Research on removal of NOX, SO2 and PM from flue gas of coal-fired boilers and engineering application

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Abstract: Removal of NOX and SO2 from flue gas by Ozone (O3) oxidation and NaOH absorption was carried out in practical engineering. The effects of the liquid to gas ratio (L/G), the molar ratio of O3 dosage and initial content of NOX (O3/NOX), pH and NaOH concentrations on the removal efficiencies of NOx and SO2 were investigated. In addition, the influences of O3/NOX and voltage on the removal of PM were analyzed. The results show that the NOX removal efficiency increases with the increasing of O3/NOX (0~2.0), solution pH (4~7) and L/G (2~8), while is slightly affected by NaOH concentration (0.05~1%). The SO2 removal efficiency increases with the increase of L/G from 2 to 8 L/Nm³, but is hardly changed by O3/NOX (0~2.0), NaOH concentration (0.05~1%) and solution pH (4~10). It was found that the outlet concentration of PM (CPM) decreased with the rise of voltage ranging from 0 to 40 kV, however, slightly increases with the increment of O3/NOX at a range from 1.6 to 2.0. The optimal operating conditions can be established when taking running costs and rigorous ultra-low emission standards into consideration. Under the optimal conditions, the removal efficiencies of NOX and SO2 reached more than 75% and 98% respectively, and CPM could be also controlled within 5 mg/Nm³.

1. Introduction
In China, the typical air pollutants are sulfur dioxide (SO2), nitrogen oxides (NOX) and particulate matter, which are emitted into atmosphere from coal-fired boilers giving rise to acid deposition and hazy weather [1-2]. In recent years, the wet flue gas desulfurization (WFGD) units are considered as optimized method for SO2 removal due to their high removal efficiency and wide applicability [3]. The selective catalytic reduction (SCR) with ammonia is applied widely for NOX reduction [4-5]. However, it is unsuitable for the flue gas treatment of small industrial boilers because of its high cost and strict temperature requirements of catalyst. The advanced techniques for simultaneous removal of SO2 and NOX from flue gas have been studied, including non-thermal plasma (NTP) [6-7], chemical absorption [8-9] and gas-solid phase absorption [10]. The advantages of NTP are simple process, low resistance and high oxidation efficiency. O3 injection [11-12] is a kind of NTP, which has been widely used in the flue gas reconstruction of small and medium-sized boilers. The bag dust collector is commonly used for PM removal before WFGD, furthermore the outlet concentration of PM (CPM) can be controlled below 20 mg/Nm³. The wet electrostatic precipitator (WESP) is installed downstream of WFGD to remove fine PM and sulfuric acid mists to satisfy the rigorous ultra-low emission standards (SO2≤35 mg/Nm³, NOX≤ 50 mg/Nm³, PM≤ 5 mg/Nm³) [13-14].

In this paper, simultaneous removal of NOX and SO2 from flue gas by O3 oxidation and sodium hydroxide (NaOH) absorption was carried out in practical engineering. The effects of L/G, O3/NOX, pH
and NaOH concentrations on the removal efficiencies of NO\(_X\) and SO\(_2\) were discussed, meanwhile the mechanism of the reaction in the process was hypothesized. In addition, the influences of O\(_3\)/NO\(_X\) and voltage on the removal of PM were analyzed in order to establish the optimal operating conditions.

2. Engineering Situation

The emissions of SO\(_2\), NO\(_X\) and PM of the coal-fired boilers in coal mine couldn’t meet the ultra-low emission requirements, so it was urgent to upgrade the flue gas treatment system of the coal-fired boilers. In this paper, the research was performed on an eight t/h coal-fired boiler and a ten t/h coal-fired boiler. Fig. 1 displayed the renovated flue gas treatment process. The O\(_3\) generator (Guolin Co., Ltd. Qingdao, China), the WESP (designed by HERI of CCTEG, Hangzhou, China) and the boost up fan (Zhanggu Co., Ltd. Jinan, China) were newly built. The concentrations of NO\(_X\) and SO\(_2\) at the inlet were 200 mg/Nm\(^3\) and 1200 mg/Nm\(^3\), respectively, with a precision of ±10 mg/Nm\(^3\). The flue gas temperature at the inlet of WFGD was about 423 K. The gas flow rate and water flow rate were controlled at approximately 35000 Nm\(^3\)/h and 280 m\(^3\)/h, respectively. The desired pH of solution was adjusted by adding NaOH and HNO\(_3\). The inlet concentrations of SO\(_2\) and NO\(_X\) and the outlet concentration of SO\(_2\), NO\(_X\) and PM was measured by flue gas analysers (Beijing SDL Technology Co., Ltd, China). Under the actual working conditions, the gas flow rate, the initial concentrations of NO\(_X\) and SO\(_2\) have a slight change in the numerical value.

