# **Use of Magnesium Hydroxide for Reduction of Plume Visibility in Coal-Fired Power Plants**

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#### **ABSTRACT**

Combustion of high-sulfur coal combined with use of selective catalytic reduction (SCR) produces a high concentration of sulfur trioxide (SO<sub>3</sub>) in flue gas. Sulfur trioxide combines with water at lower temperature to form sulfuric acid. When wet FGD is also in use, the sulfuric acid condenses to a sub-micron aerosol which can produce a visible plume. As a result, many existing coal-fired generating units equipped with both wet FGD and SCR are seeking retrofit of systems to remove SO<sub>3</sub>. Reduction of sulfuric acid concentration to less than about 5 ppmv at the stack is necessary to eliminate visibility due to SO<sub>3</sub>. Injection of magnesium hydroxide into flue gas is potentially a low-capital cost retrofit technology for this purpose. Commercial magnesium hydroxide can be used for this purpose, however power stations with wet FGD using magnesium-enhanced lime can produce magnesium hydroxide as a low-cost byproduct, and this byproduct is suitable for injection to capture SO<sub>3</sub>.

The paper presents results of 1.6 MW-scale pilot testing of injection of byproduct Mg(OH)<sub>2</sub> into flue gas ahead of a Lungstrom<sup>®</sup>-type air preheater which demonstrate efficient removal of SO<sub>3</sub>. The results also demonstrate beneficial effects of SO<sub>3</sub> capture on air preheater operation. To simulate flue gas from a generating unit burning high-sulfur coal and equipped with SCR, SO<sub>3</sub> was added to a slipstream of flue gas from a bituminous coal-fired unit to increase SO<sub>3</sub> concentration to 35-55 ppmv.

The pilot air preheater was sized to allow a greater than normal reduction in flue gas exit temperature to demonstrate potential for an increase in generation efficiency and a corresponding reduction in CO<sub>2</sub> emissions. Removal of SO<sub>3</sub> from the flue gas allowed the air preheater flue gas exit temperature to be reduced to 220°F. The pilot was operated at this low exit temperature for 32 days to allow evaluation of the air preheater baskets under this condition. No increase in flue gas side pressure drop occurred during this period. Magnesium hydroxide injection protected the air preheater from severe deposits due to acid condensation.

#### INTRODUCTION

Sulfuric acid is present in flue gas from combustion of high-sulfur bituminous coal because a small fraction, approximately 1%, of sulfur dioxide (SO<sub>2</sub>) produced when coal is burned is converted to SO<sub>3</sub>. Sulfuric acid can cause air heater fouling and equipment corrosion. For generating units equipped with selective catalytic reduction (SCR), additional SO<sub>3</sub> is formed by catalysis. Below approximately 800°F and with typical flue gas water content, a portion of the SO<sub>3</sub> reacts with water to form sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) vapor. Below approximately 400°F, essentially all the SO<sub>3</sub> is present as H<sub>2</sub>SO<sub>4</sub> vapor. Although SO<sub>3</sub> vapor, H<sub>2</sub>SO<sub>4</sub> vapor, or aerosol H<sub>2</sub>SO<sub>4</sub> can be present in flue gas depending on flue gas temperature, water content and other conditions, they are often referred to simply as SO<sub>3</sub>, and this convention is used here.

When flue gas containing sulfuric acid vapor is rapidly cooled immediately after entering a wet FGD spray absorber, the sulfuric acid condenses to form a sub-micron aerosol. Most wet FGD absorbers are designed with a low flue gas pressure loss across the absorption zone, and as a result typically less than 50% of the aerosol is captured by the sprays, and the remainder exits with the flue gas to the stack. The aerosol scatters light and can form a visible plume that persists long after moisture has dispersed. The size distribution of the aerosol has a large impact on visibility, with aerosols that have a large fraction near 0.5 microns having the highest visibility. Visibility can be high enough to exceed permitted visual opacity limits.

As a result, many existing coal-fired generating units equipped with both wet FGD and SCR are seeking retrofit of systems to remove SO<sub>3</sub>. Reduction of the sulfuric acid aerosol concentration to less than about 5 ppmv at the exit of a large diameter stack is generally necessary to eliminate or greatly reduce visibility due to SO<sub>3</sub>.

One option for retrofit of SO<sub>3</sub> control is injection of magnesium hydroxide [Mg(OH)<sub>2</sub>] into the flue gas. Injection trials for reduction of SO<sub>3</sub> to reduce air preheater fouling and downstream corrosion were conducted in coal-fired boilers 30 years ago. Since 2001, magnesium hydroxide injection has been tested in several generating units fired with high-sulfur coal specifically for reduction of SO<sub>3</sub> emissions, and a 1300 MW generating unit has been injecting Mg(OH)<sub>2</sub> into the furnace for this purpose since 2004. However, although this technique very efficiently captures SO<sub>3</sub> generated in the furnace, the remaining Mg(OH)<sub>2</sub> that exits the furnace with the flue gas does not also efficiently capture SO<sub>3</sub> generated downstream in the SCR, as described later.

