

# SICK

## SO<sub>3</sub> CEMs in Power Plants

Deborah Padwater – Strategic Industry Manager – Power;  
SICK AG Nimburger Strasse 11, D-79276 Reute Germany

*The real-time, continuous measurement of SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> in power plants has been a long discussed desire of the industry. Here we will show the design, implementation and testing of an SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> CEM in an operational coal fired power plant. Real time data will show how process changes effect SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> concentrations. All aspects of the system performance will be discussed including theory, calibration, and testing.*

*Formation and emissions of SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> can potentially lead to plant operation-related problems and environmental concerns. The emissions of SO<sub>3</sub> from a boiler depend on a number of complex factors including coal sulfur content, combustion conditions, flue gas characteristics and which type of air pollution control devices (FGD/SCR/ESP) are being used. Real-time analysis of the SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> concentration can assist plant engineers and operators in better control of process parameters. It also can be used to directly control injection of reduction reagents, such as Trona, Hydrated Lime and Sodium Bisulfate, leading to lower operating costs.*

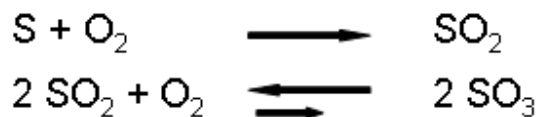
### 1. The Problem

SO<sub>3</sub> formation in the flue gas of a coal fired power plant is undesirable for many reasons. First, it causes the formation of a blue plume exiting the stack even at low concentrations of 3 – 4 mg/m<sup>3</sup> which is disconcerting to the public. In addition, it can lead to a higher corrosion potential in the air pre-heater and subsequent ductwork through the formation of other acid gases such as H<sub>2</sub>SO<sub>4</sub> and ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>). Finally, it can inhibit the effectiveness of absorbent material injection such as activated carbon used to remove Hg from the flue gases.

SO<sub>3</sub> forms in boilers and within the Selective Catalytic Reduction system (SCR) so-called thermal and catalytic oxidation of SO<sub>2</sub>.

#### - SO<sub>3</sub>-formation:

- In the furnace from Sulfur in coal (typ. 1 – 2% of SO<sub>2</sub>):



- In the catalyst of a DeNO<sub>x</sub> plant (typ. + 1 – 2 % of SO<sub>2</sub>):



Figure1: Chemical reaction showing SO<sub>3</sub> formation in a coal fired power plant.

# SICK

Thermal oxidation occurs in the high temperature zones of the boiler while catalytic oxidation is supported by the presence of metals such as iron ore, platinum or and vanadium typically used as catalysts in the SCR. While vanadium in the SCR promotes the positive reaction of NO<sub>x</sub> removal from flue gas, it has the negative side effect of generating SO<sub>3</sub>.

The SCR process uses NH<sub>3</sub> for its reaction of NO<sub>x</sub> to N<sub>2</sub> and H<sub>2</sub>O. Unfortunately NH<sub>3</sub> will also react with SO<sub>3</sub> and form undesirable byproducts such as ammonium bisulfate. This chemical is a highly corrosive and sticky deposit that combines with fly ash rendering it unusable for resale and can foul downstream components. As this reaction occurs at temperatures lower than 200°C, normally happens in the primary air heat exchangers. This leads to a loss of efficiency and eventually to plant outages for cleaning and repair due to corrosion.

It is the combination of all of these negative effects which has lead to a demand from the power industry in the United States to come up with an effective way of monitoring SO<sub>3</sub> concentrations in the flue gas in order for them to take appropriate countermeasures to inhibit it's formation and/or to neutralize once SO<sub>3</sub> formation occurs.

## 2. The Research

In 2008, SICK's Research and Development Department in Meersburg, Germany began investigations into possible technologies which could accurately and continuously monitor the concentration of SO<sub>3</sub>. This is a particularly daunting task because SO<sub>3</sub> is extremely unstable and difficult to obtain.

The first round of basic research confirmed earlier findings by EPA<sup>1</sup> that the SO<sub>3</sub> will convert to H<sub>2</sub>SO<sub>4</sub> vapor in the presence of H<sub>2</sub>O. H<sub>2</sub>SO<sub>4</sub> is also corrosive and as with SO<sub>3</sub> combines with the NH<sub>3</sub> to form ammonium bisulfate leading to fouling and corrosion as previously indicated.

