Investigation on NO Oxidation during Ozone Oxidation Denitration of Sintering Flue Gas

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Abstract. With the intensified requirements on ambient air quality, controlling NO_x emission from sintering flue gas has become the most important priority in steel industry. Ozone oxidation denitration process has become the most closely watched sintering flue gas denitration technology. In order to investigate the influence of different operating conditions on NO oxidation in practical engineering application of ozone oxidation denitration process, an ozone oxidation system was built, and sintering flue gas was extracted from the pipeline between the induced draft fan and the desulfurization tower. The influence of discharge power and O_2 flow rate of ozone generator on O_3 concentration, O_3 yield and NO oxidation efficiency were investigated. The results indicated that NO oxidation efficiency increased with the discharge power. And the increase of O_3 dosage imposed a significant influence on NO oxidation efficiency. However, little effect of O_2 flow rate on NO oxidation efficiency was observed.

1 Introduction

With the intensified requirements on ambient air quality, controlling NO_x emission from sintering flue gas has become the most important priority in steel industry. However, the performance of flue gas denitration technology implemented in steel industry is not satisfactory compared with other air pollution control technologies such as desulfurization.

It is widely acknowledged that NO_x generated by sintering process of steel industry is mainly comprised of NO (95% vol.) [1] which is difficult to be removed from flue gas due to its stability especially the limited solubility. The solubility can be improved by oxidation where NO is transformed into high-valence nitrogen oxides (such as NO_2, NO_3, N_2O_5, etc.), thus the removal could be readily performed by wet scrubber. As a reactive oxidant, ozone has drawn great attention in oxidation denitration since it exhibits many advantages which are low economic costs, high selectivity to NO, and resistance to temperature fluctuations [2]. In the research conducted by Mok [3], after the exhaust gas passed through the ozonizing chamber and the absorber sequentially, NO_x removal efficiency of about 95% and SO_2 removal efficiency of 100% were obtained. Similar results were observed by Wang [4] who found that 97% of NO and nearly 100% of SO_2 can be removed simultaneously by alkaline washing tower after the injection of ozone.

According to the research results of Wang [5], the oxidation reactions between O_3 and NO could be expressed by equation (1) to (3) where NO was oxidized into NO_2 which further transforms into N_2O_5 in the presence of excessive O_3.

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (1)$$

$$O_3 + NO_2 \rightarrow O_2 + NO_3 \qquad (2)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad (3)$$
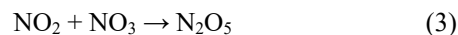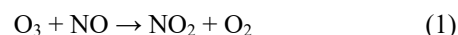
As a result, the O_3 concentration would not only dominate the performance of NO oxidation effect, but also play a significant role in the removal of NO in the whole process of oxidation denitration. In order to investigate the influence of different operating conditions on NO oxidation in practical engineering application of ozone oxidation denitration process, an ozone oxidation system was built, and sintering flue gas was extracted from the pipeline between the induced draft fan and the desulfurization tower. The influence of discharge power and O_2 flow rate of ozone generator on O_3 concentration, O_3 yield and NO oxidation efficiency were investigated.

2 Experiment part

2.1 Process description

The on-site operation of ozone oxidation experiments were conducted at a steel-making plant in Tangshan, Hebei province. An ozone oxidation system was built, and sintering flue gas was extracted from the pipeline between the induced draft fan and the desulfurization tower at 30000 m^3/h. The temperature of flue gas was about 140℃. The NO concentration was 70 mg/m^3. As shown in figure 1, O_3 generated by an ozone generator (GUOLIN, CF-G-2-7kg) was injected into the flue gas

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by ozone feeding distributor at the inlet of the mixing chamber where O_3 and flue gas were mixed thoroughly. The mixed flue gas resided in the system for 0.6~1.0 s. Finally, the oxidized flue gas entered into the desulfurization tower to remove the SO_2 and NO_x from the flue gas simultaneously.
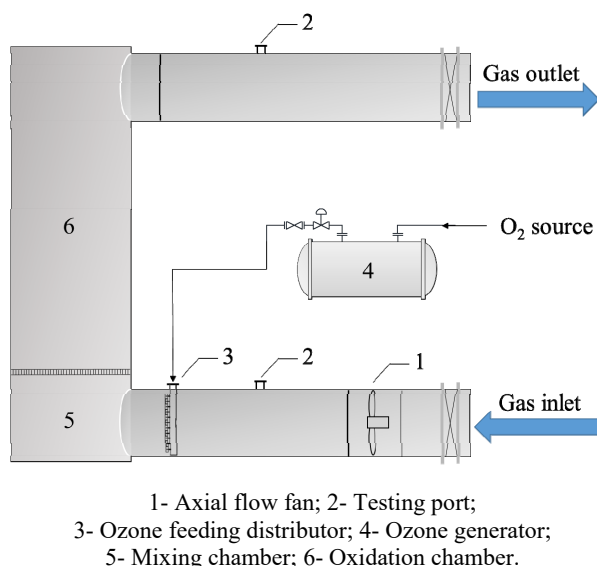