# Magnesium Hydroxide Products for Injection

Magnesium hydroxide slurry and magnesium oxide (MgO) powder are commercial products available for use in injection. For generation units fitted with wet FGD using magnesium-enhanced lime (MEL or Thiosorbic® Lime), Mg(OH)<sub>2</sub> can be produced as a byproduct slurry. Four generating units totaling about 2800 MW currently produce byproduct Mg(OH)<sub>2</sub>. The byproduct has been demonstrated to be as effective as

commercial magnesium hydroxide for removal of SO<sub>3</sub> across the furnace. Byproduct generation associated with the MEL FGD process is described in detail elsewhere.<sup>2</sup>

Magnesium compounds are highly soluble in water, so injection of Mg(OH)<sub>2</sub> is unlikely to form hard-to-remove deposits on equipment or ductwork.

Table 1 gives typical properties of byproduct Mg(OH)<sub>2</sub> and commercial Mg(OH)<sub>2</sub> used for injection.<sup>3</sup> The byproduct has a high specific surface area, 55-75 square meters per gram (dry basis) compared with 12 square meters per gram for commercial Mg(OH)<sub>2</sub>. The byproduct contains 12-14% Mg(OH)<sub>2</sub> compared with 60% for the commercial product. As noted above, SO<sub>3</sub> removal performance of the products was similar at the same molar injection ratio in one series of tests, but the products have not been tested side-by-side in other injection trials.

**Table 1.** Typical Properties of Byproduct and Commercial Magnesium Hydroxides

	Byproduct Mg(OH) <sub>2</sub> slurry	Commercial Mg(OH) <sub>2</sub> slurry
Mg(OH) <sub>2</sub> , wt. % dry basis	55-65	98.5
Total suspended solids, %	20	61
Mg(OH) <sub>2</sub> , wt. %	12-14	60
CaSO <sub>4</sub> • 2H <sub>2</sub> O and inerts, wt. %	7 - 9	<1
BET specific surface area, m <sup>2</sup> /g, dry basis	55-75	12
Median particle size, microns	3	3

# **Earlier Magnesium Hydroxide Injection Trials**

#### Furnace Injection

Byproduct magnesium injection into the furnace has demonstrated high reduction of furnace-generated SO<sub>3</sub> but much lower reduction of SCR-generated SO<sub>3</sub>. In 2001, the National Energy Technology Laboratory (NETL) of the U.S. Department of Energy (DOE) tested full-scale furnace injection of byproduct magnesium hydroxide at American Electric Power's 1300 MW Gavin Unit 1 to determine SO<sub>3</sub> reduction efficiency across the boiler and across the SCR. Byproduct Mg(OH)<sub>2</sub> slurry was provided by Allegheny Energy from their Pleasants power station, which includes a byproduct Mg(OH)<sub>2</sub> recovery system as part of the magnesium-enhanced lime wet FGD. The byproduct slurry was injected into the upper furnace of the 1300 MW unit above the nose where flue gas temperature was ~1900 F. At an injection rate of 7 moles Mg(OH)<sub>2</sub> per mole of uncontrolled SO<sub>3</sub> at the economizer exit, 90% reduction of furnace-generated SO<sub>3</sub> was achieved, but only about 20% of SCR-generated SO<sub>3</sub> was captured. This lower removal

of SCR-generated SO<sub>3</sub> was surprising, since the remaining Mg(OH)<sub>2</sub> amounted to at least 6 moles per mole of generated SO<sub>3</sub> in the SCR. Commercial magnesium hydroxide was also tested with the same result.

A possible explanation for the lower removal of SCR-generated SO<sub>3</sub> is that after injection into the upper furnace at ~1900°F, a portion of Mg(OH)<sub>2</sub> reacted immediately with SO<sub>3</sub>, but most of the remainder sintered from the high temperature, greatly reducing its specific surface area, or formed fusion products with molten flyash. As a result, little reactive Mg(OH)<sub>2</sub> remained, resulting in little SO<sub>3</sub> reduction across the SCR. Consistent with this explanation, one company that produces commercial Mg(OH)<sub>2</sub> and MgO products for SO<sub>3</sub> control recommends injection after the furnace where gas temperature is 650-750°F to avoid these possible adverse reactions.<sup>5</sup> Moreover, injection before an SCR or ahead of an air preheater would offer an opportunity to capture all the SO<sub>3</sub> generated in the furnace and the SCR in a single step.

#### Mg(OH)<sub>2</sub> Injection Ahead of an Air Preheater

Results of pilot tests sponsored by NETL at another coal-fired generating station suggested that byproduct Mg(OH)<sub>2</sub> injection after the boiler could yield greater reduction of overall SO<sub>3</sub> (furnace-generated plus SCR-generated) than in the furnace injection demonstration.<sup>6</sup> In these tests, byproduct Mg(OH)<sub>2</sub> identical to that used in the furnace injection demonstration was injected into flue gas at about 650°F ahead of a pilot-scale Ljungstrom (regenerative-type) air preheater (APH). The APH is normally located downstream of the SCR. At this temperature, inactivation of Mg(OH)<sub>2</sub> that apparently occurred in the furnace injection demonstration is unlikely to occur.<sup>7</sup> Consol Energy's R&D group designed and installed the pilot plant and carried out the testing. Alstom Air Preheater Co. provided the APH, multiple sets of hot-end and cold-end baskets, and performed thorough analysis of APH baskets at the end of the test program. Environmental Elements Corp. provided a pilot ESP, and Carmeuse provided support related to use of byproduct Mg(OH)<sub>2</sub>. Allegheny Energy provided its 285 MW Mitchell generating station as host site for the pilot.

