

Orthogonal Experiments on Ozone Oxidation Denitration of Sintering Flue Gas

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Abstract. Ozone oxidation denitration process has become the most closely watched sintering flue gas denitration technology currently. In order to investigate the influence of different operating conditions on NO oxidation in practical engineering application of this technology, 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 flue gas flow and inlet NO concentration on NO oxidation was investigated by orthogonal experiments. The results indicated that NO oxidation efficiency increased with the O₃ yield of ozone generator and O₃ dosage under any flue gas conditions. Under the same inlet NO concentration, NO oxidation efficiency decreased with the increase of flue gas flow. Under the same flue gas flow and O₃ dosage, with the increase of inlet NO concentration, the O₃ utilization rate increased while the average oxidation energy consumption of each NO molecule decreased, which was beneficial to promote the NO oxidation efficiency. In practical engineering application, the setting of O₃ dosage should take into account both engineering design indicators and economy. Ozone oxidation denitration process could achieve NO oxidation efficiency higher than 90% through reasonable design, indicating a good industrial application prospect in the treatment of sintering flue gas.

1 Introduction

Nitrogen oxides (NO_x) is one of the major air pollutants discharged by steel industry. The NO_x generated by sintering process whose major components are NO (95%) and NO₂ (5%) [1] accounts for 48% [2] of the whole steel smelting process. 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.

At present, the technology combining ammonia-selective catalytic reduction (NH₃-SCR) denitration with wet flue gas desulfurization (WFGD) has been widely used in coal-fired power plants. This combination could achieve high desulfurization and denitration efficiencies, but the optimal active temperature of catalysts in NH₃-SCR process is 320~450 °C, and it exhibits disadvantages including high economic costs, catalyst poisoning, ammonia escape, and so on [3]. As a result, it is unsuitable for dealing with the sintering flue gas that is at low temperature (120~180 °C) and high humidity (10~12%). In addition, the composition of sintering flue gas is complicated, while the flue gas flow and concentrations are wildly fluctuating [4]. Therefore, it is urgent to develop a high efficiency flue gas desulfurization and denitration technology which does

not involve catalytic reaction devices, and could adapt to characteristics of sintering flue gas.

Ozone oxidation denitration process incorporates the enhanced oxidation by O₃ and the improved absorption of WFGD system, such that it is able to oxidize the insoluble NO into high-soluble nitrogen oxides (such as NO₂, NO₃, N₂O₅, etc.) and remove them by the desulfurization facilities. It has become the most closely watched sintering flue gas denitration technology due to its good properties of low economic costs, broad applicable temperature range, high selectivity to NO, and so on [5]. LoTO_x technology developed by BOC Gases [6] uses O₂/O₃ gas mixture to oxidize NO_x into high-valence state and two stage washing process with CaCO₃/NaOH to realize desulfurization and denitration simultaneously. Finally the achieved NO_x removal efficiency is over 90%. In the research conducted by Mok [5], after the exhaust gas passed through the ozonizing chamber and the absorber sequentially, NO_x removal efficiency of about 95% and SO₂ removal efficiency of 100% were obtained. Similar results were observed by Wang [1] who found that 97% of NO and nearly 100% of SO₂ can be removed simultaneously by alkaline washing tower after the injection of ozone.

The oxidation of NO is the key step to realize high NO_x removal efficiency [1]. In order to investigate the influence of different operating conditions on NO oxidation in practical industrial 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

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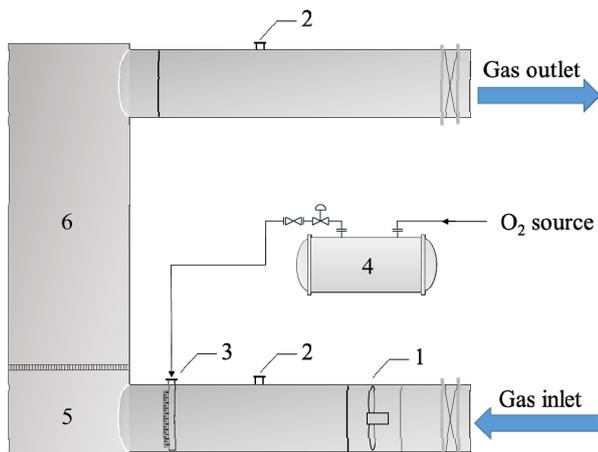
desulfurization tower. The influence of flue gas flow and inlet NO concentration on NO oxidation was investigated by orthogonal experiments.

