

Automatic On-line Monitoring of SO₃ Condensables

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Charles A. Lockert

Breen Energy Solution, 104 Broadway Street, Carnegie, PA 15106

ABSTRACT

The negative effects of varying and elevated levels of SO₃ in utility flue gas streams have been well documented. Air Heater fouling and corrosion, diminished unit heat rate, compromised ESP performance, compromised mercury capture when using Activated Carbon Injection 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 SO₃/Sulfuric Acid Vapor in full scale plant settings. The presentation will cover control of mitigation chemical injection at various locations in the gas stream, the impact of SO₃ control on SCR Minimum Operating Temperature and SCR NO_x reduction capability.

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 have become increasingly evident.

To counter the negative effects of SO₃ 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 SO₃ related problems and requires a unique solution.

While the economic benefit to the plant for removing SO₃ 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 SO₃

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

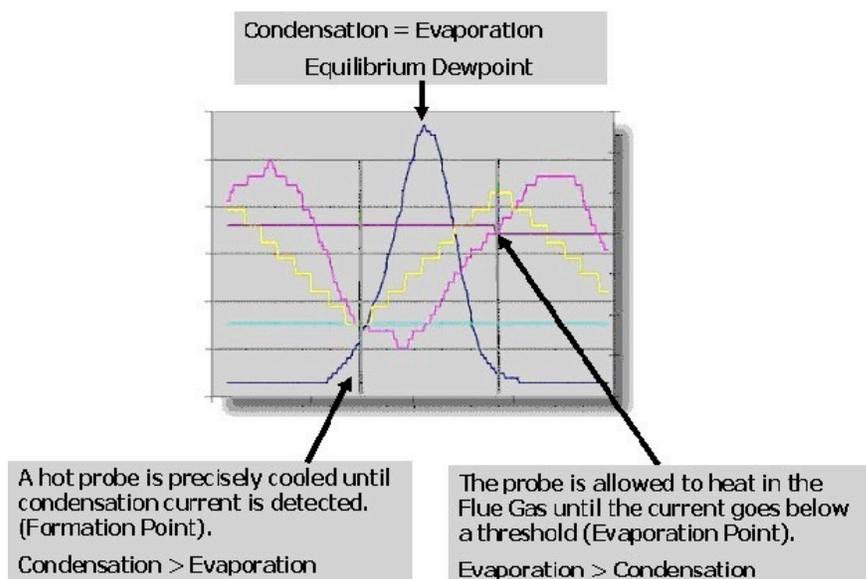
Additionally, as chemical mitigation has moved from the back end of the generating station to locations ahead of the SCR, the interaction between furnace generated SO_3 , SCR generated SO_3 and pre-SCR injected ammonia must also be considered. Results from several different programs will be discussed including:

- Pre-ESP Trona Injection
- Pre Air Heater Lime Injection
- Pre-SCR and Post SCR Sodium Carbonate Dual Injection (Hot Side ESP)

Condensables Measurement 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.

Figure 1 Graphical Description of AbSensor Instrument Operating Curve

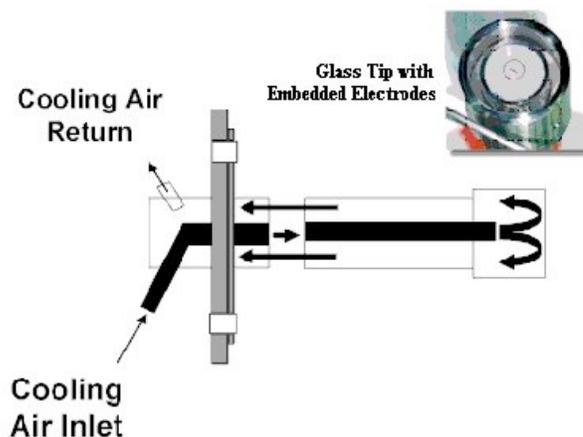


The Breen Energy AbSensor - Condensables measurement device consists of a highly polished glass surface with electrodes embedded therein. The kinetic algorithm then

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 metal plates in 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.

