

# Dual Flue Gas Conditioning Processes, Technology and Experience

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## 1 FOREWORD

Altering the flue gas environment through gaseous additives (flue gas conditioning or FGC) is a common technique to improve ESP performance. The deposition of layers of liquid on the surfaces of fly ash particles is the most common mechanism for altering the behavior of these particles during precipitation [1].

Over the years, SO<sub>3</sub> flue gas conditioning (FGC), without a doubt demonstrated its ability to modify the fly ash resistivity via surface conductivity modification. On the other hand, Dr. Dismukes clearly demonstrated that fly ash shows no significant change in resistivity as a result of ammonia conditioning<sup>[2]</sup>. However, it does improve the efficiency of fly ash precipitation through two mechanisms, the first consisting of a space-charge effect and the second involving an increase in the cohesiveness of fly ash.

In fact, ammonia works as a scavenger, hunting down each free molecule of the SO<sub>3</sub> and/or H<sub>2</sub>SO<sub>4</sub> producing several ammonium salts. Consequently, the reaction of ammonia with sulfur trioxide to produce ammonium sulfate or ammonium bisulfate appears to have been a key event in the occurrence of either type of conditioning process.

Ammonium bisulfate, generated on fly ash particle surfaces during conditioning with ammonia in the presence of SO<sub>3</sub>, has been shown to be effective in field applications for reducing resistivity and for increasing cohesivity. The effectiveness of this compound for increasing cohesivity is linked to the fact that it melts at 146.67°C (296°F). Since it may exist as a liquid at the flue gas temperatures encountered in many particle control devices, it can collect at the contact points between particles through capillary action. When this occurs, liquid bridges are formed between adjacent particles. These liquid bridges form strong bonds between particles and significantly increase the bulk cohesivity of the ash. This is the most common mechanism for increasing ash cohesivity. Water adsorbed from the flue gas can also form these liquid bridges.

Since fly ash resistivity and cohesivity are among key parameters in determining electrostatic precipitators (ESP) performance, the Dual FGC, which had been defined as

simultaneous but independent injection of ammonia and  $\text{SO}_3$  presents the best way to influence these key parameters.

## 2 $\text{SO}_3$ FLUE GAS CONDITIONING

By far the largest body of work in the art of flue gas conditioning ash has been devoted in lowering the dust resistivity<sup>[12,3,4,6,7,8,9,11,12,]</sup>. Conditioning is as old as the art of precipitation itself. As early as 1912, it was discovered that copper converter dust precipitation was considerably enhanced by the presence of sulfur trioxide or increased moisture of exhaust gases.

Acceptance of the process called flue gas conditioning (FGC) as an engineering solution to a common environmental problem has come slowly. To start with, the process is misnamed. It is not the gas which is conditioned, but the particles of dust in the gas, or in the most common application, the fly ash. Adjusting the resistivity of fly ash particles by application of a dilute acid solution to their surfaces is an easily understood and straightforward task. The very idea that the behavior of a gas stream might be adjusted in any useful way by addition of a few parts per million of a reagent boggles the mind.

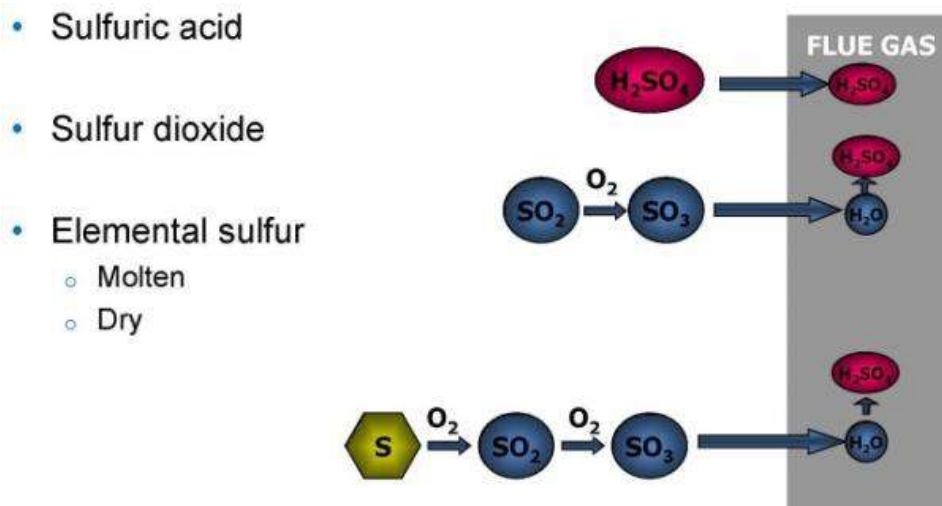


Figure 1.  $\text{SO}_3$  Flue Gas Conditioning

In spite of an inappropriate name and some bungled efforts, early trials of FGC showed benefits which justified continued experimentation, and encounters with several dozens of ways of doing it wrong eventually developed a set of reliable rules for doing it right. One result is that use of sulfur trioxide ( $\text{SO}_3$ ) for adjustment of the resistivity of fly ash from low sulfur coal has been widely applied and became an accepted part of the option of switching to low sulfur coal for compliance with the mandated  $\text{SO}_2$  emissions reduction regulations.

Sulfur occurs in coal as organic and inorganic compounds. When coal is burned, more than 95% of the sulfur becomes  $\text{SO}_2$ . A small fraction is converted to gaseous  $\text{SO}_3$ . When the flue gas temperature drops below approximately 600°F (316°C),  $\text{SO}_3$  begins to react with water vapor to produce sulfuric acid vapor. The reaction is essentially complete when the temperature drops to about 300° - 350°F (149°-177°C), where precipitators normally operate.

Thus, in a strict sense, conditioning results from sulfuric acid vapor ( $H_2SO_4$ ), rather than  $SO_3$  being absorbed onto the surface of the fly ash particles (Figure 1).

$SO_3$  may come from two sources: (a) combustion, i.e. native or indigenous conversion of the  $SO_2$  formed during the combustion of the sulfur contained in the coal to  $SO_3$  and (b) as the  $SO_3$  flue gas conditioning (FGC), which is  $SO_3$ /air mixture injected to assist in electrostatic precipitators (ESP) performance enhancement.

## 2.1 INDIGENOUS $SO_3$ FGC

$SO_3$  content has a significant impact on particle resistivity, which is one of the most important parameters in ESP collection efficiency. For high resistivity ashes,  $SO_3$  reduces the back corona phenomena. However,  $SO_3$  is also the source of the sub-micron particles, and the source of higher opacity level at the stack through the production of  $H_2SO_4$ . Typically,  $SO_3$  is generated inside of the boiler as well as the SCR process, but the  $SO_3$  quantity in the flue gas changes along the path from the furnace to the stack<sup>[1]</sup>.  $SO_3$  concentration is modified from the boiler to the ESP: in the SCR if present, and in the regenerative air preheater.

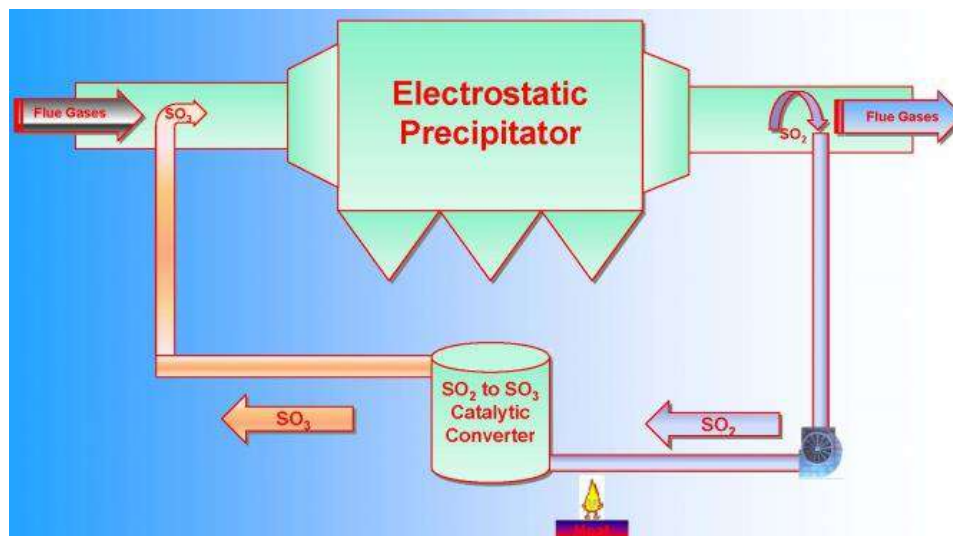


Figure 2. Indigenous Flue Gas Conditioning (iCON®) - Conceptual Schematic

Another approach to creating  $SO_3$  is to utilize "native"  $SO_2$  formed during combustion of sulfur contained in fossil fuels as a feedstock for its subsequent conversion to  $SO_3$ . Extensive experiments at Lehigh University<sup>[14]</sup> confirmed that, at conditions typical for coal-fired applications, a substantial portion of the "native"  $SO_2$  could be oxidized to  $SO_3$ . The rate of such process will depend on the temperature; the concentrations of  $SO_2$ ,  $O_2$  and water vapors; as well as catalyst's properties. Systems implementing this technique have been proposed, but none were free of major deficiencies<sup>[23,24,25]</sup>.

