

## BENCHMARKING SO<sub>3</sub> REMOVAL – THE CLEANSTACK® PROCESS

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### ABSTRACT

This paper presents the results of a full-scale demonstration of a proprietary technology for the reduction of sulfur trioxide (SO<sub>3</sub>) emissions from coal-fired power plant flue gases. The technology, trademarked CleanStack®, was developed jointly by Marsulex Environmental Technologies, the Energy & Environmental Research Center, and ALSTOM Power, Inc., Air Preheater Company. Dominion Energy hosted the demonstration of the technology at its Chesterfield Unit 5, utilizing one of the 350-MWe unit's two air preheaters for the project. Higher SO<sub>3</sub> emissions, which result from the retrofit of selective catalytic reduction (SCR) technology to control NO<sub>x</sub> emissions, are considered significant corrosion and opacity concerns for high-sulfur coal-fired boilers. The additional quantities of SO<sub>3</sub> generated by the oxidation catalysis of SCR elements on SO<sub>2</sub> have led to serious plume conditions from chimneys and higher rates of downstream corrosion. The CleanStack® technology utilizes the injection of ultrafine alkaline particles upstream of the boiler's air preheater to aid in the condensation and subsequent neutralization of SO<sub>3</sub>. Collected SO<sub>3</sub> is absorbed by the alkaline particles and

disposed of with the fly ash constituents. Advanced-design air preheater heating elements that resist fouling and enable more effective cleaning, ensure the reliable operation of the air preheater under CleanStack<sup>®</sup> operation. In addition to solving a growing emission problem, the CleanStack<sup>®</sup> technology may enable certain plants to increase their boiler thermal efficiencies by as much as 1% due to the increased heat transfer taking place across the air preheater. This benefit also translates into lower corrosion rates of downstream ductwork and electrostatic precipitator components, as well as enabling owners to more seriously evaluate fabric filters for high-sulfur applications. Fabric filters may enhance the company's ability to comply with future fine particulate and mercury regulations. The paper presents the results of the full-scale demonstration program, including SO<sub>3</sub> reduction performance, air preheater operation, and the discussion of several collateral benefits such as those cited above.

## INTRODUCTION

Emission reduction strategies implemented by electric utilities on coal-fired plants include installation of flue gas desulfurization (FGD) systems for SO<sub>2</sub> control and SCR technology for NO<sub>x</sub> control to meet the specific reductions in SO<sub>2</sub> and NO<sub>x</sub> emissions required by the 1990 Clean Air Act Amendments. These technologies result in the potential for emission of SO<sub>3</sub> and sulfuric acid aerosols that can result in increased stack opacity. The installation of FGD systems also allows the firing of high-sulfur fuels, which generate more SO<sub>3</sub> than do more expensive low-sulfur coals. While effective for SO<sub>2</sub> capture, wet FGD systems have been shown to have a minimal effect on removal of SO<sub>3</sub>.

The use of SCR for NO<sub>x</sub> control also may result 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. This problem may be aggravated by ultrafine particles formed by the reaction of SO<sub>3</sub> with excess ammonia present from the SCR process, resulting in a highly visible "blue plume" emitted from the stack.

In the coal combustion process, SO<sub>3</sub> comprises approximately 0.7% of total sulfur emissions. Chemical equilibrium modeling shows essentially all the SO<sub>3</sub> is converted to gaseous H<sub>2</sub>SO<sub>4</sub> at a flue gas temperature of 400°F (204°C). Below the sulfuric acid dew point temperature (260°–300°F, 127°–149°C) when a sufficiently high SO<sub>3</sub> concentration and a low ash particle loading is present in the flue gas, homogeneous condensation can occur, producing a submicron acid fume which is very difficult to collect in a dry electrostatic precipitator (ESP) or wet scrubber. Emission of SO<sub>3</sub> and acid fume may result in increased opacity and a conspicuous blue stack plume.<sup>1</sup>