The Multi-Pollutant Emission Control Pilot Plant included injection of byproduct magnesium hydroxide upstream of the APH. The pilot operates on a slip-stream of flue gas, equivalent to about 1.6 MW, at approximately 650°F taken upstream of the station air preheater of Mitchell Unit 3. The unit typically burns eastern bituminous coal with a sulfur content of 3.5-4% and does not include an SCR. SO<sub>3</sub> concentration in flue gas during the pilot tests ranged from 8 to 32 ppmv (adjusted to 3% O<sub>2</sub>).

The primary goal of the tests was not to remove SO<sub>3</sub> but rather to evaluate mercury control by lowering flue gas temperature ahead of an ESP, allowing mercury to adsorb onto unburned carbon in flyash. Byproduct Mg(OH)<sub>2</sub> slurry was injected via a dual-fluid atomizer at a rate of about 4 moles of Mg(OH)<sub>2</sub> per mole of uncontrolled SO<sub>3</sub>. The pilot air preheater was operated with a flue gas exit temperature of 230°F. Further cooling reduced temperature to as low as 200-220°F at the pilot ESP entrance. At this low temperature, Hg adsorption on flyash increased substantially.

To allow air preheater operation at this low flue gas exit temperature and avoid fouling of the APH baskets, byproduct Mg(OH)<sub>2</sub> was injected ahead of the air preheater to remove SO<sub>3</sub>. For the range of uncontrolled SO<sub>3</sub> concentrations noted, without an SCR, byproduct Mg(OH)<sub>2</sub> reduced flue gas SO<sub>3</sub> concentration to 3 ppmv or less at the entrance to the APH, and little or no fouling occurred during operation at the low flue gas exit temperature. However, the low-temperature operation only occurred for 3 day periods due to equipment problems. Alstom recommended an additional test run of longer duration to better evaluate the ability of Mg(OH)<sub>2</sub> injection to prevent fouling during operation at low flue gas exit temperature.

# TESTS OF BYPRODUCT Mg(OH)<sub>2</sub> INJECTION AHEAD OF AN APH WITH HIGH SO<sub>3</sub> CONCENTRATION

After completion of the NETL-sponsored project, Carmeuse decided to sponsor follow-up tests using the Mitchell pilot plant. These tests would focus only on SO<sub>3</sub> capture and a longer low-temperature run. Alstom Air Preheater Co. agreed to provide technical support and equipment for the tests, and the host site agreed to allow continued pilot testing. Consol Energy R&D agreed to operate the pilot plant and provide testing services to Carmeuse.

First, short-term, parametric tests were conducted to determine if the high SO<sub>3</sub> reduction that was obtained with byproduct Mg(OH)<sub>2</sub> injection in the NETL test program could be sustained with a higher uncontrolled SO<sub>3</sub> concentration characteristic of flue gas from burning high-sulfur coal and with SCR.

One goal of the short-term tests was to find a Mg(OH)<sub>2</sub> injection rate that would reduce SO<sub>3</sub> concentration at the APH entrance to 10 ppmv from a higher uncontrolled SO<sub>3</sub> concentration than in the NETL tests. For many cases, reduction to 10 ppmv at the APH entrance would yield a stack SO<sub>3</sub> concentration of 5 ppmv or less due to incidental SO<sub>3</sub> removal across the APH, ESP, and wet FGD.<sup>8</sup> For example, with 10 ppmv SO<sub>3</sub> at the APH entrance, and assuming 20% removal across each of the APH and ESP, and 30% removal across the wet FGD, and allowing for an increase in excess air from 20% at the APH inlet to 40% at the FGD outlet, flue gas exiting the stack would contain about 4 ppmv SO<sub>3</sub>. At this SO<sub>3</sub> concentration, little or no visual opacity due to SO<sub>3</sub> would be expected to occur.

A second goal was to find a  $Mg(OH)_2$  injection rate that would reduce  $SO_3$  concentration at the APH flue gas entrance to 5 ppmv or less. For operation of the APH with a low flue gas exit temperature, Alstom suggested that the  $SO_3$  concentration be reduced to this low level to avoid fouling of the APH baskets.

Following the short-term tests, a long continuous run would be carried out with byproduct Mg(OH)<sub>2</sub> injection and with the average flue gas exit temperature reduced to 220°F. A longer run would provide better opportunity to determine if byproduct

Mg(OH)<sub>2</sub> injection could prevent APH fouling over a longer period under this extreme condition. This would provide useful information for a future full-scale demonstration at a site with a normal flue gas exit temperature. In addition, for new generating units which could choose to install a larger APH, the test results could provide a basis for allowing regular operation with a lower flue gas exit temperature, thereby improving heat rate and reducing fuel use and CO<sub>2</sub> emissions.

Finally, if necessary, a third test period would be conducted to operate the APH with a low flue gas exit temperature but without Mg(OH)<sub>2</sub> injection. In the NETL tests with Mg(OH)<sub>2</sub> injection and low exit temperature, although operated for only short periods, the APH baskets remained so clean that it was considered possible that factors other than Mg(OH)<sub>2</sub> injection could have been responsible for keeping the baskets clean. So operation without injection would provide a direct comparison between periods of operation where the presence or absence of Mg(OH)<sub>2</sub> was the only variable.

