

Controlling Ammonia-in-Ash through Direct Measurement of Ammonium Bisulfate

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ABSTRACT

It is well known, and well documented, that ammonia contamination of fly ash results from excessive use of ammonia in DeNO_x, SO₃ mitigation and flue gas conditioning applications. For DeNO_x applications, laser based ammonia slip monitors have been used to try to control the total level of ammonia injected. Flue gas conditioning and SO₃ mitigation applications generally operate in open loop control with no sensory feedback at all.

The main contributor to fly ash ammonia contamination is ammonium bisulfate. This condensable material forms when free ammonia and sulfuric acid vapor combine, either through the air heater transition, or directly ahead of the electrostatic precipitator. Ammonia slip monitors supply only marginal levels of feedback since they cannot measure or report the ammonia bound in the ammonium bisulfate compound.

This paper will describe an instrument designed to directly measure ammonium bisulfate on-line and report on full scale plant installations for closed loop control of SCR and SNCR applications, ammonia injection for SO₃ mitigation and ammonia injection for flue gas conditioning.

BACKGROUND

The process of converting harmful NO_x compounds into nitrogen and water through chemical interaction with NH₃ has been well documented and is well understood. It is also fairly well understood and documented that increased levels of un-reacted NH₃ (ammonia slip) can lead to increased levels of ammonia salt formation, either as ammonium sulfate or ammonium bisulfate.

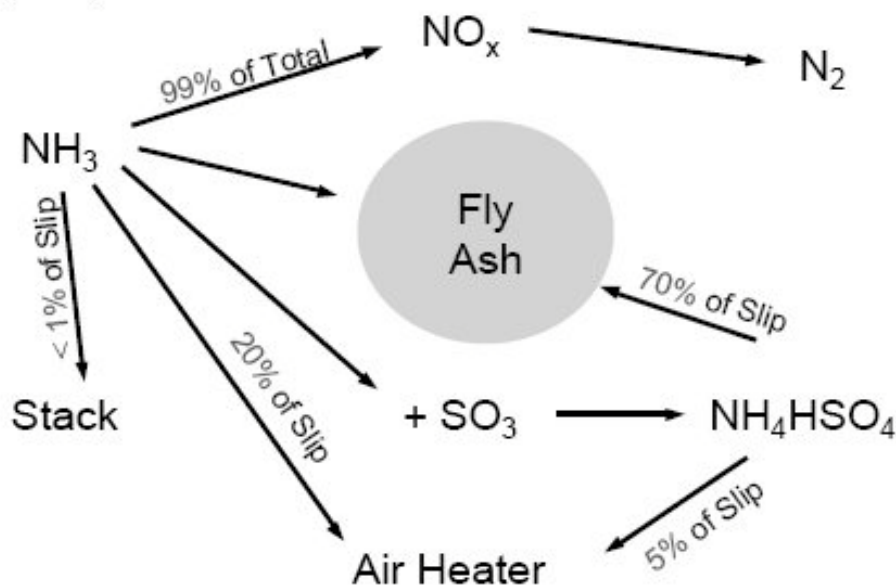
When SCR and SNCR systems first achieved widespread deployment in the United States a great deal of attention was paid to the increased levels of ammonia found in post ESP fly ash. Several comprehensive reports were written and presented at earlier ash conferences documenting the species of the ammonia salts predominantly present in ash and various technologies for removing or treating the unwanted ammonia content. However, while considerable effort has been made toward controlling the NH₃ injection process to mitigate SCR and air heater fouling, less effort has been spent on controlling the ammonia injection process for the purpose of ash quality improvement.

AMMONIA IN ASH

When discussing the topic of “Ammonia in Ash” it is interesting to discover the general misconception that exists regarding the actual nature of the “ammonia”. In fact “ammonia” exists predominantly in the forms of ammonium sulfate and ammonium bisulfate. Ammonia as a pure element generally stays in gaseous form and exits through the stack without adsorbing onto the fly ash.

In a 1999 presentation at the Ash Utilization Symposium, and summarized in a follow on document available from www.anl.gov, Lamar Larrimore of Southern Company Services succinctly summarizes the disposition of ammonia in ash as follows:

“Unreacted ammonia slip typically represents less than 1% of the injected ammonia. In conditions where there is adequate sulfur present (from coal or sulfur burners for ESP performance), Figure 1 shows that the majority of sulfur will form ammonium bisulfate, which is a sticky liquid that adheres to the surface of flyash or to downstream equipment such as air preheaters. For subbituminous coal, ammonia does not have an affinity for the alkaline Class C ash. In such cases, most of the ammonia slip goes up the stack.”