The Indigenous Flue Gas Conditioning (iCON®) concept<sup>[26]</sup> (Figure 2) consist of withdrawing a portion of the clean flue gases containing sulfur dioxide ( $SO_2$ ) generated by a combustion process from a location downstream of the electrostatic precipitator (FGC process carrier gas flow), preheating process carrier gases, passing the process carrier gases through the catalyst bed where a portion of the  $SO_2$  is converted into sulfur trioxide ( $SO_3$ ), and returning the carrier gases with the additional  $SO_3$  to a location ahead of the electrostatic

precipitator. The process of generating the SO<sub>3</sub> for the FGC and subsequent carrier gases delivery, distribution and mixing is very simple and straightforward.

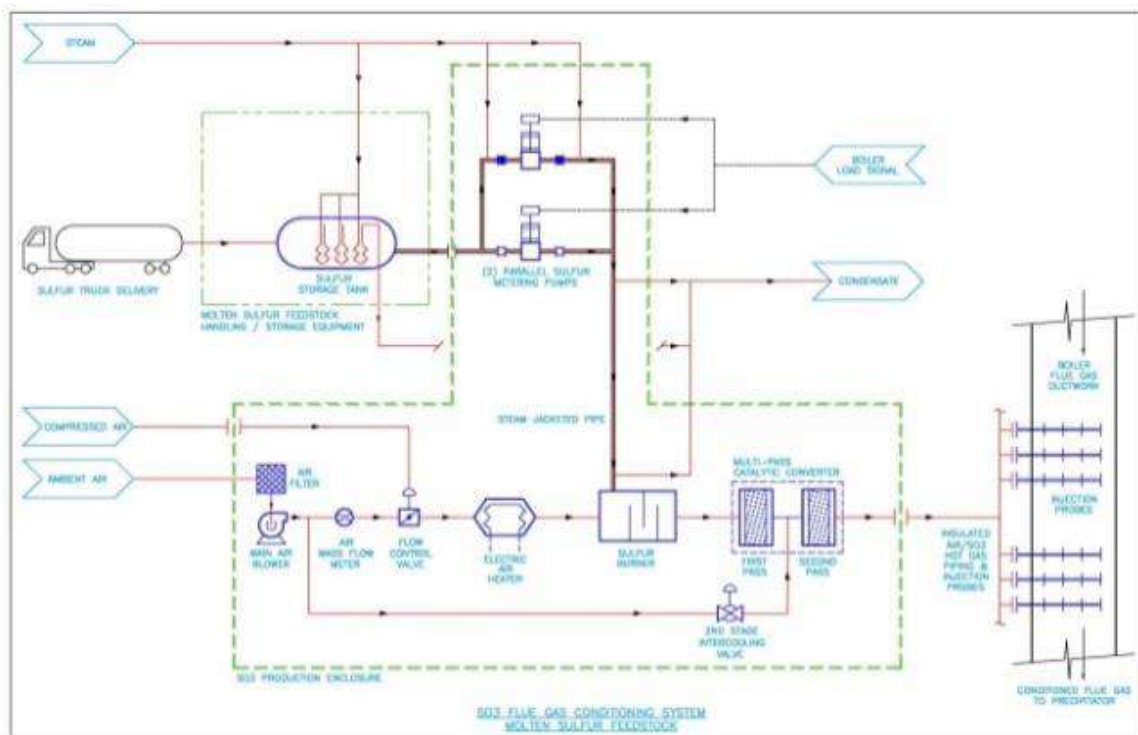
## 2.2 SO<sub>3</sub> FLUE GAS CONDITIONING

With very few exceptions, all commercial SO<sub>3</sub> FGC systems installed to date are based on catalytic conversion of sulfur dioxide (SO<sub>2</sub>) which is either supplied in molten form or obtained by burning dry granular sulfur<sup>[11,12]</sup>. Elemental molten sulfur used to be the preferred feedstock for long-term permanent operations due to its low operating costs. However, it has recently been surpassed by the systems based on the use of granular (pelletized) dry sulfur. This shift towards the use of granular dry sulfur has been primarily due to the inability of the end users to provide molten sulfur feedstock.

The catalytic conversion process was chosen over other methods of making SO<sub>3</sub> largely due to the fact that it minimizes the quantity and the difficulty of handling hazardous materials in the system.

### 2.2.1 Molten Sulfur Feedstock

Elemental molten sulfur is the preferred feedstock for long-term permanent operation because of lower operating cost, however, liquid SO<sub>2</sub> may be used for trials and small or short-term situations where reduced capital costs can offset increased feedstock expense.



**Figure 3. Molten Sulfur Based SO<sub>3</sub> FGC System.**

The sulfur feedstock system handles the storage and delivery of molten sulfur. Molten sulfur is stored in an elevated steam heated storage vessel. The tank is elevated to create flooded conditions for the suction side of the sulfur metering pumps. The sulfur is metered

via positive displacement metering pumps and is transported in steam jacketed piping to the sulfur burner for combustion.

Figure 3 is a diagrammatic representation of a molten sulfur-burning system for SO<sub>3</sub> conditioning. Molten sulfur is delivered by thermally insulated tank trucks fitted with steam coils for melt-out. In locations where sulfur cannot be delivered in molten form, bagged or bulk granular or prill sulfur may be supplied for melting on site. The sulfur grade is designated as "Bright Yellow" which contains very low levels of contaminating materials. The exact analysis varies slightly among suppliers, however it completely lacks chemicals, which could act as catalyst poisons and contains only very minute quantities of hydrocarbons. Storage in insulated steel tanks with steam-blanketing provisions for fire suppression is standard, but concrete-lined pits have been used with poor results. Tanks and molten sulfur piping are heated by steam controlled to a saturation temperature of approximately 143 °C (290 F) at which the sulfur has ideal flow characteristics. Steam tracing is preferred because of the ease with which controllable highly uniform temperatures can be maintained throughout the system. Typically, sulfur metering pumps are supplied in duplicate so that one may be serviced while the other is in operation.

Combustion of the sulfur to generate SO<sub>2</sub> is realized by introducing sulfur into an air stream which has been preheated for startup purposes to the temperature at which the catalyst becomes active. Since this temperature exceeds the auto-ignition point of molten sulfur, burning is initiated immediately upon the introduction of sulfur and SO<sub>2</sub> is delivered to the catalyst for conversion to SO<sub>3</sub>. Roughly, 4,000 Btu of heat are generated per pound of sulfur burned. This replaces a portion of the startup heat input required. Typically, at full system rating all the required heat to maintain the catalyst at operating temperature is supplied by sulfur combustion. Clearly, operation of the system in this manner allows the generation of any quantity of SO<sub>3</sub> as a function of any selected control signal used to determine the rate at which sulfur is delivered.

### 2.2.2 Dry Sulfur Feedstock Technology (Molten Sulfur on Demand)

Dry sulfur configuration (Figure 4) combines the advantages of dry sulfur storage with the precision by which molten sulfur can be metered to the burner.

