DRY INJECTION OF SODIUM SORBENTS FOR AIR POLLUTION CONTROL

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Introduction

Coal-fired boilers in the utility power plants or process industry emit air pollutants, such as SO_2, SO_3, hydrochloric acid (HCl), hydrofluoric acid (HF) and Mercury. Ever stricter environmental regulations around the world demand efficient removal of these air pollutants.

One popular SO_2 control, or flue gas desulfurization (FGD), technology is wet scrubbing. In a wet scrubber, a liquid sorbent is sprayed into the flue gas in an absorber vessel. Most wet FGD systems use alkaline slurries of limestone or slaked lime as sorbents. Sulfur oxides react with the sorbent to form calcium sulfite and calcium sulfate.

While wet scrubbers are often used at large boilers due to their high SO_2 removal efficiency (> 95%), their high capital and O&M costs make them uneconomical for small utility boilers (i.e. < 250 MW), industrial coal-fired boilers, and waste-to-energy boilers. The majority of these boilers have neither enough physical space nor the capital funding necessary for wet scrubbers. Another drawback of a wet scrubber is that it makes SO_3 more visible as blue plume.

A good alternative air pollution control technology is dry injection of sodium sorbents (trona or sodium bicarbonate). In a dry sorbent injection system, sodium sorbent is injected into the hot flue gas duct and reacts with SO_2, SO_3, HCl, HF and some NO_x. Due to its low capital cost and ease of operation, dry injection of sodium sorbents is being used at more and more boilers, and is able to remove up to 95% of SO_2 and nearly all SO_3, HCl and HF.

Figure 1

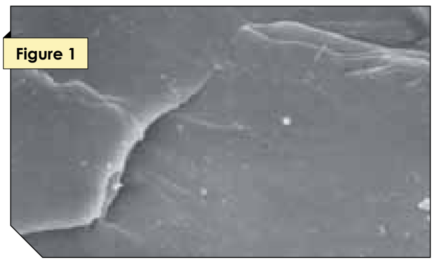
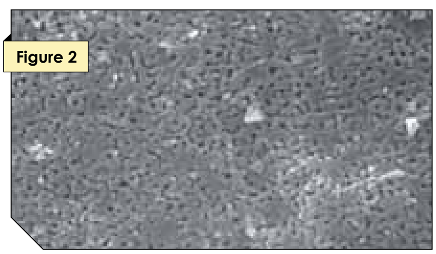


Figure 2

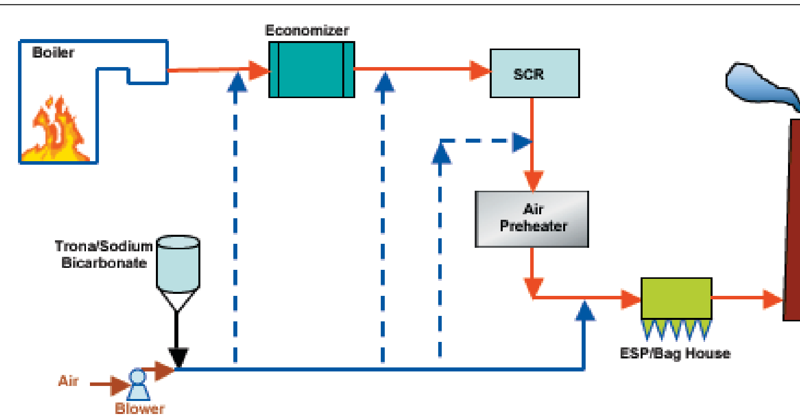


With increasing implementation of Selective Catalytic Reduction (SCR) for NO_x control, there are higher concentrations of SO_3 in the flue gas. In addition to forming blue plume after exiting the stack because of condensation of the resultant H_2SO_4, SO_3 can react with NH_3 slip to form sticky NH_4HSO_4 (ammonium bisulfate or ABS) that can plug up the air preheater. Furthermore, SO_3 can pose serious corrosion problems to air preheater, electrostatic precipitator (ESP) and any downstream equipment. Among various SO_3 mitigation technologies, dry injection of sodium sorbents, such as trona, has been proven to be very effective and cost-competitive.