Note: Example values shown for bituminous coal

Figure 1 Fate of Ammonia in Flue Gas

Additionally, the following chart created by Hitachi Zosen is often used to show the relationship between temperatures.

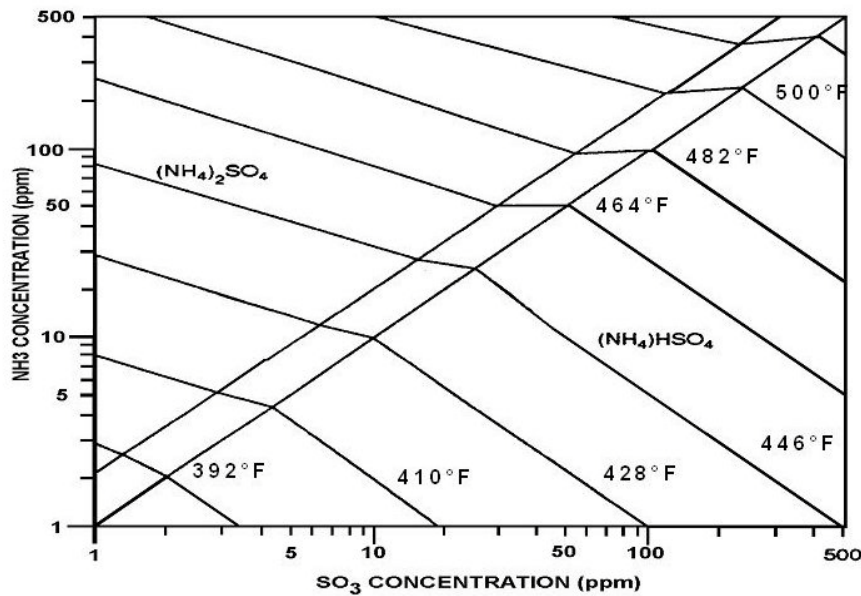


Figure 2 Hitachi Zosen Formation Curve

With the recent proliferation of wet flue gas desulfurization systems (FGD), significant commercial incentives exist for utilities to convert to higher sulfur content fuels. For these plants, flue gas SO_2 is often in the 1,000 to 2,000 ppm range resulting in furnace generated SO_3 values in the 10-20 ppm range. Plants employing SCR equipment may add another 10-20 ppm SO_3 giving a typical 20-40 ppm SO_3 level prior to the air heater. With great efforts made to keep ammonia slip below 5 ppm, it is clear from the graph that NH_3 : SO_3 ratios favor ammonium bisulfate formation.

The main focus, then, for control of ammonia deposition on fly ash must be on controlling the formation of ammonium bisulfate during the SCR and SNCR NO_x reduction processes.

INSTRUMENTATION

Over the last 5 years a technology has been developed and commercialized for the direct measurement of sulfuric acid and ammonium bisulfate condensables in the flue gas stream directly ahead of the air heater. This instrument, developed by Breen Energy Solutions and branded as “AbSensor”, uses a modified dewpoint approach to measure the presence and concentration of acid and ABS condensables.

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.

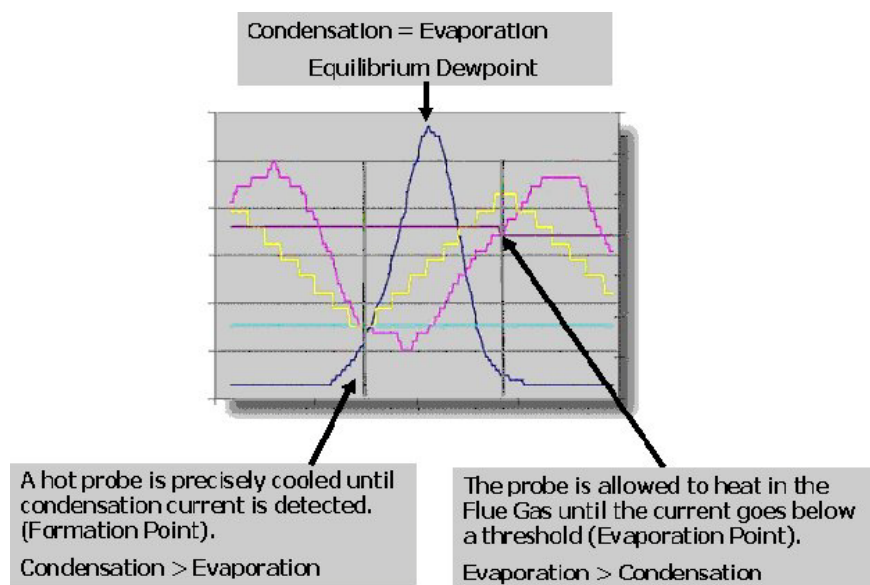


Figure 3 Instrument Operating Cycle

The Breen Energy AbSensor 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.

