

# **MEGA 2008**

## **Field Experience with On-line Measurement of SO<sub>3</sub> and Sulfuric Acid Dewpoint**

**Paper # 68**

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### **ABSTRACT**

The negative effects of varying and elevated levels of SO<sub>3</sub> in utility flue gas streams have been well documented. Air Heater fouling and corrosion, diminished unit heat rate, compromised ESP performance, compromised mercury capture through ACI and Blue Plume release have all captured center stage in technical conferences and research investigations.

To effectively mitigate these problems several viable technologies have been introduced and field tested. However, only recently has an equally viable method for measurement and control of these processes been introduced. This presentation will document the field experience of the Breen AbSensor technology for on-line measurement of SO<sub>3</sub>/Sulfuric Acid Vapor in full scale plant settings. The presentation will cover control of mitigation chemical injection, on-line heat rate improvement, high sulfur baghouse experience and control of ESP Gas Conditioning systems.

### **INTRODUCTION**

Much has been written and presented about the negative effects of sulfuric acid and ammonium bisulfate vapor in the flue gas stream from the economizer outlet to eventual gas discharge from the stack. As the installed base of Selective Catalytic Reactors (SCR) and Wet Scrubbers (FGD) increases, and as plants subsequently move to higher sulfur coal for economic value, these problems become increasingly evident.

To counter the negative effects of SO<sub>3</sub> and ammonia slip, multiple vendors have developed and commercialized chemical injection systems to remove the acid vapor and mitigate the acid and ammonium bisulfate deposition problems. As might be assumed, each technology has a primary application zone where the combination of chemical effects and temperature make it competitively effective. Simply put, each generating station has a unique set of SO<sub>3</sub> related problems and requires a unique solution.

While the economic benefit to the plant for removing SO<sub>3</sub> compounds can easily run into the millions of dollars, so also can the cost of operation. Over-injection can result in significant chemical waste and unnecessary burden on the particulate collection system. Under-injection can result in compromised plant performance and, in some cases formation of secondary compounds that can be as detrimental as the initial SO<sub>3</sub>

derivatives. As these technologies move from experimental to commercially implemented, a means for on-line control and optimization is required.

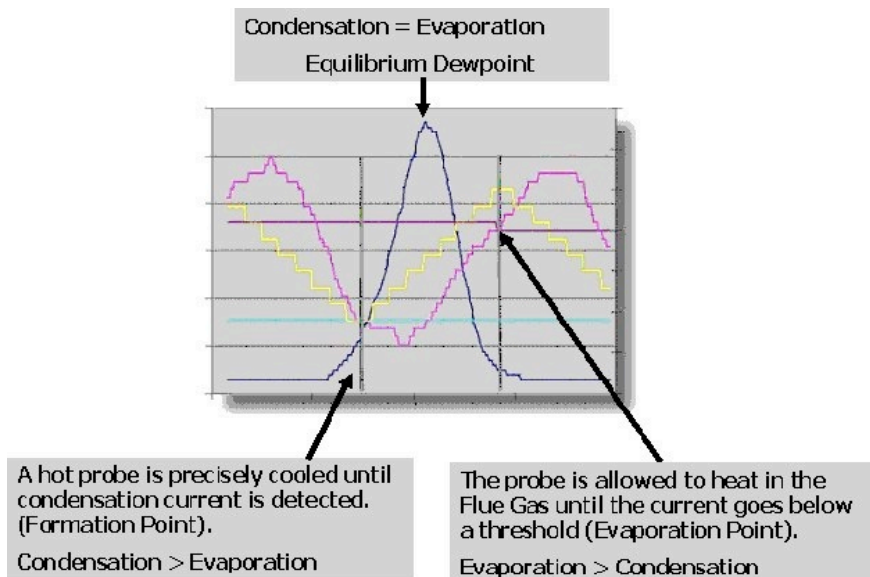
Additionally, as chemical mitigation has moved from the back end of the generating station to locations ahead of the SCR, the interaction between furnace generated  $\text{SO}_3$ , SCR generated  $\text{SO}_3$  and pre-SCR injected ammonia most also be considered. The most recent data on the interaction between  $\text{SO}_3$ ,  $\text{NH}_3$  and ammonium bisulfate has been presented by J. Wei in cooperation with FERCo and EPRI. This data will be expanded and explained here.

In light of that information, the balance of the discussion will relate to control results from a dual injection point  $\text{SO}_3$  mitigation process at a Midwest generating station.