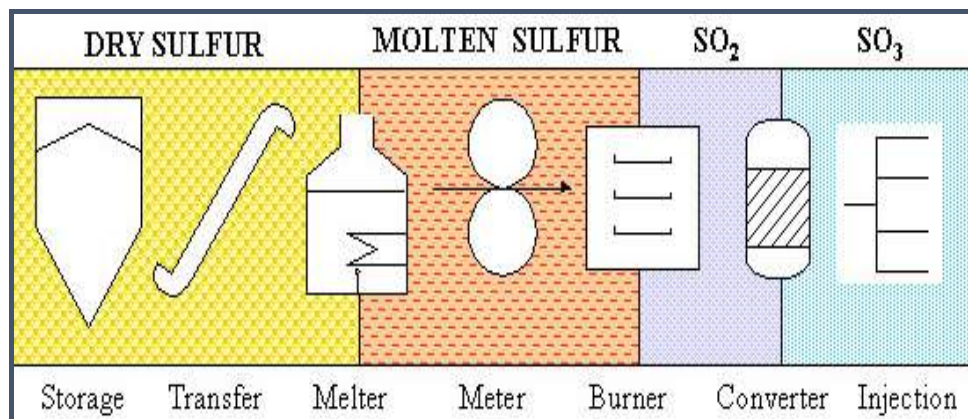


Figure 4 – Dry Sulfur Based SO<sub>3</sub> FGC Process

Sulfur is delivered in dry form and then melted for use in various processes (Figure 5). Using this tried and true proven method, dry sulfur is melted via the use of saturated steam coils (in the melter vessel) to molten sulfur for conventional process metering. This takes advantage of dry sulfur storage and handling while maintaining the good burn characteristics of molten sulfur as well as accurate and reliable metering. With the proper provisions, a permanent system could accept both dry and molten sulfur feed stock so that the process is not dependent on one source or method of sulfur delivery.

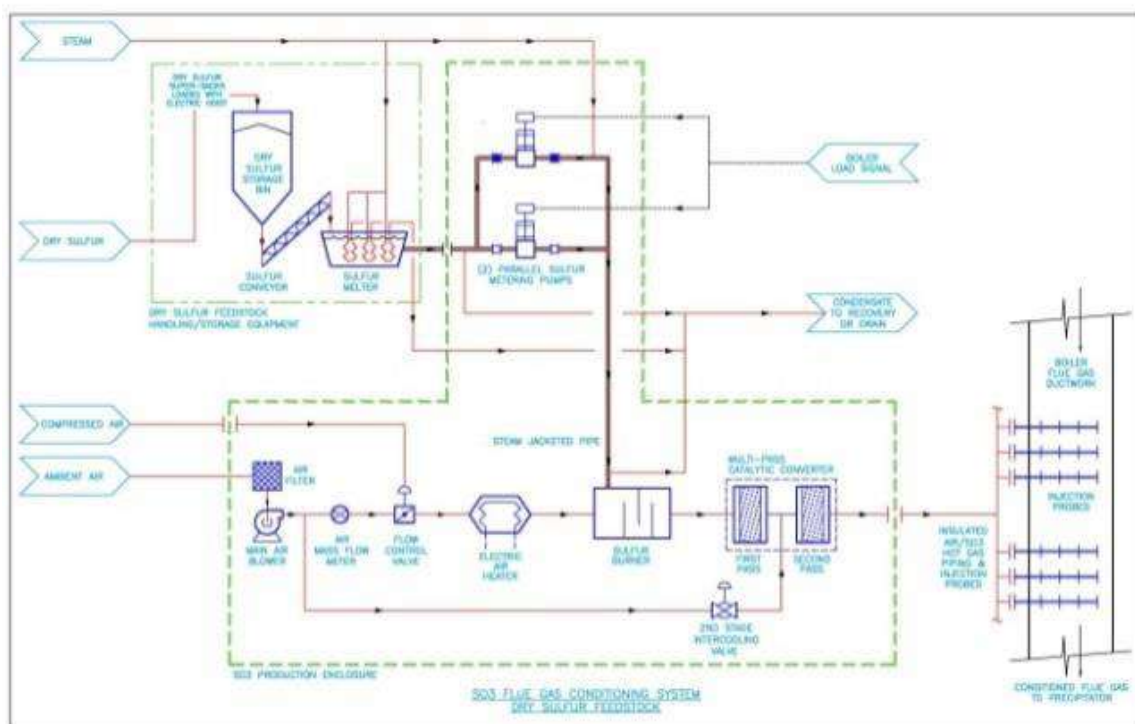


Figure 5. SO<sub>3</sub> Flue Gas Conditioning System Layout with Dry Sulfur Supply

### 2.2.3 SO<sub>2</sub> to SO<sub>3</sub> Conversion

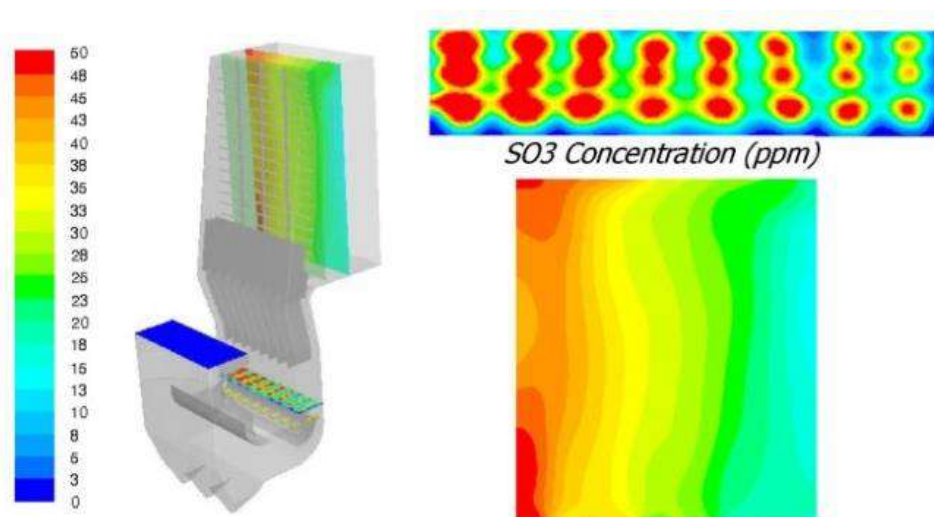
In conventional FGC systems, the catalyst for conversion of SO<sub>2</sub> to SO<sub>3</sub> is usually chosen from any of the types developed for the manufacturing of sulfuric acid and similar applications. Vanadium pentoxide is the active ingredient in these catalysts, and is classified as a hazardous material. Care should be taken to remove dust and water from the air intake to the maximum extent possible and to service the air intake filter on a regular basis.

The hot air stream containing the generated SO<sub>3</sub> exits the SO<sub>2</sub> to SO<sub>3</sub> converter at temperatures between 399 °C (750 °F) to about 538 °C (1,000 °F), depending on the production rate of SO<sub>3</sub>. It is essential that this stream be held above its acid dew point temperature throughout the delivery manifold and injection probes. If the temperature goes below the dew point, the acid will condense out in the manifold or the injection probes. This is undesirable for two reasons. First, none of the acid will reach the flue gas to do the intended conditioning job, and, secondly, the condensed acid will corrode the piping and nozzles. Since the SO<sub>3</sub> concentration is a few percent in this stream, the acid dew point will be on the order of 238 °C (460 °F), but maintaining the delivery end of the system in a condensation-free state requires that the calculated gas temperature be no less than 260 °C

(500 °F) as it exits the injection probe nozzles. As a result, the distribution manifolds are heavily insulated. In addition, the injection probes are thermally insulated as well when installed on the cold side of the air preheater.

## 2.2.4 Injection Probes or Lances

Since installation of injection probes are more easily accomplished in the ESP-type ductwork on the cold side of the air preheater compared with the boiler-type construction on the hot side, most of the present FGC installations inject on the cold side. However, it should be noted, that hot side injection probes installation has some advantages including the fact that air/SO<sub>3</sub> mixture does not approach acid condensation temperatures in the probes, and provides excellent mixing and contact between the SO<sub>3</sub> and the fly ash as it passes through the air preheater. Probes for hot side installation are less expensive than for the cold side since no thermal insulation is required and the erosion-protective outer sheathing can usually be eliminated. As far as operation is concerned, every existing hot side installation works as well as or better than equivalent cold side installations.