The condensed sulfuric acid also has the potential to result in fouling and corrosion on surfaces in the air preheater, ductwork, and stack. Conventional wisdom dictates that flue gas exiting a regenerative air preheater should not fall below minimum temperatures dictated by the percentage of sulfur in the coal to avoid fouling and corrosion. However, local metal temperatures are always lower than the flue gas temperature, and the metal surface temperature at the cold end of an air preheater is typically below the acid dew point. Thus acid condensation is normally occurring at the cold end of an air preheater under typical operating conditions. Deliberate control of metal temperature gradients within the air preheater offers a potential method for enhanced SO<sub>3</sub> and acid capture.<sup>2</sup>

Dominion Generation has committed to upgrades to significantly reduce particulate and sulfur emissions at its Chesterfield facility. A wet FGD and fabric filter baghouse are to be in service on Unit 6 by June 2008. The wet FGD will make possible the burning of higher-sulfur coals. However, this entails the need to reduce SO<sub>3</sub> concentrations to less than a dew point temperature of 270° F to avoid back-end corrosion, damage to fabric filters, and visible stack emissions. The operating criteria for the SO<sub>3</sub> control technology imposed the requirements of having no negative effect on unit operations, such as increased air preheater pressure drop or accumulation of material in the ductwork, high levels of reliability, operability and maintainability, low operating cost, and a reasonable capital cost. CleanStack<sup>®</sup> meets these requirements. As a result, Dominion Generation entered into a full-scale plant demonstration of this technology. Other SO<sub>3</sub> abatement technologies considered were the use of fireside reagents, reagent-based post-combustion additives, and wet ESP technology; however, they did not appear to meet all of the desired performance and operating requirements.

The basis of the SO<sub>3</sub> reduction technology demonstrated at Chesterfield Unit 5 is to provide controlled condensation of SO<sub>3</sub> by injection of ultrafine particulate material immediately upstream of the air preheater. The particle concentration provides nucleation sites for heterogeneous condensation in preference to both homogeneous condensation and condensation on metal air preheater surfaces. The condensation process does not depend on the composition of the particles, but only on the particle-size distribution and particle concentration. For the testing, limestone was chosen so as to provide a degree of acid neutralization after condensation has occurred. The Energy & Environmental Research Center (EERC), along with Marsulex Environmental Technology and the ALSTOM Power Inc., Air Preheater Company, has been working to develop solutions to SO<sub>3</sub> emission problems in boilers. The goal of the Chesterfield testing was to demonstrate the effectiveness of the CleanStack<sup>®</sup> SO<sub>3</sub> control technology for removing SO<sub>3</sub> from flue gas as a function of limestone feed rate and flue gas SO<sub>3</sub> concentration.

## EXPERIMENTAL

### Field Testing

The site selected for the demonstration was Dominion Generation's Chesterfield Station. The Chesterfield Station consists of four tangentially fired units with a total electrical capacity of 1298 MW. The testing was performed on Unit 5 which is a nominal 350-MW unit firing 183,000 lb/hr of a bituminous coal. The unit is a split-backpass design with SCRs for NO<sub>x</sub> control and cold-side ESPs for particulate removal. Dominion had previously upgraded the air preheaters on Unit 5 to include the advanced-design heating elements which would minimize the fouling concerns with CleanStack<sup>®</sup>. Specific objectives were to determine the baseline SO<sub>3</sub> concentration at the air preheater inlet (SCR outlet), air preheater outlet, and ESP inlet; determine the particle-size distribution and feed rate of the limestone injection system using multicyclones; and determine SO<sub>3</sub> removal efficiency across the air heater and at the inlet to the ESP at different limestone injection rates. This testing was performed during the summer of 2006.

A commercial SO<sub>3</sub> generator that the plant uses for ESP conditioning was used to catalytically generate an elevated SO<sub>3</sub> concentration that is anticipated to result from firing a higher-sulfur coal (~35 ppm SO<sub>3</sub>) with an SCR installed. The SO<sub>3</sub> was injected into the flue gas at a location far enough upstream of the air heater to ensure uniform dispersion of the SO<sub>3</sub>.

The control technology uses finely ground limestone injected immediately ahead of the air preheater as the SO<sub>3</sub> removal media. Limestone was injected upstream of one of the air preheaters and ESPs of Unit 5. Figure 1 shows the general locations for SO<sub>3</sub> and limestone injection and for sampling. Details of the limestone injection system are shown in Figure 2.

