

WHITE PLUME REMOVAL USING FUEL ADDITIVES IN THERMAL POWER PLANTS

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Flue gas desulfurization (FGD) facilities have been operated to reduce the air emissions of sulfur oxides in many thermal power plants. Even though they satisfy the strict air emission standards in terms of sulfur oxide concentrations, power plants that use heavy oil, having high sulfur content, as fuel have been troubled with their visible plume opacity such as white plume. The general public who lives near the power plants has complained about the plume opacity from the power plant stacks. In this study we investigated causes of the white plume produced from the thermal power plants in Ulsan, Korea. Fuel additives, containing magnesium slurry and emulsifiers, were injected into the burner systems of the boilers to remove the white plume from the stacks. The average temperature of the cold end section in the air pre-heater was maintained below the acid dew point of sulfuric acid. Significant emission reduction of SO₃ in the flue gases by injecting fuel additives resulted in successful removal of the visible white plume. In addition, the combustion characteristics and thermal efficiency of the boilers have been significantly improved. The catalyst operation temperature, flue gas temperature and excess air volume significantly reduced. Finally, we solved the complaints concerning the visible white plume and also saved a large amount of the power plant operation costs through improvement of thermal efficiency of the systems and improvement of the combustion efficiency of the boilers.

INTRODUCTION

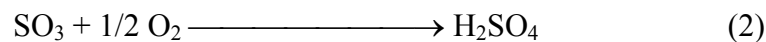
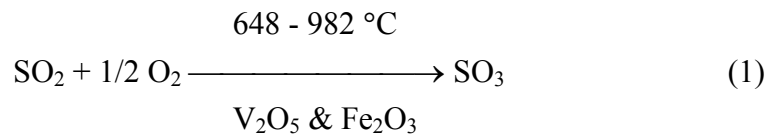
Electric power plant is usually considered as one of large stationary emission sources of sulfur oxides (SO_x). Many power plants are operating flue gas desulfurization (FGD) facilities to reduce the air emissions of sulfur oxides. Even though the strict air emission regulations of sulfur oxides have been well-satisfied by maintaining well-operated FGD facilities, the general public who lives near power plants has complained about the plume opacity, such as white plume visibility, emitted from power plant stacks. Chain reactions among materials included in fuels, various chemical reactions among materials exhausted from stacks into the atmosphere, improper combustion or combustion condition changes in fuel combustion processes and meteorological conditions may become important causes of plume opacity occurrence. Some examples of visible plume or plume opacity are as follows [1]: 1) If the exhaust gases were not sufficiently heated above the dew point of water vapor, a visible plume is produced by the humidity difference between the exhaust gases and the ambient air. The visible plume, however, disappears instantly after exhausting from stacks. 2) The second example is a visible plume produced by nitrogen oxides (NO_x) included in the exhaust gases. The color of this plume is mainly yellow. This colored plume is primarily a result of scattering and absorbance of sunlight. In fact, the color of the plume is slightly different from different angles. 3) Another important cause of a visible plume is due to the emission of condensed sulfuric acid mist. Sulfuric acid mist is produced by a condensation of gaseous SO₃ in the air temperature below a dew point of sulfuric acid.

In the previous study of plume opacity produced from the power plants operating in Ulsan, Korea, it is identified that a main cause of the white plume was due to the formation of sulfuric acid mist. As such, even though only 5 – 10 ppm of SO₃ is included in the exhaust gases from power plant stacks, it still can produce plume opacity. The power plants under the study were producing about 50 – 60 ppm of SO₃. If the maximum SO₃ concentration that the white plume is not to be observed is assumed as less than 2ppm, approximately 95% of the current concentration of SO₃ should be removed. Currently, installation of wet electrostatic precipitator (ESP) and injection of alkaline absorbents are mainly considered as removal methods of SO₃ in the flue gases [2]. In fact, it is not easy to adopt the wet ESP option requiring high initial investment and additional modification in the outlet section of absorption tower. It is easy to apply the injection of alkaline absorbents into the inlet of the ESP for removal of SO₃, however, this option has low removal efficiency and may produce severe drawbacks for a normal operation of the ESP. One feasible technology is considered as a real