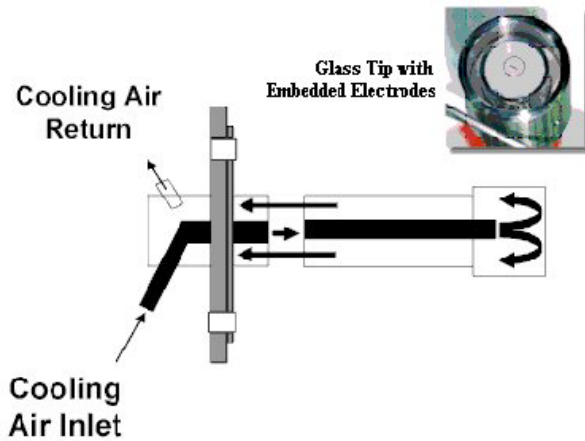


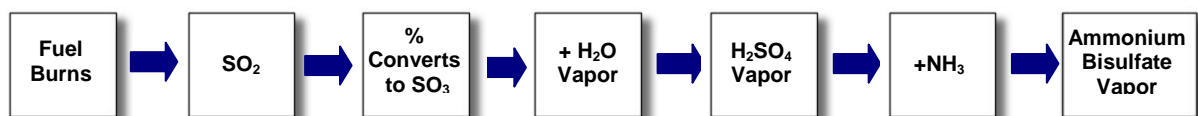
Figure 4 Instrument Physical Description

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:

- The dominant species detected is reflected by the value of EvT
- The concentration of the dominant species is reflected by the FmT value
- In general terms:
 - sulfuric acid species is represented by EvT values below 330°F
 - Ammonium bisulfate species is represented by EvT values in the general range of 450 °F to 500 °F

CONTROLLING AMMONIUM BISULFATE FORMATION

From a “non-chemical engineering” perspective, the process of ABS formation progresses something like this:



As can be seen, there are many variables influencing the formation and concentration of ABS. Because flue gas SO_3 , moisture and NH_3 can all vary over the course of a few hours, it is not sufficient to simply know the level of free ammonia slip after the catalyst.

The only way to predict and avoid air heater fouling is to directly measure the condensable end product, ammonium bisulfate.

The Double Peak Measurement

Significant field experience with the AbSensor-AFP instrument in both SCR and SNCR applications has led to the discovery of a measurable precursor to ABS formation. This point is only measurable using a controlled tip measurement process and has been termed the “double peak”. It is the point where the formation temperature of the condensate corresponds to the sulfuric acid range, but the evaporation point lies in the AbS range.

