SO_3 Removal System for Flue Gas in Plants Firing High-sulfur Residual Fuels

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With the recent demand for higher quality refined petroleum products, the sulfur content in petroleum residues is increasing. These residues are called residual fuel oils and can be burned as fuel for boilers. However, SO_3 levels in the flue gas emitted by combustion are very high, which becomes a cause of machinery corrosion or a visible blue plume. The installation of a removal system is essential. The major conventional methods applied for SO_3 removal are ammonia injection and the use of wet electrostatic precipitators (ESP). These methods, however, have technical difficulties when SO_3 concentrations are high (60–100 ppm or higher). Therefore, Mitsubishi Heavy Industries, Ltd. (MHI) has developed a new technology called the salt solution spray system. This report compares these different SO_3 removal technologies and also shows the high SO_3 removal capability of our salt solution spray system, and its proven performance for long-term stable operation in plants.

1. Introduction

The petroleum residues obtained after oil refinement, such as vacuum residual (VR) oil, petro coke (PC) and solvent de-asphalting (SDA) pitch, are often disposed of as waste. However, from the perspective of recovering the unused energy and reducing waste disposal costs, these residues have been used as fuel for thermal power plants. The residues are rich in sulfur and thus their flue gas contains high levels of SO_2 as well as SO_3, which is formed by the oxidation of SO_2. In the quenching process of flue gas desulfurization (FGD) system, SO_3 gas changes to form fine sulfuric acid mist and becomes a cause of corrosion or a visible, trailing blue plume from the stack. This may result in a serious problem. It is essential to take measures for SO_3 treatment in plants firing petroleum residues as fuel.

The most common method to deal with SO_3 is the ammonia injection system, in which gaseous ammonia is used to react with SO_3 gas to produce ammonium sulfate. Ammonium sulfate is then collected by a dry ESP. This method has been used commercially since the 1970s. However, as a high sulfur content in fuel means an elevated SO_3 level in flue gas, the production of ammonium sulfate is subsequently increased. Intermediates such as ammonium bisulfate are also involved in the functioning of the system. These cause problems for dry ESP (e.g., ash-clogged hoppers or energization problems due to a build-up of ash deposits on the electrodes), thus making long-term continuous operation difficult.

Another technology applied commercially is the use of wet ESP to capture the sulfuric acid mist formed from SO_3. Sulfuric acid mist can be very effectively removed by wet ESP. For stable operation, however, it is desirable to maintain SO_3 concentrations of 60 ppm or lower at the wet ESP inlet. Because the droplets of the sulfuric acid mist produced are extremely fine, high SO_3 concentrations can lead to the occurrence of a space charge effect, interfering with the discharge

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current in wet ESP. As a result, the collection efficiency by wet ESP will be lowered significantly. Therefore, to ensure the designed levels of collection efficiency, wet ESP need to be built extremely large. This makes the application of wet ESP difficult.

As a technology applicable to the conditions where the inlet SO_3 levels are 60 ppm or higher, we have developed a salt solution spray system in which the FGD circulating solution is sprayed on the upstream side of the FGD equipment. The following sections introduce each of these SO_3 removal technologies and their actual operational achievements.

2. Ammonia injection method[1]

2.1 Configuration of the system

Figure 1 shows a flow diagram of the ammonia injection system. In this system, gaseous ammonia is sprayed on the upstream side of the dry ESP and reacts with SO_3 gas to produce solid ammonium sulfate particles. It takes a second or longer to complete the reaction after ammonia is sprayed. Therefore, considering that the flow rate of flue gas is 10–15 m/s, a horizontal duct of 10–15 m should be used to connect between the nozzle for ammonia injection and the inlet of the dry ESP.

As shown in the chemical equation given below, the reaction occurs between 1 mol of SO_3 and 2 mol of ammonia. To ensure that the reaction proceeds as expected, a few dozen additional ppm of ammonia is also supplied.

