

SO₃ Mitigation Technologies or Sorbents, Carbon Burn Out and impacts upon Fly Ash

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Utilities and operators of power plant and industrial boilers face challenges associated with implementing current and future regulations. In recent years, there has been increasing public and government concern over the environmental impact of nitrogen oxides (NO_x) emissions. In order to meet the new NO_x emission requirements, many utilities install pollution control equipment, using a combination of combustion management and post-combustion processes. Unintended consequences associated with the installation of pollution control equipment have surfaced.

Two approaches are typically used for the control of NO_x emissions. These are combustion tuning and post combustion treatment of flue gas. Combustion tuning techniques include low NO_x burners, over-fired air systems, reburning, and flue gas recirculation. Post combustion treatments include, but are not limited to, Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR). SCR and SNCR chemically reduce NO_x to nitrogen and water.

While ammonia has been used successfully to reduce nitrogen oxide emissions, the ammonia is typically introduced in excess of the reaction requirement and is not totally consumed. These fugitive ammonia emissions are called ammonia slip. SCR systems typically operate with ammonia slip values in the stack gas in the 5 ppm range while SNCR systems operate considerably higher. Ammonia slip can be expected to vary widely depending on changes in operating conditions. Some of the slip reports to the gas stream and some to the combustion by-products. Therefore, residues from the combustion process such as fly ash and other combustion by-products will contain ammonia and/or ammonia compounds, such as ammonium sulfate, ammonium bisulfate, ammonium chloride, ammonium hydroxide and ammonium carbonate.

Ammonia slip results in a significant portion of the ammonia compounds being deposited on fly ash. Because the fly ash has much lower mass than the stack gas, the concentration of these compounds is much higher (in the range of 50-100 ppm for SCR and up to about 1000 ppm for SNCR). As more post combustion NO_x control systems are placed in operation, increasing amounts of fly ash will contain ammonia.

Requirements for reduction of emissions from coal combustion have often resulted in the coupling of two or more pollution control devices. For example, SCR for reduction of NO_x is combined with flue gas desulfurization (FGD or “scrubbers”) for reduction of sulfur dioxide emissions. The coupling of these two devices has resulted in the unintended consequence of increasing the SO₃ emissions of the host utility.

During coal combustion, the majority of sulfur in the coal is converted to SO₂, with a small percentage of that being further oxidized to SO₃. The use of SCR for the control of NO_x emissions directs the hot SO₂ laden flue gas through the SCR system. The vanadium containing catalyst commonly associated with SCR systems also serves as a catalyst for the oxidation of SO₂ to SO₃. This results in a significant portion of the SO₂ in the flue gas being oxidized to SO₃. Higher sulfur fuel produces higher SO₂ concentrations in the flue gas thereby increasing the SO₃ emissions potentially emitted in this scenario.

Before the SO₃ containing flue gas is released into the atmosphere, the flue gas may pass through a FGD system. However, the SO₃ capture efficiency of FGD systems is low. This results in emissions of SO₃, the precursor of “Blue Plume”. Blue Plume is formed when SO₃ is converted to sulfuric acid (H₂SO₄) mist. Sulfuric acid is formed as SO₃ aerosols cool as they enter the atmosphere and combine with moisture from the ambient environment. Because H₂SO₄ within a plume, flowing from a stack, is heavier than air, the plume’s direction, which was previously upward, changes to an undesirable lateral, or even downward, direction. The visible effect of this phenomena is referred to as “Blue Plume.” Thus, while SCR reduces NO_x emissions, it may increase SO₃ emissions.

There are multiple approaches to reduce the SO₃. In general, they involve addition of a sorbent that captures the SO₃ in a compound that is (or becomes) a solid. These solid compounds become part of, and are captured with, the fly ash. Our involvement has been limited to determining the impact of whatever additive is used to reduce the SO₃ on the ash when used in conjunction with a particular proprietary beneficiation system known as Carbon Burn Out (CBO).

Currently there are several types of reagents being proposed or used for SO₃ control in power plant exhaust streams: Magnesium Oxide, Trona, Sodium Carbonate, Sodium bisulfite, Hydrated Lime and ammonia. Our testing included three(3) of the main types of reagents being proposed for SO₃ control are: ammonia (at much higher concentrations than used for NO_x treatment), hydrated lime (which is calcium hydroxide – Ca(OH)₂) and Trona (a naturally occurring Hydrated Sodium BiCarbonate Carbonate).

The following table briefly describes: the additive being used, its impact on the CBO process, its potential impact on product ash and measurements of its actual impact on CBO processed ash being used as a partial replacement for Portland Cement.

