Experiences of Systems to Reduce SO_3 from Flue Gas of Combusting High Sulfur Content Residual Materials in Oil Refinery

Chikayuki Nagata — chikayuki_nagata@mhims.mhi.co.jp
Kazuaki Miyake — kazuaki_miyake@mhims.mhi.co.jp
Hiroyuki Nagasawa — hiroyuki_nagasawa@mhims.mhi.co.jp
Toshihide Noguchi — toshihide_noguchi@mhims.mhi.co.jp

Mitsubishi Heavy Industries Mechatronics Systems, Ltd.
4-22 Wadamiya-dori 5-chome, Hyogo-ku, Kobe 652-0863, **JAPAN**

1 Abstract:

Due to recent higher quality requirement for oil-refined-products, sulfur content is increasing in the residual materials, which are used as boiler fuel, from economical reasons and viewpoint of effective resource utilization. In such case, reducing SO_3 such as high as 120ppm in flue gas is needed to avoid corrosion and bluish plume. Herein, experiences of improving energization difficulties and clogging in hopper in ordinary “Ammonia Injection + Dry-type ESP” system, according to the intermediate byproducts of NH_4 – SO_4, are introduced. Furthermore, “Salt Solution Spray + Wet-type ESP” system, which enables more stable and continuous operation, is also introduced.

2 Introduction

In accordance with the global tendency of environmental regulation becoming more stringent, higher quality oil-refined-products with lower sulfur content are being required more and more, and as the result, the residual materials in the oil refining process, such as vacuum residual oil (VR), petroleum coke (PC), SDA pitch (SDA), etc. are also increasing, and sulfur content in such residual materials is becoming higher and higher.

Such residual materials are often treated as waste materials, however in order to recover thermal or electrical energy from the limited resources and also, from the economical point of view, to save the treatment cost of waste material, using them as the fuel of thermal power station is becoming a tendency. In such case, due to high sulfur content in the residual materials, sulfur-dioxide (SO_2) gas shall be reduced of course, and sulfur-trioxide (SO_3) gas, which is furthermore oxidized from SO_2 and forms sulfuric acid (H_2SO_4) mist combined with water vapour in the flue gas, shall also be reduced, since the sulfuric acid mist causes serious corrosion problem in the flue gas treatment system and also bluish plume problem if it is discharged from stack.

In Japan, many oil fired thermal power stations were constructed at the time of high economic growth in 1970s, and in such power stations, “Ammonia (NH_3) Injection + Dry-type ESP (DEP)” system that injecting diluted NH_3 gas at the inlet of DEP, and removing solid particles of ammonium sulfate [$(NH_4)_2SO_4$], which is formed by the reaction of SO_3 gas in the flue gas and injected NH_3 gas.[1]

This system is the most popular and proven technology for SO_3 reduction in the flue gas, it is also most generally used when residual materials with very high sulfur content are used as the fuel. However, when the sulfur content is much increased, SO_3 content in the flue gas becomes much higher, and amount of NH_3 injection and reacted materials of NH_3 and SO_3 increase significantly, DEP suffers many troubles, such as energization problem due to ash adhesion on the electrodes, ash discharge difficulty in hoppers, etc., and long time continuous operation becomes often very difficult. In this paper, we introduce our various experience of improvement of “NH_3 Injection + DEP” system applied to very high sulfur content fuel, to realize more stable operation and to enable the long time continuous operation.

At the same time, we also introduce a newly developed SO_3 reduction technology of “Salt Solution Spray (SSS) + Wet-type ESP (WEP)” system, which enables more stable and continuous operation, compared with “NH_3 Injection + DEP” system. The first commercial installation of the new system has been operated continuously for one year, several times, without problem, and it is considered to be predominant alternative of ordinary “NH_3 Injection + DEP” system.

Our delivery record of “NH_3 Injection + DEP” system and “SSS + WEP” system, applied to very high sulfur content fuel, is shown in Table 1.

