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Dynamic Control of SCR Minimum Operating Temperature

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ABSTRACT

On January 1, 2009 many additional SCR operators were required to begin year-round operation. The value of NOx credits and the negative dispatch effects of artificially established minimum load have rapidly driven many operators to closely examine the Minimum Operating Temperature (MOT) of their catalyst.

It is well known that ammonium bisulfate (ABS) can be formed through the interaction of SO3 and NH3 in the flue gas stream. The temperature at which ABS will condense out of the gas stream onto various nucleation sites (including air heater baskets, duct walls and particulate matter) has been the subject of a great deal of research in recent years. Generally speaking ABS forms when the temperature of the surface reaches 330°F - 390°F and will evaporate when the same surface reaches a value of 450°F - 500°F. These values are dependent on the combined concentrations of the SO3 and the NH3 as well as the localized gas pressure and moisture.

However, the temperature at which the ABS condenses inside the catalyst is additionally determined by the localized surface geometry. The pore structure of the catalyst surface creates an additional influence known as capillary enhanced condensation whereby ABS may condense out (in the pores) at temperatures much higher than the temperatures typically associated with the freely moving gas stream. The temperature where a known level of SO3 and a known level of NH3 will condense in the specific catalyst’s pores is known as the Minimum Operating Temperature. The lower the actual level of SO3 into the catalyst, then the lower the MOT.

This presentation will document the field experience of the Breen AbSensor technology for on-line measurement of SO3/Sulfuric Acid Vapor as it applies to dynamic control of MOT and will cover the impact of SO3, and SO3 control, on SCR Minimum Operating Temperature and how MOT can be continually adjusted to optimize performance. Case studies on adjustment of MOT based on measured SCR Inlet SO3, including plants with and without pre-SCR SO3 mitigation technology will be presented. Also included in the presentation will be the results of work done to measure the dynamic uptake and release of ABS from the catalyst at varying loads, temperatures and ammonia injection rates.
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. One of the issues associated with higher sulfur fuel is the Minimum Operating Temperature (MOT) of the SCR catalyst.

The curve below is a composite collection of data representing the minimum operating temperatures of most catalyst manufacturers. Clearly there will be specific conditions where a selected catalyst may operate significantly outside of these boundaries, but for the general industry these curves apply.

![Figure 1 - Composite Catalyst MOT vs SO3 curve](image)

MOT is essentially the flue gas temperature at the SCR inlet below which ammonia should not be employed. The rationale behind the temperature floor is that ammonium bisulfate (ABS) forms, in the presence of the small pores of the catalyst, at a much higher temperature than it does in bulk space. This is due to the impact of capillary enhance condensation. Therefore, knowing the geometry of the pores, each catalyst supplier can define the relationship that exists between SO3 concentration and capillary enhance ABS formation temperature.

However, most coal fired generating units have an operating floor that is significantly lower (in MW) that the floor established by SCR driven MOT. This difference in minimum load achievement can have several significant impacts on the station and the utility as a whole:
Depending on the total load factor of the plant (in other words does it cycle to a lower load every night or maintain a generally constant base load) a significant amount of time may be spent at load below the MOT. When this happens, any NOx generated is released to the atmosphere without the benefit of the SCR process. Simply put, NOx emissions are higher than they would be if a lower MOT were permitted, and

For utilities with multiple generating units, if the unit(s) constrained to operate at higher loads (MOT) are less efficient that other units in the fleet, the dispatch flexibility is compromised and significant total efficiency dollars can be wasted.

The goal of dynamically controlled MOT is to identify the actual operating conditions present at the catalyst input and controlling the operation of the SCR at the lowest possible operating temperature.

**FURNACE GENERATED SO₃**

Much has been written about the conversion of SO₂ to SO₃ in the furnace. This is the SO₃ that will be present at the SCR inlet. Rather than dwell on the total process, let’s just look at the variability of temperature and oxygen on the iron based catalytic effects.

The curve below shows the relationship of SO₂:SO₃ conversion to excess oxygen at various temperatures. What is clear is that:

The higher the level of excess O₂, the higher the formation rate of SO₃,

The lower the temperature at which the SO₂ meets the iron catalyst, the higher the formation rate of SO₃.
Figure 2 - SO2:SO3 Conversion vs. O2 and Temperature

Figure 3 below is provided for physical understanding of the temperature ranges within the boiler system.

