Effect of technology application of NO\textsubscript{x} removal by O\textsubscript{3} on fly ash concentration

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Abstract. An experimental study was carried out on the concentration of dust in flue gas from the outlet of desulphurization system under the conditions of different ammonia and ozone recharge. When the dust samples were dried at different temperatures, the mass concentration of dust was quite different. Analysis of samples by TG-DSC and XPS, It was concluded that the great change in the mass concentration of soot is mainly due to the influence of the combined denitrification process of SNCR and O\textsubscript{3} on the composition of the original flue gas. The formation of Soluble salt was carried by droplets in the flue gas and retained on the filter membrane. It led to a great change in the concentration of dust. The main substances of the soluble salt were carbonic acid, ammonium nitrate and calcium nitrate.

1. Introduction

At present, in order to implement the Circular of the General Office of the State Council on the issuance of the Strategic Action Plan for Energy Development (2014-2020) (issued by the State Office (2014) No. 31). more than 90% of the thermal power units in China had completed the transformation of ultra-low emissions. The emission standards could meet the emission limits of NO\textsubscript{x}, SO\textsubscript{2} and dust emission concentrations 50, 35 and 10mg/m\textsuperscript{3} (standard, dry base, 6%O\textsubscript{2}) specified in the notice\textsuperscript{[1]}. In order to meet the NO\textsubscript{x} emission target value, Low nitrogen Combustion Technology (LNB) and selective Catalytic reduction Technology (SCR) were generally used in Coal-fired generating sets of large Power Plant boilers\textsuperscript{[1,2]}, Selective non-catalytic reduction technology (SNCR) was generally used in small pulverized coal units or circulating fluidized bed units. More than 90% of NO\textsubscript{x} was NO in flue gas of coal-fired units\textsuperscript{[3-5]}. Because of the very low water solubility of NO, it could not be effectively absorbed by desulphurization absorption liquid. According to the very low water solubility of NO. Some small coal-fired units adopt a new denitrification process to meet the emission requirements of NO\textsubscript{x} after using SNCR. Such as non-thermal plasma oxidation\textsuperscript{[6]}, electron beam flue gas treatment\textsuperscript{[7]}, direct oxidation of O\textsubscript{3} and NaClO\textsubscript{2} oxidants\textsuperscript{[8-12]} to promote the absorption of NO in flue gas. Among them, O\textsubscript{3} oxidants had the advantages of high oxidation efficiency, strong oxidation selectivity and no secondary pollution of oxidation products at low temperature\textsuperscript{[13]}. However, the application of these new denitrification technologies only took into account the oxidative absorption of NO or the synergistic removal of NO\textsubscript{x}, SO\textsubscript{2} and mercury, and did not study and discuss the effect of the application of this technology on the emission of fly ash concentration.

This paper took a small boiler as the research object, using ammonia as reducing agent, using SNCR denitrification process and desulphurization inlet using O\textsubscript{3} oxidation process. the concentration
of dust in flue gas was measured, and the filter membrane was analyzed by comprehensive thermal analysis (TG-DSC) and X-ray photoelectron spectroscopy (XPS). The composition of dust was qualitatively analyzed after SNCR and O₃ denitrification, and the effect of ozone denitrification on soot emission was discussed.

2. Test object and method

2.1 Brief introduction of Test Unit

This paper mainly aimed at the 210t/h circulating fluidized bed of a chemical enterprise in Zhejiang Province as the test object. The unit used environmental protection facilities as shown in the following figure.

![Figure 1. Process flow chart of test unit.](image)

The unit adopt SNCR and ozonation process, high efficiency limestone-gypsum wet desulfurization process, high efficiency dedusting device and wet electric dedusting process. In the denitrification process, SNCR was arranged at the inlet of the cyclone separator, and ozone was injected into the inlet of the desulfurization absorption tower for denitrification.

2.2 Analytical instruments and methods

Under different ozone consumption conditions, samples of dust were done at the outlet of desulfurization absorption Tower by using LaoYing 3012H Dust Sampler. The filter membrane was dried at 105°C, 175°C and 250°C. The dried samples were weighed after constant weight, and analyzed by TG-DSC and XPS.