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 m³/h. The temperature of flue gas was about 140°C.

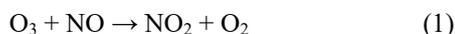
The O₃ gas used in experiments was generated by an ozone generator (GUOLIN, CF-G-2-7kg) through dielectric barrier discharge (DBD) with an adjustable discharge power ranging from 13 to 45 kW. O₂ gas (99.5% vol.) was used as the gas source of generator, and its rated consumption was 70 kg/h (50m³/h). The energy consumption of generator to generate 1kg O₃ was 7.5 kWh. The rated O₃ concentration and O₃ yield of generator were 148 mg/L (50m³/h) and 7 kg/h (with an adjustable range from 10 to 100%) respectively.



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

As shown in figure 1, O₃ generated by ozone generator was injected into the flue gas by ozone feeding distributor at the inlet of the mixing chamber where O₃ and flue gas were mixed thoroughly. The oxidation reactions between O₃ and NO could be expressed by equation (1) to (3) [7]. And 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 SO₂ and NO_x from the flue gas simultaneously.



2.2 Setting of orthogonal experiment

Orthogonal experiment was conducted to investigate the influence of flue gas flow (Q) and inlet NO concentration (C₀) on NO oxidation. The flue gas flow was set to 8500 m³/h, 16500 m³/h, 25000 m³/h corresponding to residence time of flue gas in the system for 6.2 s, 3.5 s, 2.1 s, respectively. The inlet NO concentration was set to 107 mg/m³, 188 mg/m³, 241 mg/m³, respectively. The combinations of two factors in the orthogonal experiments have shown in table 1.

Table 1. Setting of orthogonal experiment

Sequence number	C ₀ (mg/m ³)	Q (m ³ /h)
1	107	8500
2	107	16500
3	107	25000
4	188	8500
5	188	16500
6	188	25000
7	241	8500
8	241	16500
9	241	25000

2.3 Evaluation of NO oxidation efficiency

The O₃ concentration at the outlet of ozone generator was monitored online by ozone concentration detector, and O₃ 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).

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

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 flue gas flow on NO oxidation

3.1.1 Influence of ozone yield on NO oxidation under different flue gas flow

As shown in figure 2, under the same inlet NO concentration, NO oxidation efficiencies of different flue gas flow increased along with the O₃ yield of ozone generator. And under the same O₃ yield, NO oxidation efficiency decreased with the increase of flue gas flow.