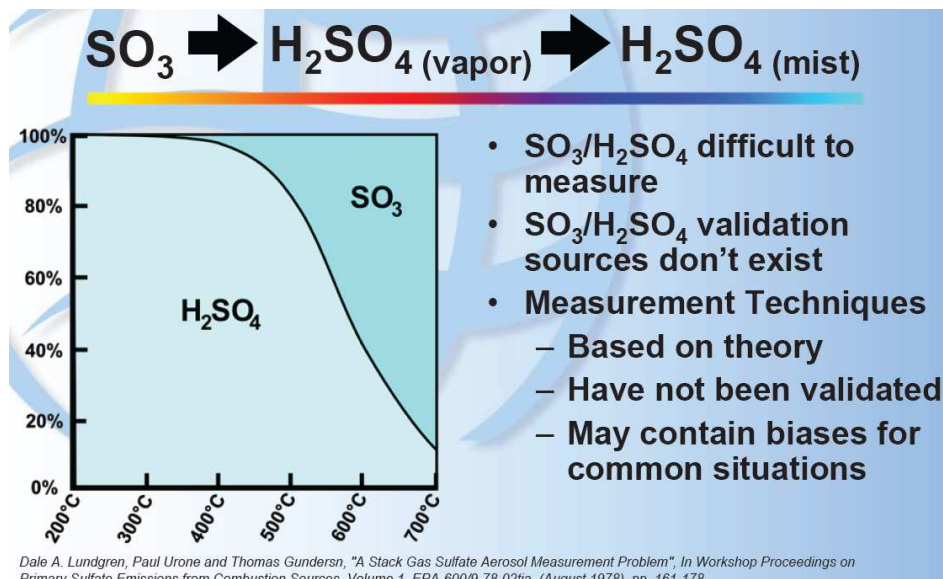


Figure 2. Equilibrium curve H<sub>2</sub>SO<sub>4</sub>, SO<sub>3</sub>. EPA-600/9-78-02tia (August 1978). Dale A. Lundgren, Paul Urone and Thomas Gunderson

The first step was to determine the absorption spectra of the 4 basic components of interest, namely  $\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$  and  $\text{SO}_2$  with the help of a laboratory Fourier Transform Infrared Spectrophotometer.

The  $\text{SO}_2$  and  $\text{SO}_3$  spectral response was generated by flowing  $\text{SO}_2$  over a palladium catalyst first at  $20^\circ\text{C}$  then heated to  $450^\circ\text{C}$ .

## SO<sub>2</sub>/SO<sub>3</sub> measurement setup & calibration via catalyst

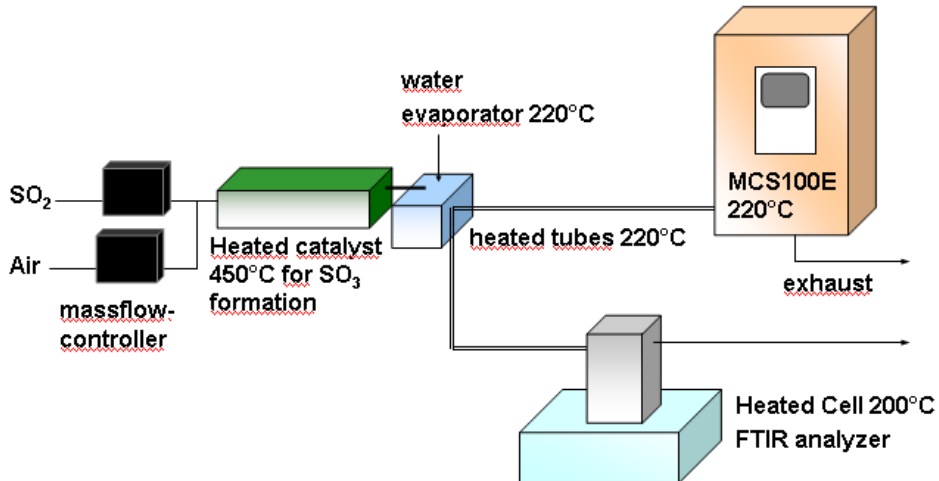


Figure 3.  $\text{SO}_2/\text{SO}_3$  measurement and calibration set-up via catalyst