3. Results and Discussion

Simultaneous removal of the NO\(_X\) and SO\(_2\) by ozone oxidation and NaOH absorption is categorized as two types. In the primary process, NO, the main component of NO\(_X\), is oxidized by O\(_3\). Meanwhile, the existence of SO\(_2\) in the flue gas will slightly inhibit the oxidation of NO. This can be ascribed as the following Eqs. (1) to (5):

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \\
\text{NO}_2 + \text{NO}_3 & \rightarrow \text{N}_2\text{O}_5 \\
\text{SO}_2 + \text{O}_3 & \rightarrow \text{SO}_3 \\
\text{SO}_2 + \text{NO}_2 & \rightarrow \text{NO} + \text{SO}_3
\end{align*}
\]
Secondly, NO₂, NO₃, N₂O₅, SO₃ and the remaining SO₂ in the gas phase are transmitted into the liquid phase and absorbed by NaOH solution. The processes in the liquid phase may be expressed from Eqs. (6) to (9):

\[
\begin{align*}
\text{NO} + \text{NO}_2 + 2\text{NaOH} & \rightarrow 2\text{NaNO}_2 + \text{H}_2\text{O} \\
2\text{NO}_2 + 2\text{NaOH} & \rightarrow \text{NaNO}_2 + \text{NaNO}_3 + \text{H}_2\text{O} \\
\text{SO}_2 + 2\text{NaOH} & \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \\
\text{SO}_2 + \text{NaOH} & \rightarrow \text{NaHSO}_3
\end{align*}
\]

3.1. Effect of L/G on removal efficiencies of NOx and SO₂

As displayed in Fig. 2a, NOx removal efficiency slightly increased with the increasing of L/G in the range from 2 to 12 L/Nm³ at the O₃/NOx from 0.0 to 1.5. It finds that NOx removal efficiency had a large difference between with O₃ oxidation and without O₃ oxidation. The removal of NOx only reached 6% at 8 L/Nm³ of L/G without O₃ oxidation, while got a removal efficiency of 75% at 8 L/Nm³ when O₃/NOx was 1.5. It can be explained that NO, the main component of NOx, has a very low solubility in aqueous solution. The main byproducts of the O₃ oxidation process of NO are NO₂, NO₃, and N₂O₅, which were captured by NaOH solution.

As shown in Fig. 2b, SO₂ removal efficiency increased with the increasing of L/G in the range from 2 to 8 L/Nm³, then retained stable varying from 10 to 12 L/Nm³ at the O₃/NOx from 0.0 to 1.5. SO₂ removal efficiency nearly reached 82.2% at 2 L/Nm³ without O₃ oxidation while only got 84.7% at 2 L/Nm³ as O₃/NOx rose 1.5. This is consistent with previous works that the activation energies of Eq. (1) and Eq. (4) are 3.176 kJ/mol and 58.17 kJ/mol, respectively [15]. The reaction between SO₂ and O₃ is difficult to occur due to the higher activation energy of Eq. (4). In addition, the activation energy of Eq. (4) is as high as 113 kJ/mol [16-17]. It is concluded that SO₂ removal efficiency had a little influence on the O₃/NOx.

3.2. Effect of pH on removal efficiencies of NOx and SO₂

The effect of solution pH on NOx and SO₂ removal efficiencies was investigated experimentally and the result is shown in Fig. 3. As displayed in Fig. 3, the average removal efficiencies of SO₂ were slightly affected by the solution pH and were greater than 98.5% with the change of solution pH from 5 to 10. A sharp increase in NOx removal efficiency from 50.0% to 68.7% was observed when the pH varied from 4 to 6. After that, it was almost retained stable at 76% when the solution pH varied from 7.0 to 10.0. It can be explained that strong acidic conditions are not conductive to the absorption of NOx. Conversely,
SO₂ tends to dissolve even in acidic solutions due to its high Henry’s law constant. Therefore, the solution pH is controlled above 8 during the actual operation.