**Figure 6. Biased SO<sub>3</sub> Probes Design**

As more power generating stations install SNCR and SCR systems for NO<sub>x</sub> reduction the potential for NH<sub>3</sub> slip at the air heater inlet has forced suppliers to re-evaluate the cold side injection strategy. This has led to unique innovations in the use of a “dense grid” design with biased injection probes. This approach has greatly enhanced application of the injection of SO<sub>3</sub> after the air heater with much less concern to the retention time. The biased grid design has also helped mitigate any potential of mild corrosion, which may be caused by over injection of SO<sub>3</sub> on the cold side of the flue gas duct. See example of biased injection grids, Figure 6.

## 3 AMMONIA FLUE GAS CONDITIONING

The value of ammonia as a conditioning agent was reportedly discovered in 1942 in efforts to deal with high resistivity of catalyst dust in the petroleum industry<sup>[1,2,6,7,9,11]</sup>. The use of the ammonia for treating fly ash in coal-fired power plants, on the other hand, is "comparatively" new.

First reports of the *intermittently* successful use of ammonia as a conditioning agent were reported in Australia by Watson and Blecher<sup>[13]</sup> in 1966. The results of this study showed effectiveness of using the ammonia as a conditioning agent. There, the SO<sub>3</sub> flue gas conditioning was proven to be ineffective due to the highly acidic ash (pH of 3.5-4) and, thus, speculations were that conditioning with a basic, rather than acidic agent, might prove more effective.

### 3.1 PROCESS AND CHEMICAL REACTIONS

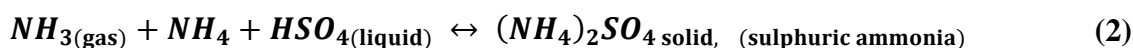
Fundamental explanations of the effects of ammonia conditioning have assumed that the chemical compounds formed when ammonia is injected, either concurrently with injection of sulfur trioxide (Dual FGC) or when the latter is formed by "natural" (combustion) processes in sufficient quantities, are ammonium bisulfate NH<sub>4</sub>HSO<sub>4</sub> or, if the stoichiometric ratio is appropriate, the normal sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub><sup>[12,6,9,11,12,13]</sup>. Besides these, the existence of intermediate chemical compounds is possible. The melting points change continuously according to the H<sub>2</sub>SO<sub>4</sub>/NH<sub>3</sub> stoichiometric ratio, and there is a possibility that compounds with very low melting points may be formed in the process. In addition, the ones which are stable in solid form at temperatures above 150 °C (300 °F) are those with stoichiometric ratios 1.2 and above.

The chemical reactions postulated by Rendle and Wildson<sup>[14]</sup> suggest that ammonia will react with any natural sulfur trioxide present and moisture to produce ammonium bisulfate (Eq. 1). In the presence of excess ammonia this reaction will slowly continue to produce ammonium sulfate (Eq. 2).

Melting point of ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>) is 146.9°C (297°F). Therefore, lacking excess ammonia or as cooling occurs the liquid ammonium bisulfate will freeze at temperatures below 147°C (297°F) into a sticky solid. It is this adherent nature of the resultant that is thought to play a major role in the precipitator performance improvement.

When flue gas temperatures are 140.9°C (284 °F), NH<sub>4</sub>HSO<sub>4</sub> will become solid. Melting points of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> are 513°C.

In the Eq. (2), (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is dissociated at higher than 200°C temperatures. When flue gas temperatures are above 200°C, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> produced will decompose into NH<sub>4</sub>HSO<sub>4</sub>. Reactions taking place in this equation are usually slower than those in equation (3).



Reactions of NH<sub>3</sub> with H<sub>2</sub>SO<sub>4</sub> are as follows:



The ammonium sulfate shown as the product of the Eq. (2) would exist as a solid in a wide range of flue gas temperatures, as indicated in the equations (2 – 3). The ammonium bisulfate shown as the product of the first Eq. (1) would exist as a liquid above 144°C (291°F)

or as a solid below this temperature; hence, the physical state is indicated in the equation as either liquid or solid. (There is some uncertainty about the temperature where ammonium bisulfate solidifies. The indicated temperature is based on the data of Kelley et al.<sup>[15]</sup> Thermodynamic information indicating that either of the two reactions can occur under flue gas conditions is also included in the data published by Kelley.)

While ammonium bisulfate has been studied extensively in the context of atmospheric aerosols, very little fundamental work has been conducted at conditions relevant to the electrostatic precipitators in coal based power generation. Since ammonium bisulfate is a sticky material, an accurate determination of its formation temperature can help accurately determine its impact on the ESP operation as well as its operational limitations<sup>[16,17,18,19]</sup>.

Wei, et al.<sup>[17]</sup> experimentally investigated the formation (i.e. condensation) temperature of ammonium bisulfate to determine how much NH<sub>3</sub> slip an air preheater can tolerate given the flue gas sulfur content and temperature.

Johnson et al.<sup>[18]</sup> noted the importance of one of, perhaps, the most important principle chemical reaction for the formation of ammonium bisulfate (Eq. 5):



Eq. (5) is important because the presence of H<sub>2</sub>SO<sub>4</sub> reduces the amount of SO<sub>3</sub> available in the flue gas to react with NH<sub>3</sub>, which tends to reduce the ammonium bisulfate formation temperature<sup>[18]</sup>. Alternatively, however, Eq. (5) can be viewed as governing the equilibrium concentrations that control whether Eq. (1) or Eq. (2) is the dominant pathway to ammonium bisulfate formation at any given temperature.

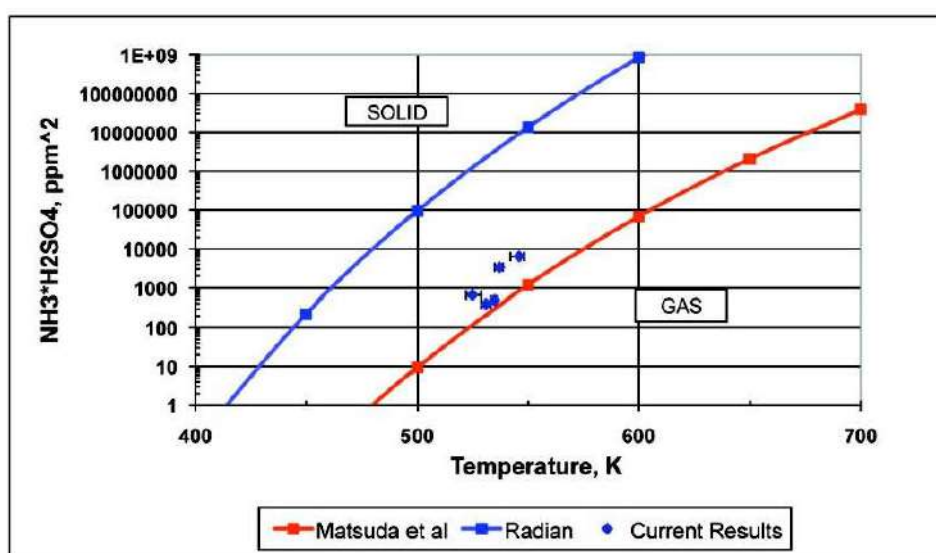


Figure 7. Reactant Concentration vs. Ammonium Bisulfate Formation Temperature<sup>[17]</sup>.

On the other hand, Matsuda, et al.<sup>[19]</sup> took an experimental approach and defined the vapor pressure of ammonium bisulfate as the product of vapor pressures of H<sub>2</sub>SO<sub>4</sub> and NH<sub>3</sub>. Essentially, this is based on Eq. (2) under the assumption that equilibrium favors H<sub>2</sub>SO<sub>4</sub> over SO<sub>3</sub> as the sulfur repository at ammonium bisulfate formation temperatures.