## **Description of Pilot Plant**

The 1.6 MW pilot pilot plant includes an Alstom air preheater which takes flue gas from a bituminous coal-fired unit. To simulate flue gas from a generating unit burning high-sulfur coal and equipped with SCR, SO<sub>3</sub> was added to the flue gas to increase SO<sub>3</sub> concentration to approximately 50 ppmv. Byproduct magnesium hydroxide slurry was atomized and injected into flue gas ahead of the air preheater.

The pilot plant includes insulated piping, byproduct Mg(OH)<sub>2</sub> slurry feed, dilution, and injection, air preheater, fans, monitoring instrumentation, and computer control and data logging system. A schematic of the pilot plant is shown in Figure 1.

Flue gas to the pilot plant is taken from ductwork immediately upstream of the station air heater. The flue gas at approximately  $650^{\circ}$ F enters a 20 inch diameter insulated duct. SO<sub>3</sub> is injected into the duct, then the gas flows horizontally to gas sampling location "A" followed immediately by the Mg(OH)<sub>2</sub> injection location.

A single dual-fluid nozzle from Lechler (model 170164 XX, hardened stainless steel) located in the center of the 20 inch horizontal flue gas duct was used for Mg(OH)<sub>2</sub> slurry atomization. The byproduct slurry containing about 20 weight percent solids was diluted to approximately 10% solids prior to injection, which was necessary to satisfy the minimum liquid flow required for nozzle operation.

After Mg(OH)<sub>2</sub> injection, the flue gas flowed horizontally in the 20 inch duct for about 46 feet, entered a long-radius 90 degree bend, turning the flow vertically downward to the entrance of the APH. Total duct length from the injection point to the top of the air heater baskets was about 81 feet. A flue gas sampling port labeled "H" was located 4 feet from the top of the baskets.

The pilot air preheater is a Ljungstrom-type. Flue gas flows downward through the preheater, and air flows upward. The hot-end (top) baskets are uncoated metal, and the

cold-end (bottom) baskets are coated. Total basket vertical length is 72 inches. The unit includes soot-blowing with high-pressure air directed at the bottom of the cold-end baskets. A water wash system is also included.

The air preheater has a rated capacity of ~16,500 lb/hr or ~3,500 scfm of air with regenerative elements sized to cool flue gas from about 650°F to an average cold-end exit of 200°F. Automatic controls vary the supply of cooling air (typically the combustion air side of the air heater) to produce the desired flue gas exit temperatures for the Hg. The heated air and cooled flue gas from the pilot air heater are returned to the station flue gas ductwork.

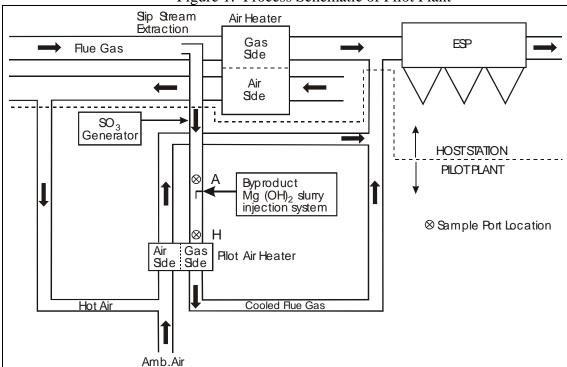


Figure 1: Process Schematic of Pilot Plant

The only significant change to the pilot plant equipment from the earlier NETL tests was the addition of a  $SO_3$  spiking system. To increase pilot flue gas uncontrolled  $SO_3$  concentration to a range typical for a station equipped with SCR, a  $SO_3$  generator was installed. The generator was designed by Consol R&D with assistance from Carmeuse. It included a liquid  $SO_2$  vaporization and metering system, a  $SO_2$ -air mixing station, a gas heater, and a tubular reactor containing a vanadium-based catalyst.  $SO_2$  vapor was fed to the mixing station at a rate of about 56 lbs per day and mixed with about 5 scfm of air. The mixture at about 10 psig flowed to a heater which increased gas temperature to about  $770^{\circ}F$ . The heated gas then entered the catalytic reactor. The reactor was well-insulated and equipped with electrical band heaters along its entire length to bring the reactor to temperature during start-up and to make-up for heat losses during operation.

Reactor exit temperature was controlled at 850°F. The converter exit gas then flowed though a flow orifice and then immediately into the pilot flue gas slipstream from the power station economizer exit. The spiked flue gas in the 20 inch diameter duct flowed through a flow straightener, and then to the gas sampling and Mg(OH)<sub>2</sub> injection sections prior to entering the pilot air preheater.