## Spectra of $\text{SO}_2 + \text{SO}_3$

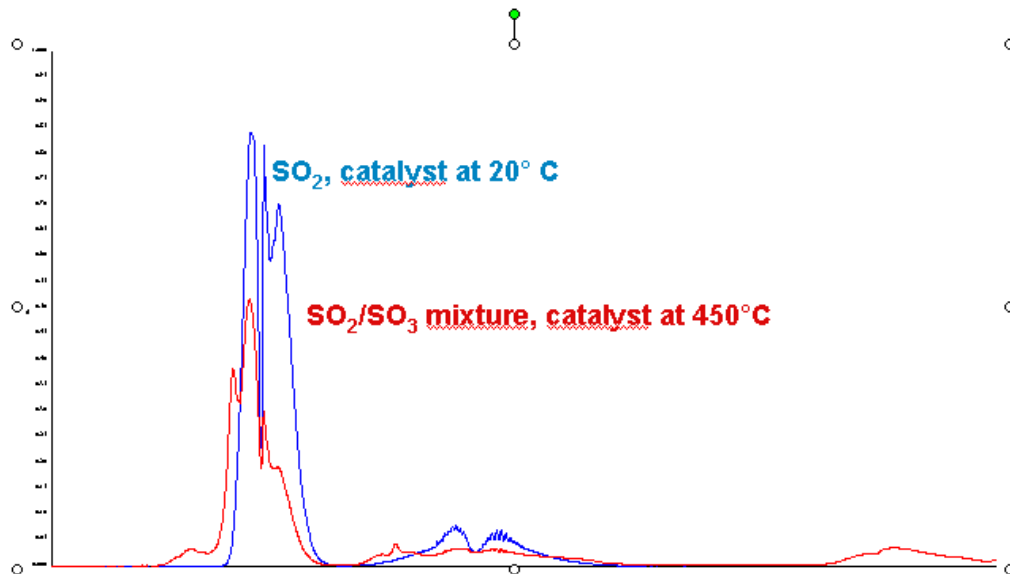


Figure 4. Infrared absorption Spectra of  $\text{SO}_2$  and  $\text{SO}_3$

# SICK

The second phase was to determine the  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  absorption spectra,  $\text{H}_2\text{O}$  is well documented, the second proved particularly difficult due to the corrosive nature of this acid gas. The laboratory apparatus used for the generation of acid vapor was destroyed more than once, causing delays with the research.

An evaporator was used to generate concentrations of  $\text{H}_2\text{SO}_4$  vapor and subsequently the absorption spectrum was measured in parallel in the FTIR and also in the MCS100E multi-component analyzer.

