# 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 $O_3$ yield of ozone generator and $O_3$ 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 $O_3$ dosage, with the increase of inlet NO concentration, the $O_3$ 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 $O_3$ 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 $NO_2$ (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 ($NH_3$-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 $NH_3$-SCR process is 320~450℃, 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℃) 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 $O_3$ and the improved absorption of WFGD system, such that it is able to oxidize the insoluble NO into high-soluble nitrogen oxides (such as $NO_2$, $NO_3$, $N_2O_5$, 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]. Lo$TO_x$ technology developed by BOC Gases [6] uses $O_2/O_3$ gas mixture to oxidize $NO_x$ into high-valence state and two stage washing process with $CaCO_3$/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 $SO_2$ removal efficiency of 100% were obtained. Similar results were observed by Wang [1] 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.

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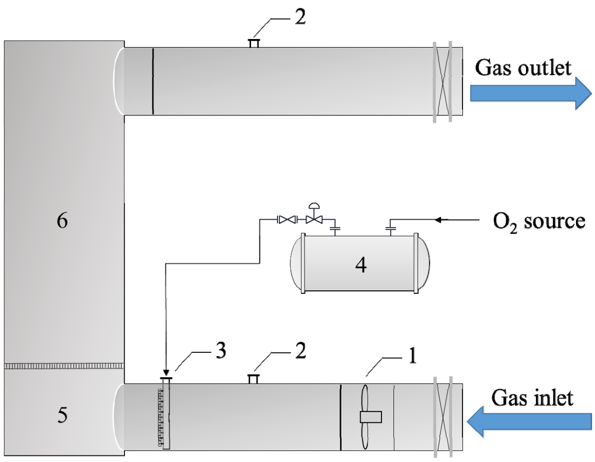
desulfurization tower. The influence of flue gas flow and inlet NO concentration on NO oxidation was investigated by orthogonal experiments.

# 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 m$^3$/h. The temperature of flue gas was about 140℃.

The $O_3$ 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. $O_2$ 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.




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, $O_3$ generated by ozone generator was injected into the flue gas by ozone feeding distributor at the inlet of the mixing chamber where $O_3$ and flue gas were mixed thoroughly. The oxidation reactions between $O_3$ 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 $SO_2$ and $NO_x$ from the flue gas simultaneously.

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{1}$$

$$O_3 + NO_2 \rightarrow O_2 + NO_3 \tag{2}$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \tag{3}$$

## 2.2 Setting of orthogonal experiment

Orthogonal experiment was conducted to investigate the influence of flue gas flow (Q) and inlet NO concentration ($C_0$) on NO oxidation. The flue gas flow was set to 8500 m$^3$/h, 16500 m$^3$/h, 25000 m$^3$/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/m$^3$, 188 mg/m$^3$, 241 mg/m$^3$, 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 $O_3$ 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).

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

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 $O_3$ yield of ozone generator. And under the same $O_3$ yield, NO oxidation efficiency decreased with the increase of flue gas flow.

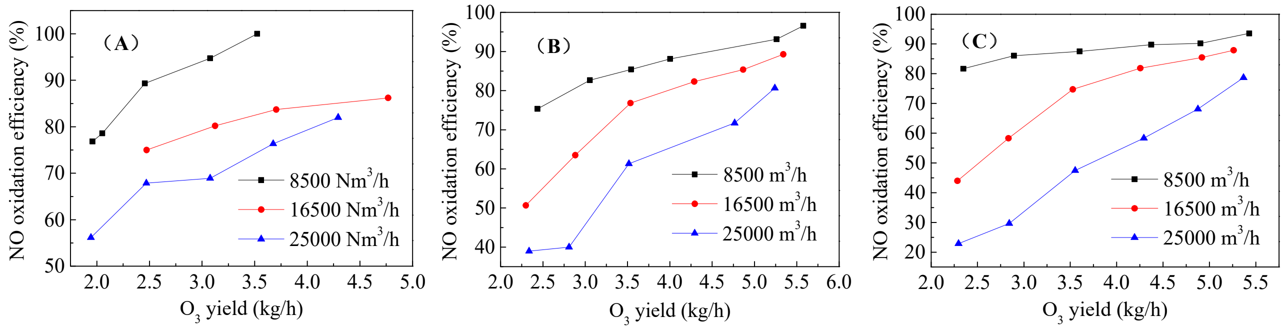



**Fig. 2** Influence of ozone yield on NO oxidation efficiency under different flue gas flow
(A) $C_0$(NO)=107 mg/m$^3$; (B) $C_0$(NO)=188 mg/m$^3$; (C) $C_0$(NO)=241 mg/m$^3$