Figure 2 AbSensor Measurement Tip and Air Flow Diagram



A great deal of information can be determined from the Formation (FmT) and Evaporation (EvT) temperatures of condensable material. For the purposes of this discussion the following is important:

- When the differential between FmT and EvT is less than 30 degrees, the condensed material is essentially a single compound and the dewpoint is, for all practical purposes, the average of the two values,
- When the differential between FmT and EvT is greater than 30 degrees, the condensed liquid contains more than one compound. For the purposes of SO₃ mitigation, we are generally looking for the Acid dewpoint, which in the case of a complex condensable is assumed to be FmT + 15°F.

- In all cases, we interpret the dominant species in the condensable to be determined by its EvT and the relative concentration by the FmT.

SO₃ Mitigation Technology Background

Much has been written elsewhere on the benefits of reducing SO₃ in the flue gas. Benefits for heat rate, corrosion, acid gas emissions and mercury collection are clearly available. The three pictures below identify both the time line and main locations in the gas stream for SO₃ mitigation chemical injection.

Figure 3 Early trona and lime injection points

The Initial work was generally done here, and included Trona, SBS and hydrated lime. Sodium products provided ESP performance support, but affected fly ash salability. Hydrated lime was cheaper but negatively influenced the ESP.

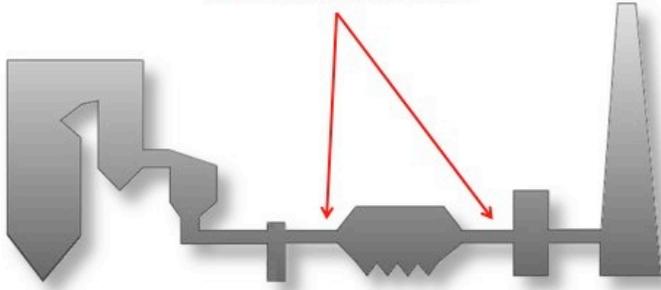


Figure 4 Injection ahead of the air heater for better mixing and increased residence time

When the negative effects of SO₃ on Mercury capture and air heater fouling/corrosion were considered, more effort was placed on mitigation here. Issues with air heater pluggage from SBS formation still linger.

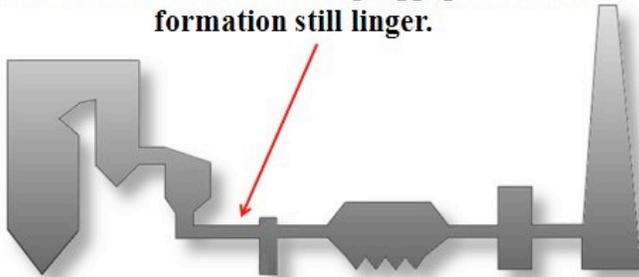
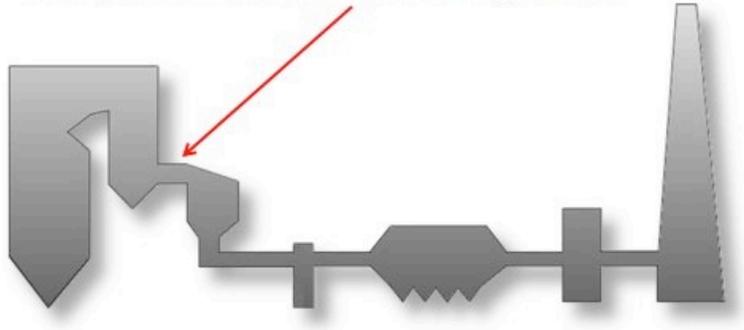


Figure 5 Na and Ca injection ahead of the SCR for improving MOT

Efforts to reduce the minimum operating temperature of the SCR have pushed mitigation technology to here. Concerns with Na effects on catalyst life and CaSO₄ blinding remain.