## ∴ $\text{H}_2\text{SO}_4$ Calibration via evaporator/steamer

### - Evaporator calibration

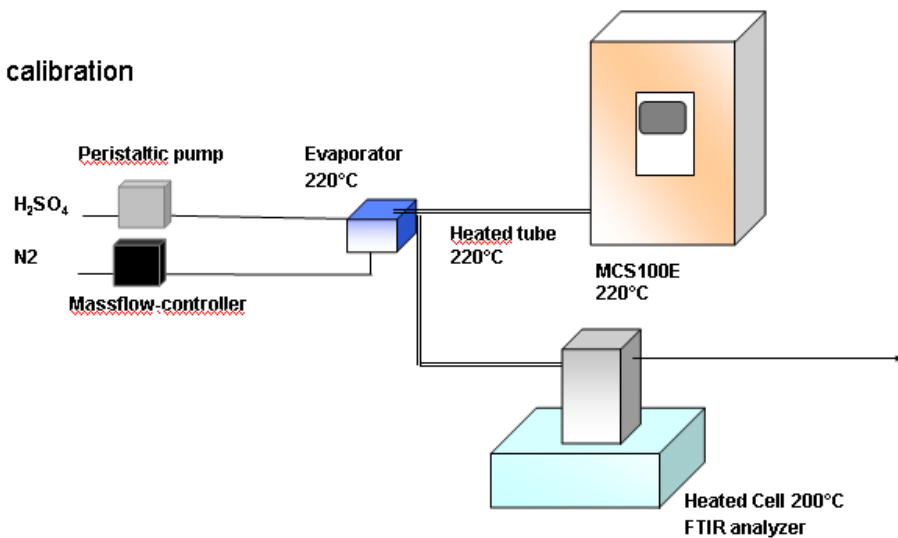


Figure 5. Generation of  $\text{H}_2\text{SO}_4$  concentrations to determine Infrared Absorption Spectra

Finally the absorption spectra of all 4 components had been measured and appropriate optical filters could be selected for the MCS100E HW photometer for continuous analysis.

## : Spectra of SO<sub>2</sub>, SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>

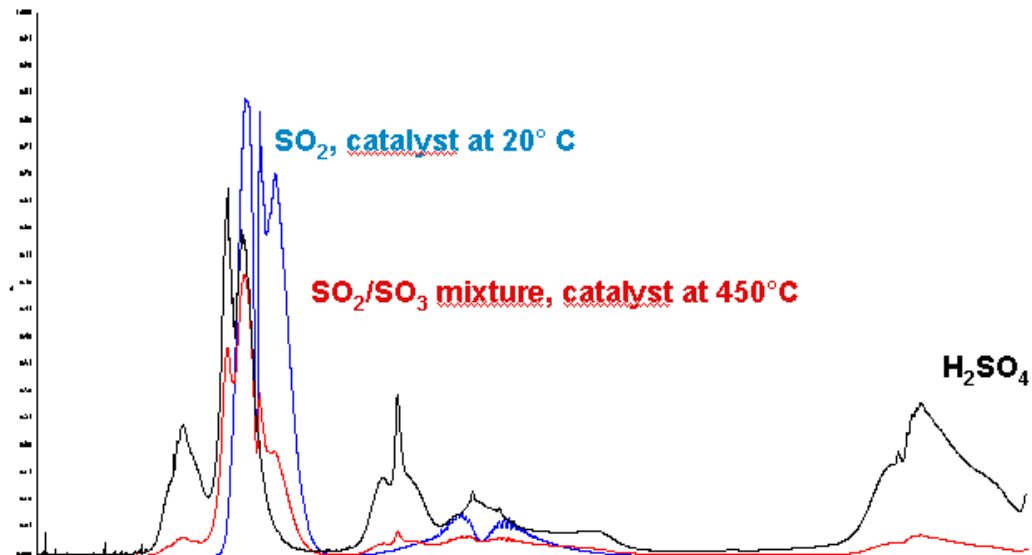


Figure 6: IR absorption spectra of SO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>.

The reproducibility of the gas generation system was repeated to insure stability, also to test the stability of the measurement results. The interferences of other gases typically found in flue gas stacks were measured and then a system of optical compensation was found and implemented.

The results from the lab evaluation were conclusive: SO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> can be measured with one multi-component filter photometer. The interesting and important result however, is the sum of both SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> as both components are present in the flue gas and both contribute to corrosion.

In addition, it was determined that by measuring other gases in parallel, SO<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and NO a complete picture without cross interferences can be made.

The calibration of SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> is challenging. The catalyst for SO<sub>3</sub> formation does not show 100% conversion rate. The SO<sub>3</sub> concentration data was indirectly determined by measuring the un-reacted SO<sub>2</sub>. In the case of the H<sub>2</sub>SO<sub>4</sub>, the calibration using the evaporator is reproducible. The material problems are under control, but still subject to optimization.

### 3. Field Trial

Based on the results of the laboratory tests, SICK determined that the most suitable analyzer for the real time measurement of SO<sub>3</sub> / H<sub>2</sub>SO<sub>4</sub> is the MCS100 E HW multi-component infrared photometer. The reasons for their decision were numerous. The MCS100 E HW systems are well known, and have been used for continuous emission monitoring of acid gases as a CEM for decades. To date, more than 4000 MCS100 units have been installed worldwide. Secondly the MCS100E HW is a hot-wet device that

# SICK

maintains the temperature of the gas above the acid dew point throughout the entire sampling and measurement sections. The hot wet multi-component gas analyzer utilizes an NDIR process photometer and can simultaneously measure up to eight active IR gas components.