Principles of Dry Injection of Sodium Sorbents

In a dry sorbent injection (DSI) system, a fine powder, such as trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) or sodium bicarbonate ($NaHCO_3$), is injected into the flue gas duct. After injection, either sodium sorbent is calcined into porous sodium carbonate (Na_2CO_3), which reacts with acid gases, such as SO_2, SO_3, HCl and HF. The resulting products (Na_2SO_4, NaCl and NaF) are collected by the particulate control device, such as an Electrostatic Precipitator (ESP) or bag filters. Figure 1 shows raw sodium bicarbonate under a microscope.

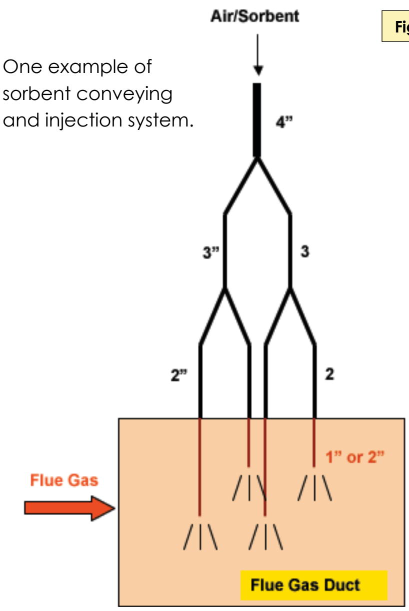
Figure 3



Click HERE to return to Table of Contents

Figure 4

One example of sorbent conveying and injection system.



After being injected into hot flue gas (> 275°F), sodium bicarbonate or trona is calcined into sodium carbonate (Na_2CO_3), as shown in the following equations:

- $2NaHCO_3$ Æ $Na_2CO_3 + H_2O$ (gas) + CO_2(gas)
- $2Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ Æ $3Na_2CO_3 + 5H_2O$ (gas) + CO_2(gas)

The release of water vapor and CO_2 in the above calcination process creates numerous micropores inside the sorbent, a phenomenon called the "pop-corn" effect. The BET specific area of calcined sorbent is approximately 10 m^2/g. This relatively high surface area enables fast reactions between sodium carbonate and acid gases, such as SO_2, SO_3, HCl and HF. The photo of calcined sodium bicarbonate under a microscope is shown in Figure 2.

The overall reactions between calcined sodium sorbents and acid gases are as follows:

- $Na_2CO_3 + SO_2 + 1/2\ O_2$ Æ $Na_2SO_4 + CO_2$
- $Na_2CO_3 + SO_3$ Æ $Na_2SO_4 + CO_2$
- $Na_2CO_3 + 2HCl$ Æ $2NaCl + H_2O + CO_2$
- $Na_2CO_3 + 2HF$ Æ $2NaF + H_2O + CO_2$

The sorbent can be injected at almost any location of the flue gas duct, as shown in Figure 3, as long as the flue gas temperature is above 275 °F.

No supplemental water injection is needed when using sodium sorbents, unlike when using lime or hydrated lime. A simple blower delivers the sorbent into the duct through injection lances.

The efficiency of Dry Sorbent Injection (DSI) system depends on many factors, such as:

- Sorbent particle size: Finer particles result in better performance.
- Sorbent residence time in flue gas stream: Longer residence time gives more time for mixing and chemical reactions, thus better performance.
- Sorbent penetration and mixing with flue gas: Better sorbent penetration into flue gas and mixing gives higher removal efficiencies.
- Particulate control device used (ESP or Baghouse): Since sorbents can build up on the fabric filters of the bag house and provide a layer of sorbent for further reactions with acid gases, baghouse filters have higher efficiencies.
- Temperature at injection site: The minimum flue gas temperature at the sorbent injection should be at least 275 °F. Higher temperatures normally result in better performance. The recommended maximum temperature is 1500 °F.

