

Successful Mitigation of SO₃ by Employing Dry Sorbent Injection of Trona Upstream of the ESP

Session B1
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ABSTRACT

Mitigation of SO₃ can have some dubious results in a coal fired utility boiler. On one hand there are corrosion issues in the air heater if the air temperature is too low or there is duct work corrosion if SO₃ is not mitigated and a visible blue plume will form out of the stack. But if the SO₃ is removed the ESP operation can be negatively affected if the flue gas stream is not conditioned.

The effort to reduce NO_x emissions from coal-fired power plants via selective catalytic reactors (SCRs) has resulted in the unintended consequence of oxidizing SO₂ to SO₃ and thereby increasing total SO₃ emissions. Although the higher stack SO₃ concentrations are still very low (measured in ppm) the emissions can sometimes produce a highly visible secondary (blue) plume, which, although unregulated, is nonetheless perceived by many to be problematic. Efforts to reduce the SO₃ levels to a point where no secondary SO₃ plume is visible can impede particulate collection for stations that employ electrostatic precipitators (ESPs). SO₃ in the flue gas absorbs onto the fly ash particles and lowers fly ash resistivity thereby enabling the ESP to capture the particle by electrostatic means. Many plants inject SO₃ to achieve optimal fly ash resistivity when ash resistivity is too high.

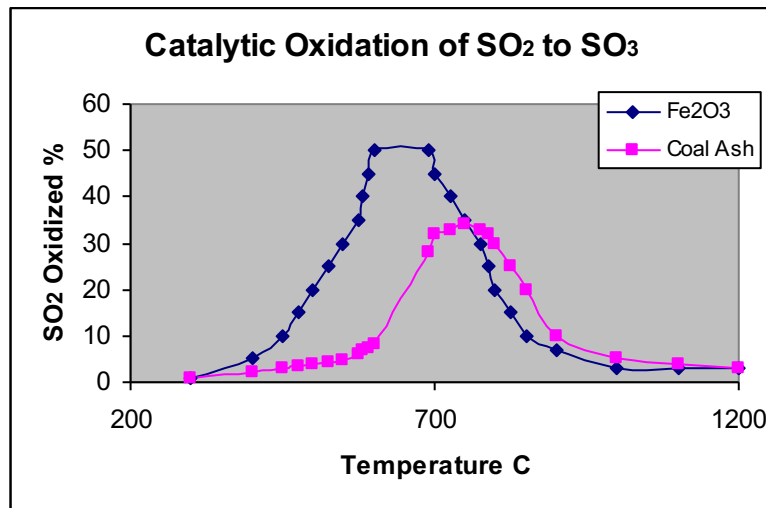
Recently several coal fired power plants have begun using dry sorbent injection of T200 a mechanically refined trona product. Dry sorbent injection is preferable to liquid injections due to the ease of handling, reduced risk of fouling downstream duct or equipment, and improved safety (including lower conveying pressures). Since T200 is a sodium compound it conditions the ash to lowers its resistivity having a positive effect on the operation of both cold and hot side ESP's. Test results using the controlled condensation method verified visual indications that stack SO₃ levels below 10 ppm were routinely attainable without opacity excursions.

INTRODUCTION

In reaction to having to meet emission requirements of Title I of the Clean Air Act Amendments of 1990 the power industry responded with the installation of NO_x abatement systems. These NO_x abatement systems took many forms but the most complete abatement system is the selective catalytic reactors (SCRs).

SCR's employ a catalyst (typically vanadium pentoxide) to convert NO_x to N₂ and H₂O with the addition of NH₃ but there is also an unintended oxidation of the SO₂ to SO₃. The oxidation of SO₂ to SO₃ was already occurring in the furnace and high temperature areas downstream of the boiler as a result of catalytic oxidation of the SO₂. The catalysts were the coal ash and various metals such as iron oxide (See Fig 1). The SO₃ generated was probably helping some of the ESP's because of its surface conditioning effect that lowers the resistivity of the ash. This positive effect was especially obvious as coal companies switched to lower sulfur coals. This switch led to conditioning agents to be used such as SO₃ to the flue gas stream prior to the ESP when sufficient SO₃ was not available or the ash resistivity of the coal is high.