Temperature rise across the SO<sub>2</sub> to SO<sub>3</sub> reactor was monitored as a means to confirm the SO<sub>3</sub> generation and injection rate. For the SO<sub>2</sub> and air flows noted above, the exothermic reaction increased the gas temperature by typically 60-70°F from reactor inlet to outlet. A heat balance around the well-insulated converter with this temperature rise indicated a SO<sub>2</sub> to SO<sub>3</sub> conversion efficiency of 27-32%. At this conversion efficiency and a SO<sub>2</sub> feed rate of 2.3 lbs/hr (56 lbs/day), the SO<sub>3</sub> injection rate was determined to be 0.8-0.9 lbs per hour. If the injected SO<sub>3</sub> would all remain in the gas phase, this injection rate would be sufficient to increase pilot flue gas SO<sub>3</sub> concentration by 20-24 ppmv (in 3100 scfm of flue gas). The temperature increase across the converter was recorded daily to confirm the approximate injection rate and as a check on the condition of the conversion catalyst, and the (nearly adiabatic) temperature rise remained approximately constant during the test program. SO<sub>3</sub> measurements via flue gas sampling, prior to the Mg(OH)<sub>2</sub> injection point, indicated that the SO<sub>3</sub> spiking system increased flue gas SO<sub>3</sub> concentration by 15-20 ppmv when the SO<sub>2</sub> to SO<sub>3</sub> converter was initial operated, and an increase of 10-15 ppmv near the end of the test program.

#### SO<sub>3</sub> Measurement Method

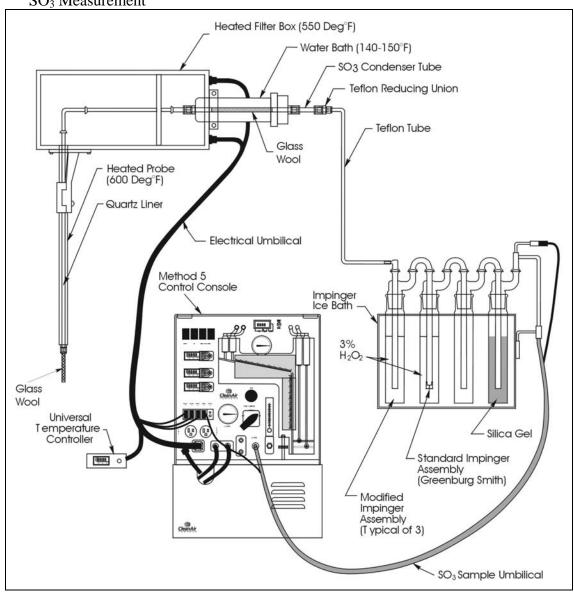
SO<sub>3</sub> concentration in flue gas was measured by Carmeuse with support from Consol R&D using a modification of Clean Air Engineering's Proposed Test Method 8B, which uses controlled condensation to collect SO<sub>3</sub>. The Method 8B apparatus was obtained from Clean Air Engineering, and the modified apparatus is shown in Figure 2.

It is known that SO<sub>3</sub> results can be biased low when sampled flue gas passes through alkaline flyash collected in the heated filter located ahead of the condenser in a controlled condensation apparatus. In the present tests, alkaline Mg(OH)<sub>2</sub> was present in the collected flyash. So in attempt to avoid a low bias, modifications were made to reduce incidental capture of SO<sub>3</sub> by Mg(OH)<sub>2</sub> contained in particulate from gas sampled immediately ahead of the APH. Consol Energy suggested two modifications which were adopted. A quartz filter holder with filter thimble which is normally used in Method 8B was removed from the heated filter box and replaced with a quartz tube. Instead, the tip of the quartz probe was packed with glass wool as recommended by Consol and others.<sup>9</sup> To reduce the amount of flyash or flyash/Mg(OH)<sub>2</sub>/reaction products collected in the glass wool at the probe tip, the gas sampling rate was maintained at about 2-3 cubic feet over about 30 minutes of sampling time. The same sampling apparatus and sampling rate was used for sampling flue gas at location "A" prior to Mg(OH)<sub>2</sub> injection and at location "H" immediately ahead of the APH.

Following gas sampling, an 80% ethanol aqueous solution was used for rinsing the condenser tube to recover collected SO<sub>3</sub>. Each of three other parts of the probe were rinsed separately: the glass wool from the probe tip, the quartz probe liner, and the quartz tubing in the heated filter box. Each separate rinse was diluted with additional ethanol solution and then each SO<sub>3</sub> catch was analyzed for sulfate content. Sulfate was determined by titration with the barium chloride standard solution specified in Method 8B with a thorin indicator. A Mettler Toledo DL 58 autotitrator was used, fitted with a DP5 Phototode optical probe to detect the thorin color endpoint.

SO<sub>2</sub> concentration in flue gas was also determined as described in Method 8B.

Figure 2: Modified Clean Air Engineering Method 8B Gas Sampling Equipment for SO<sub>3</sub> Measurement



# **Pilot Operation and Testing**

Testing began on December of 2005, and consisted of three phases as described below.

#### Short-Term Tests

Baseline tests to determine the uncontrolled SO<sub>3</sub> concentration with SO<sub>3</sub> spiking were begun in December. Mg(OH)<sub>2</sub> injection was started in early January. The Mg(OH)<sub>2</sub> injection rate was set to yield molar ratios of Mg(OH)<sub>2</sub> to uncontrolled SO<sub>3</sub> (based on 55 ppmv SO<sub>3</sub> in flue gas) equal to 4, 3, and 2. Tests with different injection ratios were conducted on different days, and each rate was maintained for at least a day with steady-state operation of the APH before flue gas sampling to determine SO<sub>3</sub> concentration were conducted. The purpose of these tests was to find a molar ratio which reduced SO<sub>3</sub> concentration to less than 10 ppmv in flue gas entering the APH.