The key of good DSI system design is to distribute the sorbent evenly in the flue gas so that the sorbent and acid gases will be well mixed. The desired design guidelines are as follows:

- Residence time: > 1 second
- Flue gas temperature: 275 ~ 1500 °F
- Conveying air: < 140 °F

Sodium Sorbents: Trona and Sodium Bicarbonate

The trona is produced in Green River, Wyoming. It is a naturally occurring mineral with a chemical formula of $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ and its typical physical properties are:

- d_{50}: ~ 30 μm
- d_{90}: ~ 160 μm
- Bulk density: 49 lb/ft^3

Since it is produced as a fine powder, it is not necessary to mill trona. Although milling can increase the removal efficiency, the additional cost of equipment and maintenance have discouraged most users from using mills.

Sodium bicarbonate is produced in several locations in the US and its typical physical properties are:

- d_{50}: ~ 110 μm
- d_{90}: ~ 250 μm
- Bulk density: 68 lb/ft^3

Raw sodium bicarbonate is too coarse to be injected directly. Therefore, an air-classifying hammer mill or pin mill needs to be used. At one power plant, the particle sizes of milled sodium bicarbonate were d_{50}=12 μm and d_{90}= 30 μm.

Performance of Dry Injection of Sodium Sorbents

Both trona and sodium bicarbonate are effective in removing SO_2, SO_3, HCl and HF. In order to compare the performance of different dry sorbent systems, Normalized Stoichiometric Ratio (NSR) is used to represent sorbent feedrate. The NSR is expressed as:

"A GOOD ALTERNATIVE AIR POLLUTION CONTROL TECHNOLOGY IS DRY INJECTION OF SODIUM SORBENTS (TRONA OR SODIUM BICARBONATE)."

- mass of sodium injected
- mass of acid gas entering system
  NSR = mass of sodium theoretically needed to react with a unit mass of acid gas

(a) SO_2

Figure 5 and Figure 6 show the SO_2 removal rates vs. Normalized Stoichiometric Ratio (NSR) using trona or sodium bicarbonate, respectively.

The curves in Figures 5 and 6 were created with the application data of numerous systems over the last 20 years. Sodium bicarbonate is more efficient than trona in removing SO_2. However, the increased efficiency comes at a higher sorbent price. Several factors need to be evaluated to determine which sorbent is best for a specific application. Some of those factors include the level of SO_2 removal required, particulate control device used, injection location and flue gas temperature, plus many more. Generally speaking, trona should be used if the SO_2 removal rate is lower than 50%, and sodium bicarbonate should be the choice if over 70% of SO_2 must be removed. Anything in between requires a careful study of all factors in order to select an economical sorbent.

Figure 5

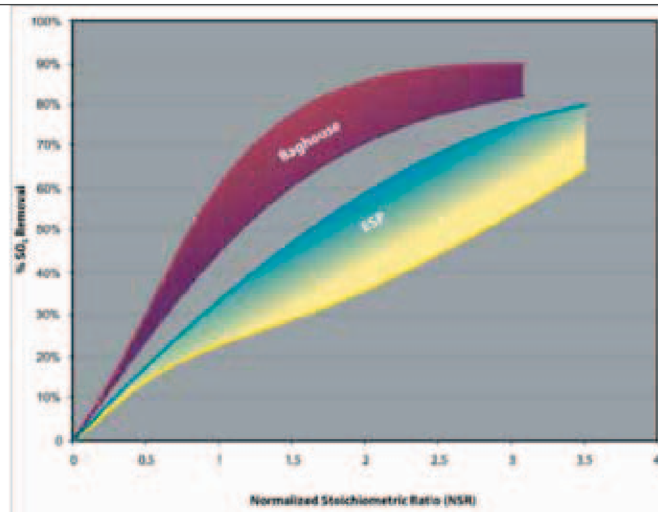
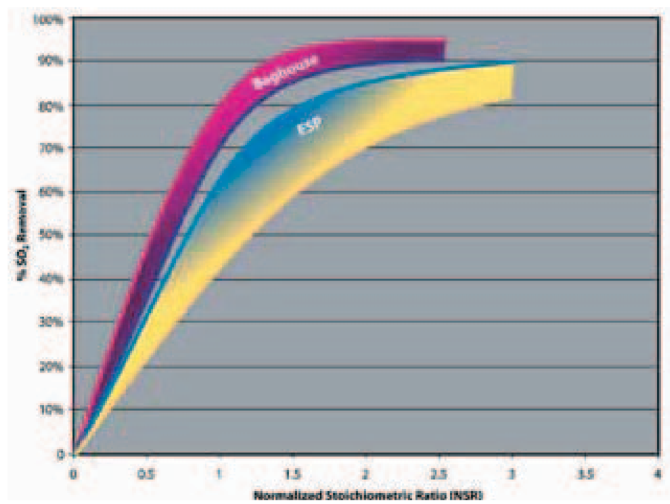