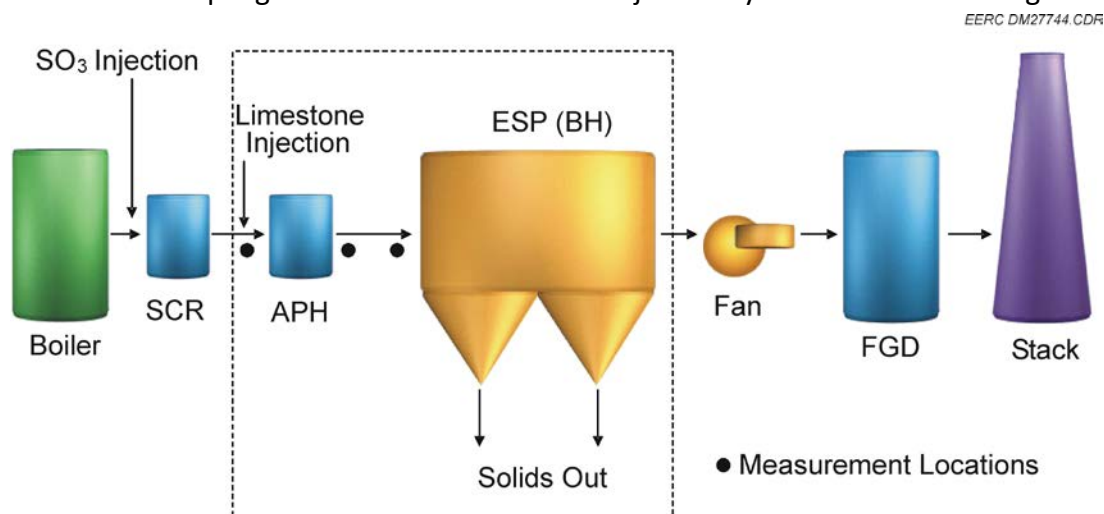


Figure 1. Injection and sampling locations.

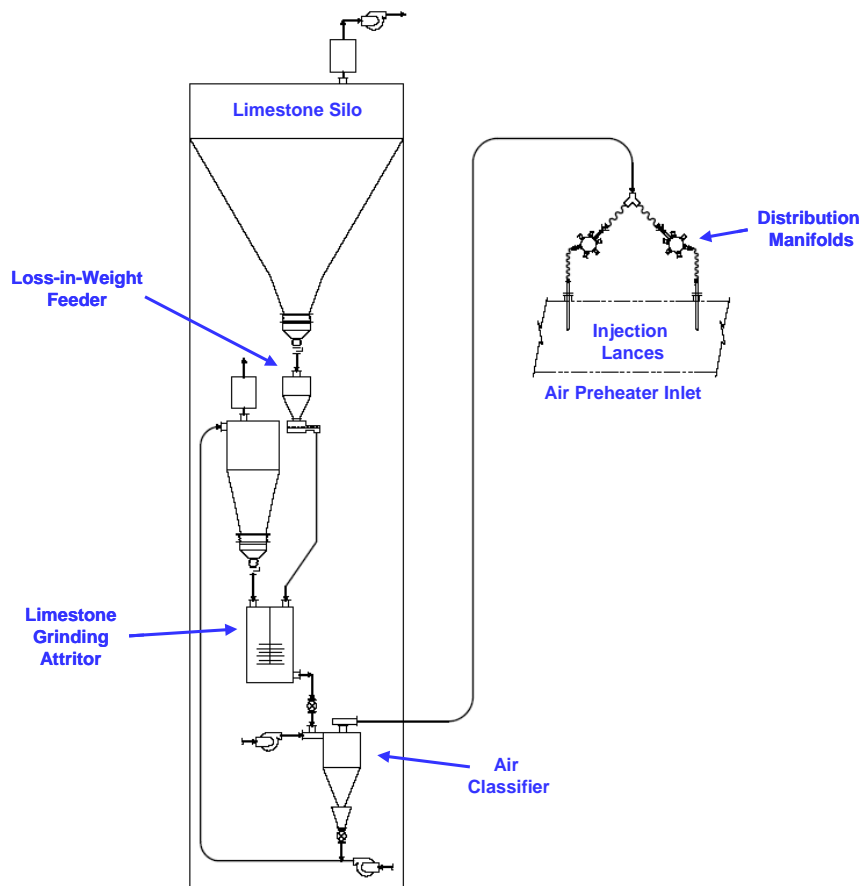


Figure 2. Equipment requirements for the limestone injection system.