Table 1 Delivery Record of Flue Gas Treatment System for High Sulfur Content Fuel Fired Boilers

Customer	Plant	Flue Gas Treatment System	Delivery	Fuel	Boiler Evaporation Rate (t/h)	SO_3 actually measured at AH Outlet (ppm-dry)	Remarks
A	P1	NH_3 + DEP (+ FGD) + WEP	1998	VR	475	32	New Plant
C	P2	NH_3 + DEP (+ FGD) + WEP	2003	VR	750	28	New Plant
A	P3	MC + NH_3 + DEP (+ FGD)	2004	PC	500	117	New Plant
A	P4	NH_3 + DEP (+ FGD)	2004	VR	485	47	New Plant
D	P5	NH_3 + DEP (+ FGD)	2005	PC	430	79	New Plant
B	P6	NH_3 + DEP (+ FGD)	2008	PC	500	(No Data)	Fuel Conversion in Existing Plant
B	P7	NH_3 + DEP (+ FGD)	2009	PC	520	69	Fuel Conversion in Existing Plant
E	P8	NH_3 + DEP (+ FGD)	2009	SDA + VR	400	29	New Plant
F	P9	NH_3 + DEP (+ FGD)	2009	SDA + VR	450	47	Fuel Conversion in Existing Plant
A	P10	DEP + SSS (+ FGD) + WEP	2006	VR	300	132	Fuel Conversion in Existing Plant

Symbol :
NH3 : Ammonia Injection
DEP : Dry-type Electrostatic Precipitator
MC : Multi-Cyclone
SSS : Salt Solution Spray
WEP : Wet-type Electrostatic Precipitator
FGD : Wet-type Flue Gas Desulfurization System
VR : Vacuum Residual Oil
PC : Petroleum Coke
SDA : SDA (Solvent Deasphalting Process) Pitch

3 "Ammonia Injection + Dry-type ESP" System

3.1 Basic Concept of the System

A part of SO_2, generated in boiler combustion due to sulfur content in the fuel, oxidized furthermore to SO_3 in boiler and SCR for NOx reduction. The conversion rate from SO_2 to SO_3 fluctuates depending on the catalytic effect of heavy metals on the surface of heat exchanging tube in boiler and the conditions of SCR catalyst, but anyway SO_3 concentration becomes high when sulfur content in fuel is high.

When diluted NH_3 gas is injected at air pre-heater outlet (namely, DEP inlet), the following chemical reaction occurs basically.

$$\underset{(gas)}{SO_3} + \underset{(gas)}{NH_3} + H_2O \rightarrow NH_4HSO_4$$

$$NH_4HSO_4 + \underset{(gas)}{NH_3} \rightarrow \underset{(solid\ particle)}{(NH_4)_2SO_4}$$

Injecting excess NH_3 and completing the reaction thoroughly to form solid particles of $(NH_4)_2SO_4$, they can be collected effectively in DEP.

Above equation is the most ideal case, and ammonium bisulfate [NH_4HSO_4] is shown as the representative, but there are so many kinds of intermediate products of NH_4 – SO_4 system. Most of such intermediate products show high deliquescency, and they are very difficult to be treated in DEP. The formation of the intermediate products depends delicately on the balance of the process, such as partial pressure of gas components, and the control of NH_3 injecting amount is so difficult especially when SO_3 content is high, that it is somewhat inevitable to prepare the formation of such intermediate products, which cause adhesive property and deterioration of fluidity in ash, and as the result, serious problems often occur in DEP.