Figure 7 presents the experimental temperature ranges as defined by Wei et al.<sup>[17]</sup>, in addition to results from Matsuda et al. and Johnson et al. for comparison. For each reactant combination, three temperatures are marked: (i) the lower temperature at which an increase in current is recorded => left x error bar; (ii) the temperature at which the sensor current appears steady => data point; (iii) the high temperature at which a decrease in current is recorded => right x error bar.

Wei et al. concluded that in commercial practice, most operators tend to use ammonium bisulfate formation temperature close to the Johnson et al.<sup>[18]</sup> curve while catalyst manufacturers tend to use the Matsuda et al. curve to set minimum SCR operation temperatures. The Wei et al. results suggest that the ammonium bisulfate may be forming at much lower temperatures than predicted by the Johnson et al. curve.

From our point of view, one of the most important points of the Wei et al. work was that the study has shown, that SO<sub>3</sub> remains an important contributor to the ammonium bisulfate formation.

### 3.2 AMMONIA FLUE GAS CONDITIONING AND FLY ASH RESISTIVITY

Generally, the volatility of a gas can be roughly correlated with the ease of adsorption of the gas on a solid. Ammonia is highly *volatile*, having a boiling point of -33°C (-27.4°F), and its adsorption on fly ash at elevated temperatures would require high partial pressures of the gas. Moreover, adsorption of ammonia on fly ash would be greatly aided if the surface of the ash is acidic; thus in the case of Dual FGC when the occurrence of an acidic surface material is the result of the adsorption of sulfur trioxide, the resistivity of the ash had been already modified.

The reaction of ammonia with sulfur trioxide to produce ammonium sulfate or ammonium bisulfate appears to have been a key event in the occurrence of either type of conditioning process.

Dismukes<sup>[2,20]</sup> investigated concentrations of ammonia, sulfur oxides, and water vapor found at the inlets ESP fields (Table 1). In each instance, the injection of ammonia lowered the concentration of sulfur trioxide. This observation is consistent with the occurrence of increased adsorption of sulfur trioxide on the surface of the fly ash as the acid on the surface is neutralized by ammonia. It is also consistent with the reaction of ammonia and SO<sub>3</sub> (present as sulfuric acid) to produce particles of ammonium sulfate or ammonium bisulfate, as shown by the chemical Equations 1 through 4 above.

Direct measurements of resistivity were made with a point-to-plane probe in situ as described by Dr. Harry White<sup>[3,5]</sup>. Comparative values of the data obtained with ammonia injected at concentrations of 7 to 20.ppm by volume show no significant change in resistivity due to ammonia conditioning.

The pH data indicate that ammonia injection produced mildly acidic slurry, however, the samples collected during ammonia injection were less acidic than those collected without injection. The ammonia concentrations appear to confirm the postulate that ammonia was present either in the form of a discrete particulate (such as ammonium sulfate), or a surface

deposit on the fly ash. The sulfate concentrations varied randomly as changes were made in ammonia injection.

**Table 1. Concentrations of Flue Gases from a Low-Sulfur Coal.**

Precipitator	Gas temp, °C	Injected NH <sub>3</sub> concn, ppm	Concentrations			
			NH <sub>3</sub> , ppm	SO <sub>3</sub> , ppm	SO <sub>2</sub> , ppm	H <sub>2</sub> O, %
7A	138	0	0.0	2.9	617	-
			0.0	1.7	621	-
		14	1.0	0.2	556	8.1
			0.4	0.3	626	8.3
			0.0	-	-	-
7B	132	0	0.6	4.0	565	-
			-	5.0	560	-
		10	0.9	0.8	554	8.4
			0.7	0.9	549	-
			-	0.6	528	-
7B	143	0	1.4	7.2	676	-
			0.6	5.0	670	-
			0.4	5.9	543	8.9
		13	0.9	1.5	638	8.7
			0.5	1.3	679	-
			0.6	-	-	-
7B	149	0	0.5	5.1	578	9.5
			0.5	4.2	577	-
		9	0.4	1.5	578	-
			-	0.9	599	-

Therefore, the Dismuke's<sup>[2,20]</sup> experiments proved that ammonia conditioning altered the electrical properties of the flue gas rather than the fly ash resistivity.

It should be noted that Indian researches (Kumar et al.<sup>[21]</sup>) reported diametrically opposite results claiming "...a considerable reduction in the resistivity of fly ash in the temperature range between 120°C and 180°C. It was also observed that the resistivity has not shown any further reduction beyond critical amount of ammonia dosage."

### 3.3SPACE-CHARGE EFFECT

Dual FGC improves the ESP performance due to an additional space charge, which alters the electrical characteristics of the flue gas in a precipitator. Specifically, it produces a space charge enhancement of the electric field by which fly ash particles are:

- i. initially charged and collected or
- ii. recollected following rapping reentrainment.

Indeed, the most probable process by which the space-charge effect occurs is reaction of the ammonia with the sulfur trioxide and water vapor normally present in flue gas to

produce fine particles of ammonium sulfate or ammonium bisulfate and subsequent charging of the particles of reaction product in the precipitator.

### 3.3.1 Creation of Ultrafine Particles

Injection of ammonia ( $\text{NH}_3$ ) into the flue gases in the presence of  $\text{SO}_3$  results in the formation of submicron particles of ammonium sulfates.

Particle formation due to chemical reaction between  $\text{NH}_3$  and  $\text{SO}_3$  species is a complex phenomenon. When the molar ratio between  $\text{NH}_3$  and  $\text{SO}_3$  is less than 1.0, ammonium bisulfate ( $\text{HSO}_4$ ) is created which is semi-liquid at the operating temperature range, hence it promotes ash agglomeration serving a “binding” agent. However, when the molar ratio between  $\text{NH}_3$  and  $\text{SO}_3$  is more than 1.0, there is an increase in the ammonium sulfate production, resulting in the creation of fine particles.

Ultrafine particle creation is a recognized problem arising, for example, when an SCR device is added in the flue gas path.  $\text{SO}_2$  to  $\text{SO}_3$  conversion level in the SCR is indeed a guaranteed value given by SCR manufacturers in order to lower submicron particle creation as well as the opacity increase due to the presence of  $\text{SO}_3$ .

On the other hand, fine particles increase the space charge load and yield enhanced voltage-current curves in the electrostatic precipitator. However, to maintain the same level of current as existed without the fine particles, the voltage must be increased.

The NEP model simulations on a 600 MW power plant (while not limiting voltage on the power supplies), show that particle concentration at the ESP could be changed up as little as from  $13 \text{ mg/Nm}^3$  to  $15 \text{ mg/Nm}^3$ . However, although the ultrafine particles do not significantly contribute to the mass based outlet emission of an ESP they might become extremely important if stricter regulations concerning  $\text{PM}_{2.5}$  (particle smaller than 2.5 micron) would be imposed.

Sample calculations have shown that with 10 ppm of ammonia added to the flue gas, the ammonia sulfate creation is estimated to be close to  $30 \text{ mg/Nm}^3$ . This value is compared to approximately  $12,000 \text{ mg/Nm}^3$  of coal ash at the ESP inlet. Therefore, un-optimized Dual FGC (incorrect  $\text{SO}_3/\text{NH}_3$  injection stoichiometry) may produce excess submicron particles which are harder to collect, thus, in a sense, altering particle size distribution at the ESP outlet, since even such a small quantity of submicron particle could impact the ESP performance.

### 3.3.2 Experimental Validation

As discussed earlier, occurrence of the space-charge effect was suggested by the electrical behavior of the precipitators investigated. From a theoretical point of view, postulation of this effect is warranted on the basis of the available thermodynamic data for the indicated reactants and products, as published by many authors. Experimentally, the occurrence of the effect is supported not only by the precipitator electrical data but by certain additional experimental data discussed by Dismukes<sup>[2]</sup> and Dahlin et al.<sup>[9]</sup>.