The APH average flue gas exit temperature was maintained at approximately 330°F during the tests to avoid sulfuric acid condensation on the APH baskets prior to the long-term test. Flue gas flow rate was 14,500 scfm. Flue gas temperature prior to the Mg(OH)<sub>2</sub> slurry injection point was 630-650°F depending on station load.

#### Long-Term Test Run with Mg(OH)<sub>2</sub> Injection

Following the short-term tests, the pilot plant was shutdown to remove one pair of APH baskets (hot-end and cold-end) and replace them with a new pair provided by Alstom. This pair would then be removed for examination at the end of the long-term run.

The long-term run began in mid-February. Equipment maintenance and periodic gas sampling were conducted during day-shift Monday through Friday. Pilot operation continued under automatic control during the off-shift and over weekends. The computer data logging system monitored APH operation and Mg(OH)<sub>2</sub> injection. Diluted Mg(OH)<sub>2</sub> slurry for injection was prepared by an automatic dispensing and dilution system. Supplies of concentrated byproduct Mg(OH)<sub>2</sub> for the injection system and liquid SO<sub>2</sub> for the SO<sub>3</sub> spiking system were replenished as needed during day-shift and over weekends.

The APH flue gas exit temperature was maintained at 220°F. Air entering the APH air side was maintained at 90°F. Air preheater operating conditions were monitored and recorded via the computer data logging system. The flue gas-side pressure loss was checked regularly. Flue gas flow was maintained at 15,000 lbs/hr.

The Mg(OH)<sub>2</sub> injection ratio was set initially at 4, based on an uncontrolled SO<sub>3</sub> of 55 ppmv. The injection ratio was reduced to 3 later in the run. After Mg(OH)<sub>2</sub> injection was begun, the APH flue gas exit average temperature was reduced to 220°F. The APH soot-blower was operated every 8 hours, but there were periods when soot-blowing was omitted. Periodic flue gas sampling was performed by Carmeuse with assistance from

Consol to determine  $SO_3$  and  $SO_2$  concentrations in flue gas prior to  $Mg(OH)_2$  injection (sample location A) and immediately ahead of the APH (sample location H).

The pilot plant was operated in this condition for a total of 32 days, excluding three periods of downtime for repair of equipment. Initial operation was for 11 days; then an expansion joint failure in the 20 inch pilot flue gas duct caused a three week outage for repairs. The pilot was then operated for an additional 22 days with two short outages for slurry pump and agitator repairs. After a total of 17 days operation, no increase in APH flue gas side pressure loss was observed. The injection ratio of Mg(OH)<sub>2</sub> to SO<sub>3</sub> was then reduced to 3 and held at this rate for the remainder of the test run. Flue gas temperature was 630-650°F just prior to the Mg(OH)<sub>2</sub> slurry injection point.

#### Test Run without Mg(OH)<sub>2</sub> Injection

In the third phase of testing, the pilot plant was operated under the same conditions as in the long-term run, including SO<sub>3</sub> spiking and a flue gas exit temperature of 220°F, but with no Mg(OH)<sub>2</sub> injection. The purpose was to confirm that the Mg(OH)<sub>2</sub> injection was directly responsible for keeping the APH baskets relatively clean in the earlier testing.

This test period lasted only 4 days due to rapid fouling of the air preheater. At Alstom's, request, soot-blowing was not performed during this period.

#### RESULTS

#### **Short-Term Tests**

 $SO_3$  removal vs.  $Mg(OH)_2/SO_3$  ratio

Figure 3 shows measured SO<sub>3</sub> concentration, based on the condenser catch only, at the APH flue gas entrance versus molar injection ratio of Mg(OH)<sub>2</sub> to SO<sub>3</sub>. For the data when no Mg(OH)<sub>2</sub> was injected, SO<sub>3</sub> was measured prior to Mg(OH)<sub>2</sub> injection or immediately prior to the APH flue gas entrance. SO<sub>3</sub> concentration was reduced to 5 ppmv or less at molar ratios of 3 or 4 except for one measurement obtained at an injection ratio of 4 when flyash broke-though the glass wool filter in the sampling probe tip and contaminated the condenser. Generally at all injection ratios, for gas sampling runs where little or no flyash broke-though to contaminate the condenser, low-single digit SO<sub>3</sub> concentrations were obtained based on the condenser catch alone.

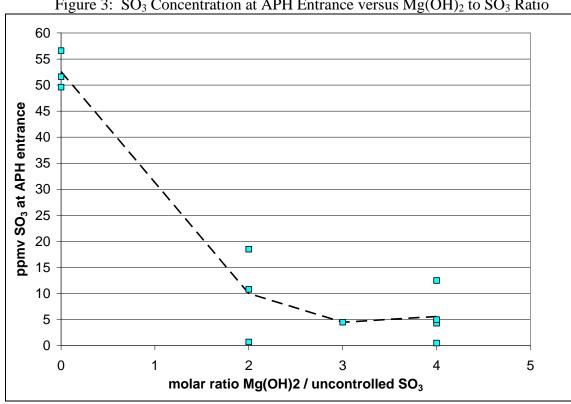


Figure 3: SO<sub>3</sub> Concentration at APH Entrance versus Mg(OH)<sub>2</sub> to SO<sub>3</sub> Ratio

Method 8B makes measurement of SO<sub>3</sub> in the other sample catches optional, and accordingly some other workers have omitted analysis of the catches from the flyash filter in other controlled condensation sampling for SO<sub>3</sub>. In the present study, the catches from rinsing the parts of the sample train that contained particulate (flyash only at location A, or a mixture of flyash/Mg(OH)<sub>2</sub>/reaction products at location H) gave significant apparent SO<sub>3</sub> readings. These apparent SO<sub>3</sub> results could have been due to SO<sub>3</sub> collected onto particulate prior to entering the probe, in which case the results should not be counted as part of the total vapor-phase SO<sub>3</sub> readings. On the other hand, some SO<sub>3</sub> could have been absorbed by flyash or the mixture collected in the probe tip or probe liner during sampling.