Figure 3 - Boiler/Backpass Temperatures
Comparing the data from Figures 2 & 3 shows that the primary conversion of SO₂ to SO₃ occurs in the region between the reheat pendants and the economizer inlet. What should also be understood is:

- As loads change, excess O₂ often changes,
- As loads change, FEGT changes and results in a shifting of temperatures throughout the critical SO₂:SO₃ conversion region,
- As mill configurations change, even at essentially constant load, temperatures and locations can also change.

The bottom line to all of this is that the conversion rate of SO₂ to SO₃ ahead of the SCR is rarely a constant number and application of a fixed MOT curve based on a fixed level of SO₃ input is generally over conservative. What is required is a real-time measurement of the actual SO₃ entering the SCR and subsequent closed loop control of the ammonia injection curve based on the dynamic number.

**ON-LINE SO₃ CONDENSABLES MEASUREMENT**

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 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**.

**PLANT OPERATING DATA**

A rigorous control strategy would desire one instrument ahead of the SCR AIG for dynamic adjustment of the MOT and a second instrument after the SCR to monitor the presence, and release, of any low temperature ABS deposits.

**Pre-SCR Measurement**
The curve below is typical of many implementations of the condensables instrument ahead of the SCR.

Figure 4 - Economizer Outlet SO3 vs. Load & O2

What is clear here, and presented only to show that it does happen, is that contrary to the plant’s expectations the SO3 actually went up dramatically during periods of light load. Even though the measured SO2 value dropped, the increase in available O2 and the changing of the temperature position in the Backpass resulted in SO3 numbers at light load being more than double the same values at high load.

Pre-Air Heater Measurement

Figure 5 - AH Inlet Condensables Spike w/ESP Spike
Figure 5, above, shows two curves superimposed. The upper traces (purple and aqua) are the instrument condensable readings at the air heater inlet. Notice:

1. The “B” side dropped from ABS into acid condensable range during the evening hours but the “A” side showed some ABS activity during the first half of the overnight load reduction,
2. The ammonia was off during the overnight period,
3. Notice the spike in both AH inlet probes just after the 6:00 AM ramp followed by a drop in the “B” side back into the acid range. Around 9:00 both instruments reported ABS activity.
4. The ammonia was re-started at the 6:00 ramp
5. Notice that the ESP outlet instrument indicates an 11 ppm SO3 spike coincident with the load ramp spikes.
6. It is presumed that the spikes are all a result of re-vaporization of ABS inventory deposited in the catalyst during normal operation,

Figure 6 - Baseline data showing cycled unit operation without ammonia

Figure 6 above shows normal, less than MOT operation for a unit burning typical Eastern Bituminous coal. Notice the following:

1. At ramp up the normal SCR outlet SO3 spike is shown as 8 ppm. This is a raw figure that was not temperature compensated. The compensated number is closer to 15 ppm.
2. At ramp up the normal AH outlet SO3 spike is shown as 9 ppm. This raw figure is accurate and does not require temperature compensation.

3. At load shed the ammonia was curtailed and was not restarted until 4 hours after ramp up so that the true SO3 release could be seen.

Figure 7 shows exactly the same operating conditions as Figure 6 but with the ammonia run at normal NOx target overnight. The ammonia was again curtailed so that the SO3 release could be identified. Notice the following:

1. The temperature compensated SO3 release from the SCR is in the order of 32 ppm,
2. The actual SO3 release from the Air Heater is 15 ppm.
3. Clearly ABS was deposited in the catalyst during low load operation when compared with the SO3 release from figure 6.
4. Also, the SO3 release spike is seen to subside indicating that the re-vaporization at higher temperature operation was successful.
Figure 8 - SO3 release from normal, below MOT operation

Figure 8 is the same set of conditions as Figure 7 except the ammonia is not curtailed at ramp up. Notice that the ammonia operation masks, or scrubs, the SO3 release at load ramp.

Also notice that during operation of Figures 7 and 8, the ABS concentration (evaporation temperature) dropped concurrent with load drop but then ramped up continuously over time. Assuming that ammonia injection rate, NOx and SO3 are all relatively constant through that period, the change in concentration could be attributed to material lost to the catalyst. However, this would suggest that the greatest deposition rate is while the catalyst is at the early stage of cooling off, which seems counter-intuitive.
SUMMARY

• Commercial drivers for operation of SCR systems below supplier specified Minimum Operating Temperatures is highly compelling.

• Plant programs have determined that using on-line condensables instruments to monitor real-time SO3 levels allows continuous bias to the MOT figure.

• Additional monitoring of condensables at the SCR outlet provides information into the presence, and level, of ABS deposits in the catalyst during low load operation.

• Lastly, field experience suggests that even if ABS does deposit in the catalyst, at any load, it can be re-vaporized and released during high temperature ramp and operation.