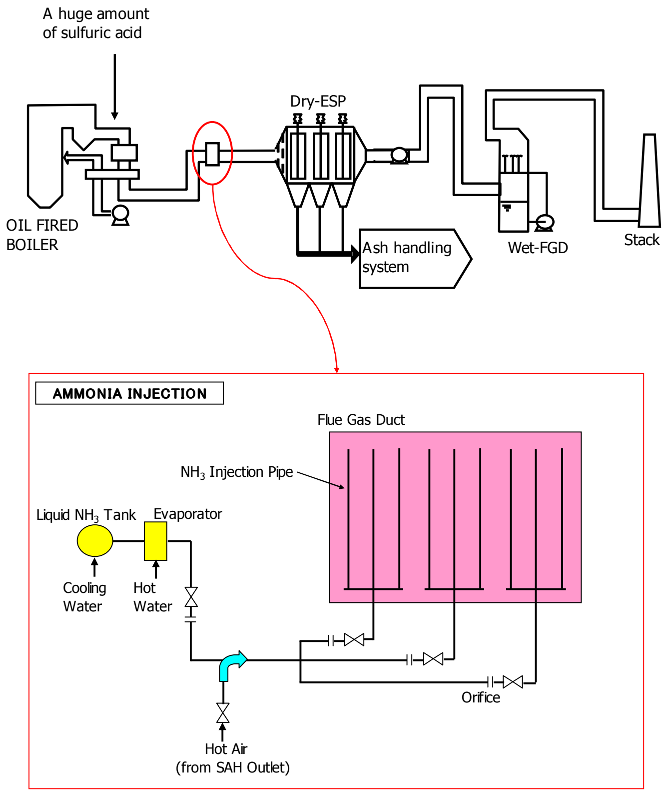


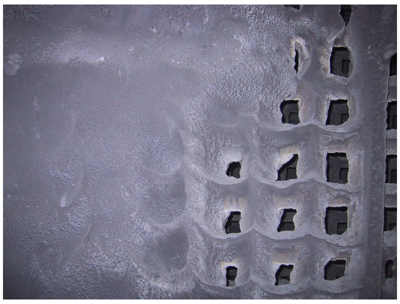
Fig 2: NH_3 Injection + Dry-type ESP System

3.2 Ash Adhesion on Gas Distribution Plate of DEP

Intermediate products such as NH_4HSO_4 and others of NH_4 – SO_4 system show very high deliquescency, and if it is mixed up with boiler dust and solid particles of $(NH_4)_2SO_4$, the ash will be very adhesive. Through DEP, the highest concentration of ash contained in the flue gas at the gas distribution plate, which is equipped inside of inlet nozzle of DEP and is exposed to the flue gas, so that it causes adhesion of ash most easily upon its surface.

Examples of the gas distribution plate whose paths of gas are almost clogged are shown in the photos of Fig 3-1. Thus, when the paths are mostly clogged, gas pressure loss increases significantly, and over load of fan is invited, and the plant cannot be operated in the worst case. Gas flow distribution in DEP is disturbed too much, and mechanical failure is sometimes experienced according to the extremely high gas velocity caused locally in DEP. Fig 3-2 shows the situation of broken collecting electrode due to hydrodynamic vibration caused by extremely high gas velocity generated locally. When collecting electrode drops like this, energization problem is caused and serious failure such as trip of the T/R unit at the bus section may easily occurs. The reason of this high gas velocity has been confirmed to be caused by the clogging of the gas distribution plate, through CFD analysis, whose result is shown in Fig 3-3, and the fundamental countermeasure is to avoid the clogging of the gas distribution plate.

This kind of clogging phenomenon of gas distribution plate was not used to be experienced in "NH_3 injection + DEP" in ordinary oil fired boiler plant, and it is recently confirmed since high sulfur content fuel has been popularly used and the tendency of increasing SO_3 concentration in flue gas has been clearly appeared. To avoid this phenomenon is very important to protect from the serious failure of DEP and to keep the long time operation of the plant. To solve the problem, we have changed the design of the form of gas distribution plate to avoid clogging, and rapping devise for the gas distribution plate has been reinforced and also its optimum arrangement has been investigated and realized.


(Example A)


(Example B)

Fig 3-1: Sticky Dust Adhesion on Gas Distribution Plate

Fig 3-2: Broken Collecting Electrode Due to Hydrodynamic Vibration Caused by High Velocity

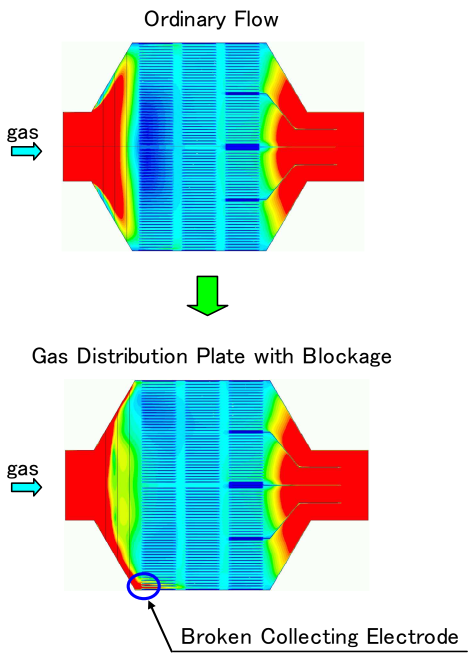


Fig 3-3: CFD Analysis Result

3.3 Ash Adhesion on Electrodes of ESP

Precipitability of intermediate products such as NH_4HSO_4 and others of $NH_4 – SO_4$ system is comparatively good, and they are very adhesive, so that problems are often caused by ash adhesion on the surface of collecting electrode and discharge electrode. Examples of ash adhesion on electrodes are shown in Fig 3-4.