1- Axial flow fan; 2- Testing port;
3- Ozone feeding distributor; 4- Ozone generator;
5- Mixing chamber; 6- Oxidation chamber.
Fig. 1 Diagram of ozone oxidation system

2.2 Generation of ozone

The ozone generator generated O_3 through dielectric barrier discharge (DBD) with an adjustable discharge power ranging from 13 to 45 kW. O_2 gas (99.5% vol.) was used as the gas source of generator, and its rated consumption was 70 kg/h (50m^3/h). The energy consumption of generator to generate 1kg O_3 was 7.5 kWh. The rated O_3 concentration and O_3 yield of generator were 148 mg/L (50m^3/h) and 7 kg/h (with an adjustable range from 10 to 100%) respectively.

2.3 Evaluation of NO oxidation efficiency

The O_3 concentration at the outlet of ozone generator was monitored online by ozone concentration detector, and O_3 yield was calculated by the control system of generator. The NO concentration at the inlet and outlet of ozone oxidation system was measured by an exhaust gas analyser (Testo 350). Based on the monitoring results, the NO oxidation efficiency can be estimated by equation (4).

$$\eta_{NO} = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \times 100\%$$
(4)

In equation (4), $[NO]_{in}$ and $[NO]_{out}$ represent the NO concentration at the inlet and outlet of system respectively.

3 Results and discussion

3.1 Influence of discharge power of ozone generator

3.1.1 Influence of discharge power on ozone concentration and yield

As shown in figure 2, when the O_2 flow rate was 30 Nm^3/h, the discharge power of ozone generator in the preheating stage was 12.9 kW, while the concentration of generated O_3 was 65 mg/L which was equivalent to 2.52 kg/h. With the increase of discharge power, O_3 concentration and yield increased.
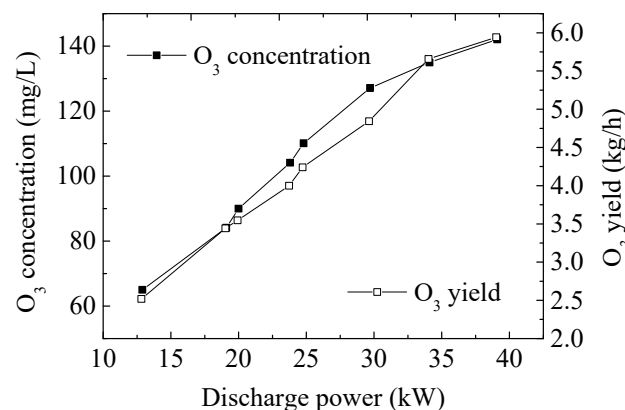

Fig. 2 Influence of discharge power on ozone concentration and yield

3.1.2 Influence of discharge power on NO oxidation

According to the previous section, the change of discharge power of ozone generator would result in the change of the generated O_3 concentration. It is thus expected that NO oxidation was enhanced under high discharge powers due to the increased O_3 concentrations. As shown in figure 3, NO oxidation efficiency increased along with the discharge power. When the discharge power increased from 12.9 kW to 29.7 kW, O_3 concentration increased correspondingly from 65 mg/L to 127.1 mg/L, and NO oxidation efficiency increased from 70.8% to 87.7%.
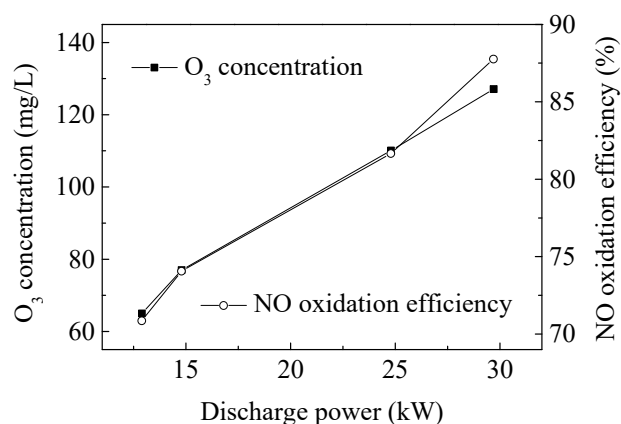

Fig. 3 Influence of discharge power on ozone concentration and NO oxidation efficiency
(The O_2 flow rate is 30 Nm^3/h.)