**Table 2. Stack Emissions - Test Data (Low Sulfur Coal with Dual FGC)**

REAGENT/TEST No.		14-1	14-2	15-1
SO <sub>3</sub>	Injected, ppmV	17	17	17
SO <sub>3</sub>	Exiting Stack, ppmV	1.8	2	1.5
NH <sub>3</sub>	Injected, ppmV	17	17	17
NH <sub>3</sub>	Exiting Stack, ppmV	0.13	0.04	0.16

If injected ammonia were to react to produce a particulate of ammonium sulfate or bisulfate, the concentration of ammonia as a gas downstream from the plane of injection would have to be lower than the concentration injected and the concentration of SO<sub>3</sub> would have to be lower than the normal concentration of this gas. The ammonia and sulfur trioxide concentrations as tested indicate that both predictions were satisfied.

Loss of the injected ammonia from the gas stream through the formation of a particulate should lead to the appearance of ammonia as a constituent of fly ash sampled from the gas stream or from the precipitator hoppers. The latter, indicating that part of the reaction product would be electrostatically precipitated, is borne out by the results of other analytical data for fly-ash samples removed from the hoppers. An additional important finding was that the ammonium products concentration changes were smaller at the precipitator outlets than at the inlets, as expected from the analytical evidence that part of the ammonia-containing particulate was electrostatically precipitated.

Table 2 presents the stack test data measured downstream of a 525 MW unit firing low sulfur coal with the Dual FGC.

### 3.4 INCREASED COHESIVENESS OF FLY-ASH PARTICLES

Dual FGC by producing ammonium bisulfate increases the cohesiveness of fly ash particles and thus *lowers the reentrainment of ash deposited on the collection electrodes.*

#### 3.4.1 Cohesion

As discussed previously, depending on the NH<sub>3</sub> to SO<sub>3</sub> (H<sub>2</sub>SO<sub>4</sub>) stoichiometric rates, ammonia can produce low melting point substances. Low stoichiometric rates produce substances with a high tendency to absorb humidity, promoting cohesion between particles. To simplify the cohesion mechanisms, only the ammonium bisulfate is being considered. Since it has a melting point around 150°C, it is in a semi-liquid state at the typical operating temperatures of an electrostatic precipitator and therefore it acts as a particle-bonding agent. Cohesion has a positive effect on the electrostatic precipitator efficiency by:

- i. Increasing the average particle size (the larger particles are easier to collect in the electrostatic precipitator)
- ii. Reducing the re-release of particles on the plates.

To quantify the particle cohesion effect on ESP, simulation using NEP model was carried out with the same configuration described above. A 10% decrease in re-entrainment parameter reduces particle concentration at the ESP outlet from 13 mg/Nm<sup>3</sup> to approximately 10 mg/Nm<sup>3</sup>.

This effect should be of greater consequence in improving the overall collection efficiency of low resistivity ash when compared to high resistivity ash because the greater electric force across a deposit of the latter material will prevent excessive reentrainment. There were numerous types of qualitative observations indicating that an increase in cohesiveness indeed occurred.

Observations of fly ash collected in a Brink impactor indicated that conditioned ash scatters/disperses less than unconditioned ash on the impaction surfaces. Finally, photomicrographs of ash have shown that conditioned ash particles are bridged by feather-like material thought to consist of ammonium sulfate.

#### 4 DUAL FLUE GAS CONDITIONING

A Dual FGC system, by providing the independent and simultaneous injection of SO<sub>3</sub> and NH<sub>3</sub> in strictly controlled stoichiometric ratios, allows for a further collection efficiency improvement when compared to SO<sub>3</sub> injection on its own. The mechanisms responsible for improved precipitator performance appear to include phenomena such as space-charge effects, agglomeration and increased cohesiveness of the fly ash. Additionally, some evidence suggests that the injection of ammonia promotes improved attachment of the available sulfuric acid to fly ash particles, making it more effective for resistivity control.

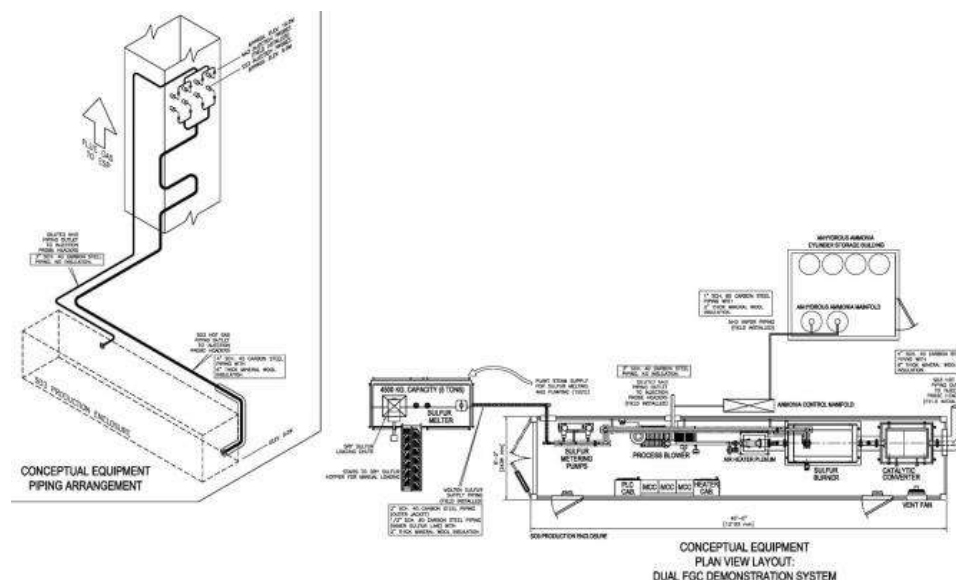


Figure 8. Dual FGC - Conceptual Equipment Layout

Generally speaking, when SO<sub>3</sub> and NH<sub>3</sub> are concurrently injected into a gas stream, a fine fume consisting of a variety of ammonium sulfate particles, all much less than 1 micron in size, is produced. These particles alter the electrical characteristics of the flue gas between the discharge electrodes and the collecting plates, and produce a space-charge enhancement of

the electric field. The higher field strength increases the overall collection efficiency of the ESP. DFGC creates a thin conductive film on the surface of the fly ash believed to consist of low melting point ammonium sulfate products which contributes to the resistivity modification. It has been suggested that the addition of ammonia improves upon the efficiency of the SO<sub>3</sub> conditioning by an additional charge carrier, the NH<sub>4</sub><sup>+</sup> ions.

Figure 8 depicts a conceptual Dual FGC system layout. When design for joint operation, both SO<sub>3</sub> and ammonia injection systems may share a number of the system components.

For example, a slipstream of process air from the SO<sub>3</sub> system blower could be used for dilution of the ammonia gas stream. An ammonia storage container, which houses the one-ton cylinders of NH<sub>3</sub> are equipped with internal racks for the stabilization of the cylinders, electric space heaters for vaporization of the NH<sub>3</sub> as well as the manifold and necessary connectors required for the vaporization and transportation of the gaseous NH<sub>3</sub> to the SO<sub>3</sub> production skid where it combines with the dilution air. The vaporized ammonia mixes with the slipstream air from the SO<sub>3</sub> process air blower. The diluted ammonia/air mixture travels through piping to the injection probes located downstream of the air preheater and upstream of the ESP. All equipment is factory assembled and incorporated into the SO<sub>3</sub> system central control cabinet, air inlet filter/silencer, and process air blower.

## 5 CASE STUDIES

### 5.1 SHENHUA ZHUNGEER POWER PLANT

Zhungeer Power Station is a 1,570-megawatt (MW) coal-fired power plant located at the suburbs of Jungar, Ordos (E'erdusi) Prefecture, Inner Mongolia Autonomous Region. The local coal is being delivered from the Zungeer mine. It is thought that Zhungeer coal ash is one of the most difficult to collect in electrostatic precipitator<sup>[36]</sup>.



Zhungeer Power Station is a four-unit coal-fired power plant with a total capacity of 1,320 MW, completed between 2002 and 2007. It is known as Zhungeer-2. The plant's first two units of 125 MW each, known as Zhungeer-1, were commissioned in 1992-1993 and retired in 2013. The units 1 and 2 are 330 MW tangentially fired boilers.