Photo 1. MCS 100 E HW System measuring  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ .

Moreover, the system can be equipped with a calibration filter system to do periodic upscale calibration and adjustments without the need for using cylinder gas. Considering the difficulty with obtaining stable concentrations of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ , the use of the calibration gas filter was thought to be the best for continuous operation in a power plant environment.

The first installation was made at a coal fired power plant in the United States in June 2010. The system was installed on the stack at the same elevation as the existing CEMS monitors. The coal fired plant is equipped with a wet flue gas desulfurization system and uses dry sorbent injection (DSI) for control of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ .



Photo 2: Installation of the MCS100 E HW at the stack with heated filter probe.

Process conditions at this plant were as follows:

Stack gas temperature: 50 °C

Solids / Particulate: < 30 mg/m<sup>3</sup>

Gas components /measuring range:

O <sub>2</sub> :	0 – 15 vol%	O <sub>2</sub> was not installed
CO <sub>2</sub> :	0 – 10 vol%	0 – 25 Vol.%
NO:	0 – 10 ppm	0 – 75 ppm
SO <sub>2</sub> :	0 – 20 ppm	0 – 400 ppm
SO <sub>3</sub> :	0 – 50 ppm	0 – 100 ppm
H <sub>2</sub> SO <sub>4</sub> :	0 – 50 ppm	0 -100 ppm
H <sub>2</sub> O	0 – 30 Vol.%	

Shortly after start-up the analyzer system immediately began to respond to process conditions and track the SO<sub>3</sub> concentration in relation to SCR operations and sorbent injection. When the SCR temperature was reduced, or during bypass mode, the levels of

# SICK

SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> also decreased. This was expected based on the fact that the conversion to SO<sub>3</sub> due to catalytic reaction was eliminated.

⋮ 24-h data w/o SCR operation during night

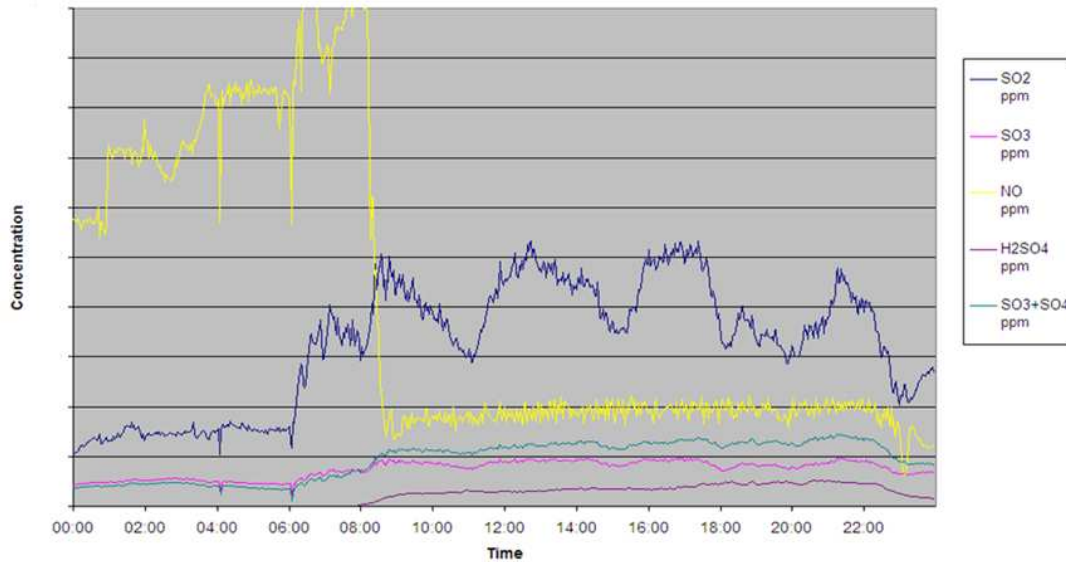


Figure 7. Process data 24 hours without SCR operation

After more than 6 months of continuous operation, the customer conducted a series of comparison measurements to insure that the measurements of SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> were indeed valid. As mentioned the ability to test with a known quantity of either substance was limited.