## MAIN BODY TEXT

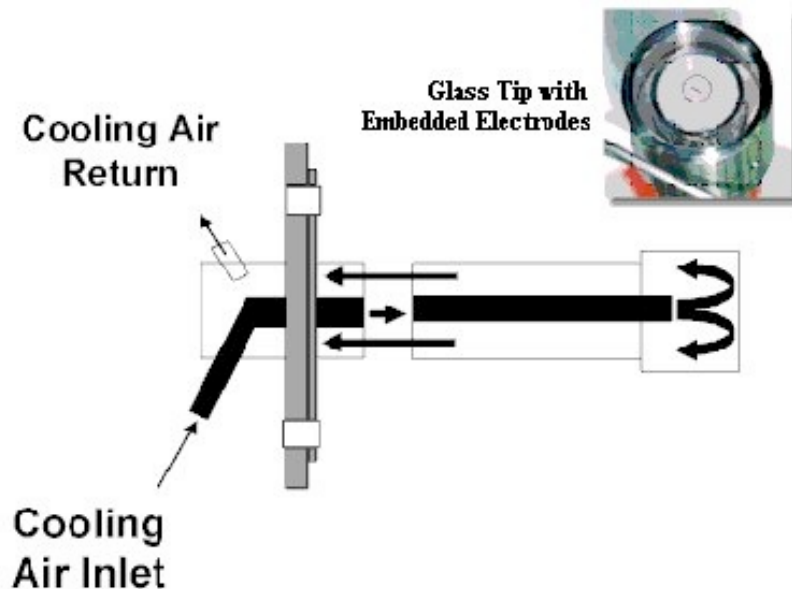
### Condensables Measurement Instrument

The ammonium bisulfate data associated with the Wei work as well as the sulfuric acid, ammonium bisulfate and sodium bisulfate data presented on the full scale mitigation process were taken using the Breen AbSensor condensables instrument. The AbSensor - Condensables measurement device uses a kinetic algorithm to detect condensables related temperatures. These temperatures are labeled as Formation Temperature and Evaporation Temperature as seen in the figure below.



The Breen Energy AbSensor - Condensables measurement device consists of a highly polished glass surface with electrodes embedded therein. The kinetic algorithm then varies the cooling flow rate to the back of this glass tip to change the temperature of the glass surface which sits in the flue gas. At the beginning of a measurement cycle the tip temperature is high enough to not cause any material to condense. The tip temperature is then varied at a controlled rate creating a temperature dynamic similar to the Air Heater. When the temperature of the tip is sufficiently low, material begins to condense on the tip and a current is recorded by the device. This temperature is noted as the Formation Temperature. The cooling air to the tip is then reduced in a controlled fashion and the tip temperature begins to rise.

As long as the tip temperature is below the equilibrium dewpoint, more material continues to condense on the tip thereby increasing the current as measured by the device. As the tip temperature crosses the equilibrium dewpoint, the material starts to vaporize faster than it condenses and the total material on the tip begins to go down. This results in the current going down until it goes to 0. The temperature at which the current goes back to 0 is noted as the Evaporation Temperature.

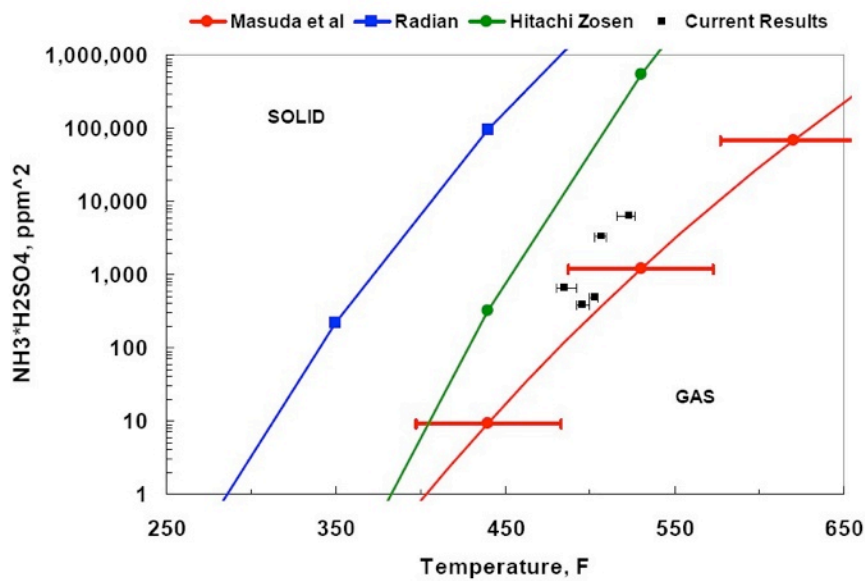


### **SO<sub>3</sub> versus NH<sub>3</sub> and the Formation of ABS**

In general sulfuric acid will exhibit formation temperatures from 230F to 280F with corresponding evaporation temperatures about 30F higher. Ammonium bisulfate

