C
oal-fired boilers in the utility power plants or process industry emit air pollutants, such as SO₂, SO₃, hydrochloric acid (HCl), hydrofluoric acid (HF) and Mercury. Ever stricter environmental regulations around the world demand efficient removal of these air pollutants.

One popular SO₂ 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 SO₂ 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 SO₃ 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, a fine powder, such as trona (Na₂CO₃ • NaHCO₃ • 2H₂O) or sodium bicarbonate (NaHCO₃), is injected into the flue gas duct. After injection, either sodium sorbent is calcined into porous sodium carbonate (Na₂CO₃), which reacts with acid gases, such as SO₂, SO₃, HCl and HF. The resulting products (Na₂SO₄, 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.

In a dry sorbent injection (DSI) system, a fine powder, such as trona (Na₂CO₃ • NaHCO₃ • 2H₂O) or sodium bicarbonate (NaHCO₃), is injected into the flue gas duct. After injection, either sodium sorbent is calcined into porous sodium carbonate (Na₂CO₃), which reacts with acid gases, such as SO₂, SO₃, HCl and HF. The resulting products (Na₂SO₄, 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.

Dry Injection of Sodium Sorbents for Air Pollution Control

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After being injected into hot flue gas (> 275°F), sodium bicarbonate or trona is calcined into sodium carbonate (Na₂CO₃), as shown in the following equations:

- 2NaHCO₃ → Na₂CO₃ + H₂O (gas) + CO₂(gas)
- 2Na₂CO₃·NaHCO₃·2H₂O → 3Na₂CO₃ + 5H₂O (gas) + CO₂(gas)

The release of water vapor and CO₂ 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 m²/g. This relatively high surface area enables fast reactions between sodium carbonate and acid gases, such as SO₂, SO₃, 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:

- Na₂CO₃ + SO₂ + 1/2 O₂ → Na₂SO₄ + CO₂
- Na₂CO₃ + SO₃ → Na₂SO₄ + CO₂
- Na₂CO₃ + 2HCl → 2NaCl + H₂O + CO₂
- Na₂CO₃ + 2HF → 2NaF + H₂O + CO₂

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 bicarbonate is produced in several locations in the US and its typical physical properties are:
- d₅₀: ~ 110 µm
- d₉₀: ~ 250 µm
- Bulk density: 68 lb/ft³

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.

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 d₅₀=12 µm and d₉₀= 30 µm.

Both trona and sodium bicarbonate are effective in removing SO₂, SO₃, 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:

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\text{NSR} = \frac{\text{Feedrate of Sorbent}}{\text{Feedrate of Acid Gas}}
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A GOOD ALTERNATIVE AIR POLLUTION CONTROL TECHNOLOGY IS DRY INJECTION OF SODIUM SORBENTS (TRONA OR SODIUM BICARBONATE).
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, SO₃ can cause the following problems:

• Formation of ammonium bisulfate (ABS) in the SCR system. Depending on its concentration, SO₃ can also react with NH₃ 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. SO₃ and ammonia (NH₃) will react to form ABS in the air heater if SO₃ is present in molar concentration in excess of the molar concentration of NH₃ 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 SO₃ dew point and acid condensation occurs. The SO₃ dew point increases with SO₃ concentration.

• Increased corrosion to the downstream equipment.

(b) SO₃

The vast majority of sulfur in coal is oxidized into SO₂ during combustion but a small portion – typically 1% to 2% – is further oxidized to sulfur trioxide (SO₃) in the boiler. If there is a SCR system for NOₓ control, a small fraction of SO₂ is oxidized to SO₃ by the SCR catalyst. The amount of SO₂ 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 SO₃, it can remove only some of the SO₃. Typically, the amount of SO₃ 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.

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Trona is very reactive with SO₃. At one power plant, trona was injected between the air preheater and ESP. The SO₃ was measured upstream of the trona injection ports and downstream of the ESP. Figure 7 shows one example of SO₃ removal performance with trona. Since the SO₃ concentration is
much lower than SO₂, high efficiency removal (i.e. > 95%) requires good mixing between trona and flue gas. In other words, the SO₃ removal efficiency is limited by the mass transfer, not the reactivity between SO₃ and trona.

Sodium bicarbonate is as reactive with SO₃ as trona. However, since sodium bicarbonate is also very reactive with SO₂, some injected sodium bicarbonate can be consumed in reacting with SO₂, which could result in higher operation cost if SO₂ 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 SO₂, SO₃, 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.