3.1.3 Influence of ozone dosage on NO oxidation

To investigate the influence of O_3/NO molar ratio on NO oxidation efficiency, O_3 concentration at the outlet of ozone generator was converted into concentration in the flue gas. As shown in figure 4, there was a significantly positive correlation between NO oxidation efficiency and O_3/NO molar ratio, and the increase of O_3 dosage imposed a significant influence on NO oxidation efficiency. When the O_3/NO molar ratio increased from 0.84 to 1.37, NO oxidation efficiency increased correspondingly from 70.8% to 87.7%.

It was observed that NO oxidation efficiency was 75% under the O_3/NO molar ratio of 1 which was lower than the theoretical value indicated by equation (1). This could be ascribed to that O_3 oxidized generated NO_2 into high-valence nitrogen oxides (such as NO_3, N_2O_5, etc.) or reacted with other components in flue gas, which made some of O_3 not be used for NO oxidation.
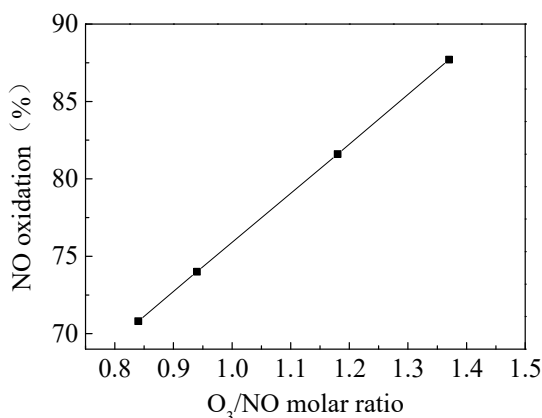

Fig. 4 Influence of ozone dosage on NO oxidation efficiency
(The O_2 flow rate is 30 Nm³/h.)

3.2 Influence of oxygen flow rate of ozone generator

3.2.1 Influence of oxygen flow rate on ozone concentration and yield

Figure 5 indicated a significantly negative correlation between O_3 concentration and O_2 flow rate, while O_3 yield was positively associated with O_2 flow rate. Within a range of O_2 flow rate from 28.6 Nm³/h to 45.2 Nm³/h, the O_3 generation rate increased with O_2 flow rate, leading to a higher O_3 yield. However, the generated O_3 gas was diluted by the increased feed of O_2 gas leading to a reduced observed concentration.
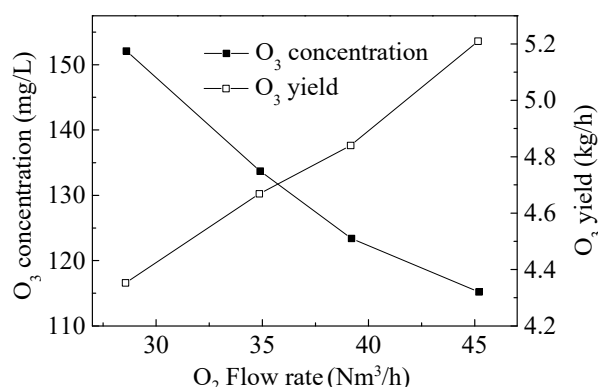

Fig. 5 Influence of oxygen flow rate on ozone concentration and yield
(The discharge power is 30 kW.)

As shown in figure 6, O_3 yield increased with discharge power which was consistent with the above conclusion. Besides, O_3 yield of different discharge power increased gently with O_2 flow rate.
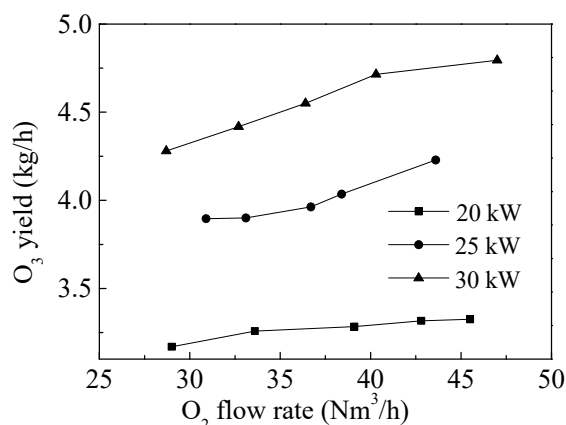