Limestone is fed from the storage silo into an attritor mill followed by a classifier. The classifier recycles oversized material back to the attritor mill for regrinding while allowing the fine material (mean size approximately 3  $\mu\text{m}$ ) to be pneumatically conveyed to the distribution manifolds and the injection lances located upstream of the APH inlet. A total of 12 limestone injection lances were used, providing a reasonably even distribution across the gas stream going into the air preheater.

$\text{SO}_3$  sampling was performed at three locations: the inlet to the air preheater (after the  $\text{SO}_3$  injection location), the exit of the air preheater and the inlet to the ESP. All  $\text{SO}_3$  sampling was accomplished using the controlled condensation method. At each location, four ports were sampled across the duct for 1 hour each (two ports were sampled simultaneously) providing a 4-point traverse. The  $\text{SO}_3$  concentration reported was an average across the four ports. The  $\text{SO}_3$

concentration in the sample collected at each point was measured using ion chromatography. To compare the results from each of the sampling locations, the data were put on the same O<sub>2</sub> basis (3%, with the O<sub>2</sub> concentration at each sampling location measured using a portable O<sub>2</sub> analyzer).

The testing parameters are provided in Table 1. The plant process conditions for the tests are listed in Table 2. The plant operated at nearly full load and, in general, provided very steady operation during the tests.

**Table 1. Testing Parameters.**

Test	Limestone, lb/hr	Sulfur, lb/hr	Comments
T0	0	0	Baseline
T1	500	90	Probe was hot (>600°F)
T2	0	90	Probe was hot (>600°F)
T3	500	60	
T4	0	60	Tube leak in boiler occurred during testing
T5	0	60	
T6	500	60	
T7	300	60	Boiler load was low
T8	500	60	
T9	300	60	
T10	0	60	

**Table 2. Process Conditions at Dominion's Chesterfield Plant During SO<sub>3</sub> Sampling.**

Test	Baseline	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Barometric Pressure, in. Hg	NA*	30.15	30.00	30.00	30.00	30.06	30.06	30.00	30.00	30.03	30.03
Boiler Load, MW	341	342	337	339	338	337	348	347	267	340	341
Stack Flow, scfm	769,900	778,900	766,200	759,800	766,600	773,000	770,000	645,500	766,700	775,900	782,500
Opacity, %	5.70	5.72	7.06	13.17	7.77	5.42	5.52	4.48	9.21	8.81	10.05
Air Heater Inlet, °F	682	680	675	673	674	671	672	644	673	672	671
Air Heater Outlet, °F	285	292	304	292	294	292	293	280	295	290	291
∞ Air Heater ΔP, in. H <sub>2</sub> O	5.28	5.42	5.12	5.20	5.25	5.24	5.34	3.68	5.21	5.20	5.22
Boiler O <sub>2</sub> , %	3.0	3.1	2.7	2.6	2.9	2.8	2.8	3.4	2.5	2.9	3.2
NH <sub>3</sub> Feed Rate, lb/hr	173.9	171.0	133.9	131.7	128.9	158.5	161.6	138.2	132.9	150.2	159.7
SCR in NO <sub>x</sub> , ppmv	241	239	195	193	188	198	202	237	190	209	224
SCR out NO <sub>x</sub> , ppmv	30	30	29	30	29	29	30	30	30	30	30
Stack SO <sub>2</sub> ppmv	681	639	625	640	639	649	659	640	670	629	633

\* Not available.

