High Activity Magnesia Use for SCR Related SO_3 Problems

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Summary

Magnesia as a fuel oil additive and flue gas additive has long been used for ash modification and SO_3 scavenging to allow more efficient boiler operation at lower exit flue gas temperatures allowed by reduced acid dew point. This paper presents additional advantages for magnesium compounds to provide efficient back end SO_3 control and ash modification to counter several detrimental side effects associated with selective catalytic reduction (SCR) technology in oil and coal fired furnaces.

Historically fuel oil and flue gas additives have been used by power plants to treat or prevent a combination of combustion and flue gas related problems. Magnesia based fuel oil additives have been used for more than twenty five years to protect against high temperature corrosion from sodium-vanadium complexes, to minimize SO_2 conversion to SO_3 due to vanadium's catalytic effect, to improve ash friability, and to reduce cold end corrosion resulting from sulfuric acid condensation. Likewise, magnesium oxide (MgO) powder was used as a flue gas additive to reduce stack gas plume opacity and protect against back end corrosion resulting from SO_3 formed with the higher sulfur content coals and oil burned during the 1980's. Combining good combustion operation along with the proper magnesia additive and application has been proven to improve thermal efficiency while also providing benefits of reduced corrosion, prolonged boiler campaign with reduced maintenance costs and reduced stack gas plume opacity resulting from sulfur trioxide emissions.

The use of Selective Catalytic Reduction (SCR) technology to meet mandated NO_X emissions is expected to increase the SO_3 related opacity problems at both coal and oil fired power plants in the near future. Several recent SCR start-ups have already confirmed these troublesome consequences. SCR technology, designed to reduce NO_X emission in the presence of ammonia, also increases the conversion of SO_2 to SO_3 in the flue gas. Depending on the fuel type and operating conditions, nearly all the sulfur present in the fuel forms SO_2 during combustion. Some of this SO_2 is converted to SO_3 as the flue gas travels from the furnace to the exhaust stack. Typically about 1.0 % of the SO_2 is converted to SO_3 following combustion. The SCR however, depending on design, can contribute up to an additional 2% conversion of SO_2 to SO_3. This can easily double or triple the total SO_3 concentrations exiting a SCR unit. The SO_3 vapor combined with water vapor in the flue gas readily converts to gaseous sulfuric acid. As gas and surface temperatures cool through the system these vapors form a fine aerosol mist of sulfuric acid. The sub-micron particles of this acid aerosol often evade separation or capture in gas cleaning devices and exit the stack. Despite relatively low acid or SO_3 concentrations exiting the stack, the light scattering properties of these fine particles can easily create a visible plume and high opacity reading. It is generally accepted that every 1 ppm-v SO_3 will contribute 1 to 3 % opacity making exhaust gas concentrations of 10-15 ppm-v SO_3 or higher likely conditions for opacity and acid plume problems. In addition, deposition or formation of acid on any metal surfaces below the acid dew point causes corrosion within the unit. This can be a common problem at the air heater depending on operating temperatures and the flue gas's acid dew point. As more of these conditions develop, injection of magnesium oxide powder into the flue gas stream is again being evaluated and used to control SO_3 problems similar to those encountered with higher sulfur content fuels of the past. High activity magnesium oxide's proven performance at scrubbing SO_3 from flue gas provides an efficient means to reduce SO_3 emission levels to pre-SCR conditions.

Not only can high activity magnesium oxide be used to treat opacity and acid plume problems created or aggravated by SCR units on line, it should also be considered to protect against chemical poisoning or blinding of the catalyst and to reduce corrosion and fouling. Benefits for this application of high activity magnesia can provide catalyst protection and less frequent and easier cleanup of downstream equipment. Sulfur trioxide not only contributes to opacity and acid problems noted, but it also reacts with ammonia (injected at SCR) and water vapor to form ammonium bisulfate (1) and ammonium sulfate (2).

$$(1) \quad NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$$

$$(2) \quad 2NH_3 + SO_3 + H_20 \rightarrow (NH_4)_2SO_4$$

Both of these ammonia salts can cause fouling and corrosion problems in the system. Ammonium bisulfate has a melting point at 297 °F and ammonium sulfate at 455 °F, making them molten or tacky at typical SCR and air heater operating temperatures. Coating and fouling of the air heater and even the catalyst can result. Corrosion from these deposits will also be an issue since ammonium bisulfate has an acid pH (2% wt. solution measures < 1.4 pH).

Lime (CaO) has been considered as an additive to treat the reaction by products. However, lime reacts with the ammonia salts to form gypsum

$$CaO + NH_4HSO_4 \rightarrow CaSO_4 \cdot 2H_2O$$

The gypsum formed creates similar fouling problems for the air heater and potential poisoning problems for the catalyst. Gypsum forms a hard, non-friable deposit with very low solubility (2 g/l) that is difficult to remove or wash clean.

Using magnesium oxide as an additive to the flue gas provides a remedy for these problems. Magnesium oxide not only captures SO_3 from the flue gas to form magnesium sulfate but also reacts with the ammonia salts to form ammonium magnesium sulfate.

$$MgO + 2NH_4HSO_4 \rightarrow (NH_4)_2Mg(SO_4)_2 + H_2O$$

$$MgO + SO_3 \rightarrow MgSO_4$$

The ammonium magnesium sulfate formed is friable and has a melting point at 750 °F. These properties in the ash not only make deposits less likely, but also make removal easier and more feasible with conventional soot blowers and sonic horns. Unlike gypsum, ammonium magnesium sulfate is very soluble (160 g/l) making it easy to remove by water washing. Unlike ammonium bisulfate's corrosive characteristic, ammonium magnesium sulfate is non-corrosive (2% wt solution measures 9 pH). Magnesium sulfate is also non-corrosive, water soluble, and easily cleaned.

In summary, magnesia compounds are again emerging as back end additives to the flue gas to treat new problems that have developed from the use of SCR technology. Back end injection of high activity magnesium oxide powder (UtiliMag 40) has been demonstrated to efficiently reduce SO_3 emissions by more than 85%, to maintain visual opacity below 5%, and provide stack opacity control to pre-SCR operating levels. Additionally, magnesium oxide in the presence of sulfur trioxide and ammonia has been documented to form ammonium magnesium sulfate, a friable, water soluble, non-corrosive salt that is easier to clean and less prone to ash build up and blockage. Magnesium oxide injection can provide an effective and efficient method to treat SO_3 related issues as more SCR units are put in service in the industry. Benefits from this magnesia application will assure prolonged unit life, corrosion prevention, reduced maintenance costs, and control of stack gas plume opacity.