To help identify the net effects of total SO₃ formation (furnace and SCR) coupled with the mitigating effects of ammonia injection (SCR) and process chemistry (Na/Ca) an on-line sensor was required. What must be understood by the reader is that FGD inlet SO₂ is not, in and of itself, an accurate predictor of flue gas SO₃. Changes in both furnace conversion and SCR conversion are complex and must include consideration for:

- Ash Chemistry
- Boiler Cleanliness
- Boiler excess O₂ and the spatial distribution of that O₂
- Boiler Outlet NO_x & NO_x Distribution
- Catalyst Temperature
- Catalyst Cleanliness (LPA)
- Catalyst Age
- Catalyst Inlet NO_x levels

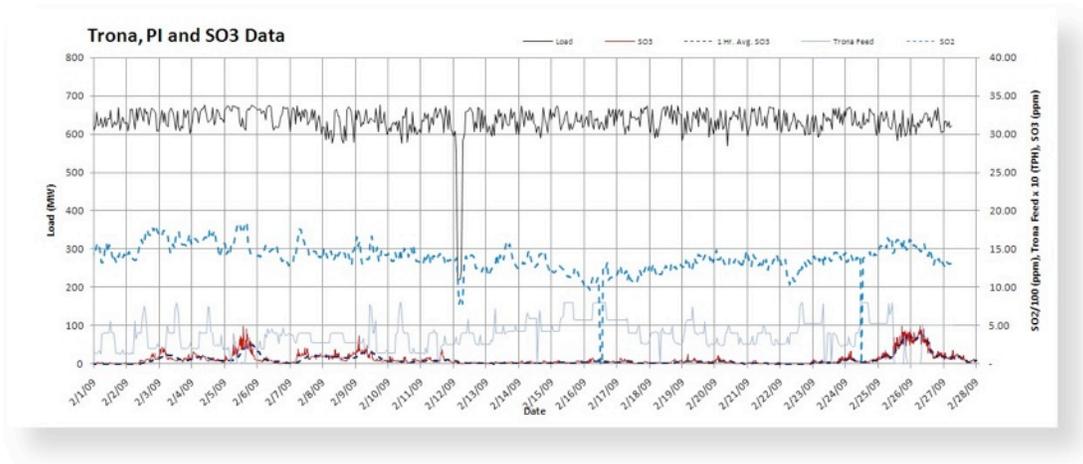
Additionally, removal of 100% of the free acid vapor can often prove detrimental to ESP performance.

The following Case Histories document full scale findings for both sodium and calcium based systems at all three locations in the flue gas train. They also discuss some of the modifications that have been made to the instrument to provide reliable data at the various test locations.

Single Injection Pre-ESP Trona SO₃ Mitigation

The data below shows the Trona feed, load, SO₂ and SO₃ data for a Midwestern plant using pre-ESP injection for mitigation of blue plume.

Figure 6 Plot of SO₃ vs. load, SO₂ and trona injection rate



Note that the SO₃ level as measured by the instrument only reaches the level of 5 ppm twice in the one month period. Also note that the Trona feed rate during the period averages just under 0.5 tons/hr. Assuming a cost of \$150/ton for Trona delivered to the duct then the total Trona cost for the month of February at this site would be just over \$50,000. Controlling the Trona feed rate to yield an SO₃ level of 3 ppm will save the plant 50% in chemical usage.

Lessons learned at this site:

1. The instrument includes a self cleaning air jet that executes at the end of every cycle. This process has proven very effective in removing stagnant ash buildup and assuring system reliability. However, during early testing at this location, high evaporation levels were found consistent with the presence of Trona injection. Process investigation revealed that the early version cleaning system directed the cleaning air directly at the sensor tip. In the presence of Trona, it appears that the cleaning air stream would cause impingement of the SO₃ laden Trona onto the sensor tip resulting in localized formation of sodium bisulfate deposits. A re-design of the cleaning tip to blow across the sensor tip instead of at the sensor tip relieved the problem.
2. Changes in plant fuel/air ratio during load transition can result in high transient levels of SO₂: SO₃ conversion. In the absence of Trona feed, this high SO₃ level can lead to deposition of acid condensate on the sensor tip with a dewpoint higher than the

localized gas temperature. This would not allow the material to evaporate and essentially fouled the sensor tip. To remedy this condition, a localized heating element was added to the sensor head allowing additional of 50F to 70F in localized heat. This has proven sufficient to induce evaporation of any level of sulfuric acid deposit regardless of gas temperature.