3. Results and discussion

3.1 Filter membrane weight at different drying temperatures

| num
ber | Inlet
flue
gas
temperature | Outlet
flue
gas
temperature | Flue
gas
volum
e | Ammonia
consumption
per hour | Ozone
consumption
per hour | Weight after
drying at 105°C--
mgm⁻³ | Weight after
drying at 175°C--
mgm⁻³ | Weight after
drying at 250°C--
mgm⁻³ |
|------|-----------------|-----------------|---------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1st
day | 100 54 20000 | 108 90-120 5.2 8.7 5.9 0.8 2.1 0.9 / / / |
| 2nd
day | 125 49 20000 | 262 150-170 35 2 30.1 25.0 25.5 21.4 12.6 2.06 / 2.7 |
| 3rd
day | 145 49 44299 | 488 281 9.7 8.3 / / / / 4.5 3.7 / |

Remarks: Numbers ①、②、③ were three samples, the quality of the same sample at different drying temperatures.
According to the Method of performance tests for electrostatic precipitator (GB 13931-2017) and Stationary source emission-Determination of mass concentration of particulate matter at low concentration-Manual gravimetric method(HJ 836-2017), the sampling heads should be placed at a constant temperature of 105℃ and 110℃, dried for 2h and 1h, and then cooled in constant temperature and humidity equipment, and weighed after meeting the corresponding prescribed conditions.

From the comparison of the data on the 1st and 2nd days in Tab.1, Under the condition that the load of the unit remained unchanged and the dedusting system was running normally, When the inlet flue gas temperature increased, the amount of ammonia and ozone recharge in the SNCR region increased, and the smoke concentration at the desulfurization outlet increased from 5.2mg/m³, 8.7mg/m³, 5.9mg/m³ to 35.2mg/m³, 30.1mg/m³, 25.0mg/m³. The average value increased from 6.6mg/m³ to 30.1mg/m³, and the absolute value of weight increased by about 78%. The increase of the soot concentration was mainly due to the chemical reaction between the escape ammonia and the unreacted NO in the SNCR region and the ozone supplied at the inlet of the desulfurization system, resulting in the formation of substances that were easily soluble in water. After desulfurization and washing, the soot sampler captures the droplets in the flue gas and leaves the soluble salt and insoluble or slightly soluble substances on the filter membrane, which lead to a significant increase in the concentration of soot.

From the comparison of the data on the 1st and 3rd days in Tab.1, Under the condition that the load of the unit remained unchanged and the dedusting system was running normally, With the increase of load, the amount of ammonia and ozone recharge in SNCR region increased, and the smoke concentration at the outlet of desulfurization increased from 5.2mg/m³, 8.7mg/m³ and 5.9mg/m³ to 9.7mg/m³ and 8.3mg/m³. The average value rose from 6.6mg/m³ to 9.0mg/m³, and the absolute value of weight increased by about 7%. The smaller increase in fly ash concentration was mainly due to the increase in the load of the unit, although the amount of ammonia and ozone recharge increases. However, with the increase of unit load, the initial NOx concentration increased greatly, and the ammonia water consumption and ozone consumption increased. The reaction degree of unreacted NO and escape ammonia equal to desulphurization inlet ozone was lower than that of excess recharge reaction. The formation of soluble matter decreased, so the concentration of smoke and dust increased slightly.

3.2 Filter membrane composition analysis

Under the condition of different load, different consumption of ammonia and ozone. There was a great difference in the concentration of dust at the outlet of the desulfurization system. It was mainly due to the existence of a large number of decomposing substances in the residual substances of the filter membrane. In view of this phenomenon, the qualitative analysis of filter membrane was carried out by using TG-DSC and XPS.

3.2.1 Analysis of existing substances in filter membrane.

In the denitrification, desulphurization and dedusting process adopted by the unit, the participation of ozone led to the change of flue gas composition in the desulfurization system and the change of ions in the slurry of the desulfurization system.

Table 2 lists several major elementary reactions in the process of O₃ oxidation of industrial flue gas. The kinetic parameters of the reaction were taken from the NIST (National Institute of Standards and Technology) database of the American Institute of Standards. The reaction rate constant was:

\[ k = AT^b \exp(-E_a/RT) \]

| Reaction         | A        | b | Ea/(cal/mol) |
|------------------|----------|---|--------------|
| O₃+NO→NO₂+O₂     | 8.43×10¹¹| 0 | 2600         |

Table 2. Reaction kinetic parameter [14-16].
| Reaction | A         | b  | Ea/(cal/mol) |
|----------|-----------|----|--------------|
| O$_3$+NO$_2$==NO$_3$+O$_2$ | 8.40×10$^{10}$ | 0 | 4910 |
| NO$_2$+NO$_3$==N$_2$O$_5$ | 7.98×10$^{17}$ | -3.9 | 0 |
| O$_3$+SO$_2$==O$_2$+SO$_3$ | 1.81×10$^{12}$ | 0 | 13910 |
| O$_3$+CO==O$_3$+CO$_2$ | 6.02×10$^{2}$ | 0 | 0 |
| O$_3$+H$_2$O==O$_2$+H$_2$O$_2$ | 6.62×10$^{10}$ | 0 | 0 |
| O$_3$+HCl==HOC$l$+O$_2$ | 2.83 | 0 | 0 |

By the reaction parameters, in the process of O$_3$ oxidation of NO$_x$, the formation rate of NO$_2$ and N$_2$O$_5$ was higher than that of NO$_3$. The generated NO$_3$ was easy for NO$_2$ to react to generate N$_2$O$_5$, the final products of O$_3$ oxidation of NO were NO$_2$ and N$_2$O$_5$. The resulting N$_2$O$_5$ was easily soluble in water to form HNO$_3$. The reaction rate of O$_3$ oxidation of NO$_x$ was higher than that of O$_3$ oxidation of SO$_2$, so O$_3$ had a certain selectivity $^{[17]}$.