Fig. 1



As coal plants began to tackle the problems meeting regulations requiring SO_x and NO_x new problems began to crop up. Switching coals resolved some problems but the ever changing economic picture and the variability of the ash resistivity, along with increased burdens on the particulate collection devices caused the situation to be in a state of flux. As SCR's were put into service the generation of a secondary plume became evident. This plume was not regulated but it could create opacity excursions and if it touched down possible exposure problems to the surroundings and life in the area of the touchdown could occur.

“Although the higher stack SO₃ concentrations are still very low (measured in ppm) the emissions can sometimes produce a highly visible secondary plume, which, though unregulated, is nonetheless perceived by many to be problematic.”¹

“SO₃ reacts with water vapor in the flue gas ducts of the coal power plant and forms vaporous H₂SO₄. A portion of this condenses out in the air heater baskets. Another portion of the sulfuric acid vapor can condense in the duct if the duct temperature is too low, thereby corroding the duct. The remaining acid vapor condenses either when the plume is quenched when it contacts the relatively cold atmosphere or when wet scrubbers are employed for flue gas desulfurization (FGD), in the scrubber’s quench zone. The rapid quenching of the acid vapor in the FGD tower results in a fine acid mist. The droplets are often too fine to be absorbed in the FGD tower or to be captured in the mist eliminator. Thus, there is only limited SO₃ removal by the FGD towers. If the sulfuric acid levels emitted from the stack are high enough, a secondary plume appears. Levels as low as 7-10 ppmvd (corrected to 3% O₂) can be visible, depending upon meteorological conditions.”²

Trona is a sodium based sorbent that is relatively low in cost, is highly reactive, and requires minimal capital for injection into the duct. Trona is typically injected in flue gas streams in various processes for acid gas mitigation. The use of trona for SO_x mitigation is well established. The use of sodium conditioning as an alternative to SO₃ conditioning has been documented.³ The practical application of dry sodium injection for simultaneous SO₃ mitigation and ash conditioning is the subject of this report.

TRONA: ITS FORMATION, MINING, USE AND APPLICATION AT GAVIN PLANT

Background of Trona Ore

Trona’s formation at Green River, Wyoming is the result of rapidly repeated evaporation cycles of Lake Gosiute approximately 50-60 million years ago. The original lake was fresh water and supported abundant flora and fauna. When the climate changed from humid to arid, Lake Gosiute evaporated and trapped the remnants of the once abundant life. The lake bottom became a mixture of mud and organic sediments that formed oil shale. Runoff water from the nearby mountains continued to supply sodium, alkaline earth, and bicarbonate to the lake. Since the rate of evaporation was high, the clear waters changed to brine that finally precipitated a sodium carbonate-bicarbonate compound known as the mineral “trona” (chemical formula: Na₂CO₃•NaHCO₃•2H₂O). Alternating climates prevailed for about two million years. Periods of rains washed mud into the lake to cover previously formed carbonate type precipitates while interim periods of arid climate produced new precipitates. This caused numerous beds of trona to be formed. In total, they contain billions of tons of trona and related minerals.

The tropical rains eventually returned to expand Lake Gosiute. This washed sand and mud from the surrounding mountains into its waters. Sediments of clay and shale built new formations as the geological evolution of the Green River Basin progressed. Buried

under these sediments remain the trona beds that have become the basis of the present soda ash and sodium-based industry located around Green River, Wyoming.

Solvay Chemicals, Inc. currently mines trona ore from bed number 17 located at an approximate depth of 1500 feet. This ore body under Solvay's lease holdings is approximately 12 feet thick and of very high quality. Bed 17 will provide ore for many years; however, should the need arise, additional trona ore may be extracted from other beds as well.

Solvay Chemicals employs the "room and pillar" method of mining. Long drifts (tunnels) are mined with cross cuts at specified distances and the remaining pillars support the roof of the mine.