3.3. Effect of NaOH concentration on removal efficiencies of NOX and SO₂
The effect of NaOH concentration on NOX and SO₂ removal efficiencies is shown in Fig. 4. As shown in Fig. 4, NOX and SO₂ efficiencies were slightly affected by NaOH concentration. The removal efficiencies retained more than 75% and 98% respectively when the concentration of NaOH solution increases from 0.1% to 1.0%. This is attributed to Eqs. (6) to (9). Therefore, when the NaOH use costs and the removal efficiencies were taken into accounts, the concentration of NaOH solution is controlled at 0.1% during the actual operation.

3.4. Effect of O₃/NOx on removal efficiencies of NOx, SO₂ and PM
Fig. 5a shows the effect of O₃/NOx on NOX and SO₂ removal efficiencies. By increasing the O₃/NOx from 0 to 1.4, the NOX removal efficiency significantly increased from 4.0% to 82.5%. By further increasing O₃/NOx from 1.4 to 2.0, NOX removal efficiency slightly increased from 84.2% to 90.5%. The phenomenon indicates that the NO oxidation efficiency became higher with more O₃ injected.
Conversely, SO₂ removal efficiency was as maximum up to 99.5% and retained stable by increasing the O₃/NOₓ from 0 to 2.0.

Fig. 5b shows the effect of O₃/NOₓ on CPM. As exhibited in Fig. 5b, CPM decreased with the rise of voltage from 0 to 40 kV. CPM reached 3.0 mg/Nm³ with 40 kV while 18.5 mg/Nm³ without voltage when O₃/NOₓ is set to 1. This is due to WESP which is installed after WFGD to realize the effective capture of dust and deep removal of fine PM.

It was seen CPM remained nearly stable by varying O₃/NOₓ from 0.0 to 1.4, then increased from 18.4 mg/Nm³ to 28.6 mg/Nm³ and from 3.0 mg/Nm³ to 8.0 mg/Nm³ by O₃/NOₓ in the range from 1.6 to 2.0 when voltages are 0 and 40 kV respectively. CPM can be controlled within 5 mg/Nm³ when the voltage was set as 40 kV. So it is deduced that a rise in O₃/NOₓ can promote the reaction of Eq. (4). Sulfuric acid aerosols are then formed mainly in the desulfurization process due to simultaneous heat, mass transfer and subsequent homogeneous nucleation [18-19]. Hence, O₃/NOₓ is controlled in the range from 1.0 to 1.2.

**4. Economic Study**

| Table 1. Fundamental data   | gas flow rate Nm³/h | NOₓ mg/Nm³ | SO₂ mg/Nm³ | PM mg/Nm³ |
|-----------------------------|---------------------|------------|------------|-----------|
| Actual flue gas             | 35000               | ≤200       | 1200       | 5000      |
| Emission standard           | ≤50                 | 35         | 5          |

Table 1 shows the fundamental data of flue gas from coal-fired boilers. A simple analysis of operating costs is displayed in Table 2. Annual working hours are 4000 h. The power consumption mainly includes booster fan, circulating pump, ozone generator and WESP.

As shown in Table 2, the operating costs for removal of NOₓ, SO₂ and PM are about 677250 yuan every year. A large amount of the costs results from power consumption. So, it is important to control the optimal operating conditions.

**5. Conclusion**

In this paper, the effects of L/G, O₃/NOₓ, pH and NaOH concentrations on the removal efficiencies of NOₓ and SO₂ were investigated. The influences of O₃/NOₓ and voltage on the removal of PM were carried out in order to establish the optimal operating conditions. Meanwhile, the mechanism of the reaction of removal in the process was hypothesized.

It is found that the NOₓ removal efficiency increases with the increasing of O₃/NOₓ, solution pH and L/G, while is slightly affected by NaOH concentration. The SO₂ removal efficiency slightly increases with the increase of L/G, whereas is hardly changed by the O₃/NOₓ, NaOH concentration and solution pH. The optimum removal efficiencies of NOₓ and SO₂ were 90.5% and 99.5%, respectively. CPM slightly increases with the increment of O₃/NOₓ from 1.6 to 2.0. Voltage has a significant effect on PM removal. CPM can be controlled below 5 mg/Nm³ when the voltage was set as 40 kV. Therefore, when running costs and rigorous regulation were taken into consideration, the optimal operating conditions can be concluded as follows: L/G is 8 L/Nm³, O₃/NOₓ is 1.0, NaOH concentration is 0.1%, pH is above
and voltage is 40 kV. Under the optimal conditions, the removal efficiencies of NOX and SO2 reached more than 75% and 98% respectively, CPM could be controlled within 5 mg/Nm³.

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