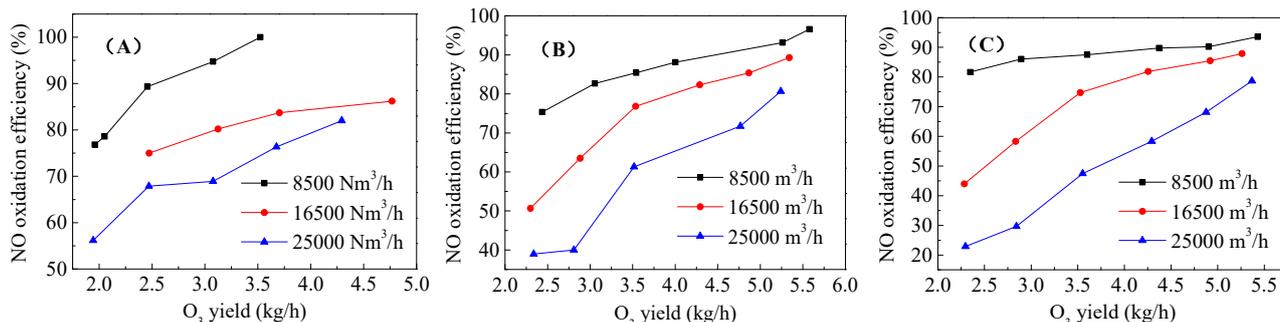


Fig. 2 Influence of ozone yield on NO oxidation efficiency under different flue gas flow
 (A) $C_0(\text{NO})=107 \text{ mg/m}^3$; (B) $C_0(\text{NO})=188 \text{ mg/m}^3$; (C) $C_0(\text{NO})=241 \text{ mg/m}^3$

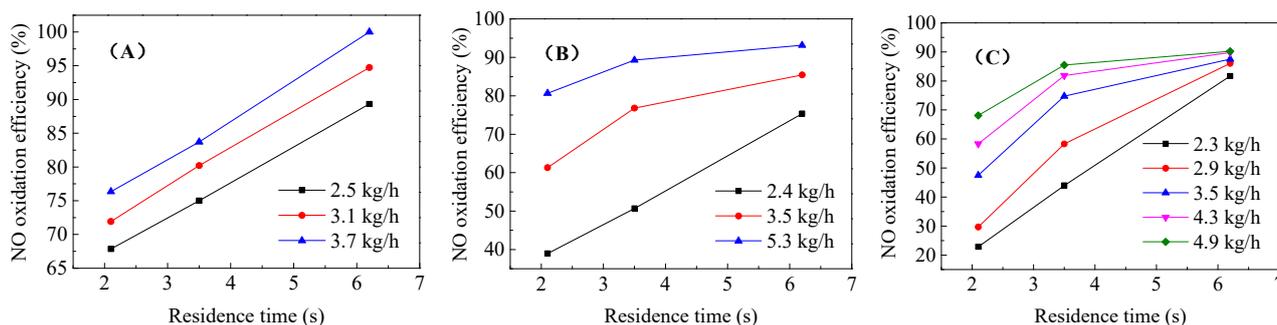


Fig. 3 Influence of retention time on NO oxidation efficiency under different ozone yield
 (A) $C_0(\text{NO})=107 \text{ mg/m}^3$; (B) $C_0(\text{NO})=188 \text{ mg/m}^3$; (C) $C_0(\text{NO})=241 \text{ mg/m}^3$

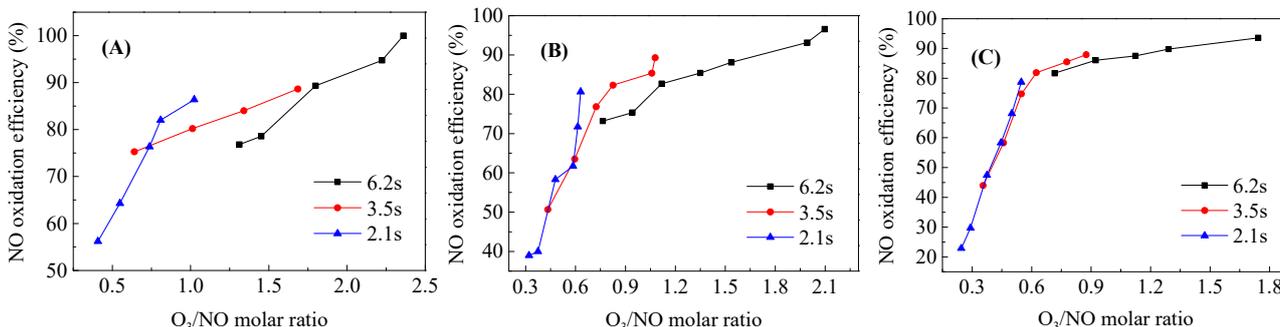


Fig. 4 Influence of ozone dosage on NO oxidation efficiency under different flue gas flow
 (A) $C_0(\text{NO})=107 \text{ mg/m}^3$; (B) $C_0(\text{NO})=188 \text{ mg/m}^3$; (C) $C_0(\text{NO})=241 \text{ mg/m}^3$