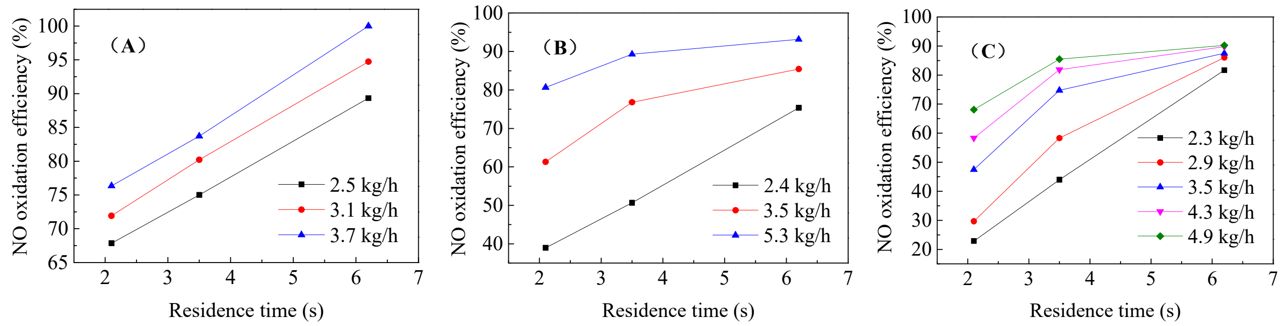



**Fig. 3** Influence of retention time on NO oxidation efficiency under different ozone yield
(A) $C_0$(NO)=107 mg/m$^3$; (B) $C_0$(NO)=188 mg/m$^3$; (C) $C_0$(NO)=241 mg/m$^3$

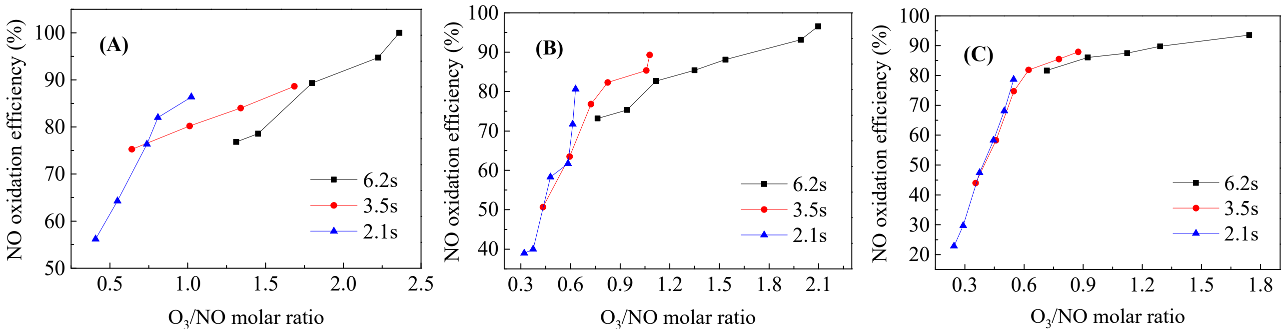



**Fig. 4** Influence of ozone dosage on NO oxidation efficiency under different flue gas flow
(A) $C_0$(NO)=107 mg/m$^3$; (B) $C_0$(NO)=188 mg/m$^3$; (C) $C_0$(NO)=241 mg/m$^3$

### *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 m$^3$/h, 16500 m$^3$/h, 25000 m$^3$/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.

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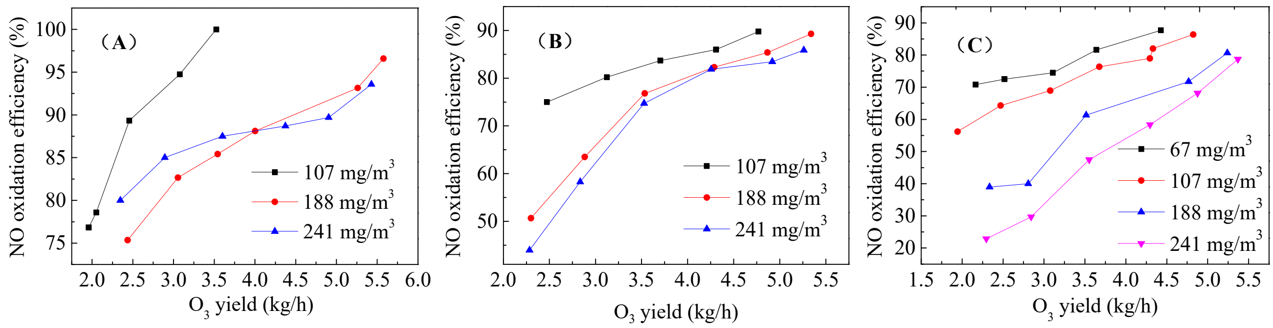


**Fig. 5** Influence of ozone yield on NO oxidation efficiency under different inlet NO concentration
(A) Q = 8500 m³/h; (B) Q = 16500 m³/h; (C) Q = 25000 m³/h