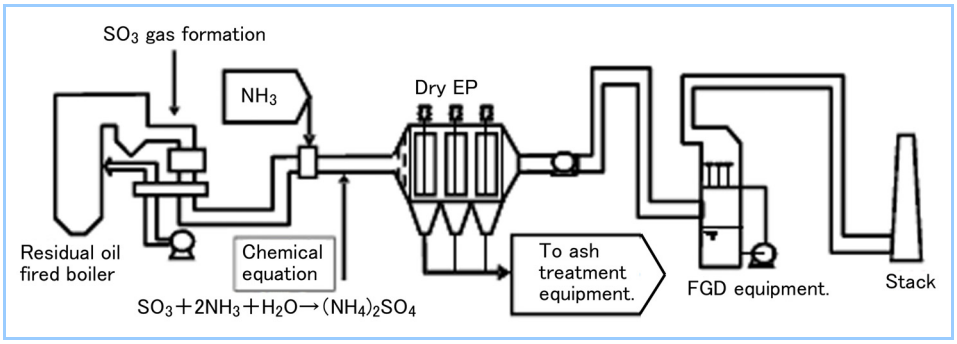

Figure 1 Flow diagram of ammonia injection system
The figure illustrates the course of actual operation for an ammonia injection system.

2.2 Behavior of dust comprised mainly of ammonium sulfate

The resulting dust contains reaction products mainly consisting of ammonium sulfate, and can be collected thoroughly by dry ESP. The removal rate of SO_3 through this system reaches almost 100%. However, these reaction products have a highly adherent property. If the SO_3 levels are high enough, continuous operation for just a few months can cause the dust to build up on the electrodes in a dry ESP (**Figure 2**), thus interfering with the discharge current. As the collection efficiency by dry ESP is lowered with the decrease of discharge current, the sizing of dry ESP should be determined with an estimation of the decreased electric current caused by the build-up of dust deposits. Recent study results indicate that SO_2 in flue gas is involved in the precipitation mechanism of reaction product (i.e., ammonium sulfate dust). Higher concentrations of SO_2 induce more adherence of ammonium sulfate dust.

Dust particles adhered to dry ESP electrodes grow gradually, and become detached as an agglomerate of dust particles when reaching a certain size. As shown in **Figure 3**, such dust agglomerates that have separated from the collecting electrode may lean over to the discharge electrode, thus causing a short circuit. Dust comprised mainly of ammonium sulfate has a relatively high conductivity, and therefore high voltages cannot be applied in a short-circuited ESP. In the worst-case scenario, the plant operation has to be stopped to clean the inside of the dry ESP. If the dust collection efficiency is sufficiently good, the charging area in a dry ESP can be divided into several sectors in advance. The power can be cut off only in the disturbed charging area and the plant operation can continue. However, the build-up of dust deposits in the ammonia injection method still remains a serious obstruction to the long-term stable operation of plants where SO_3 levels are high.

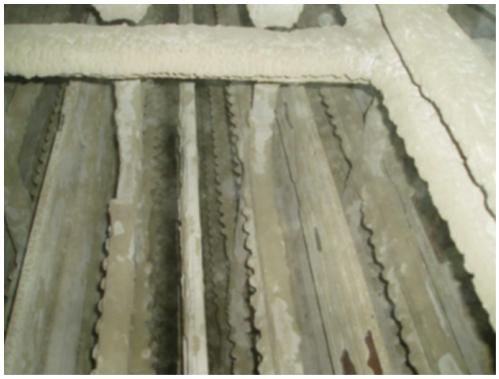

Figure 2 Build-up of dust deposits inside dry ESP
The figure shows the build-up of dust deposits on the electrodes in a dry ESP, which occurred in the ammonia injection system. The dust is comprised mainly of ammonium sulfate and acid ammonium sulfate.

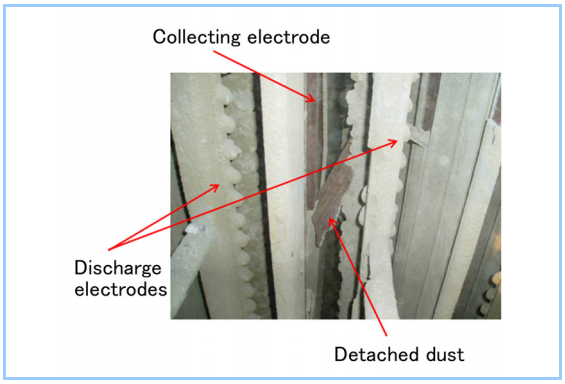

Figure 3 Dust-caused short circuit in dry ESP
The figure shows a short circuit, caused by dust deposits that were built up on the collecting electrode in a dry ESP and became detached to lean over to the discharge electrode.