3.1.2 Influence of residence time on NO oxidation under different ozone yield

Flue gas flow determined the residence time of flue gas in the ozone oxidation system, which would influence the NO oxidation effect. Numerous studies have shown that with a certain amount of O_3 dosage, the longer residence time was, the more beneficial it would be to NO oxidation. On the other hand, when the residence time was fixed, the more excess of O_3 dosage, the higher NO oxidation efficiency would be.

In this investigation, when the flue gas flow was $8500 \text{ m}^3/\text{h}$, $16500 \text{ m}^3/\text{h}$, $25000 \text{ m}^3/\text{h}$, the corresponding residence time of flue gas in the system was 6.2 s, 3.5 s, 2.1 s, respectively. As shown in figure 3, under the same inlet NO concentration, NO oxidation efficiencies of

different O_3 yield decreased along with the residence time. And under the same residence time, NO oxidation efficiency increased with the O_3 yield.

3.1.3 Influence of ozone dosage on NO oxidation under different residence time

When the inlet NO concentration and O_3 yield were fixed, the longer residence time of flue gas in the system was, the greater O_3/NO molar ratio was, the more beneficial it would be to promote NO oxidation effect. As shown in figure 4, under the same inlet NO concentration, NO oxidation efficiencies of different residence time increased along with O_3/NO molar ratio. Compared to residence time of 2.1 s and 3.5 s, the O_3/NO molar ratio and NO oxidation efficiency under residence time of 6.2 s were much higher.

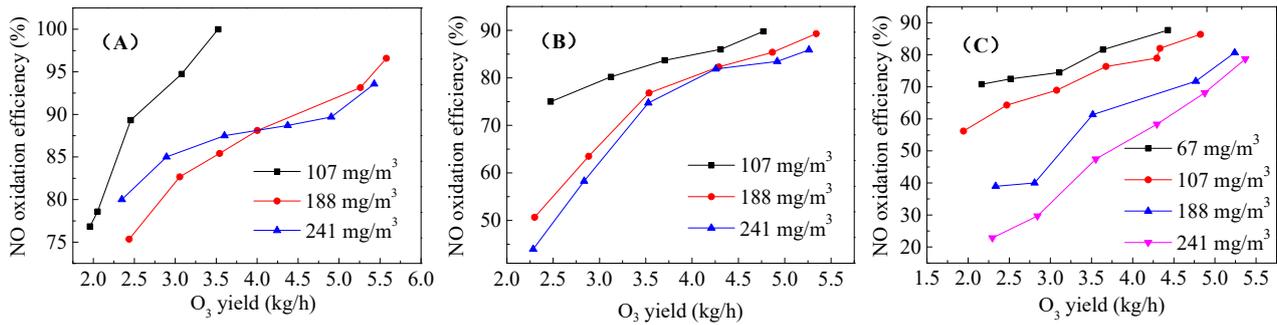


Fig. 5 Influence of ozone yield on NO oxidation efficiency under different inlet NO concentration
 (A) $Q = 8500 \text{ m}^3/\text{h}$; (B) $Q = 16500 \text{ m}^3/\text{h}$; (C) $Q = 25000 \text{ m}^3/\text{h}$

