modeling the Interaction of Vapor-Phase and Particulate Species at Low Temperatures

DURATION

Start Date: 04/01/2001

End Date: 08/31/2002

Соѕт

Total Project Value \$100,000

**DOE/Non-DOE Share** \$40,000 / \$60,000

## **PROJECT 3:**

Modeling of Limestone Injection at Chesterfield Unit 5

DURATION

Start Date: 07/01/2005

End Date: 09/30/2005

Соѕт

Total Project Value \$32,043

DOE/Non-DOE Share \$10,813 / \$21,230

## PARTNERS

Energy & Environmental Research Center (EERC) Grand Forks, ND

Marsulex Environmental Technologies, LLC Lebanon, PA formation model to predict the particle loading and properties (particle-size and composition distribution [PSCD]) of particles entering the APH, 2) FLUENT<sup>TM</sup> computational fluid dynamics (CFD) software to predict velocity and temperature profiles, and 3) Chemkin<sup>TM</sup> reaction kinetics software to predict the rate of SO<sub>3</sub> formation in the gas phase. The EERC model employs algorithms to account for heterogeneous condensation of sulfuric acid on ash particle surfaces as well as on metal surfaces, to predict particle impaction and accumulation rates in the APH and, finally, to predict the gas-phase SO<sub>3</sub> concentration at the entrance to the electrostatic precipitator (ESP).

The results of the modeling work indicated a significant reduction of  $SO_3$  in the presence of fine particles less than approximately 5 µm in diameter as the flue gases containing  $SO_3$  passed through the APH and ductwork upstream of the ESP, which was corroborated by early field observations at a full-scale utility boiler. This finding provided a unique opportunity to reduce the level of  $SO_3$  in the flue gas as it passes through an APH.

## Demonstrations

The site selected for a full-scale demonstration of the technology was Dominion Energy's Chesterfield Station Unit 5, located in Chester, Virginia. The plant is a nominal 350-MW unit firing 183,000 lb/hr of a bituminous coal. The unit is equipped with SCR technology and cold-side ESPs. Unit dimensions and operating data were obtained to model the expected degree of SO<sub>3</sub> reduction using the technology.

The researchers modeled the process in three phases for the unit firing the current baseline coal (current coal) and for a higher-sulfur coal contemplated for future use:

- The first phase involved prediction of fly ash size and composition distributions. The chemical and physical transformations of the inorganic components of coal to ash or slag during combustion depend on the design of the system, operating conditions, and fuel composition. During the combustion and gas-cooling process, the inorganic species are transformed into inorganic vapors, liquids, and solid particles in the initial combustion phase. These ash precursor materials are cooled as they are transported with the bulk gas flow through the combustion system. The model uses advanced coal inorganic constituent analysis, boiler parameters, and a detailed knowledge of the chemical and physical transformations of inorganic components during combustion to predict the particle size and chemical composition of the resulting ash. An aerosol formation and evolution model component predicts submicron ash formation by homogeneous nucleation and growth by heterogeneous condensation and coagulation.
- The second phase was to determine the flue gas components at the entrance to the APH, particularly  $SO_2$ ,  $SO_3$ ,  $H_2O$ , and  $H_2SO_4$ . A simple calculation produced an estimate of gas composition at the furnace exit based on the coal chemistry, coal feed rate, and excess air. Since measurements of  $SO_2$  and  $SO_3$  concentration after the SCR at the APH entrance were available for the current coal, these were used rather than determining  $SO_3$  concentration from kinetic modeling. For the high-sulfur coal, the researchers assumed that the  $SO_2$  concentration and conversion to  $SO_3$  across the SCR would be proportional to that of the current coal.
- In the third phase, FLUENT—a CFD code—was used to model flow patterns through selected devices. The CFD model provides the flow of gas-phase and particulate-phase materials along with the velocity and temperature distribution through the APH and downstream ductwork. This determines the impacts of species mixing and impingement on the walls of particles suspended in the flue gas streams. The model outputs are then used to model the particle transport and deposition processes. When combined with an ash impaction and sticking model, this information determines the impacts of particles as well as particle sizes on the fate of SO<sub>3</sub> in the APH and ductwork between the APH and the ESP.

A full-scale field demonstration using the technology evaluated within this project was performed during late summer 2006. A commercial  $SO_3$  generator that the plant uses for ESP conditioning was used to catalytically generate an elevated  $SO_3$  concentration that was anticipated to result from firing a higher-sulfur coal (~35 ppm SO<sub>3</sub>) with an SCR installed. The control technology used finely

ground limestone injected immediately ahead of the APH as the  $SO_3$  removal medium. Precise placement of 12 limestone injection lances provided a reasonably even distribution across the gas stream going into the APH.

 $SO_3$  sampling was performed at three locations: 1) the inlet to the APH (after the  $SO_3$  injection location), 2) the exit of the APH, and 3) the inlet to the ESP. The sampling was done at the APH inlet and outlet locations and at the ESP inlet using the controlled condensation method. The measured  $SO_3$  levels in the flue gas during the tests are shown in Figure 1. There was a 53.6 percent average

reduction in  $SO_3$  (as measured at the ESP inlet location) as a result of limestone injection. No increase in APH pressure drop was observed, and there was no change in ESP performance or increase in stack opacity during the limestone injection.

From the model predictions, the calculated SO<sub>3</sub> removal results for the currently fired coal with an assumed SO<sub>2</sub> concentration of 36 ppm are shown in Figure 2 in comparison with the measurements obtained during the test program. At the ESP exit, a substantial reduction in gas-phase SO<sub>3</sub> was predicted for the case with limestone injection (25 versus 55 percent of the starting concentration) with the difference condensed on particulate material. Although the limestone only increases the particle loading from 1.5 to 3.0 to 4.0 percent, the small particle size results in significant additional condensation. The full-scale test results were in good agreement with the model predictions.







Figure 2. Calculated SO<sub>3</sub> removal results compared to actual SO<sub>3</sub> removal.

## **Commercial Opportunity**

Improved sulfur control technologies such as an FGD combined with a fabric filter baghouse make possible the burning of higher-sulfur coals. However, reduction of  $SO_3$  concentrations to less than a dew point temperature of 270°F is then required to avoid back-end corrosion, damage to fabric filters, and visible stack emissions. The operating criteria for the  $SO_3$  control technology imposed the requirements of having no negative effect on unit operations, such as increased APH pressure drop or accumulation of material in the ductwork; high levels of reliability, operability, and maintainability; low operating cost; and a reasonable capital cost. All of these requirements are met using this  $SO_3$  reduction technology. Other  $SO_3$  abatement technologies—such as the use of fireside reagents, reagent-based postcombustion additives, and wet ESP technology—do not meet all of these desired performance and operating requirements.

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