2.3 Actual operational achievements

Table 1 shows our past installations of the ammonia injection system in residual oil fired plants. One of these plants even handles SO_3 levels exceeding 100 ppm. In plants where SO_3 concentrations are high, it is difficult to operate continuously during a one-year interval between annual inspections, and the inside of the dry ESP may be cleaned once or twice in between.

Recent measures taken include dividing the charging area into several sectors (as stated above), conducting power-off rapping with a damper system, and installing a pulse air agitator in the hoppers. These measures have improved the situation considerably.

Table 1 Actual operational achievements of our ammonia injection method
Outlined specifications of residual oil fired plants in which the ammonia injection method is used.

Plant	Equipment combination for flue gas treatment	Start of operation	Fuel	Boiler load (t/h)	SO_3 level (ppm)
P1	NH_3 + DESP + FGD + WEP	1998	VR	475	32
P2	NH_3 + DESP + FGD + WEP	2003	VR	750	28
P3	MC + NH_3 + DESP + FGD	2004	PC	500	117
P4	NH_3 + DESP + FGD	2004	VR	485	47
P5	NH_3 + DESP + FGD	2005	PC	430	79
P6	NH_3 + DESP + FGD	2008	PC	500	-
P7	NH_3 + DESP + FGD	2009	PC	520	69
P8	NH_3 + DESP + FGD	2009	SDA + VR	400	29
P9	NH_3 + DESP + FGD	2009	SDA + VR	450	47

NH_3: ammonia injection, DEP: dry ESP, FGD: flue gas desulfurization equipment.
WEP: wet ESP, MC: multicyclone
VR: vacuum residual oil
PC: petro coke
SDA: solvent de-asphalting process pitch

3. Wet ESP

3.1 Configuration of system

Figure 4 shows a flow diagram of a SO_3 removal system using wet ESP. In this system, flue gas is cooled down to approximately 60°C in the cooling tower of the wet FGD system and becomes saturated with moisture. In this process, SO_3 gas changes to form a mist of concentrated sulfuric acid (≈40%) with extremely fine droplets. This sulfuric acid mist is generally called SO_3 mist despite its chemical compound, and is referred to as SO_3 mist hereafter.

The particle diameters of mist droplets vary depending on the SO_3 concentration and gas temperature at the FGD inlet, but are extremely small because their mean diameter is 0.1–0.3 μm. Therefore, the collection efficiency of SO_3 mist by the FGD equipment reaches only 20% or so, and most of the mist has to be treated by the wet ESP installed downstream from the FGD equipment.

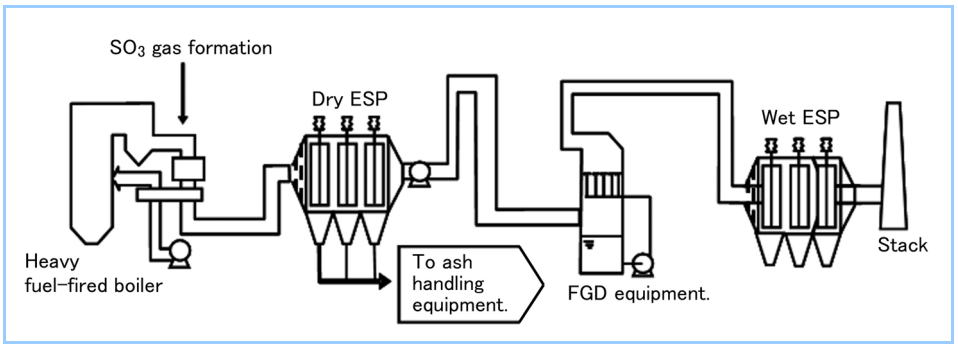

Figure 4 Flow diagram of SO_3 removal system using wet ESP
The figure illustrates the course of actual operation for SO_3 removal using a wet ESP.

3.2 SO_3 mist collection efficiency by wet ESP

As mentioned above, SO_3 mist formed in wet FGD equipment consists of extremely small droplets. When SO_3 mist is charged in wet ESP and has an electric charge, only a few dozen ppm of charged SO_3 mist create a few dozen μC/m^3N of electric charge per unit of gas volume, and the discharge current will be decreased considerably. This phenomenon is called the space charge effect, which results from the disturbed flow of electric current caused by the charge carriers present in the discharge space.