These two modifications have been included as standard design on all instruments operating after the air heater outlet.

Single Injection Pre-Air Heater Hydrated Lime SO₃ Mitigation

The following figure shows the results of a closely controlled test of hydrated lime injection ahead of the air heater.

Figure 7 Plot of condensable temperatures vs. NH₃, SO₃ and Ca injection rate



During this program levels of SO_3 and NH_3 were controlled by injection ahead of the SCR catalyst. This location was chosen to give sufficient residence time for the calcium to react with the SO_3 prior to the air heater. As can be clearly seen, the SO_3 injection leads the ammonia injection by about an hour. Response from the instrument at the SCR inlet shows the presence of the increased SO_3 , but the net effect on the SCR outlet instrument was more subdued.

At the onset of ammonia injection, the SCR Outlet instrument responded by moving from a higher acid condition to an ammonium bisulfate condition, as expected.

The yellow trace shows that three molar ratios of calcium to SO_3 were tested with the third molar ratio resulting in reduction of the SCR outlet condensable condition from ABS to zero. Removal of the lime injection resulted in a recurrence of ammonium bisulfate presence.

Lessons learned at this site:

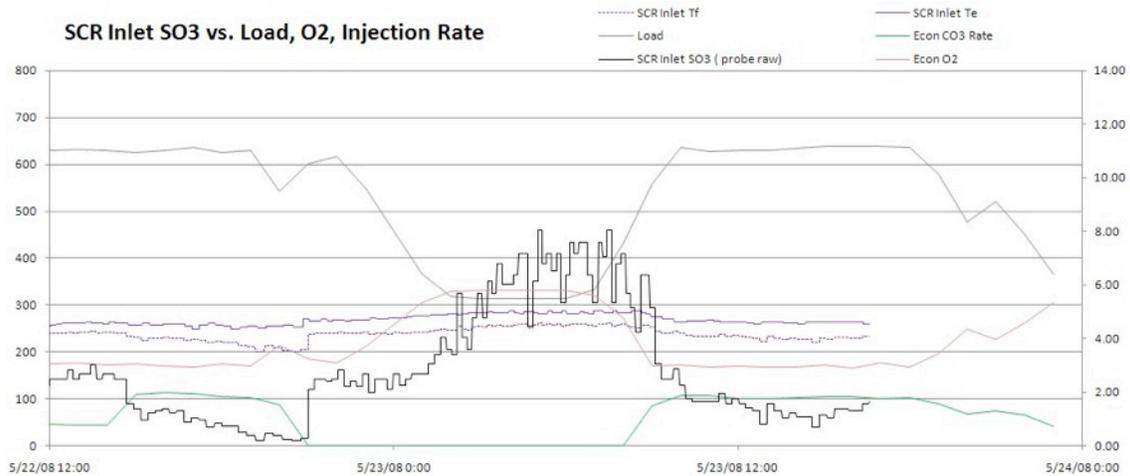
Calcium can be injected ahead of the SCR and effect a complete reduction in both acid and ABS condensable at the air heater inlet.

Dual Injection Point Na Based SO_3 Mitigation (Hot Side ESP)

In early 2008 a Midwestern US generating facility was fitted with a Na based SO_3 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_3 and after the SCR for removal of SCR generated SO_3 . 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_3 injection point. The graph below is representative of the relationship between SCR inlet SO_3 and changes in load, oxygen and Na chemical injection rate.