Fig. 6 Relationship between oxygen flow rate and ozone yield under different discharge power

3.2.2 Influence of oxygen flow rate on NO oxidation

In order to investigate the influence of O_2 flow rate on NO oxidation efficiency, O_2 flow rate was increased from 34.9 Nm³/h to 45.2 Nm³/h which resulted in a decrease in O_3 concentration from 133.7 mg/L to 115.2 mg/L. However, as shown in figure 7, NO oxidation efficiency changed slightly and sustained between 85~88%. When O_2 gas was used as the gas source of ozone generator, numerous studies have shown an ability of DBD to generate many kinds of reactive species, such as O_3, O_2, O, e, etc. With the increase of O_2 flow rate, the generated O and other reactive radical in unit volume increased which also had oxidation to NO. Therefore, the change of O_2 flow rate exhibited little influence on NO oxidation efficiency despite of the decrease in O_3 concentration.
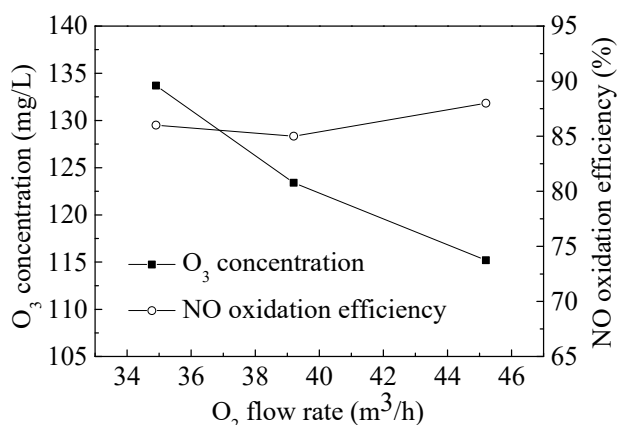
Fig. 7 Influence of oxygen flow rate on ozone concentration
and NO oxidation efficiency
(The discharge power is 30 kW.)

3.3 Assessment of NO oxidation energy consumption

When inlet NO concentration was 70 mg/m^3 and O_3/NO molar ratio was 1, the NO oxidation efficiency was 75%. In this case, the energy consumption of ozone generator to generate 1kg O_3 was 7.5 kWh which was equivalent to 62.5 g/kWh. According to these data, the average oxidation energy consumption of each NO molecule was 0.05 eV which was much lower than that of 30 eV in discharge plasma oxidation. It could be concluded that ozone oxidation denitration process was feasible and economical.

4 Conclusions

In this investigation, the influence of discharge power and O_2 flow rate of ozone generator on O_3 concentration, O_3 yield and NO oxidation were investigated. The results indicated that O_3 concentration, O_3 yield and NO oxidation efficiency increased along with the discharge power under the same O_2 flow rate and inlet NO concentration. There was a significantly positive correlation between NO oxidation efficiency and O_3/NO molar ratio, and the increase of O_3 dosage imposed a significant influence on NO oxidation efficiency. These test results showed that applying ozonation denitration process to dealing with sintering flue gas could achieve a NO oxidation efficiency higher than 90%.

Besides, under the same discharge power and inlet NO concentration, with the increase of O_2 flow rate, O_3 concentration decreased gradually while O_3 yield increased gradually. However, little effect of O_2 flow rate on NO oxidation efficiency was observed. In the application of ozone oxidation denitration engineering, when the O_2 was supplied in a certain amount, we should improve NO oxidation efficiency by adjusting the discharge power of ozone generator. But considering some of O_3 may not be used for NO oxidation in practical engineering application, O_3 dosage should be moderately higher than the theoretical value under the reasonable economic consideration.

References

1. H.Y. Jiang, Shandong Chemical Industry **45**, 150 (2016)
2. Z.L. Liu, Petroleum Refinery Engineering **42**, 23(2012)
3. Y.S. Mok, H. Lee, Fuel Process. Technol **87**, 591 (2006)
4. Z.H. Wang, J.H. Zhou, J.R. Fan, Y.Q. Zhu, Z.C. Wen, J.Z. Liu, K.F. Cen, Fuel Process. Technol **88**, 817 (2007)
5. Z.H. Wang, J.H Zhou, J.R. Fan, K.F Cen, Energy Fuels **20**, 2432 (2006)