The collection efficiency by ESP greatly varies according to the particle diameter of mist droplets. As indicated in **Figure 5**, droplets with a diameter of 0.1–0.3 μm are the most difficult to capture, which suggests that the SO_3 mist has a natural tendency to slip through the ESP. This, together with the significantly lowered current due to the space charge effect, necessitates the considerable enlargement of the equipment in high SO_3 level conditions.

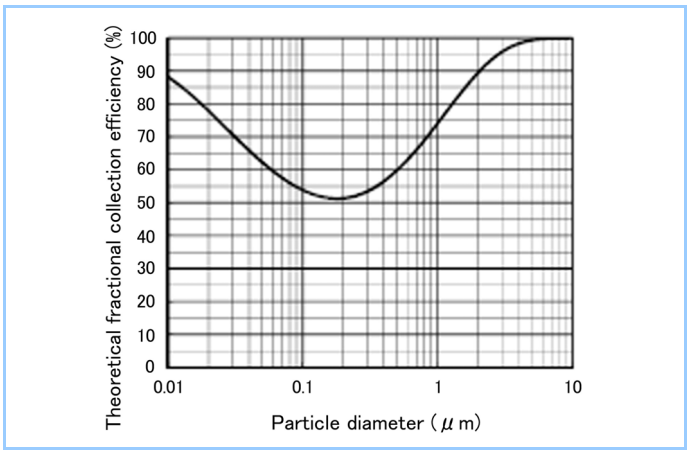

Figure 5 Collection efficiency by ESP, varying with particle diameters
The figure shows that the collection efficiency by ESP changes with particle diameters.

As a result, we have experienced difficulty using wet ESP if SO_3 concentrations are high (60 ppm or higher) and the enlargement of the equipment is not possible.

In summary, although both the ammonia injection method and wet ESP have been commercially used as effective means of removing low levels of SO_3, neither is suitable as a stable system to deal with high levels of SO_3 (especially beyond 60 ppm). It is necessary to develop a new system that can work effectively to remove high levels of SO_3 as well.

4. Salt solution spray system

4.1 Configuration of system

The flow diagram of the salt solution spray system can also be seen in Figure 4. However, a nozzle is attached in the duct of the upstream side of the FGD equipment and from there, the FGD circulating solution is sprayed downward (**Figure 6**). Although it is possible to spray upward or horizontally, problems such as blocked spray nozzles and adhesion of the sprayed solution on the

inner surface of the duct wall will become more pronounced. At present, downward spraying is adopted as the principal setting.

Considering the evaporation rate of the sprayed solution and its properties of adsorption and reaction with SO_3 gas, we have decided that two-fluid nozzles should be used for spraying to produce fine droplets with a Sauter mean diameter of 20–50 μm.

Figure 7 is a simplified illustration of the reaction mechanism. As the diameters of the sprayed FGD circulating-solution droplets are small, the moisture contained in the droplets evaporates quickly to leave the dried dust particles of salt solution behind. In this process, SO_3 gas is removed by being adsorbed on to the surface of these dust particles. The reaction product (i.e., salt solution dust) is water soluble, and most of it dissolves in the circulating solution of the downstream FGD equipment and is incorporated in FGD effluent when eventually treated. Therefore, compared with the ammonia injection method, the amount of industrial waste can be considerably reduced and running costs can also be lowered.

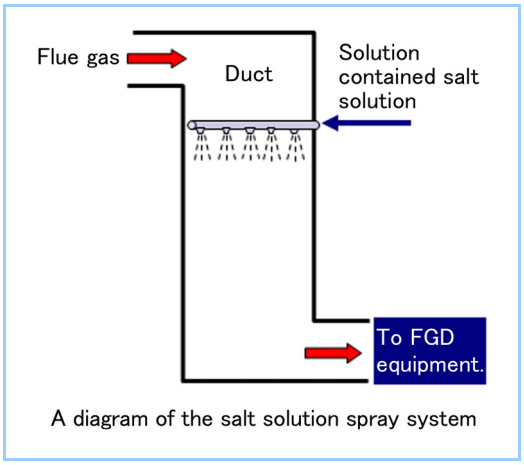

Figure 6 Diagram of nozzle installation for salt solution spraying
The figure shows a diagram of a two-fluid nozzle installation for salt solution spraying downward in a vertical flue.