Figure 8 Plot of SO₃ vs. load showing an increase in SO₃ at light load



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 NH₃ injection is curtailed until the unit reaches a certain load. During the night Na injection is also curtailed.

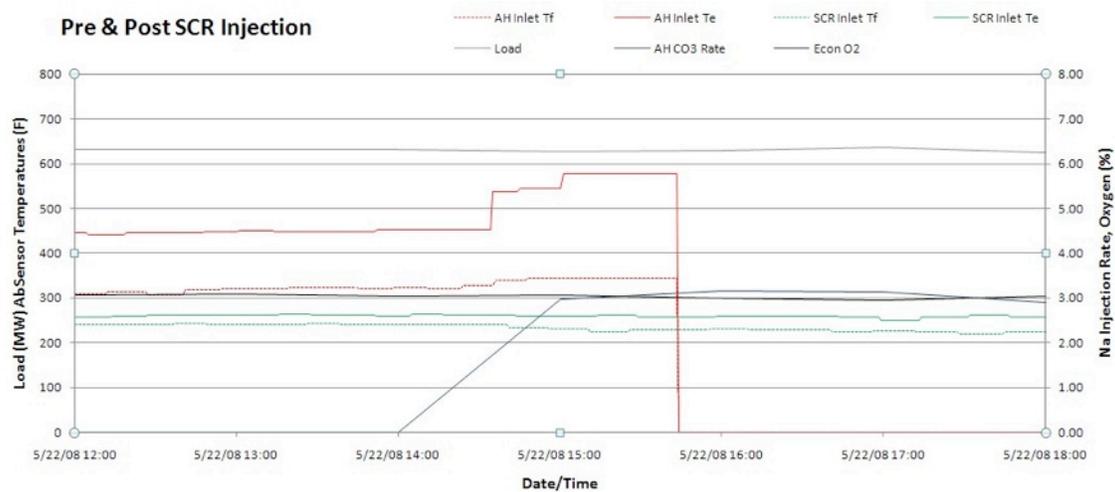
After ramp up, the secondary Na injection point was held off to monitor the effectiveness of the economizer Na injection point on removing post SCR SO₃. As can be seen, when the NH₃ injection was started the condensables specie moved from sulfuric acid to ammonium bisulfate. During the period from 9:00 AM to 12:00 noon the economizer Na injection rate was increased from its normal rate to double, and then triple its value. As can be seen, by examining the reported Formation and Evaporation temperatures, the level of ammonium bisulfate was essentially unchanged.

Figure 9 Plot of FmT and EvT changes over a 24 hour period



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.

Figure 10 Effect on condensable material with second SBS injection point activity



The green traces are the pre-SCR SO₃ formation and evaporation temperatures, the violet trace is plant load and the black trace is the furnace O₂. 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 ($FmT > 300^{\circ}F$ / $EvT > 450^{\circ}F$). 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_3 present. The AbSensor data at this point suggests a change in condensable material from ammonium bisulfate to sodium bisulfate. This can be seen by the step function increase in EvT from the approx. $450^{\circ}F$ value typical of ammonium bisulfate to a value approaching $580^{\circ}F$, more typical of 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.

Lessons learned at this site:

1. Mitigation chemicals injected ahead of the ESP in a Low-Dust SCR configuration will not be effective in removing SO_3 generated in the SCR regardless of the amount of chemical injected,
2. The combination of two systems, one to remove the furnace SO_3 and a second to remove the SCR generated SO_3 can be highly effective in removing all traces of condensable material at the air heater inlet.
3. The combination of this approach will allow significantly reduced minimum SCR operating temperature as well as potential improvement in heat rate through lower air heater outlet temperatures.

SUMMARY

As drivers for sorbent based SO_3 mitigation expand, the types of chemical used and the location for injection is moving further up the flue gas train. In the presence of higher temperatures and with the air heater temperature drop downstream, control of the injection level in direct ratio to actual SO_3 is crucial and can be aided by a direct measurement feedback instrument.