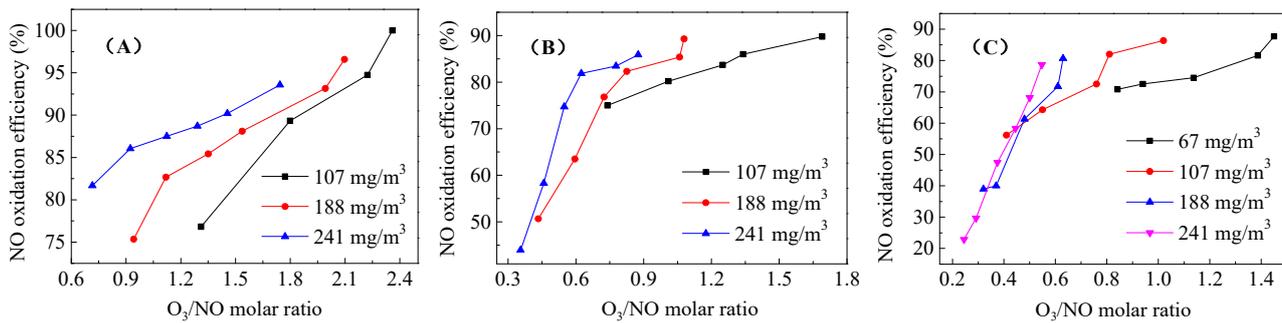


Fig. 6 Influence of ozone dosage on NO oxidation efficiency under different inlet NO concentration
 (A) $Q = 8500 \text{ m}^3/\text{h}$; (B) $Q = 16500 \text{ m}^3/\text{h}$; (C) $Q = 25000 \text{ m}^3/\text{h}$

3.2 Influence of inlet NO concentration on NO oxidation

3.2.1 Influence of ozone yield on NO oxidation under different inlet NO concentration

As shown in figure 5, NO oxidation efficiencies of different inlet NO concentration increased along with O_3 yield. And under the same O_3 yield, NO oxidation efficiency decreased generally with the increase of inlet NO concentration. This could be ascribed to the lower O_3/NO molar ratio under high inlet NO concentration, if the flue gas flow and O_3 yield was fixed.

3.2.2 Influence of ozone dosage on NO oxidation under different inlet NO concentration

As shown in figure 6, under the same flue gas flow, NO oxidation efficiencies at different inlet NO concentration increased along with O_3/NO molar ratio. Meanwhile under the same O_3/NO molar ratio, NO oxidation efficiency increased with the inlet NO concentration.

3.2.3 Influence of ozone dosage on ozone utilization rate under different inlet NO concentration

As shown in figure 7, O_3 utilization rate of different inlet NO concentration decreased along with the increase of O_3/NO molar ratio. And under the same O_3/NO molar ratio, the higher inlet NO concentration was, the higher O_3 utilization rate would be. When the O_3/NO molar

ratio was about 1.3, the O_3 utilization rate was 58.58%, 62.27%, 69.15% at the inlet NO concentration of 107 mg/m^3 , 188 mg/m^3 , 241 mg/m^3 , respectively.

This indicated that in practical engineering application, the increase of O_3 dosage was beneficial to NO oxidation, but it would reduce the O_3 utilization rate. One possible reason was that in practical oxidation process, 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.

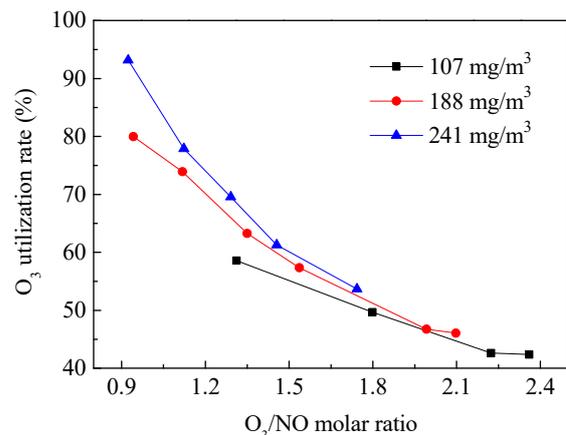


Fig. 7 Influence of ozone dosage on ozone utilization rate under different inlet NO concentration
 ($Q = 8500 \text{ m}^3/\text{h}$)