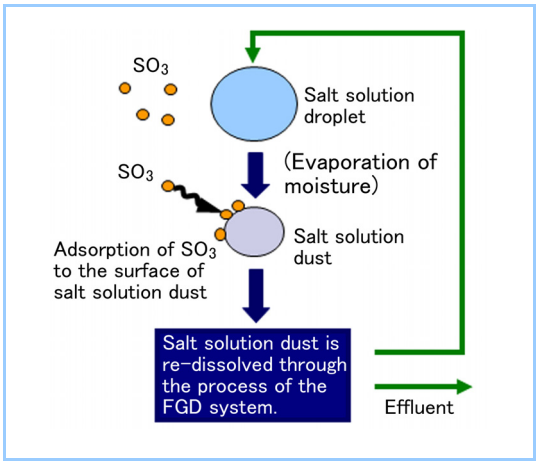

Figure 7 Mechanism of SO_3 removal by salt solution spraying
The figure illustrates the process in which salt solution spraying allows SO_3 to be incorporated in dissolved-salt dust.

The dissolved salts applicable in this system can be any salts of Na, Mg and K. If sodium hydroxide or magnesium hydroxide is used in the FGD system, the FGD equipment can be operated using the FGD circulating solution with a Na_2SO_4 or $MgSO_4$ concentration of approximately 5 wt%, respectively. Thus, the FGD circulating solution itself can be sprayed for the removal of SO_3 and no special chemicals are needed for salt solution spraying. In the case of the lime-gypsum method being applied in the FGD system, however, combination with salt solution spraying is less cost effective, because low salt levels in the FGD circulating solution requires the use of additional chemicals and the adhesion of gypsum becomes another issue that has to be dealt with.

4.2 SO_3 removal performance in salt solution spray system

As mentioned above, several types of salts can be used in the salt solution spray system. Differences in the SO_3 removal performance among these salts are small (**Figure 8**). This is because the reaction concerned is not based on a chemical change, but occurs mainly as a result of the physical adsorption of SO_3 to the surface of dust particles through the process of evaporation.

The SO_3 removal performance greatly depends on gas temperature. As indicated in **Figure 9**, the highest removal performance can be achieved when the gas temperature after the evaporation of the sprayed solution reaches approximately 145°C, below which the performance is rapidly worsened. This is because the reaction concerned is a gas-solid (or gas-liquid) reaction and once SO_3 mist is formed, adsorption to the surface of the salt solution dust particles is considered to be suppressed.

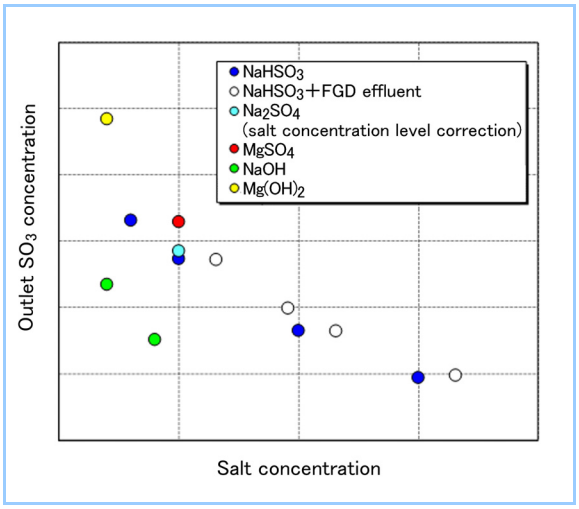

Figure 8 Influence of salt solution types on SO_3 removal performance
The figure shows the change of outlet SO_3 concentrations caused by the type of salt solution and their concentrations.

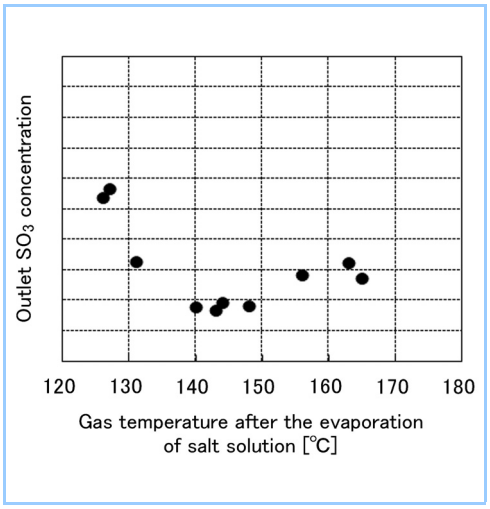

Figure 9 Difference in SO_3 removal performance according to the gas temperature after the evaporation of salt solution
The graph shows that SO_3 removal performance varies depending on the gas temperature after the evaporation of the sprayed dissolved-salt solution.