There is one (1) ESP with two (2) chambers, two (2) cells each per each unit. Each cell houses forty-seven (47) gas passages on 305 mm (12 inches nominal) centers. Each ESP has five (5) mechanical fields in the direction of the gas flow: first three fields are 3.00 m (9.85 ft.) in length and last two fields are 3.5 m (11.47 ft.) each. Collecting plates are 15.24 m (50.00 ft.) tall. The SCA is 151 m<sup>2</sup>/m<sup>3</sup>/s (767 ft<sup>2</sup>/kacfm)

Original ESP dust concentrations were 25 g/Nm<sup>3</sup> at the inlet for Unit 1 and 15 g/Nm<sup>3</sup> at the inlet for Unit 2, and 116 mg/Nm<sup>3</sup> for Unit 1 and 85 mg/Nm<sup>3</sup> for Unit 2 at outlet. Based on extensive numerical modeling, Dual FGC was proposed to improve the outlet emissions.

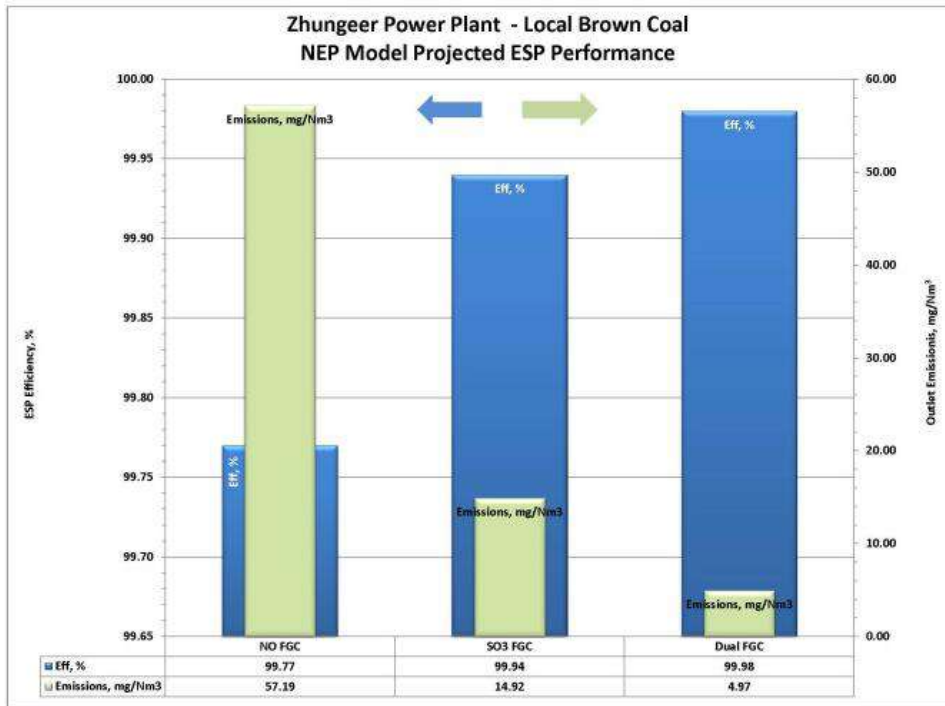


Figure 9. Zhungeer Power Plant, Units 1-2 NEP Model Projected Performance

Figure 9 presents Numerical ESP Performance (NEP) model projected performance for the Zhungeer Units 1-2 electrostatic precipitators.

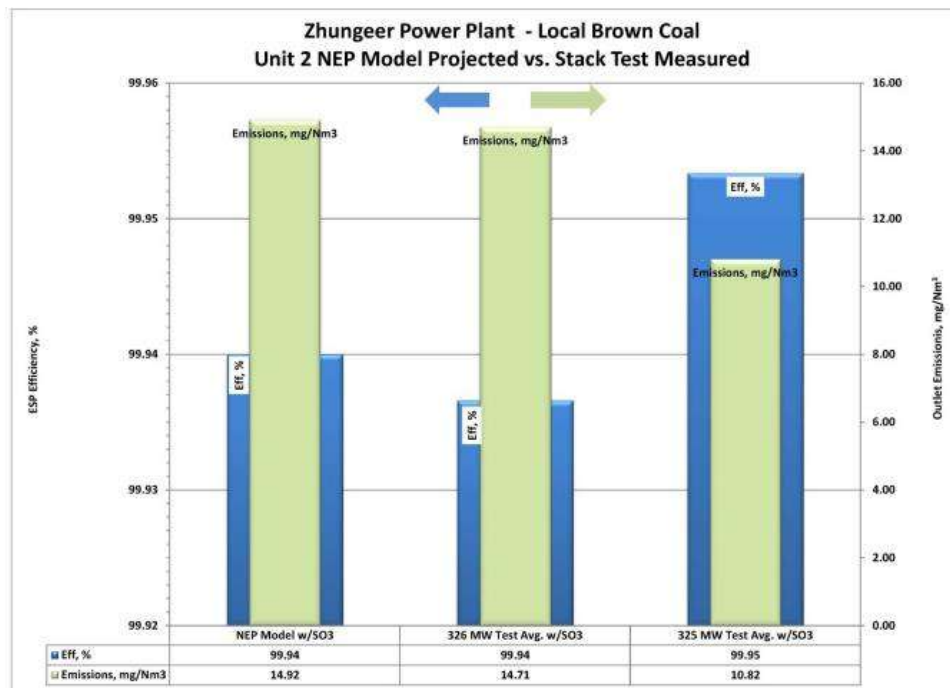


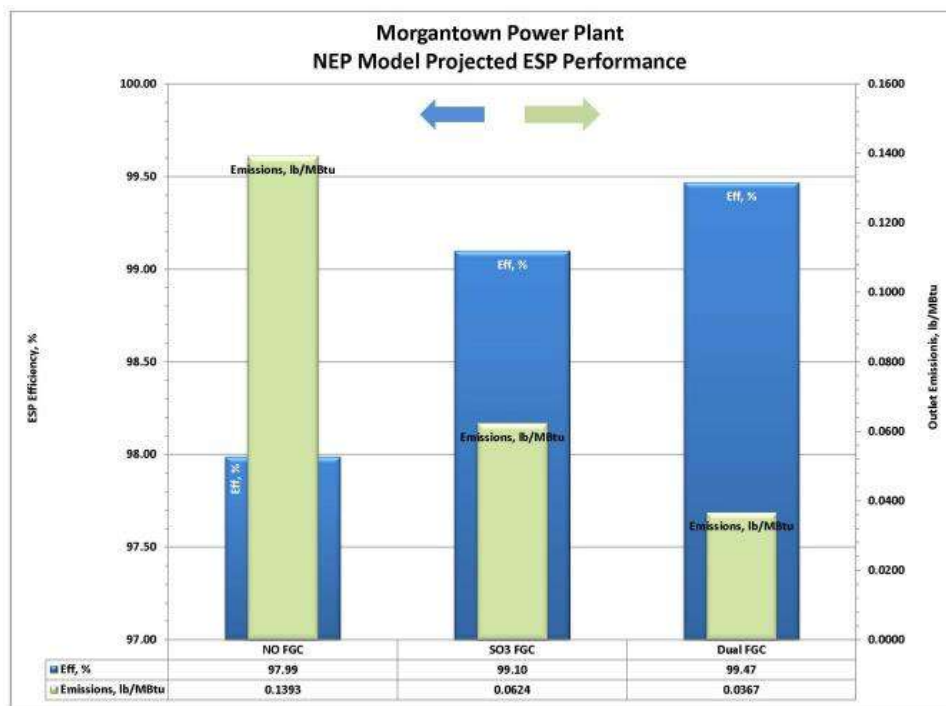
Figure 10. Zhungeer Power Plants Units 1-2 Stack Testing Results

Figure 10 depicts the results of the stack testing with and without the SO<sub>3</sub> FGC. The final emissions were tested with SO<sub>3</sub> FGC only and the results were as follows:

- Unit 1 achieved 18 mg/Nm<sup>3</sup> at ESP outlet
- Unit 2 achieved 17 mg/Nm<sup>3</sup> at ESP outlet