Solvay currently uses boring type miners and long wall mining to extract the ore. Roof bolting machines insert steel rods into the roof of the mined areas. This supports the immediate rock roof and prevents rock falls. Once cut, the ore is transported via shuttle car to a series of belt conveyors which discharge into underground storage bins. From these storage bins, the ore is hoisted to the surface in 20-ton capacity skips.

Solvay offers mechanically refined sodium sesquicarbonate (natural trona) to the merchant market. Coarse product exclusively is marketed and sold to the animal feed market by an outside company. Alternative products, Solvay T-50 (250-300µms) and T-200 (23µms), are marketed directly by Solvay for acid gas and acid neutralization applications.

Trona product operations are located in the ore-crushing portion of the soda ash plant. Trona ore is crushed and screened before being sent through a fluid bed dryer. The dryer serves to remove free moisture from the product and to separate the coarse (T-50) from fine (T-200) product. Trona products are stored in bulk quantity awaiting rail and truckload out. A bagging operation exists for the packaging of T50 products into 50-pound bags and both T50 and T200 in 2000-pound bulk sacks.

De-acidification of Acid Gases with Trona

Trona is rapidly calcined to sodium carbonate when heated at or above 408°K (275°F). The "popcorn-like" decomposition creates a large and reactive surface by bringing unreacted sodium carbonate to the particle surface for acid neutralization. The by-products of the reactions are sodium salts. For example the SO₂ chemistry is:

1. $2(\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 + 2\text{H}_2\text{O}) + 3\text{SO}_2 \rightarrow 3\text{Na}_2\text{SO}_3 + 4\text{CO}_2 + 5\text{H}_2\text{O}$
2. $3\text{Na}_2\text{SO}_3 + 1.5\text{O}_2 \rightarrow 3\text{Na}_2\text{SO}_4$

Sodium carbonate is brought in contact with acid vapor in the flue gas stream by a simple direct injection of a sodium compound such as trona that will thermally decompose to form sodium carbonate. After the initial sorbent surface of the sodium carbonate has reacted with SO₂ to form sodium sulfite, or sulfate, the reaction slows due to pore blockage -resisting gas phase diffusion of SO₂. In order for the reaction to continue, the

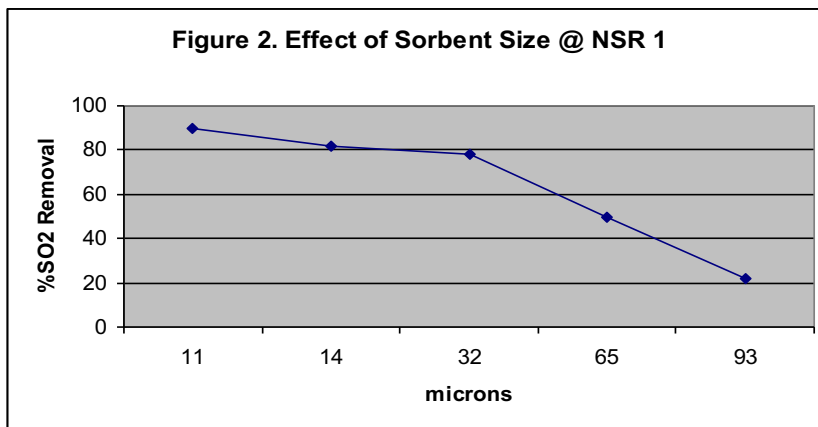
sorbent particle must decompose further. This decomposition evolves H₂O and CO₂ gases into the surrounding atmosphere creating a network of void spaces throughout the particle. This process exposes fresh reactive sorbent and allows SO₂ once again to diffuse into the particle interior. This increase in surface area (“popcorn effect”) is on the order of 5 to 20 times the original surface area.”