3.2.4 Influence of ozone dosage on oxidation energy consumption under different inlet NO concentration

As shown in figure 8, when the flue gas flow was 8500 m³/h, oxidation energy consumptions under different inlet NO concentration decreased along with the increase of O₃/NO molar ratio. Meanwhile under the same O₃/NO molar ratio, the higher inlet NO concentration was, the lower average oxidation energy consumption would be. Specifically, when the O₃/NO molar ratio was about 1.3, average oxidation energy consumption of each NO molecule was 0.04865 eV, 0.04375 eV, 0.04214 eV at the inlet NO concentration of 107 mg/m³, 188 mg/m³, 241 mg/m³, respectively.

According to the above test results, under the same flue gas flow rate and O₃/NO molar ratio, with the increase of inlet NO concentration, the O₃ utilization rate increased while the average oxidation energy consumption of each NO molecule decreased, which was beneficial to promote NO oxidation efficiency.

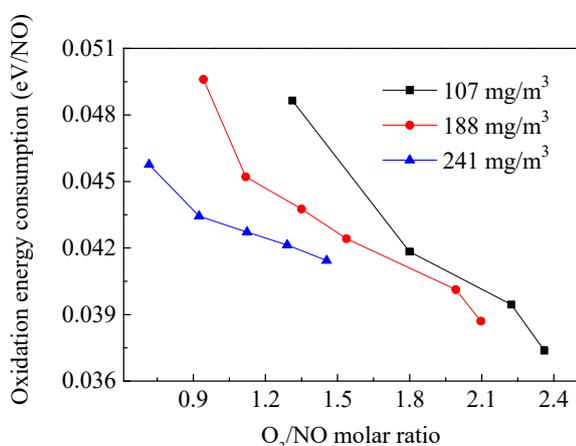


Fig. 8 Influence of ozone dosage on oxidation energy consumption under different inlet NO concentration (Q = 8500m³/h)

Table 2. Results of orthogonal experiment

C ₀ (mg/m ³)	Q (m ³ /h)	η _{NO} (%)
107	8500	77~100
107	16500	75~90
107	25000	56~86
188	8500	75~96
188	16500	50~89
188	25000	33~80
241	8500	81~94
241	16500	44~86
241	25000	23~79

3.3 Results of orthogonal experiment

In this investigation, the influence of flue gas flow and inlet NO concentration on NO oxidation was investigated. As shown in table 2, ozone oxidation denitration process could achieve NO oxidation efficiency higher than 90% in the practical engineering application through reasonable design, indicating a good industrial application prospect in the treatment of sintering flue gas.

4 Conclusions

Following conclusions could be drawn from the experimental results:

(1) NO oxidation efficiency increased with the O₃ yield of ozone generator and O₃ dosage under any flue gas conditions.

(2) Under the same inlet NO concentration, NO oxidation efficiency decreased with the increase of flue gas flow which was equivalent to the decrease of residence time of flue gas in the ozone oxidation system.

(3) Under the same flue gas flow and O₃ yield, NO oxidation efficiency decreased with the increase of inlet NO concentration.

(4) Under the same flue gas flow and O₃ dosage, with the increase of inlet NO concentration, the O₃ utilization rate increased while the average oxidation energy consumption of each NO molecule decreased, which was beneficial to promote the NO oxidation efficiency.

(5) In practical engineering application, the increase of O₃ dosage could reduce average oxidation energy consumption of each NO molecule which was beneficial to NO oxidation, but it would reduce the O₃ utilization rate. Therefore, the setting of O₃ dosage should take into account both engineering design indicators and economy.

(6) Ozone oxidation denitration process could achieve NO oxidation efficiency higher than 90% in the practical engineering application through reasonable design, indicating a good industrial application prospect in the treatment of sintering flue gas.

Acknowledgements

The authors gratefully acknowledge financial support by Science and Technology Plan Project of Guangdong Province, China (No. 2017B090901057).

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