According to the above reaction, the following main ions might exist in the slurry of desulfurization system due to denitrification escape ammonia and other reasons.

Cation: Ca$^{2+}$, NH$_4^+$, H$^+$
Anion: CO$_3^{2-}$, NO$_3^-$, SO$_4^{2-}$, OH$^-$, Cl$^-$

### 3.2.2 TG-DCS result analysis.

According to Fig.2, the sample began to decompose at 176.62°C and stopped to decompose at 260.01°C. The weight loss rate was 26.99%.

![TG-DCS result analysis](image)

**Figure 2. Analytical atlas and test results.**

| Number | substances | Decomposition temperature - °C | Solubility          |
|--------|------------|--------------------------------|---------------------|
| 1      | CaCO$_3$   | 800                            | Slight dissolution  |
According to Fig.2 and Tab.3, the starting decomposition substances should be mainly NH$_4$HCO$_3$, NH$_4$NO$_3$, NH$_4$Cl, Ca(NO$_3$)$_2$ and (NH$_4$)$_2$SO$_4$ at 176.62 °C. After treatment at 260.01 °C, the remaining substances should be CaSO$_4$, CaCO$_3$ and fly ash.

### 3.2.3 XPS result analysis

Table 4. X-ray photoelectron spectroscopy analysis and test results.

| Name   | 1st specimen | 2nd specimen |
|--------|--------------|--------------|
|       | After treatment at 105°C | After treatment at 250°C | After treatment at 105°C | After treatment at 250°C |
| Atomic % | Atomic % | Atomic % | Atomic % | Atomic % |
| Al2p   | 5.81          | 6.21         | 5.5        | 5.33         |
| C1s    | 26.31         | 19.14        | 29.61      | 23.74        |
| Ca2p   | 1.02          | 0.79         | 0.74       | 0.67         |
| Cl2p   | 3.14          | 0.34         | 1.18       | 0.4          |
| Cr2p   | 0.6           | 0.57         | 0.58       | 0.55         |
| F1s    | 0.89          | 0.85         | 0.88       | 0.52         |
| Fe2p   | 1.39          | 1.258        | 1.23       | 0.77         |
| I3d    | 0.08          | 0.09         | 0.1        | 0.1          |
| K2p    | 0.14          | 0.19         | 0.28       | 0.13         |
| Mg1s   | 0.67          | 0.3          | 0.5        | 0.45         |
| N1s    | 5.12          | 3.92         | 3.39       | 2.23         |
| Na1s   | 1.43          | 0.95         | 1.37       | 1.28         |
| O1s    | 39.23         | 47.61        | 40.07      | 45.75        |
| P2p    | 0.73          | 0.77         | 0.74       | 0.75         |
| S2p    | 1.69          | 3.63         | 1.43       | 2.74         |
| Si2p   | 11.07         | 12.79        | 11.8       | 14.07        |
According to Tab.4, after calcination at different temperatures, the content of oxygen was maintained at 40 to 50%. Main reason: The matrix itself contains oxygen. In the process of sample preparation, oxygen existed in the microscopic gap in the process of sample preparation, mainly by physical adsorption. Oxygen adsorption occurred in the process of entering XPS\[18\].

According to Tab.4, the sample decomposed after calcination at 250°C. The main substances were nitrate and carbonate, and a small amount of hypochlorite.

### 4. Conclusion

Through the analysis of dust concentration at the outlet of wet desulphurization after using SNCR and ozone combined with denitrification process, Denitrification combined with ozone denitrification process directly affected the concentration of smoke and dust at the outlet of desulfurization system after traditional denitrification process. According to the requirements of the national and environmental standards, the soot concentration contains the soluble salts carried in the droplets, and the main substances were carbonic acid and nitrate ammonium salt and nitrate calcium salt.

Based on the results of the above analysis, in view of the combination of the traditional denitrification process and the ozone denitrification process unit, the ozone replenishment should be strictly controlled. Prevent excessive ozone emission while preventing excessive ozone from reacting with the original components in flue gas. After the reactant was dissolved in water, it reacted with escape ammonia and other substances to form a large number of soluble salt, resulting in difficulty in dehydration of gypsum. At the same time, under the condition of high droplet control index, the droplets carried soluble salt and caused the desulphurization outlet smoke to exceed the standard.

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