compounds exhibit formation temperatures as low as 300F and as high as 470F with evaporation temperatures ranging from approximately 450F to 530F. Sodium bisulfate compounds are rarer but exhibit formation temperatures in the mid 300s (F) but evaporations between 575F to upwards of 600F.

In the application of the instrument to SO<sub>3</sub> mitigation in the presence of NH<sub>3</sub> it is common to see mixtures of these compounds. In fact the desired control matrix for ammonia injection in an SCR seeks to control the process at a formation temperature of 290F and an evaporation temperature of 470F. This represents condensable formation in the upper acid region and evaporation in the ammonium bisulfate region.



The graph above shows the three most commonly referenced curves relating ammonium bisulfate formation to SO<sub>3</sub> and NH<sub>3</sub> concentrations and was presented by L. Muzio at the 2007 EPRI SCR workshop. What is most important to understand is that the formation of ammonium bisulfate is based on the multiple of SO<sub>3</sub> and NH<sub>3</sub> and is expressed in ppm<sup>2</sup> units. The black data points were generated by J. Wei in a project to independently associated the formation of ammonium bisulfate with the SO<sub>3</sub>\* NH<sub>3</sub> multiple. It is interesting to note that the data points lie between the Hitachi Zosen and Masuda predictions and in general follow the same curve shape. This data was taken in a controlled laboratory environment.

In further work done at a full scale generating station, using the same equipment, some interesting data was discovered. The graph above shows the comparison between SO<sub>3</sub>

and NH<sub>3</sub> (using wet chemistry methods) at a fixed unit load. The NH<sub>3</sub> injection level was varied and the concentrations compared with the ammonium bisulfate formation temperature determined from the AbSensor instrument

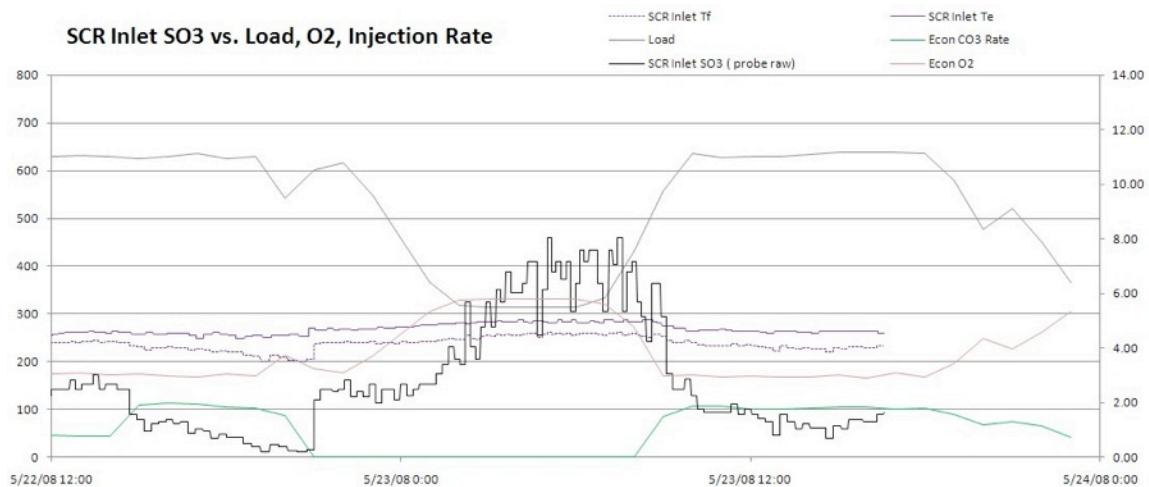
As can be seen, there is a clear trend on both ducts indicating that as NH<sub>3</sub> goes up, SO<sub>3</sub> in fact goes down. In this test program the NH<sub>3</sub> level was both increased and decreased and the data was consistent in both directions. Since the fuel, load and furnace operating conditions were unchanged over the number of hours of the exercise it can be assumed that the SO<sub>3</sub> levels entering the SCR reactor were unchanged.