Figure 4 shows the apparent SO<sub>3</sub> readings from the catches that contained particulate from the short-term tests versus the injection ratio. With no Mg(OH)<sub>2</sub> injection, the apparent SO<sub>3</sub> readings averaged 5 ppmv, only about 10% of the value from the condenser catch. When Mg(OH)<sub>2</sub> was injected, the apparent SO<sub>3</sub> values increased.

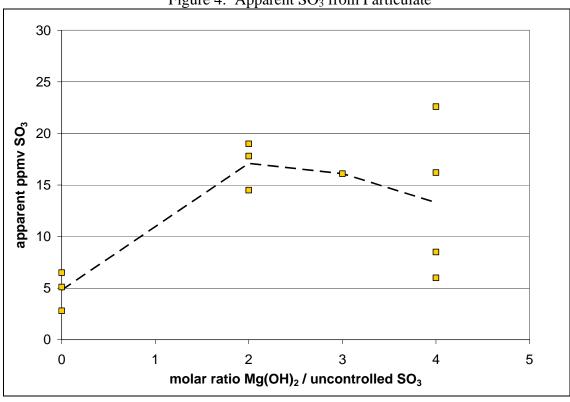


Figure 4: Apparent SO<sub>3</sub> from Particulate

Although the apparent SO<sub>3</sub> readings from the particulate catches appear to make the SO<sub>3</sub> results less certain, the average condenser-only value of 5 ppmv at injection ratios of 3 and 4 seemed reasonable in light of the 3 ppmv result from the earlier NETL tests at lower uncontrolled inlet SO<sub>3</sub> concentration. Based on this, an injection ratio of 4 was selected for the start of the long-term test run.

# Long-Term Run with Mg(OH)<sub>2</sub> Injection

#### Air Preheater Flue Gas Pressure Loss

No increase in flue gas side pressure loss across the APH was observed throughout the 32 day test run. The pressure loss remained in the range of 2.9-3.1 inches of water, the fluctuations corresponding to variations in flue gas inlet temperature from changes in power station load.

#### Measurements with Inertial Filter

In attempt to avoid the uncertainty in SO<sub>3</sub> measurements associated with the flyash collected in the filter of the Method 8B gas sampling probe, an inertial-type sintered-metal filter from Mott Co. [model 7611-½-36-0.5-(AB)F] was substituted for the Method 8B sample probe at location H for a few gas sampling runs. The filter consists of a 3 foot long, ½ inch inside diameter sintered 316 stainless tube with a 0.5 micron

pore size, inside of a larger diameter solid stainless steel tube, forming an annular space between the filter and outside tube. The filtered gas sample was withdrawn from the annulus. In this setup, a slipstream of flue gas was pulled through the filter by an air eductor located at the downstream end of the filter, and the flue gas and air were returned to the flue gas at the APH exit. The flue gas velocity inside the filter was maintained at 70 feet per second to prevent collection of flyash on the filter surface. The gas sample was withdrawn from the annular space at a rate that produces a very low radial flow through the filter compared with the slipstream velocity.

SO<sub>3</sub> results using the Mott filter were inconclusive. SO<sub>3</sub> concentrations of 1 ppmv or less were measured at location H, but these results were probably lower than actual due to sulfuric acid condensation on parts of the metal filter that were not adequately heat-traced. However, SO<sub>2</sub> results were consistent with values obtained using the Method 8B sampling probe.

#### Sulfuric Acid Dewpoint

During the week of April 3rd, a research engineer from Land Instruments visited the pilot to make sulfuric acid dewpoint measurements using a Land Instruments dewpoint analyzer. Condensation is detected by a sensor at the tip of the probe which is cooled indirectly with air. The probe is inserted into hot flue gas, and then the tip is slowly cooled until a dewpoint is detected.

The dewpoint of flue gas at location A was measured with the SO<sub>3</sub> spiking system in service and with the spiking system turned off for a few hours. The dewpoint was also measured at location H. The modified Method 8B was used to determine flue gas SO<sub>3</sub> concentration (condenser catch only), SO<sub>2</sub> concentration, and moisture content. These results are shown in Table 2 along with results of dewpoint measurements obtained at the same time as the gas sampling results.

The last column of Table 2 includes dewpoints calculated using a model recommended by Consol which estimates dewpoint temperature from SO<sub>3</sub> concentration and moisture content.<sup>11</sup> The values calculated from the model are 11-13°F higher than the measured dewpoints at location A (before Mg(OH)<sub>2</sub> injection point).

The dewpoint at location H (flue gas entrance to APH during Mg(OH)<sub>2</sub> injection) was undetectable; the probe tip was gradually cooled to 113°F without evidence of a dewpoint. This result suggests a very low SO<sub>3</sub> concentration at location H, consistent with the low values obtained during the short-term tests. The injection ratio was 3 during this portion of the long-term test.