The rates of decomposition and subsequent sulfation of a sodium compound particle are a complicated function of gas temperature, rate of heat transfer to the particle, flue gas H₂O and CO₂ partial pressure and the effects of other flue gas components present. In an actual sodium DSI system additional parameters and physical constraints will also affect overall sorbent utilization. These include:

- Sorbent injection rate
- NSR (normalized stoichiometric ratio) between the sorbent and the system inlet SO₂ concentration considering that two moles of Na are required to react with one mole of SO₂
- Sorbent particle size
- Sorbent residence time in the flue gas stream
- Sorbent penetration and mixing within the flue gas
- Particulate control device used

The optimum temperature range of sodium sorbent/gas reactions is much more forgiving than the calcium systems. The sodium sorbent has demonstrated high removal efficiencies in the temperature range of 398 -752°K (257- 894°F) on both a laboratory and commercial scale systems. Most calcium sorbents are only effective at low temperatures and the by-product salts have substantial vapor pressures at the higher temperatures of their own.

The particle size of the sorbent can have a dramatic effect on the removal efficiency of SO₂ as can be seen in Figure 2:



Gavin Plant SO₃ Mitigation Efforts

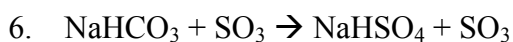
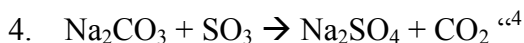
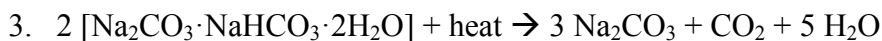
“American Electric Power sought out sorbents for testing that contained elements such as potassium and sodium that were not expected to degrade ESP performance. KOH, KHCO₃, K₂CO₃, NaOH, SBS, sodium bicarbonate/ nahcolite, trona and other chemicals were investigated. Some of these were judged to be unacceptable as sorbents. Others were expected to perform well, but were not tested due to safety concerns associated with handling the material. Others were excluded due to cost.

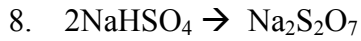
Trona was selected as a candidate for testing based on its acid neutralizing abilities coupled with its sodium content that would be utilized for conditioning the precipitators. Trona was expected to be useful for maintaining low fly ash resistivity even as SO₃ was removed from the gas stream. Trona is the least expensive sodium-based sorbent available. This made trona more attractive to test compared to sodium bicarbonate. The dry form was the preferred method of injection over slurry or solution. This was based on the relative ease of handling, simplicity, safety (e.g. lower conveying pressure), and lower probability of fouling downstream of the injection point.

Most of the trona suppliers that were contacted process trona into soda ash. Particle size is not critical for that application and thus it was difficult to find a source of trona with a small average particle size. One supplier (Solvay) was found that had experience using trona for acid gas (SO₂) mitigation and understood AEP’s needs with respect to reaction efficiencies. The material supplied for tests had an average particle size of 23-28μ. This coupled with the decrepitation effect during calcination was judged to provide sufficient surface area for to be an effective sorbent. Surface area was judged to be acceptable based on the product’s performance.

Trona, like most alkali reagents, will tend to react more rapidly with the stronger acids in the gas stream first, and then after some residence time it will react with the weaker acids. Such gas constituents as HCl and SO₃ are strong acids and trona will react much more rapidly with these acids than it will with a weak acid such as SO₂.

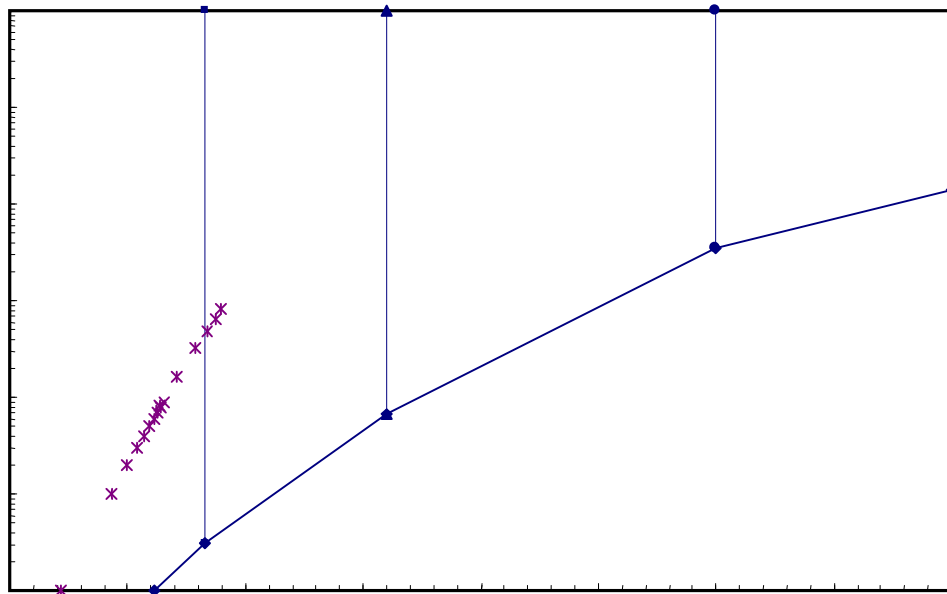
Trona is injected into the hot flue gas where it calcines to soda ash”⁴. The reaction of soda ash with SO₃ is believed to form sodium sulfate, Na₂SO₄, however; recently analyzed duct deposition suggests that sodium bisulfate may also be unintentionally forming as per the following reactions:





Chemical reactions 3 and 4 are the most common and the primary ones in most desulfurization by dry sorbent injection of T200. Most recently we have encountered circumstances in which the SO_x concentrations were very high and sodium feed rates very low relative to the amount of acid gas being treated. The chemistry of these reactions under these conditions are shown in reaction 5. Sodium bisulfate is an acid salt with a low melt temperature and unstable at high temperatures (reaction 8). Reactions 6 would occur when if the trona is not completely calcined. Reaction 7 is possible after the fact when the acid dew point is reached. This condition will occur further down stream from the feed point and under very high SO_x concentrations - which occurred at Gavin. The following figure 3 depicts the possible reaction products: (note the acid DP is depicted buy the "x" notation)

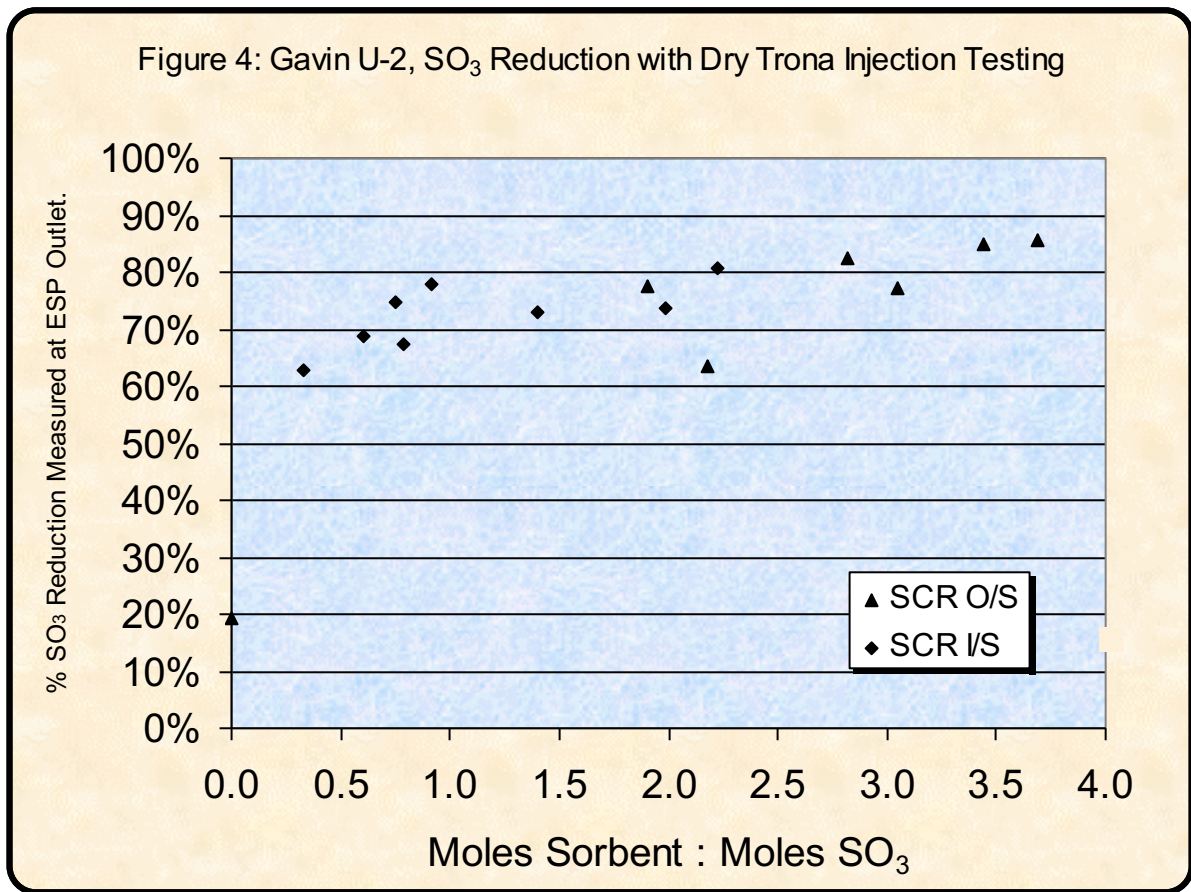
Figure 3⁶.