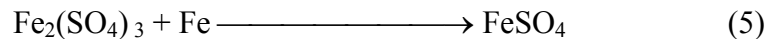
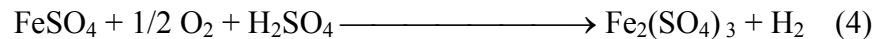
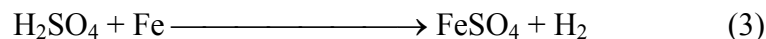
application measure for removal of white plume visibility by removing sulfuric acid mist. The feasible option is to use fuel additives, such as MgO, for formation reduction of SO₃ from flue gases and for improvement of fuel combustion efficiency at boiler. This paper reports the removal effect of white plume visibility and improvement effect of thermal efficiency using fuel additives (MgO) at power plants that use a fuel containing a high content of sulfur, such as 2.5%S.

SO₃ AND WHITE PLUME FORMATION

White plume visibility in oil-fired boiler usually originates from sulfuric acid formed by condensation of flue gases including water and sulfur oxides produced from oxidation of sulfur, contained in fuel, as follows:



The sulfuric acid exists as a vapor phase in the flue gas temperature or the temperature above the dew point of sulfuric acid. However, sulfuric acid in the temperature under the acid dew point within the boiler zone is condensed resulting in acid corrosion on the metal surfaces as follows:



When the sulfuric acid is emitted from stacks, it produces visible white plume by scattering and absorption of sunlight. The dew point of sulfuric acid in power plants depends upon sulfur content in the fuel, the oxygen (or excess air) content used for combustion, and SO₃ concentration formed in flue gases.

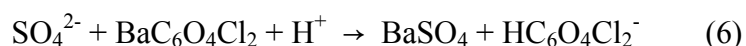
MATERIALS AND METHODS

The Power Plants

The electric power plants used for this study use bunker C oils containing a high content of sulfur as fuel and, therefore, emitting large amounts of sulfur oxides. These electric power plants operate 3 facilities with a power generation capacity of 400 MW and they use JBRs as flue gas desulfurization facilities. The FGD facilities were designed to maintain a desulfurization efficiency of above 90% and an emission concentration of sulfur oxides below 150 ppm. A wet limestone (CaCO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) method is used for desulfurization in the JBRs[3]. Gypsum with a purity above 95% is produced as a by-product. The boiler of the power plants has a water evaporation capacity of 1,184 ton/hr. The power plant stacks have a height of 150m, a diameter of 5.7m, a sampling point of 37.5m height and an exhaust gas ventilation velocity of 18.0 m/s.

Experiments

To identify that the visible plume by condensed sulfuric acid mist is formed, the process temperature was investigated as to whether or not the FGD system maintains temperatures below the dew point of sulfuric acid. Concentrations of SO_3 and SO_2 were identified at the inlet and outlet of the air pre-heater (AH) before and after adding the fuel additives (MgO and emulsifiers) into the study system. MgO slurry (Pentomag) was continuously fed into the inlet of the top burner (4PI) by a feed pump with a rate of 500ppm (0.50kg of MgO/ton of fuel). Emulsifier slurry (Pentomulus) was also continuously injected into the inlet of the F.O. daily tank by a feed pump with a rate of 350ppm (0.35kg of emulsifiers/ton of fuel). Fuel was emulsified by spraying water, 8wt% of fuel, and it was almost completely combusted with small amount of excess air. Flue gases that might include SO_3 or H_2SO_4 were absorbed into an isopropyl alcohol solution (consisting of 80% alcohol plus 20% water) using a stack gas sampler. SO_3 or H_2SO_4 would be existed as SO_4^{2-} in the absorbing medium. The solution including SO_4^{2-} produces $\text{HC}_6\text{O}_4\text{Cl}_2^-$ with passing through $\text{BaC}_6\text{O}_4\text{Cl}_2$ layer as the following reaction:



The concentrations of SO_3 or H_2SO_4 in flue gases were determined by measuring the absorbance of $\text{HC}_6\text{O}_4\text{Cl}_2^-$ ion at 535nm. In order to reduce the concentration of SO_3 by

improving the condensation efficiency of SO_3 into H_2SO_4 , the average temperature of the cold end section of the AH was adjusted below the dew point of sulfuric acid. The injected MgO could neutralize the acidic environment and significantly reduce an acid corrosion possibility expected in the cold end section of the air pre-heater. The average temperature of the cold end section of the AH was gradually reduced from 135°C to 75°C . The pH of the ash obtained from the hopper of the electro precipitator before and after adding the fuel additives was continuously monitored using a pH meter. The amount of MgO slurry injected was adjusted to maintain a proper pH range, above pH 4.0, which could prevent acid corrosion of the cold end section of the AH.

The main procedure of the study consisted of two major experiments: analysis of removal processes of white plume and effects on equipments by the removal processes. The removal processes included the stabilization tests of ash pH for three weeks and temperature reduction tests of flue gases from 160°C to 105°C for three weeks. The tests of the effects on the equipments included continuous monitoring of the degree of fouling and self-cleaning status on the walls inside combustion chamber of the boilers and the outside surfaces of the tubes supplying fuel and additives. The change of ash pH, SO_3 concentration and the temperature of the flue gases at the outlet of the AH, and the change of nitrogen oxides (NO_x) concentrations were also investigated to identify the effects on the equipments during the experiment period of two months. In addition, the combustion system efficiency concerned the injection of fuel additives and the particulate removal efficiency of the electrostatic precipitators were monitored for five weeks.

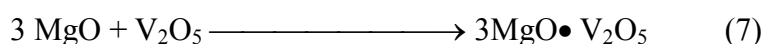
The ash pH and the slag status of the ash that was not collected in the electrostatic precipitator were continuously monitored for identification of the fouling and self-cleaning status during the injection of the fuel additives and the reduction of the flue gas temperature. The SO_3 concentrations at the inlet and outlet of the AH were monitored, and the maximum gas temperature that white plume at the stacks was invisible was identified. The reduction of excess air and the improvement of combustion efficiency could lead to reduction of nitrogen oxides. The maximum reduction degree of atomizing, combustion status, reduction degree of amount of excess air, amount of injected water, gas temperature at ECO outlet, NO_x and CO concentrations versus O_2 concentrations were measured during the NO_x reduction experiments accompanied with SO_3 reduction. In order to analyze the effects accompanied with a temperature change (reduction) of flue gases, dust and SO_3 concentrations, Ash pH, gypsum purity, and current (efficiency) of the electrostatic precipitator were monitored during the experiments. In order to identify the effects accompanied with injection of fuel additives, NO_x and SO_3

concentrations, Ash pH, gypsum purity, fraction of unburned carbon, and boiler efficiency were also analyzed. The SO₂ and NO_x concentrations were continuously obtained by tele-metering system (TMS) equipment at the stacks of the power plants during the experiments. To more easily observe the effects of visible plume reduction or removal, days with a clear sky were chosen as experimental days. By keeping the same operating conditions of the boilers in each experimental situation, the removal efficiency of the visible plume was identified with the naked eye and with photographs.

RESULTS AND DISCUSSION

Strategies of SO₃ and white plume formation prevention

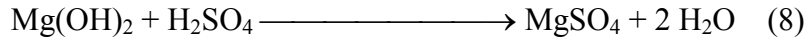
One of major strategies to prevent formation of white plume in the power plants that use bunker C oil containing a high sulfur content, 2.5 – 2.7%S, as fuel is to control SO₃ formation in the flue gases of the boilers. SO₃ is mainly formed from oxidation by excess oxygen (air) or vanadium oxide (V₂O₅) catalyst of SO₂ produced from combustion of fuel. Therefore, one method to reduce SO₃ formation level is to decrease the amount of excess oxygen without producing any problems of fuel combustion. This can be accomplished by injection of metal catalyst into fuel system or by increase of fuel combustion efficiency by emulsifying fuel. Oil containing a high content of sulfur usually includes high concentration of vanadium. Vanadium oxide exists as a liquid phase in the combustion zone or temperature. However, the vanadium oxide that has a relatively low melting point of approximately 600 °C deposits on the heat exchanger (or transfer) surface such as water wall tube or super heater, and then it roles as a SO₃ formation catalyst. Therefore, the other method to reduce SO₃ formation level is to add fuel additives such as magnesium oxide to prevent surface coating or scaling of vanadium oxide, which roles as a SO₃ formation catalyst, on the heat exchanger surface. Magnesium oxide added into the fuel reacts with vanadium oxide resulting in magnesium and vanadium oxide (3MgO• V₂O₅), which has a much high melting points of approximately 1,180°C, as follows:



The formed magnesium and vanadium oxide also can affect crystal structure of ash, and thus it can prohibit particle growth resulting in preventing fouling by ash.

Another strategy to prevent formation of white plume in the power plants is to remove the condensed sulfuric acid after conversion of SO₃ into H₂SO₄ as the following

reaction by reducing the average temperature of the cold end section of the AH:



Removal Effect of White Plume

Table 1 summarizes the results of white plume removal experiments in the power plant #6. There was no change in SO₂ concentration in the inlet of the AH between before and after injection of fuel additives. However, there was significant reduction of 92.6% in the outlet of the ESP after injection of fuel additives. 24.4% reduction in SO₂ concentration at the outlet of the flue gas desulfurization facilities and 19.1% reduction in the stack temperature were also observed between before and after the injection. If the SO₃ concentration at the outlet of the ESP under the temperature below the sulfuric acid dew point is higher than 2ppm, the white plume might be observed. Even though the stack temperature was much less than the dew point of sulfuric acid, the white plume was not observed in this study. That is because SO₃ was removed by reducing the average temperature at the cold end section of the air pre-heater from 135 °C to 75 °C. This temperature reduction is almost equivalent to the reduction of flue gases from 160 °C to 120 °C. The 2 ppm of SO₃ can be condensed into sulfuric acid, which might result in visible white plume, in the flue gas temperature below the acid dew point of 122 °C. SO₃ was condensed into sulfuric acid (H₂SO₄) at the cold end section of the air pre-heater of 75 °C and then neutralized by reacting with MgO that is an alkaline agent. Thus the pH of the ash at the outlet of the ESPs before injecting of MgO was 2.9, however, the pH after injecting MgO increased to 4.3. This pH increase can significantly contribute to the reduction of a degree of metal corrosion. Thus the SO₃ concentration at the outlet of the ESPs by adding MgO was maintained about 1.3ppm, which was much less than 2ppm, and resulted in no white plume observation.

	Before Injection	After Injection	White Plume (WP)
AH Inlet SO ₂ Conc. (ppm)	1,347	1,346	WP is not observed
ESP Outlet SO ₃ Conc. (ppm)	17.47	1.3	
FGD Outlet SO ₂ Conc. (ppm)	127	96	
Stack Temperature (°C)	94	76	

Table 1: Result summary of the white plume removal experiments in the power plant #6

Table 2 represents reduction in SO₃ concentration at the outlet of the ESPs operated in the power plants under the study. All the SO₃ concentrations were ranged from 1.3 to

0.35ppm, which represents from 92.6 to 99.0% reduction, after injection of the fuel additives. Thus all the power plants under the study can successfully remove the white visible plume problems by adding the fuel additives, MgO and the emulsifiers, into the inlet of the top burner and by reducing the temperature at the cold end section of the air pre-heater.

Power Plant	SO ₃ Concentration (ppm) at Outlet of EPs		White Plume (WP) Status
	Before Injection	After Injection	
#4	17.47	1.3	WP is not observed
#5	17.15	0.4	WP is not observed
#6	36.7	0.35	WP is not observed

Table 2: SO₃ concentration and white plume status of fuel additive injection in the power plants

Improvement of Thermal Efficiency

Table 3 compares the effects concerned thermal efficiency before and after this study. MgO addition into the fuel significantly improved the thermal efficiency of the boilers resulting in significant reduction in the temperature of the flue gases and excess air percentage of boilers. Thus significant increase in the degree of fuel combustion efficiency led to reduction in the unburned carbon fraction. Reduction of excess oxygen available to oxidation of SO₂ to SO₃ and the magnesium and vanadium oxide (3MgO•V₂O₅) contributed to significant reduction in SO₃ formation. SO₃ concentration reduction and increase in the degree of completeness of fuel combustion decreased dust formation through the entire combustion system. The MgO used as fuel additives also contributed to prevention of surface coating of vanadium oxide and fouling of ash resulting in decrease in the dust concentration of 66.3%.