Table 2. Sulfuric Acid Dewpoints versus SO<sub>3</sub> Concentration and Moisture Content

Date	Sample Location	SO <sub>3</sub> Spiking	°F	Vol. % O <sub>2</sub>	SO <sub>3</sub> ppmv	SO <sub>2</sub> ppmv	Vol. % H <sub>2</sub> O	Measured Dewpoint °F	Model Dewpoint °F
4/4/06	A	On	657	2.9	34.9	3138	10.07	290	302
4/5/06	A	Off	657	3.3	21.3	2890	6.87	275	286
4/5/06	Н	On	~600	~3			~7.7	<113	
4/6/06	A	On	645	3.0	31.0	3186	8.02	283	296

## Examination of Air Preheater Baskets

Figures 5a and 5b show the bottom of the cold-end baskets at the flue gas exit at the conclusion of the 32 day run. The baskets appear to be free of deposits. The condition of the baskets is consistent with the absence of any increase in flue gas pressure loss during the 32 day run.

The test pair of hot- and cold-end baskets were removed from the APH and returned to Alstom for detailed examination and analysis. Preliminary examination of individual cold-end basket elements shows a slight, water-soluble build-up on the side of some peaks of the element corrugations. Details of the basket examinations will be reported in a later publication of pilot test results.

The test hot- and cold-end baskets were replaced with new test baskets prior to the following test run.

Figure 5a: Pilot Air Preheater Cold-End Basket Flue Gas Exit with Mg(OH)<sub>2</sub> Injection



Figure 5b: Pilot Air Preheater Cold-End Basket Flue Gas Exit with Mg(OH)<sub>2</sub> Injection



# **Test Run without Magnesium Hydroxide Injection**

#### Air Preheater Flue Gas Pressure Loss

The test run without  $Mg(OH)_2$  injection started on May  $9^{th}$ . The APH flue gas side pressure loss started to increase after one day, apparently due to fouling of the baskets, and the air-side flow through the APH had to be gradually increased to maintain the flue gas exit temperature at  $220^{\circ}F$ . The run continued until May  $12^{th}$ , a total of 4 days, until the air flow was no longer able to be increased to compensate for fouling of the baskets. The flue gas side pressure loss increase from 3 inches  $H_2O$  at the start of the run to 4 inches  $H_2O$  at the end. As recommended by Alstom, soot blowing was not carried out during the run.

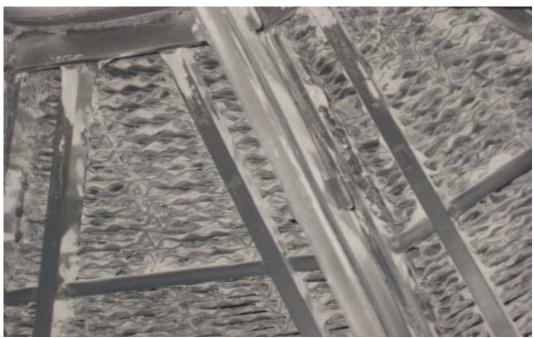
#### Examination of Air Preheater Baskets

Figures 6a and 6b show the bottom of the cold-end baskets at the flue gas exit at the conclusion of the 4 day run. The pictures show accumulation of flyash, some of which is expected to be due to lack of soot blowing. The tests baskets were removed and returned to Alstom for examination and analysis. Preliminary examination shows an accumulation of heavy deposits consistent with a large amount of sulfuric acid condensation and flyash accumulation. Details of the basket examination will be reported in a later publication.

Figure 6a: Pilot Air Preheater Cold-End Basket Flue Gas Exit without  $Mg(OH)_2$  Injection



Figure 6b: Pilot Air Preheater Cold-End Basket Flue Gas Exit without  $Mg(OH)_2$  Injection



#### **CONCLUSION**

Injection of byproduct Mg(OH)<sub>2</sub> slurry ahead of a pilot air preheater achieved high reduction of SO<sub>3</sub> from an uncontrolled SO<sub>3</sub> concentration of 30-55 ppmv characteristic of high sulfur coal-fired generating units with SCR. Injection at a molar ratio of 3 to 4 reduced SO<sub>3</sub> to 10 ppmv or less at the APH flue gas entrance. Sulfuric acid dewpoint measurements support the conclusion that SO<sub>3</sub> concentration was reduced to very low levels. APH baskets remained clean after a 32 day run with very low APH flue gas exit temperature of 220°F. Operation of the APH at this low exit temperature without Mg(OH)<sub>2</sub> injection led to rapid fouling.

Reduction of SO<sub>3</sub> concentration to 10 ppmv or less at the APH flue gas entrance is expected to produce a SO<sub>3</sub> stack concentration of 5 ppmv or less which would greatly reduce or eliminate visual plume opacity due to SO<sub>3</sub>.

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#### **DISCLAIMER**

Carmeuse makes no warranty or representation, expressed or implied, and assumes no liability with respect to the use of, or damages resulting from the use of, any information, apparatus, method or process disclosed in this document.

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#### **KEY WORDS**

Sulfur trioxide removal; SO<sub>3</sub> removal; plume opacity reduction; magnesium-enhanced lime.