These conditions appear to be unique to the Gavin plant. Other power plants using T200 for the same mitigation and conditioning effects of T200 do not have any fouling issues.

Cold Side ESP Conditioning

“Referring to Figure 4, at a DSI rate of 2.9 TPH with the SCR O/S there is an indication that ESP conditioning may improve SO₃ removal efficiencies. The first data point was taken directly after trona injection began. There was no attempt to condition the ESP prior to this first test point. This resulted in a removal efficiency of about 63%. The removal was measured again at 2.9 TPH later in the test schedule. However, for the second data point at 2.9 TPH the ESP was well conditioned and a 78% removal was seen. Looking at these two data points in Figure 4 one can see that the unconditioned point is slightly above a 2.0 molar ratio (removing 63% SO₃) while the conditioned point is actually removing a higher percentage of SO₃ (78%) while being at a molar ratio slightly lower than 2.0.



Hydrated lime injection rates were limited to 2 to 2.5 TPH due to ESP performance degradation. No such degradation was noted with trona injection, see Figure 5. It did not appear that ESP performance was negatively impacted by trona injection. VI curves were also generated during trona injection with no indication of back corona. After a permanent system was installed, it was noticed that plant operators actually injected trona for the sole purpose of enhancing ESP performance. This was done when several T/R sets were O/S due to internal grounds. Hence, the trona system actually benefited ESP performance while SCR were O/S.”⁵