4.3 Actual operational achievements

In a heavy fuel-fired plant where sodium hydroxide is used in the FGD system, the salt solution spray system has enabled the plant to operate continuously during a one-year interval between annual inspections since its installation in 2007. As shown in **Figure 10**, SO_3 levels of approximately 1 ppm or lower can be maintained at the outlet of wet ESP, in spite of the inlet levels being 60–130 ppm. None of the plants with other SO_3 removal systems designed to treat high levels of SO_3 (100 ppm or higher) have succeeded in establishing stable, one-year continuous operation over successive years, which demonstrates that our salt solution spray system is the most effective answer for SO_3 removal in residual oil fired plants.

As salt solution spraying itself can remove 90–95% of SO_3, downstream wet ESP may be considered unnecessary for the system. However, as some of the reaction products (i.e., dissolved-salt dust particles) can pass through the FGD equipment, it is recommended that salt solution spraying be used in conjunction with wet ESP from the perspective of reducing outlet dust concentrations.

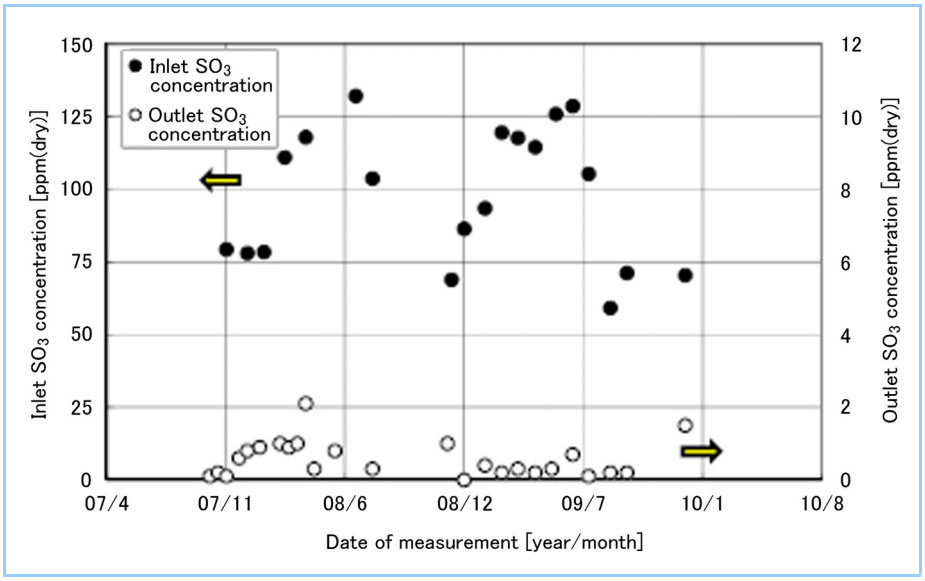

Figure 10 SO_3 removal data, obtained by the actual operation of a plant with a combined system of salt solution spraying and wet ESP
The data on SO_3 removal performance were obtained by the actual operation of a residual oil fired plant with a boiler load of 300 t/h, where a combined system of salt solution spraying and wet ESP is used.

5. Conclusions

(1) MHI has several proprietary SO_3 removal technologies which have been proven by actual operations, and can suggest an optimum SO_3 removal system depending on gas conditions, spatial limitations for installation and other factors concerned.

(2) MHI has developed a new technology for stable operation under high SO_3 level conditions, called the salt solution spray system.

(3) Since its installation in 2007, the salt solution spray system has enabled a plant to operate continuously during a one-year interval between annual inspections over successive years, and maintains high SO_3 removal performance in spite of the SO_3 levels being approximately 100 ppm. It has been demonstrated that the system is highly reliable as a technology for treating high levels of SO_3.

Reference

1. Nagata, C. et al., Experiences of Systems to Reduce SO_3 from Flue Gas of Combusting High Sulfur Content Residual Materials in Oil Refinery, International Journal of Plasma Environmental Science and Technology, vol.5, no.2, pp. 135-140, 2011