Ash adhered excessively on collecting electrode sometimes peels off when it grows to a certain degree, and the if the size of block of the peeled ash is big enough to short-circuits the collecting electrode and discharge electrode, energization at the bus section may be led to be impossible, and the continuous operation of the plant may become impossible.

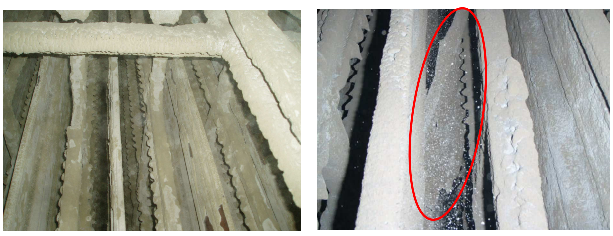
On the other hand, Ash adhesion on discharge electrode affects to the energization property of DEP very much. It reduces corona current, so that the performance of DEP deteriorates. Therefore, using high sulfur content fuel, attention should be paid, even if the initial performance of DEP is good with clean discharge electrode, to the corona current reduction and the deterioration of DEP performance, when the operation continues some time.

When the concentration of SO_3 becomes higher, ash adhesion is accelerated, and as long as this kind of very high sulfur content fuel is used, ash adhesion on electrodes is considered to be somewhat inevitable.

For the countermeasure, it is of course important to keep the condition of rapping devise always in sound condition. In order to keep the acceleration distribution of rapping very high through all the surface of the electrode, to hit the bottom part of collecting electrode, which is supported at the top, is effective, and the tumbling type rapping system is most preferable.

To equip high current type discharge electrode with long spike at the most upstream section of DEP is somewhat effective to keep current even if some ash adhesion occurs on the surface.

If long time continuous operation of the plant is the primary goal, long time operation procedure should be considered. At the starting up the operation of the plant, the ash amount adhered on the electrode is still not so much, and the corona current can be secured, so that it is possible to collect the ash, whose precipitability is comparatively good, at the maximum performance of DEP. However, if DEP is operated in its maximum performance from the plant starting up, it will only promote the ash adhesion on the correcting electrode, which may cause serious failure of energization trip due to short-circuit by peeled ash, and also ash adhesion on the discharge electrode, which reduces the corona current and deteriorates the performance of DEP. It is rather effective to operate DEP in suppressed current condition, for the purpose of expanding continuous operating time of the plant.



Example A

Example B
Peeled dust layer is marked with .

Fig 3-4: Sticky Dust Adhesion on Collecting Electrodes and Discharge Electrodes

When current tends to be reduced, continuous rapping in power-off condition may contribute to recover the current. In order to do the power-off rapping, stream in DEP should be divided and “damper system” should be adopted. In damper system, a damper is installed at the outlet of respective divided stream of DEP, and gas flow of a certain stream can be shut off by closing the damper, and power-off rapping can be done in off-flow condition, so that re-entrainment of ash is avoided. It is also effective if the collecting area is divided into many small bus sections, in order to minimize the influence of energization failure.

Continuous operation of DEP is very difficult when ash, mixed so much with intermediate products such as NH_4HSO_4 and others of $NH_4 – SO_4$ system, is treated, and it is often unavoidable to shut down the plant in order to wash the internals of DEP by water very frequently, such as once in every month or every two months. In such situation, above mentioned countermeasures are taken, and we have experience to achieve the continuous operation of DEP for about one year. Not only for DEP but also for main equipment, such as boiler, and other auxiliary equipment, continuous operation is difficult when very high sulfur content fuel is used, and we strongly do not want DEP to be critical for the continuous operation of the whole plant. For the purpose, such countermeasures mentioned above shall be considered well.