SO_x Removal with Trona (T200) at 750F

100%
90%
80%
70%
60%
50%
0

Hot Side ESP Experience

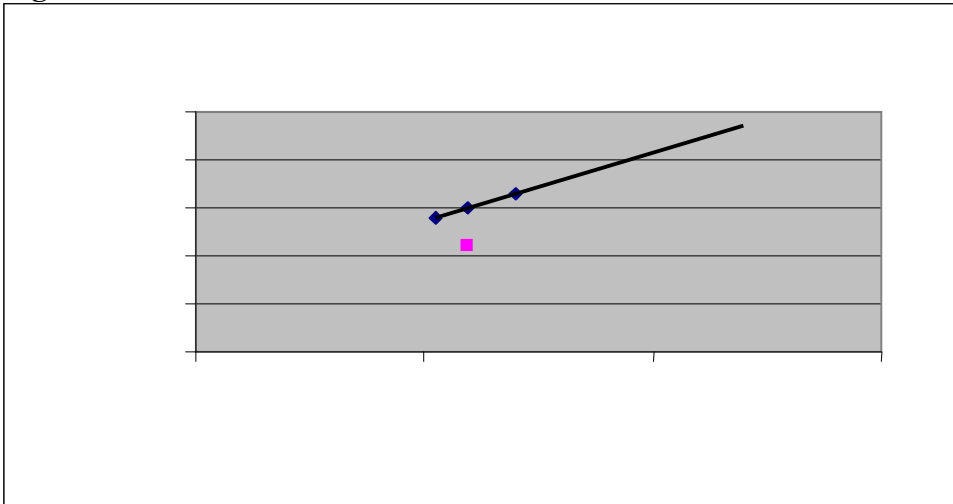
SBC

Typically dry sorbent injection (DSI) has been done at temperatures lower than 400°F because of material of construction temperature limitations of the baghouse media and possible sintering of the sorbent crystal. What we have learned is that natural mechanically refined fine trona reactivity to sulfur oxides is improved as the injection temperature is raised unlike chemically refined milled sodium bicarbonate.

NSR

The graph below shows a study that varied the trona flow rate while holding all other process variables constant in comparison to sodium bicarbonate. This study was done in a commercial plant which used a hot side ESP (no baghouse) and SO_x concentrations of 800 ppm. Typically sodium bicarbonate will out perform mechanically refined trona. In this case trona removed 81% of the SO_x when milled sodium bicarbonate removed only 72% of the SO_x under the same situation. See Figure 6

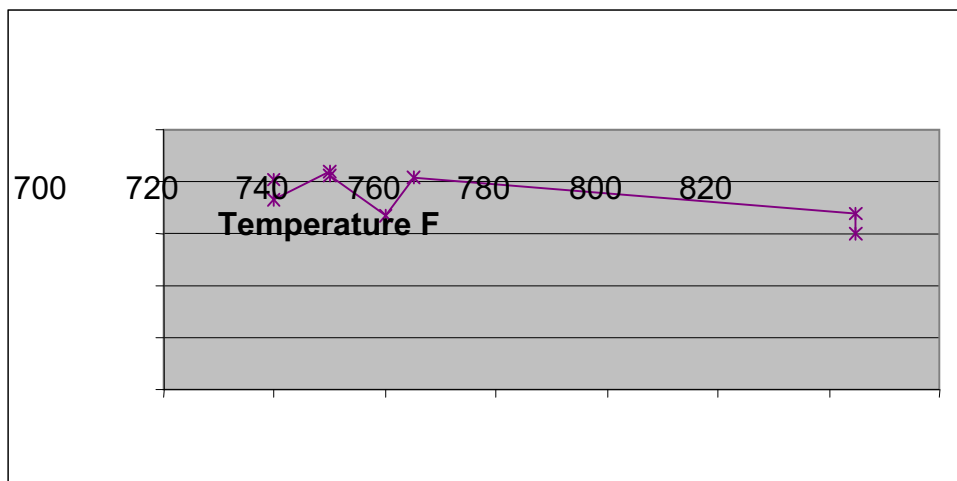
Figure 6



The data shown in the graph below is from the same commercial process in which mechanically refined trona (T200) was injected into the flue gas stream at a 1.5 normalized stoichiometric ratio (NSR) rate while varying the injection temperature. Removals as high as 91% were achieved injecting T200 into a hot ESP w/o a baghouse. At this writing the T200 injection is being done at 725°F using 25% less trona than sodium bicarbonate and getting the same SO_x removal. SO_x removals as high as 91% have been demonstrated using trona at 725°F and at an NSR of 1.5. Please see Figure 7 below:

100%
90%
80%
70%
60%
50%
680

Figure 7



As can be seen in the graphs above high SO_x removals can be achieved at higher temperatures than has been typically observed at lower temperatures unless a baghouse was used. Also, lower NSR values are needed for the high SO_x removal than observed in laboratory studies or actual plant operating data than milled sodium bicarbonate unless a baghouse was used.

Prior to injecting trona T200 the “perf plates” of the hot side ESP would plug within days of injecting sodium bicarbonate but when using trona no pluggage was encountered and the system is operating trouble free for the last year.

Conclusions

Trona T200 removed SO₃ while conditioning the Gavin Plant ESP. T200 can be used on a commercial scale to provide a reliable and cost effective SO₃ mitigation technology. T200 is used year around to condition the ESP. T200 under most conditions can be injected into the ducts providing a trouble free SO₃ mitigation process.

References

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