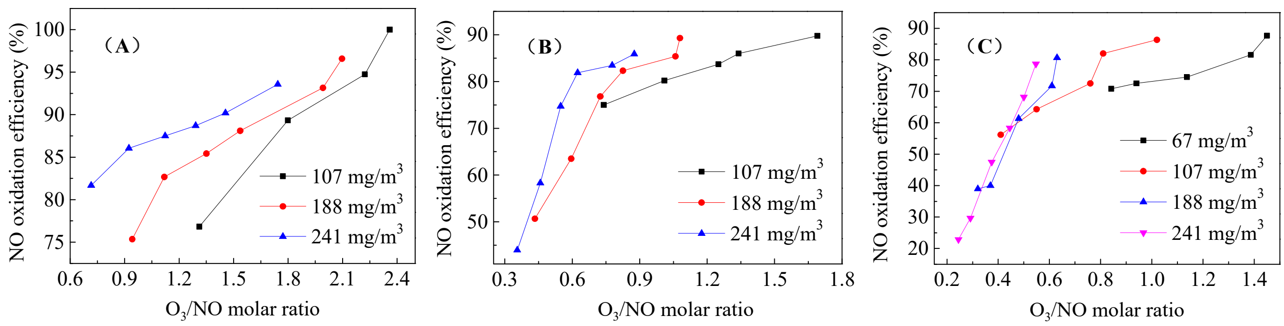


**Fig. 6** Influence of ozone dosage on NO oxidation efficiency under different inlet NO concentration
(A) Q = 8500 m³/h; (B) Q = 16500 m³/h; (C) Q = 25000 m³/h

## 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/m³, 188 mg/m³, 241 mg/m³, 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.

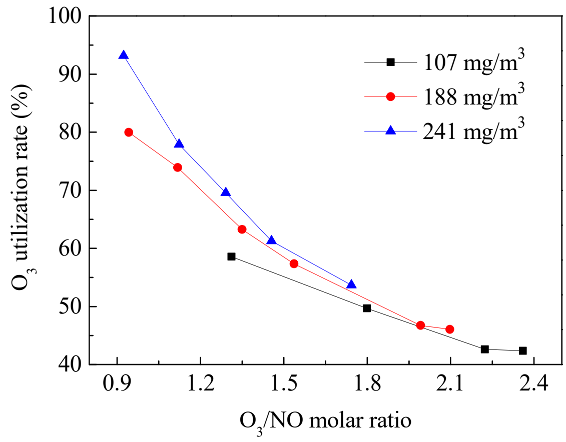


**Fig. 7** Influence of ozone dosage on ozone utilization rate under different inlet NO concentration
(Q = 8500 m³/h)

### *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 $m^3/h$, oxidation energy consumptions under different inlet NO concentration decreased along with the increase of $O_3$/NO molar ratio. Meabwhile under the same $O_3$/NO molar ratio, the higher inlet NO concentration was, the lower average oxidation energy consumption would be. Specifically, when the $O_3$/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 $mg/m^3$, 188 $mg/m^3$, 241 $mg/m^3$, respectively.

According to the above test results, under the same flue gas flow rate and $O_3$/NO molar ratio, with the increase of inlet NO concentration, the $O_3$ utilization rate increased while the average oxidation energy consumption of each NO molecule decreased, which was beneficial to promote NO oxidation efficiency.

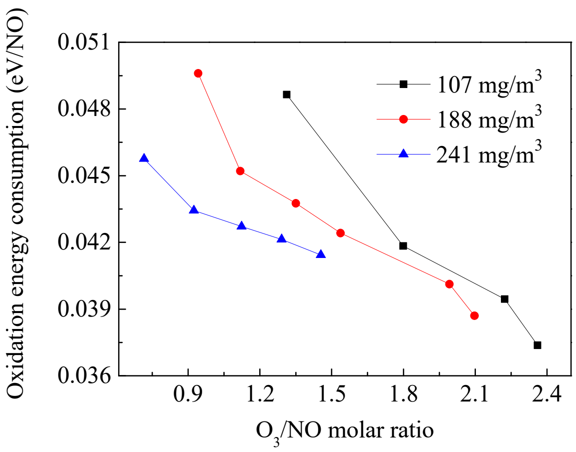


**Fig. 8** Influence of ozone dosage on oxidation energy consumption under different inlet NO concentration (Q = 8500$m^3/h$)

**Table 2.** Results of orthogonal experiment

| $C_0$ ($mg/m^3$) | $Q$ ($m^3/h$) | $\eta_{NO}$ (%) |
|---|---|---|
| 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 $O_3$ yield of ozone generator and $O_3$ 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 $O_3$ yield, NO oxidation efficiency decreased with the increase of inlet NO concentration.

(4) Under the same flue gas flow and $O_3$ dosage, with the increase of inlet NO concentration, the $O_3$ 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 $O_3$ dosage could reduce average oxidation energy consumption of each NO molecule which was beneficial to NO oxidation, but it would reduce the $O_3$ utilization rate. Therefore, the setting of $O_3$ 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.

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