Lastly, at starting up and shut down process of the plant, accumulated ash on electrodes tends to be peeled off due to thermal expansion or shrinking, and it may easily cause the short-circuit, so that every time when the plant is shut down, internals of DEP is strongly recommended to be washed by water.

3.4 DEP Hopper Clogging and Ash Discharge Difficulty

Ash, mixed so much with intermediate products such as NH_4HSO_4 and others of $NH_4 – SO_4$ system, is very adhesive, and its fluidity is bad, so that it often causes hopper clogging and difficulty of ash discharge from hoppers. We have analysed the adhesion of ash based on the actually sampled ash, and we have found that the possibility of hopper clogging can be predicted by two indexes of (1) cohesion factor and (2) ash hardening factor.

Ash adhesion on inner surface of hopper grows when additional ash accumulates on the ash still remained in hopper when ash discharge process is completed. The starting point of the ash accumulation is the mutual adhesion of ash. There are several evaluation factors of ash adhesion and we have paid attention to "cohesion factor", whose measurement is comparatively easy and the correlation with the actual phenomena is found more or less. The value of cohesion factor shows the degree how bulky it may be, due to the cohesion caused by vibration of ash. When cohesion factor is high, bulky ash increases, and the average diameter of ash after cohesion becomes large.

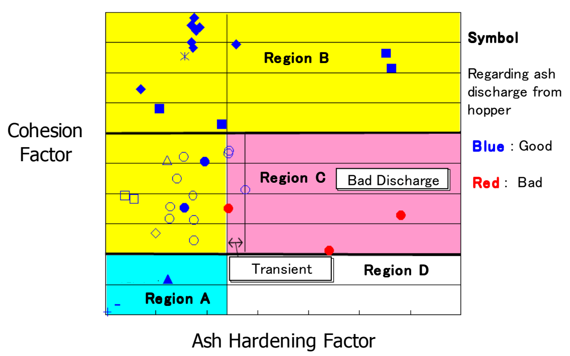
In order to find another index to represent the hardening of ash layer, the relationship between ash composition and hardening is studied. Paying attention to metal oxide, which is said to mitigate the ash hardening, we have investigated various components of ash, and we have found that ash tends to be hardened when some metal oxide components and unburned carbon is less, and ammonium sulfate is more. We have empirically defined an index of "ash hardening factor" in the combination of the above mentioned parameters.

Fig 3-5 is the chart in which the data of actual samples are plotted. Horizontal axis shows ash hardening factor and vertical axis shows cohesion factor, and the plots are distinguished in color depending on the conditions of ash discharge whether it is good or bad. We have classified the chart into four region of A, B, C, D, and we have found that the region C is most dangerous and the region B should be also paid some attention in hopper clogging.

In order to discharge ash from hoppers smoothly and without problem, the key point is how all the ash can be completely discharged without any ash remained in hopper, at one discharge process of ash handling system. In accordance with the characteristics of ash, the appropriate countermeasure shall be added to assist ash discharge from hopper, and the following design considerations are required depending on the condition.

- Conical shape hopper is adopted (with suitable valley angle).
- Hopper heater is necessary to avoid water condensation on hopper wall, however the temperature shall not be too high to avoid decomposition of ammonium sulfate. (Steam heater is preferable, since the heating temperature is constant.)
- Vibro-motor is installed.
- Air agitator is installed.
- "Pulse air agitator" is additionally installed. (Especially when ash discharge condition is bad, installation of standard air agitator is not enough, and agitator should be added. In this case, in order to save air consumption, pulse jet air, which is effectively injected at very short time, is adopted. To avoid erosion on hopper wall, the set angle of the jet is important, and the pulse jet air is injected tangentially to the wall.)

Fig 3-6 shows the typical view of hopper with air agitator, which is applied in DEP for the plant using very high sulfur content fuel.