The customer used an independent testing company which implemented EPA's Method 8A controlled condensate for comparison measurements, this is comparable to VDI Norm 2462, Page 2, issued 2011-11.



# SICK

Controlled Condensate comparison:

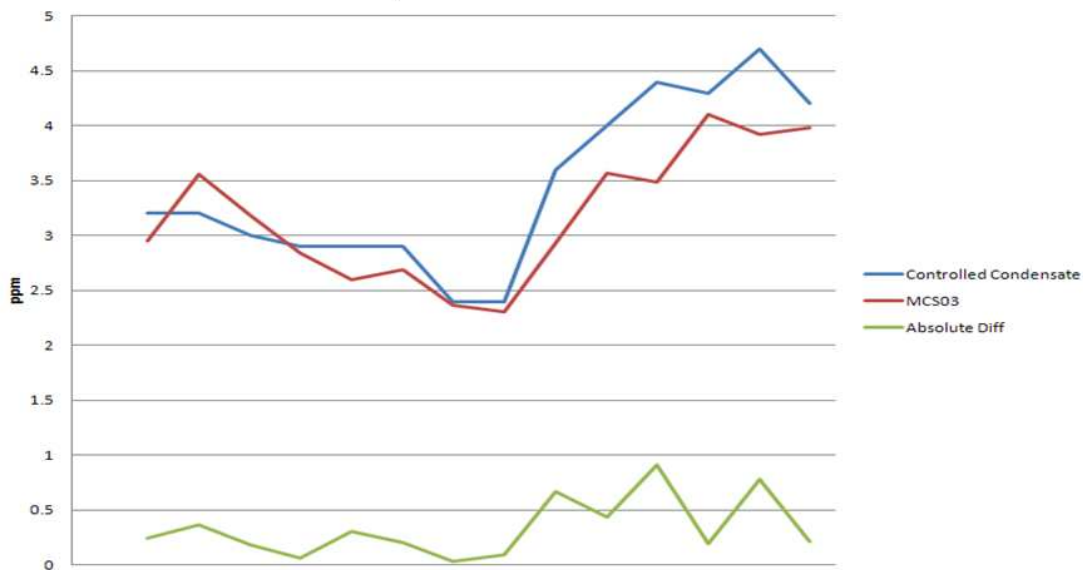


Figure 8. Comparison of wet chemical method to real time measurement system MCS100 E HW

Here the results were again conclusive, measuring in a range of 2 to 5 ppm, the on-line analyzer compares favorably with the wet-chemical method showing a deviation of measurement within 2% of full scale.

The system shown above has been in operation ever since the first field trials were conducted. A yearly check with a testing team confirms that the analyzer calibration is still valid and the measurements can be used to control and/or monitor dry sorbent injection removal efficiency.

The typical response time of the complete analyzer system is 4 minutes. Considering this the plant is using the signals received for  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  for feedback control of their dry sorbent injection and have managed to save enough money in the first 9 months to justify the cost of the system.

## 4. Conclusion

Real-time monitoring of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  in coal-fired power plants offers numerous monetary and environmental benefits. Plants can realize significant savings both in reduced use of sorbent, as well as reduced maintenance and unplanned outages due to premature corrosion of air heaters and duct work.

From an environmental point of view, the plants can better control the opacity levels in the flue gas caused by  $\text{SO}_3$  which could lead to fines and negative public opinion.

In addition, better control of  $\text{SO}_3$  levels can increase the effectiveness of activated carbon injection for mercury removal.

The well established hot wet multi-component NDIR analyzer has proven ability to measure  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  in the flue gas. For the first time, plant operators have a



reliable way to track changing conditions and adjust their control mechanisms accordingly.

Deborah L. Padwater

11 March 2013

**Literature:**

<sup>1</sup> Dale A. Lundgren, Paul Urone and Thomas Gunderson, "A Stack Gas Sulfate Aerosol Measurement Problem", In Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, Volume 1, EPA-600/9-78-02tia, (August 1978), pp 161-178.