Item	Unit	Before	After
White Plume at Stacks	-	Observed	Not observed
Flue gas temperature of boilers	°C	160	100 ~ 120
S.A./H water vapor amount	ton/h	15	0
Recirculation temperature of flue gases	°C	332	312
Excess air percentage of boilers	%	1.05	0.80
Water vapor temperature of recirculation steam	°C	524	541
Unburned carbon fraction	%	70.4	52.5
Dust concentration at inlet of EPs	mg/Nm ³	454	153

Table 3: Comparison of the effects concerned thermal efficiency before and after the study

Economy Analysis of the White Plume Removal

Table 4 shows a summary of the yearly economy analysis for solving the white plume problems by adding fuel additives into boiler and by reducing the temperature of the cold end section of the air pre-heater in the power plants under the study. Even though the purchasing costs of the fuel additives and the additional costs by loss of water from the additives are necessary, the power plants could significant amount of money by successfully solving the white plume problems. Flue gas temperature and AH supply steam heat could significantly reduce by greatly reducing SO₃ concentration resulting in significant amount of the costs. The power plants also greatly save the flue gas recirculation costs and power costs for desulfurization.

Cost comparison item	Saving Costs (Thous. US\$)	Operation Costs (Thous. US\$)	Remarks
Additives purchase	-	1,489	
Chemical injection equipment rent	-	92	
Additional water	-	8	
Water loss from additives	-	451	
Flue gas temperature reduction	1,280	-	40 °C reduction (160→120 °C)
AH supply steam heat reduction	1,540	-	48 °C reduction (90 → 42 °C)
Power saving for desulfurization	216	-	BUF power cost reduction
Flue gas recirculation	797	-	Catalyst operation temp. reduction (335 → 312 °C)
Ammonia purchasing	316	-	
Subtotal for fuel additive injection	4,149	2,040	
Net economy (saving – operation)	2,109		2.1 M USD/yr-power plant
Total saving for 3 power plants	6,329		6.3 M USD/yr-3 power plants

Table 4: The yearly economy analysis of white plume removal by fuel additives in the power plants

Ammonia, as an absorbing medium to solve the white plume problems and as a conditioning agent to improve the ESP operation efficiency, has been injected into the power plant system. However, the white problems were not completely removed. In addition, unreacted ammonia and ammonium salts, [ammonium bisulfate (NH₄HSO₄)

and ammonium sulfate ((NH₄)₂HSO₄) produced from the reaction between SO₃ and added ammonia, were adsorbed onto fly ashes. Also, ammonia might be leaked in the middle of the disposal processes of the ashes including the adsorbed materials produced an odor problem, and the workers were reluctant to handle ammonia. However, the power plants under the study did not have to use ammonia and completely solved the white visible plume problems. Thus they could save purchasing costs of ammonia. In solving their the white visible plume problems by addition of fuel additives into the boilers and by reduction of the cold end section temperature of the air heaters, the power plants which are operating three power plants of 400MW could save 6.3 million US dollars per year.

CONCLUSIONS

In order to remove the white plume problems produced from the stacks of power plants that use bunker C oil containing a high content of sulfur, the fuel additives containing magnesium slurry and emulsifiers were injected into the burner systems of the boilers. The average temperature of the cold end section in the air pre-heater was also maintained below the acid dew point of sulfuric acid. Injection of fuel additives and the temperature reduction led to significant reduction in SO₃ concentration in the flue gases and also resulted in successful removal of the visible white plume. In addition, the catalyst operation temperature, flue gas temperature and excess air volume significantly reduced. Finally, the power plants could save a large amount of the power plant operation costs concerned the white plume problem solving through improvement of thermal efficiency of the systems and improvement of the combustion efficiency of the boilers.

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