## 5.2 NRG ENERGY – MORGANTOWN POWER STATION

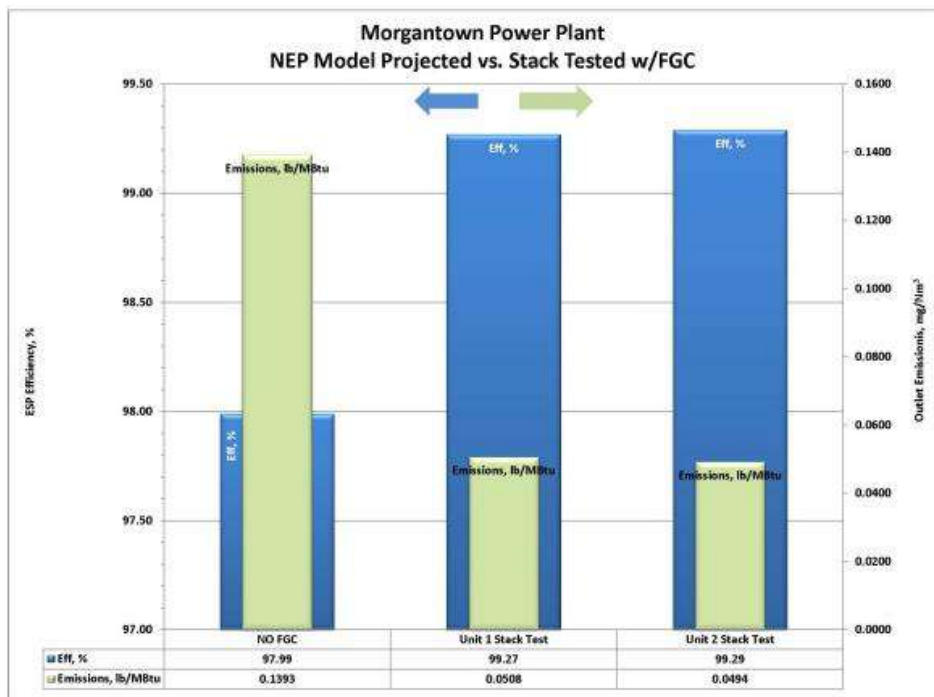
Morgantown Generating Plant is located in Newburg, Washington, D.C. area in Charles County, Maryland on the Potomac River. Its capacity is 1,492 megawatts at base load. It was designed to burn both coal and oil. Unit No 1 was placed in service in 1970 with the Unit No 2 following in 1971. Each of the two (2) boilers, manufactured by Combustion Engineering (CE), is rated at 640 MW. Each boiler is a tangentially coal fired supercritical unit with a superheater, single reheat and economizer. Units 1 and 2 are each equipped with Low NOx burners (LNBs), Electrostatic Precipitators (ESP), Selective Catalytic Reduction (SCR), Over Fire Air (OFA) and Flue Gas Desulfurization (FGD) and exhausted through a 400 foot high stack. When the FGD systems are not in use, the flue gas is exhausted through a 700 foot high by-pass stack. The units also have the capability of firing on No. 6 oil as an alternative primary fuel.



**Figure 11. Morgantown Power Plant - NEP Model ESP Projected Performance**

Existing electrostatic precipitators (ESPs) are marginal at best with the design SCA of 38 m<sup>2</sup>/m<sup>3</sup>/s (193 ft<sup>2</sup>/kacfm) at the design load and 31-33 m<sup>2</sup>/m<sup>3</sup>/s (158-169 ft<sup>2</sup>/kacfm) at the boilers' current maximum load. One of the potential upgrades that were identified early in the project definition phase was to improve the stack emissions which, when implemented, will

serve to improve the overall APC equipment effectiveness and ultimately the performance of the precipitators.



**Figure 12. Morgantown Power Plant - As Tested Stack Emissions**

The project team identified a comprehensive two-phase approach to reduce the stack opacity: (a) Phase I included the Numerical Electrostatic Precipitator (NEP) model, and (b) Phase II consisted of ESP upgrade and Dual FGC. The latter resulted in a significant recovery of the power generation:

- Unit 1 recovered 25 MW
- Unit 2 recovered 45 MW

Figure 11 depicts the NEP model ESP projected performance and Figure 12 compares stack emissions as tested.

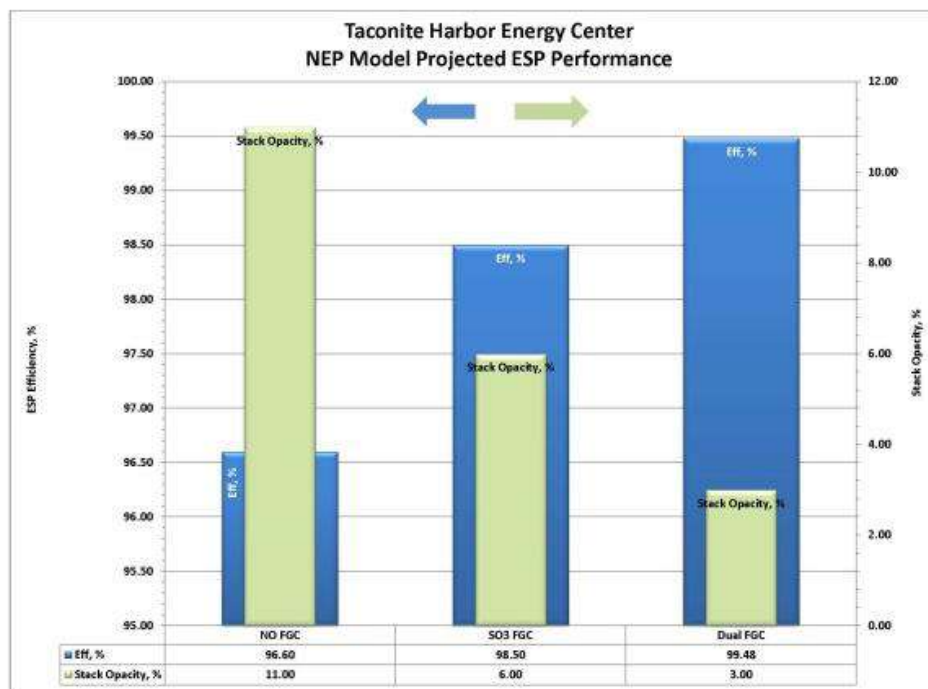
### 5.3 MINNESOTA POWER - TACONITE HARBOR ENERGY CENTER

Taconite Harbor Energy Center is a coal-fired power station near Schroeder, Minnesota. The facility is a coal-fired steam electric utility generating plant consisting of three identical tangentially-fired coal-burning units located on the north shore of Lake Superior. Boilers 1 and 2 burn bituminous and sub-bituminous coal.



Each unit is capable of a heat input of 900 MBtu/hr, with net generating capacities of 79 MW (Boiler 1) and 76 MW (Boiler 2). The plant uses western subbituminous coal which is received by boat and stored in an outdoor storage pile. Ash is pneumatically conveyed to and collected in a storage bin, then wetted and disposed of at an ash disposal site.

Due to the installation of a Lime Based Sorbent and other agents used to lower SO<sub>x</sub> and NO<sub>x</sub> emissions, particulate load had increased. The exiting precipitator was not able to handle the speed of gas flow to effectively collect the excess and highly resistive fly ash. Government regulations required the facility to reduce opacity.



**Figure 13. Taconite Harbor Energy Center NEP Model Projected ESP Performance**

The successfully performed hot-to-cold retrofit, augmented by the use of Dual FGC, enabled the plant to outperform the 0.03 lbs./MBtu outlet emissions (Figure 13). The equipment upgrade also resulted in improved reliability and performance.

## 6 SUMMARY

In conclusion, dual flue gas conditioning (Dual FGC) is a simultaneous and independent injection of the ammonia and SO<sub>3</sub> air mixture into the flue gas stream ahead of the ESP. In properly designed and implemented systems (at appropriate stoichiometric ratio) ammonia will, in effect, scavenge SO<sub>3</sub> and create certain ammonia salts.

While SO<sub>3</sub> will improve the fly ash resistivity, the ammonia salts will improve particles agglomeration and cohesivity, eliminate rapping losses, and enhance the electric field to further improve the particles migration velocity.

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