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.
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 SO₃ 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 SO₃ removal technologies and their actual operational achievements.

## 2. Ammonia injection method

### 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 SO₃ 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 SO₃ and 2 mol of ammonia. To ensure that the reaction proceeds as expected, a few dozen additional ppm of ammonia is also supplied.

$$\text{SO}_3 + 2\text{NH}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4$$

![Figure 1](image1.png)

**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 SO₃ through this system reaches almost 100%. However, these reaction products have a highly adherent property. If the SO₃ 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 SO₂ in flue gas is involved in the precipitation mechanism of reaction product (i.e., ammonium sulfate dust). Higher concentrations of SO₂ 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 SO₃ 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>
<thead>
<tr>
<th>Plant</th>
<th>Equipment combination for flue gas treatment</th>
<th>Start of operation</th>
<th>Fuel</th>
<th>Boiler load (t/h)</th>
<th>SO$_3$ level (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>NH$_3$ + DESP + FGD + WEP</td>
<td>1998</td>
<td>VR</td>
<td>475</td>
<td>32</td>
</tr>
<tr>
<td>P2</td>
<td>NH$_3$ + DESP + FGD + WEP</td>
<td>2003</td>
<td>VR</td>
<td>750</td>
<td>28</td>
</tr>
<tr>
<td>P3</td>
<td>MC + NH$_3$ + DESP + FGD</td>
<td>2004</td>
<td>PC</td>
<td>500</td>
<td>117</td>
</tr>
<tr>
<td>P4</td>
<td>NH$_3$ + DESP + FGD</td>
<td>2004</td>
<td>VR</td>
<td>485</td>
<td>47</td>
</tr>
<tr>
<td>P5</td>
<td>NH$_3$ + DESP + FGD</td>
<td>2005</td>
<td>PC</td>
<td>430</td>
<td>79</td>
</tr>
<tr>
<td>P6</td>
<td>NH$_3$ + DESP + FGD</td>
<td>2008</td>
<td>PC</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>P7</td>
<td>NH$_3$ + DESP + FGD</td>
<td>2009</td>
<td>PC</td>
<td>520</td>
<td>69</td>
</tr>
<tr>
<td>P8</td>
<td>NH$_3$ + DESP + FGD</td>
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<td>SDA + VR</td>
<td>400</td>
<td>29</td>
</tr>
<tr>
<td>P9</td>
<td>NH$_3$ + DESP + FGD</td>
<td>2009</td>
<td>SDA + VR</td>
<td>450</td>
<td>47</td>
</tr>
</tbody>
</table>

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.
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$^3$N 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.

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.

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$_2$SO$_4$ 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 SO₃ removal performance
The figure shows the change of outlet SO₃ concentrations caused by the type of salt solution and their concentrations.

Figure 9  Difference in SO₃ removal performance according to the gas temperature after the evaporation of salt solution
The graph shows that SO₃ 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, SO₃ 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 SO₃ removal systems designed to treat high levels of SO₃ (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 SO₃ removal in residual oil fired plants.

As salt solution spraying itself can remove 90–95% of SO₃, 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  SO₃ removal data, obtained by the actual operation of a plant with a combined system of salt solution spraying and wet ESP
The data on SO₃ 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