Table 1. SO₃ Mitigation Technologies

Additive	Amount Tested (% by weight)	Impact on CBO	Potential Impact on Product Ash	Impact on fly ash as a Portland Cement replacement			
				CBO product ash		Testing / Specifications	
				ASTM C618	ASTM C441	ASTM C618	ASTM C441
Ammonia	5000 ppm	None	Residue of Ammonia compounds and strong odor	NH ₃ decomposes, no impact on product ash		75% min.	100% max.
Ca(OH)₂	control @ ~ 3.75%	None	Increase in ASR, increase in available	82%	19%	75% min.	100% max.
	control + ~ 0.5%			87%	32%	75% min.	100% max.

	control + ~ 1.5%	Readjustment of normal operating parameter required	alkalies	82%	20%	75% min.	100% max.
TRONA	0.0%	None	Increase in ASR, increase in available alkalies	77%	20%	75% min.	100% max.
	4.8%			71%	28%	75% min.	100% max.
	8.0%			74%	29%	75% min.	100% max.

Fly ash samples including varying quantities of the three additives were processed in a series of tests in a CBO pilot module for Table 1. Trona and Hydrated Lime ($\text{Ca}(\text{OH})_2$) tests were performed using fly ash feed stock samples from actual power plant combustion by-products using the Trona and $\text{Ca}(\text{OH})_2$ injection. The ammonia samples were generated by adding reagent grade material to existing fly ash prior to CBO processing. This was necessary because no fly ash containing the required quantities of ammoniated compounds was available from operating power plants. Note that ammonia is injected into the flue gas stream for SO_3 control, but ends up predominately as ammonium sulfate. Therefore, the testing was performed by adding reagent grade ammonium sulfate to the fly ash feed stock to simulate actual treated ash.

Ammonia slip results in a significant portion of the ammonia compounds being deposited on fly ash, primarily as ammonium sulfate, and can be expected to vary widely depending on changes in operating conditions. Ammonia compound testing was performed by applying ammonium sulfate equivalent to approximately 5000 ppm ammonia, to a fly ash feedstock for CBO processing. An amount of 5000 ppm ammonia was determined to correspond to the maximum expected concentrations of ammonia on the fly ash. These ammoniated compounds had no effect on the CBO process. As reported in previous papers, the ammonia thermally decomposes during processing leaving no evidence of ammonia on the CBO product ash and thus no adverse impact on the fly ash ability to serve as a replacement for Portland Cement.

Fly ash with three different injection rates of calcium Hydroxide ($\text{Ca}(\text{OH})_2$), also known as Hydrated Lime, was tested.

- ❖ Control @ ~ 3.75% CaO – the control ash sample was processed without any lime addition but was noted to have an above average CaO level of approximately 3.75%. (Note that $\text{Ca}(\text{OH})_2$ is reported as CaO equivalent in mineral analyses).
- ❖ Control + ~ 0.5% - the lowest lime injection rate resulting in an increase of the final CaO measurement by approximately 0.5%.
- ❖ Control + ~ 1.5% - the highest lime injection rate resulting in an increase of the final CaO measurement by approximately 1.50%.

No impact was noted for the CBO processing of ash with $\text{Ca}(\text{OH})_2$ at levels that resulted in concentrations below approximately 4.25% CaO equivalent. At the highest level of lime injection, approximately 5.25% CaO, a minor adjustment of the normal operating parameters was required to process the ash. The $\text{Ca}(\text{OH})_2$ addition did not adversely impact the final product ash as seen above in the Table 1.

The remaining tests involved a Sodium based product. Trona, also known as Hydrated Sodium BiCarbonate Carbonate, was also tested at three different concentrations.

- ❖ 0% – Control sample with no Trona .
- ❖ 4.8% – approximately 4.8% Trona by weight.
- ❖ 8.0% – approximately 8.0% Trona by weight.

No impact was noted on CBO processing, even at the highest level of Trona. However, it appears that Trona does have some impact on the product ash and its ability to be a partial replacement for Portland Cement. As seen in Table 1, borderline strength activity index results may occur even at low concentrations of Trona. Surprisingly, no evidence of alkali problems such as ASR was noted.

The Trona results were somewhat surprising. First, there was some concern that the sodium, being a low melting element would cause problems in the CBO process similar to the well known coal fired boiler slagging problems with high sodium coals. However, the expected product of reaction of trona with SO₃ is sodium sulfate (Na₂SO₄). This compound has a melting temperature of over 1,600°f and no problems were seen in the CBO process. Second, since the sodium sulfate product of trona is quite soluble, there was concern that Alkali Silica Reaction (ASR) problems would result. The ASTM C-441 expansion tests shown in Table 1 did not indicate such problems.