Figure 6



(b) SO_3

The vast majority of sulfur in coal is oxidized into SO_2 during combustion but a small portion – typically 1% to 2% – is further oxidized to sulfur trioxide (SO_3) in the boiler. If there is a SCR system for NO_x control, a small fraction of SO_2 is oxidized to SO_3 by the SCR catalyst. The amount of SO_2 oxidized in the SCR catalyst can vary from 0.3% to around 2%, with the current market driving toward 0.1% oxidation.

Although a wet scrubber is effective in removing SO_2, it can remove only some of the SO_3. Typically, the amount of SO_3 removed is marginal to perhaps as high as 30%. As the flue gas is rapidly cooled by the sprays of liquid in the wet scrubber, the vaporous sulfuric acid undergoes a shock condensation process that produces very fine sulfuric acid aerosol particles. These aerosol particles are, for the most part, too small to be effectively captured in the scrubber and are emitted into the air as a sulfuric acid mist, which forms a blue plume and causes opacity issues.

In addition to the blue plume, SO_3 can cause the following problems:

- Formation of ammonium bisulfate (ABS) in the SCR system. Depending on its concentration, SO_3 can also react with NH_3 under the catalytic conditions that exist in the SCR system at temperatures in the range of 530 °F to 630 °F. ABS is a sticky solid that can foul the SCR catalyst and air heater.
- Formation of ammonium bisulfate (ABS) in the air heater. SO_3 and ammonia (NH_3) will react to form ABS in the air heater if SO_3 is present in molar concentration in excess of the molar concentration of NH_3 and when the flue gas in the air heater cools to between 350 °F and 420 °F.
- Increased air heater fouling. Fouling of a regenerative air heater becomes serious when the flue gas temperature is below the SO_3 dew point and acid condensation occurs. The SO_3 dew point increases with SO_3 concentration.
- Increased corrosion to the downstream equipment.

Trona is very reactive with SO_3. At one power plant, trona was injected between the air preheater and ESP. The SO_3 was measured upstream of the trona injection ports and downstream of the ESP. Figure 7 shows one example of SO_3 removal performance with trona. Since the SO_3 concentration is

Table 1

REMOVAL OF HCL AND HF BY TRONA AND SODIUM BICARBONATE	HCl at Stack (lb/MBtu)	HCl Removal Rate %	HF at Stack (lb/MBtu)	HF Removal Rate (%)
Trona	0.0011	98.8	0.0008	78.4
Sodium Bicarbonate	0.0013	97.8	0.0002	88.0
Permit Limit	0.0072		0.0026	