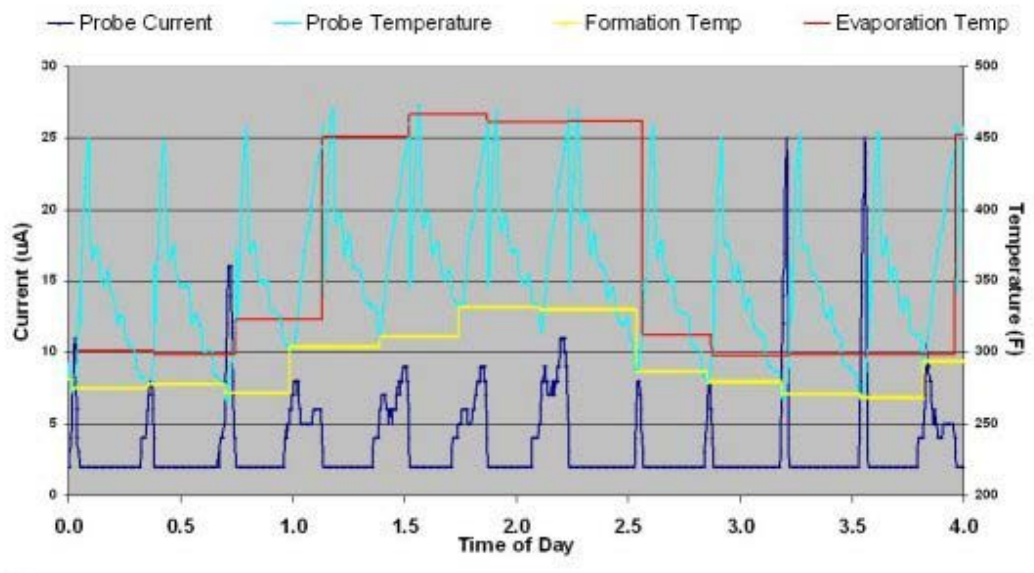


Figure 5 Instrument Response to Varying NH3 Levels

The chart above shows a progression from low ammonia feed, to higher ammonia feed, and then back to low in an SNCR installation. The waveforms (yellow/red) left of 0.7 hours show traditional sulfuric acid formation and evaporation temperatures. As NH₃ is increased, the temperature curves diverge, slowly for one cycle, and then rapidly. At 1.8 – 2.5 hours classic ABS is present. Beyond 2.5 hours the curves converge back to sulfuric acid. From 0.7 – 1.5 hours, ABS is predicted but will not yet kinetically form in the air heater or on the fly ash.

The graph below is a two week trace of both formation and evaporation temperatures (2 ducts/one probe per duct) compared to ammonia flow. It is fairly clear that the transition from sulfuric acid to ABS is related to ammonia feed rate, and that different levels of ammonia feed rate can be correlated to the presence and concentration of ABS.

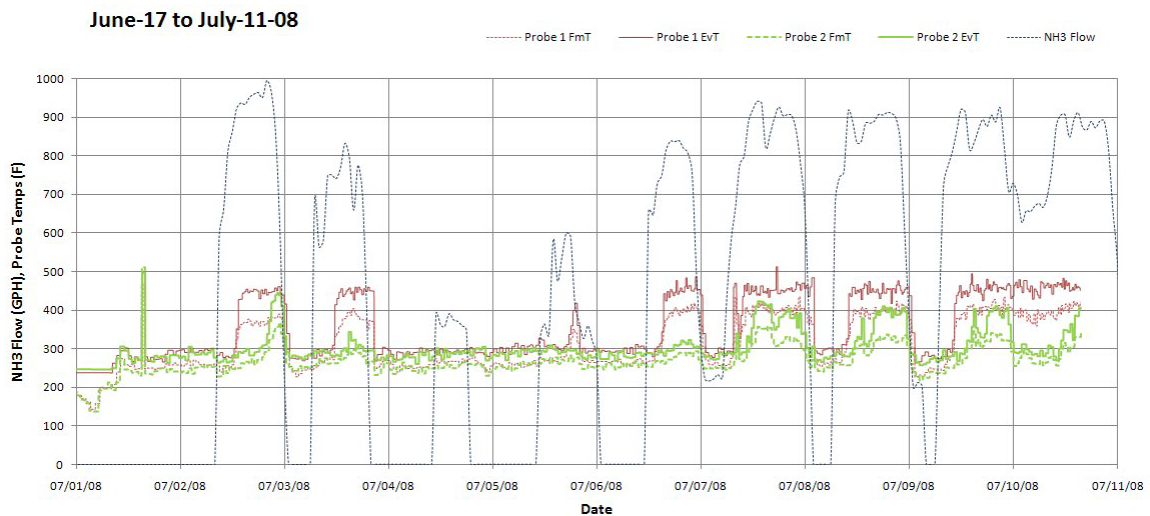


Figure 6 Typical Real-Time Instrument Data Plot Showing ABS/Acid Differentials

Notice the data from 7/2, 7/3 and 7/7. On these days a significant level of ammonia is present yet ABS (as identified by the upper 400F EvT) is only dominant on the A Duct (probe 1). The cause for this could be mal-distribution of SO₃, NO_x stratification between the ducts, or some other issue. What is clear is that ABS is being formed in the A duct which will lead to ABS deposition on the fly ash.

Also notice the variations in FmT for the various days when ABS is present in both the A and B Ducts. The ability to monitor this signal, and controlling the ammonia feed rate in response leads to lower ABS concentrations, reduced air heater fouling, and minimized ABS (ammonia) deposition in the fly ash.

CONCLUSIONS

As of this writing the Breen instrument has been successfully deployed in over 50 full scale, permanent and demonstration sites. It has been used for closed loop control of NH₃ feed rate in both SCR and SNCR applications for minimization of air heater fouling, control of SCR Minimum Operating Temperature and improvement of back end gas temperatures (heat rate). It has been used extensively for control of SO₃ mitigation chemical feed, and is finding new applications for the control of air heater speed as an alternative to steam coils/bypass dampers for ACET control.

Correlation has been found between the instrument data and ash samples taken from ESP hoppers, but no full scale demonstration for the purpose of minimizing ammonia in ash has, as yet, been undertaken.

Beta site partners for this application are currently being sought.