## RESULTS AND DISCUSSION

The SO<sub>3</sub> levels in the flue gas measured during the tests are shown in Table 3. These results are presented on a constant O<sub>2</sub> basis (3%) so that the concentration at each of the three locations can be compared to determine the actual SO<sub>3</sub> removal that occurs as a result of the limestone injection. The results in Table 3 show differences in SO<sub>3</sub> concentration across the duct, especially at the air preheater inlet sampling location. In general, the concentrations at the C and D ports were higher than those measured at the A and B ports. This was found to be the result of an uneven distribution of SO<sub>3</sub> flows being injected into the duct. Variability in SO<sub>3</sub> levels were also observed at the air preheater outlet because of the rotation of the air preheater. Previous modeling results indicated that the temperature at various points in the air preheater rotation would have an effect on SO<sub>3</sub> concentration and removal.<sup>3</sup> At the ESP inlet location, the SO<sub>3</sub> levels are more constant across the duct as the increased residence time allows better mixing of the gas. There is no explanation why the air preheater inlet location for Test T3 is so low compared to the other tests, since the feed rate of sulfur for the SO<sub>3</sub> generator for all the tests (T3–T10) was held constant at 60 lb/hr. The SO<sub>3</sub> level at the air preheater outlet location for test T3 is similar to the other tests where limestone was added.

**Table 3. Flue Gas SO<sub>3</sub> Concentrations (3% O<sub>2</sub> Basis).**

Test	T3	T5	T6	T8	T9	T10
<i>Air Preheater Inlet</i>						
A	13.1	14.1	19.2	21.0	19.6	24.8
B	16.0	27.6	15.6	15.1	27.8	35.2
C	14.1	32.1	48.5	61.7	61.8	70.5
D	25.6	61.1	66.0	52.1	59.5	67.5
Avg.	17.2	33.7	37.3	37.5	42.2	49.5
<i>Air Preheater Inlet</i>						
A	18.2	32.8	5.9	8.3	22.3	13.2
B	19.2	17.2	14.5	8.5	12.0	14.7
C	8.1	13.4	21.6	16.8	7.8	46.5
D	1.6	14.4	10.1	9.9	10.2	21.4
Avg.	11.8	19.5	13.0	10.8	13.1	23.9
<i>ESP Inlet</i>						
A	5.7	12.5	7.5	7.1	7.0	14.1
B	6.5	13.2	10.2	5.5	7.3	16.8
C	5.2	15.0	10.1	8.9	9.8	15.9
D	5.2	16.7	12.2	3.4	11.0	14.1
Avg.	5.7	14.4	10.0	6.1	8.8	15.2



A comparison of the tests with and without limestone injection is provided in Table 4. If the concentration of SO<sub>3</sub> for Test T3 was more in-line with the average SO<sub>3</sub> level, the removal for that test would be 85.4%. As stated earlier, Tables 3 and 4 provide the SO<sub>3</sub> on a 3% O<sub>2</sub> basis so that comparisons can be made across the different sample points and tests. However, the actual SO<sub>3</sub> emissions are the concentration of SO<sub>3</sub> in flue gas irrespective of the excess air. These results are shown in Table 5. There was a 49.3% reduction average in SO<sub>3</sub> (as measured at the ESP inlet location) as a result of limestone injection.

**Table 4. Comparison of Tests with and Without Limestone Addition.**

Test	AH inlet	AH Outlet	ESP inlet	Removal
<i>Without Limestone Injection</i>				
T5	33.7	19.5	14.4	57.3
T10	49.5	23.9	15.5	68.7
<b>Average</b>	<b>41.6</b>	<b>21.7</b>	<b>15.0</b>	<b>63</b>
<i>With Limestone Injection</i>				
T3	17.2	11.8	5.7	66.8
T6	37.3	13.0	10.0	73.1
T8	37.5	10.8	6.1	83.7
T9	42.2	13.1	8.8	79.1
<b>Average</b>	<b>33.6</b>	<b>12.2</b>	<b>7.6</b>	<b>75.7</b>

From previous model predictions,<sup>3</sup> the calculated SO<sub>3</sub> removal results for the currently fired coal with an assumed SO<sub>3</sub> concentration of 36 ppm is shown in Figure 3 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% 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%, the small particle size results in significant additional condensation. The test results are in good agreement with the model predictions.