Criteria for Ash Discharge from Hopper
Region A : No Problem
Region B : Caution
Region C : Danger
Region D : Pending (Few Data)

Fig 3-5: Criteria for Ash Discharge from Hopper

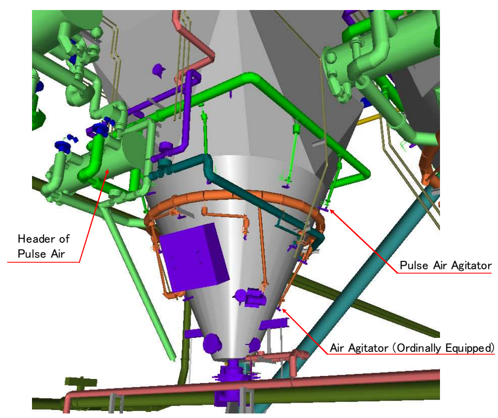


Fig 3-6: Hopper of Dry-type ESP for High Sulfur Content Fuel Fired Boiler

4 "Salt Solution Spray + Wet-type ESP" System

One of alternative SO_3 reduction system for boiler flue gas is Wet-type ESP (WEP) [2][3]. WEP can collect SO_3 mist very effectively from the water saturated gas at downstream of FGD, however the maximum concentration of SO_3 ever experienced is about 80ppm, and less than 60ppm of SO_3 is preferable for the stable operation of WEP. If SO_3 concentration becomes higher, it will be very difficult to keep performance of WEP due to space charge effect, and it will also be too severe in corrosion point of view.

When SO_3 concentration is very high such as 100ppm or more, SO_3 should be reduced prior to be introduced into WEP, and one of such pre-treatment system has was introduced at the last ICESP [4], as salt solution spray (SSS) system, which had already been in commercially applied stage. The basic information of the first commercial installation is as shown in Table 1.

The basic configuration of SSS system is shown in Fig 4-1. Salt solution included in FGD effluent is sprayed into the flue gas duct. In the first commercial installation, sodium-process FGD is installed, so that the solution of $NaHSO_3$ and Na_2SO_4 are injected. Sprayed

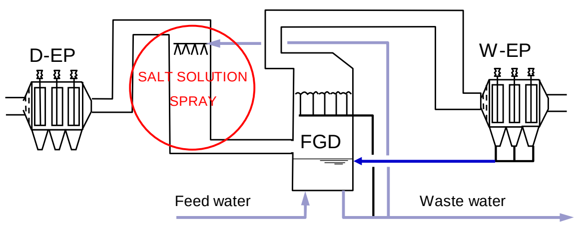


Fig 4-1: Configuration of Salt Solution Spray System

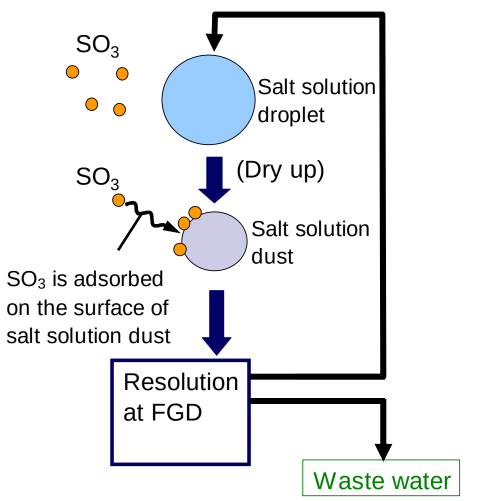


Fig 4-2: Mechanism of Salt Solution Spray

droplet including salt solution is drying up in the flue gas, and absorbing SO_3 on its surface (as shown in Fig 4-2). Salt solution droplet does not react with SO_2, and it absorbs selectively only SO_3, so that SSS is very effective for SO_3 reduction.

This plant, with first commercial installation of SSS, has never shut down except for its annual periodical shut down for maintenance, and one year continuous operation of SSS has been already achieved for several times. During the operation, 80 to 90% of SO_3 can be stably removed from the flue gas, and the concentration of SO_3 at inlet of WEP can be reduced to its allowable limit, and this "SSS + WEP" system has been proven to be effectively applied to very high sulfur content fuel.

5 Summary

Using residual materials from oil refinery with high sulfur content as boiler fuel, due to high content SO_3 in flue gas, DEP can easily be suffered with energization problem and hopper clogging, and its continuous operation is very difficult when "NH_3 injection + DEP" system is applied. However, we have achieved six months or one year level of the continuous operation of the system without any shut down for water washing of DEP internals during the operation. And when the new system of "SSS + WEP" is applied, we have achieved one year continuous operation, and it has been proven as a good alternative.

6 Literature

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