Figure 7

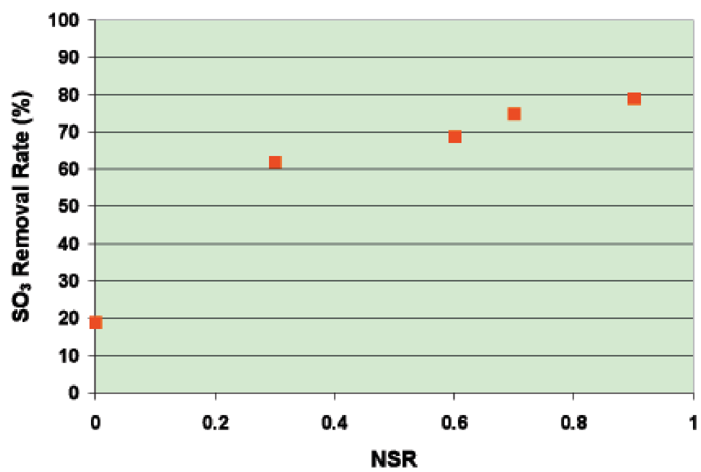
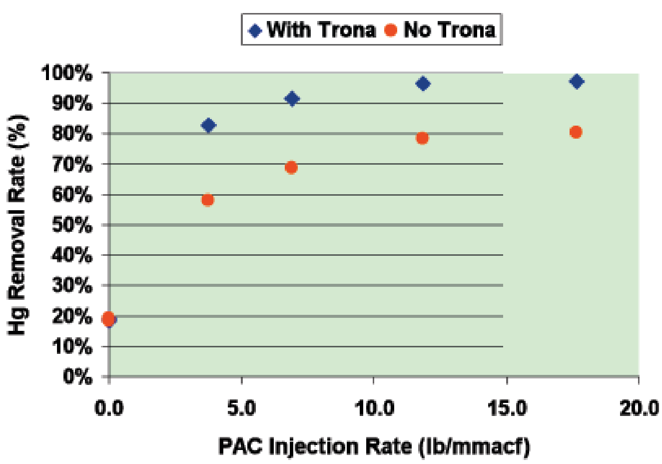


Figure 8



much lower than SO_2, high efficiency removal (i.e. > 95%) requires good mixing between trona and flue gas. In other words, the SO_3 removal efficiency is limited by the mass transfer, not the reactivity between SO_3 and trona.

Sodium bicarbonate is as reactive with SO_3 as trona. However, since sodium bicarbonate is also very reactive with SO_2, some injected sodium bicarbonate can be consumed in reacting with SO_2, which could result in higher operation cost if SO_2 is to be mitigated with other lower-cost methods.

(c) Mercury

As noted earlier, SO3 in flue gas can adsorb onto the fly ash and injected activated carbon, thus in competition with mercury for the active adsorption sites. Therefore, injecting trona to remove SO3 will greatly enhance mercury removal by fly ash and activated carbon. Figure 8 shows the effect of trona injection on the mercury removal by Powdered Activated Carbon (PAC). It was a 340 MW boiler with SCR and cold-side ESP. Trona was injected before the air preheater and powdered activated carbon was injected between the air preheater and ESP. Without trona, no more than 80% of the mercury was removed even at very high PAC feedrates. With trona injection at a NSR of 0.1 (based on SO2), high mercury removal rates (> 90%) were achieved even at low PAC feedrates. The SO3 at the SCR outlet was around 3 ppm. After trona injection, there was no measurable SO3, which was the key to the high mercury removal.

(d) HCl and HF

Trona and sodium bicarbonate are also very reactive with HCl and HF. Table 1 shows the HCl and HF removal performance of trona and sodium bicarbonate where the sorbent was injected upstream of the air preheater of a 100 MW coal-fired boiler. Around 98% of HCl and HF can be removed by injection of trona or sodium bicarbonate.

In addition to mitigating air pollutants, sodium sorbents are able to improve the performance of electrostatic precipitators. Some fly ash has high resistivity, which makes the capture of fine particulate material difficult with electrostatic precipitators. Injection of low-cost sodium sorbent, such as trona, is able to lower the resistivity of fly ash, and consequently improve the performance of ESP.

Conclusion

The high removal efficiencies of SO_2, SO_3, HCl and HF with trona and sodium bicarbonate have been demonstrated at many power plants over the last 20 years. Its low capital cost makes dry sorbent injection even more attractive in today's difficult economic environment. EE