It is not our purpose here to explain this phenomenon, but simply to point out that experimental data suggests that the SCR catalyst is not a passive device with respect to NO<sub>x</sub>/ NH<sub>3</sub>/ SO<sub>3</sub> interactions. Simply put, the level of NH<sub>3</sub> at the catalyst inlet affects the SO<sub>3</sub> level at the catalyst outlet.

## Dual Injection Point Na SO<sub>3</sub> Mitigation

In early 2008 a Midwestern US generating facility was fitted with a Na based SO<sub>3</sub> mitigation process. Since this site used a hot side ESP for particulate collection it was decided to inject mitigation chemistry ahead of the ESP (actually at the economizer outlet) for removal of furnace generated SO<sub>3</sub> and after the SCR for removal of SCR generated SO<sub>3</sub>. Due to the expected cost of the mitigation chemical, and to avoid the possible side effects of sub-stoichiometric chemical injection the Breen AbSensor system was deployed to take on-line readings of pre and post SCR condensables levels.

The pre-SCR instrument was situated downstream of the Na injection point but ahead of the NH<sub>3</sub> injection point. The graph below is representative of the relationship between SCR inlet SO<sub>3</sub> and changes in load, oxygen and Na chemical injection rate.



The post-SCR instrument was situated downstream of the second Na injection point but ahead of the Air Heater. The graph below shows the result of a typical morning load ramp. At this location the NH<sub>3</sub> injection is curtailed until the unit reaches a certain load. During the night Na injection is also curtailed.

After ramp up, the secondary Na injection point was held off to monitor the effectiveness of the economizer Na injection point on removing post SCR SO<sub>3</sub>. As can be seen, when the NH<sub>3</sub> injection was started the condensables specie moved from sulfuric acid to ammonium bisulfate. During the period from 9:00 AM to 12:00 noon the economizer Na injection rate was increased from its normal rate to double, then triple its value. As can be seen, the level of ammonium bisulfate was essentially unchanged.



The third graph below shows the effect of startup of the post SCR Na injection point with the post SCR flue gas initially in an ammonium bisulfate state.



The green traces are the pre-SCR SO<sub>3</sub> formation and evaporation temperatures, the violet trace is plant load and the black trace is the furnace O<sub>2</sub>. They are all fairly constant through the process change indicating that the post SCR condensables change is a result of the post-SCR Na injection startup.

As can be seen, at 2:00 PM the post-SCR Na injection location was activated. The condensable material was in a clear ammonium bisulfate state. Due to the physical issues with changing injection rates, it takes about 30 minutes for the change in injection rate to manifest itself. At that point, the Na level is ramping and temporarily shows a sub-stoichiometric ratio with the ammonium bisulfate and SO<sub>3</sub> present. The AbSensor data at this point suggests a change in condensable material from ammonium bisulfate to sodium bisulfate.

After an additional hour of injection ramp up and stabilization the sodium bisulfate material disappears as well as the ammonium bisulfate, sulfuric acid and any other condensable material. The flue gas entering the air heater at this location is now completely clear of any condensable material!

## **SUMMARY**

In summary, the project to remove SO<sub>3</sub> from the flue gas using controlled dual point Sodium injection has been successful. The AbSensor instruments proved reliable and essential in optimizing the level of Na injection ahead of the ESP and behind the SCR.

As a next step the NH<sub>3</sub> injection rates will be controlled in an attempt to increase the level of NO<sub>x</sub> reduction once the AH inlet condensables level is driven to zero. This effort will combine the information learned through the FERCo test program with the information learned in this experience. It is expected that improvements of 5% - 10% in NO<sub>x</sub> removal will be achievable.

## **ACKNOWLEDGEMENTS**

Breen Energy would like to acknowledge the following individuals for their help and support during this program:

Greg Quartucy, Larry Muzio; FERCO  
Jeff Stallings - EPRI  
Jim Jarvis, Sterling Grey; URS Corporation

## REFERENCES

Wei, J; Dunn-Rankin, D; UC Irvine; Muzio, L; Ferco; Stallings, J; EPRI; *Pilot Scale Study of ABS Formation Temperature*; presented at the EPRI 2007 SCR Workshop; November 12-14, 2007.