**Table 5. Actual SO<sub>3</sub> Emissions.**

<i>Without Limestone Injection</i>				
Port	T5	T10		
A	11.2	12.1		
B	11.6	14.2		
C	11.2	13.2		
D	12.2	12.8		
<b>Avg</b>	<b>11.7</b>	<b>13.1</b>		
<i>With Limestone Injection</i>				
	T3	T6	T8	T9
A	5.0	6.3	7.3	6.1
B	5.8	8.5	2.7	6.2
C	4.5	7.7	5.6	8.6
D	4.5	9.5	4.4	9.5
<b>Avg</b>	<b>4.9</b>	<b>8.0</b>	<b>5.0</b>	<b>7.6</b>

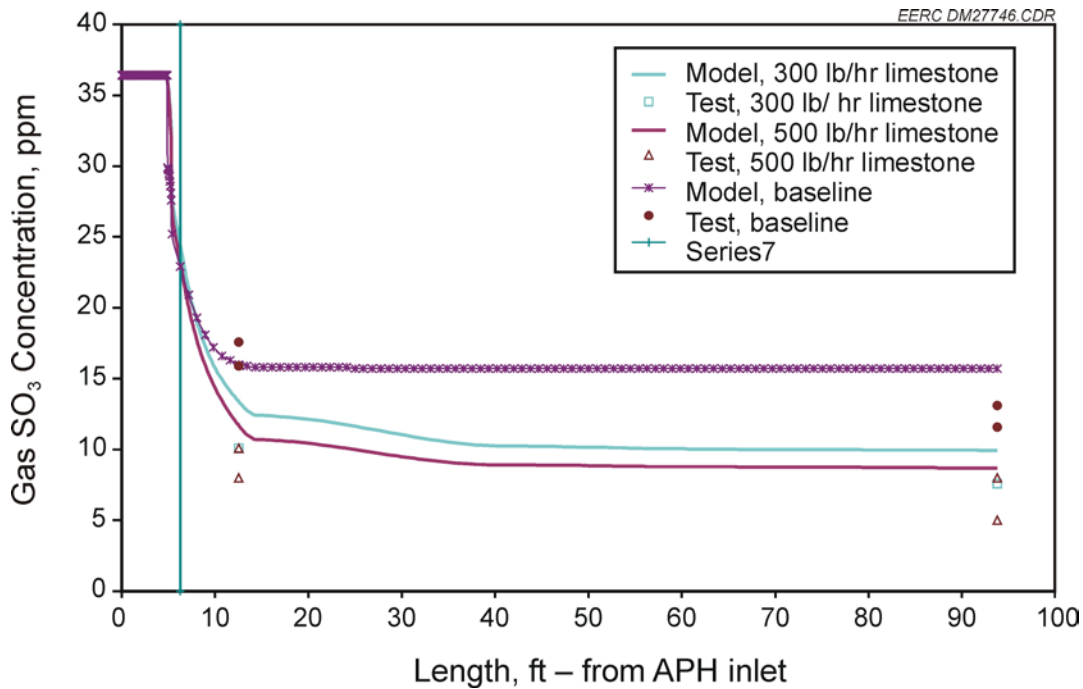


Figure 3. Comparison of test results with modeling predictions.

## CONCLUSIONS

As part of upgrades to meet regulations for particulate and sulfur emissions at its Chesterfield facility, Dominion Generation is examining control technologies to reduce SO<sub>3</sub> concentrations to less than a dew point temperature of 270°F to avoid back-end corrosion, damage to fabric filters and visible stack emissions while having no negative effects on unit operations. As a result, Dominion Generation entered into a full-scale plant demonstration of the CleanStack<sup>®</sup> technology. Testing was performed during the summer of 2006 to determine the baseline SO<sub>3</sub> concentration at the air preheater inlet (SCR outlet), air preheater outlet and ESP inlet and determine SO<sub>3</sub> removal efficiency across the air preheater and between the air preheater and the ESP as a function of limestone injection rates. The technology demonstrated a 49.3% average reduction in SO<sub>3</sub> (as measured at the ESP inlet location) as a result of CleanStack<sup>®</sup> limestone injection. The test results are in good agreement with previous model predictions.

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