



Research on the Technology and Mechanism of Flue Gas Oxidation Denitrification Based on H₂O₂/UV System

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In recent years, nitrogen oxide emissions are growing rapidly. It is imminent to study and develop a new technology of gas flue denitrification. This article shows that under laboratory condition, simulated flue gas system and used hydrogen peroxide (H₂O₂) solution to conduct de-NO_x experiment, as well as investigated influence of many factors on the de-NO_x efficiency and arrived at an optimal de-NO_x system. At the same time the mechanisms were analysed. On this basis, the research on dynamics and thermodynamics were carried on to explore the dynamics and thermodynamics theory of this de-NO_x system.

H₂O₂ solution has a certain effect on the flue gas denitrification, the removal rate with time is not significant. The results show that the removal of NO by H₂O₂ / UV system is feasible, and the removal rate of NO is about 70%, and the removal efficiency is much better than that of H₂O₂ / UV system. Stable.

Response surface method optimization experiments obtained regression equation: $R = -10.10203 \times X_1 - 0.12647 \times X_2 - 27.68087 \times X_3 + 0.62404 \times X_4 - 28071.60614 \times X_5 + 0.011653 \times X_6 + 1.66373 \times X_1 X_3 + 0.021411 \times X_2 X_3 + 2513.87184 \times X_3 X_5 + 214.3005$, predicted the nitric oxide removal efficiency well. The impact of various factors on the results for Fe catalyst descending > H₂O₂ concentration > NO initial concentration > H₂O₂ solution temperature > O₂ concentration > flue gas flow. Under optimum conditions the theoretical NO removal efficiency reached up to 89.91%.

Mechanics studies shows the apparent reaction order was 2 and thereby established kinetic model was consistent with experiment data. The H₂O₂ / UV system used in low temperature flue gas NO removal has a significant effect. This study provides data and some quotable experience for development of efficient and cleaner flue gas denitrification technology.

1. Introduction

Nitrogen oxide (NO_x) is one of the main air pollutant in China, and also an important reason for the formation of acid rain. According to statistics, in 2008, China's nitrogen oxide emissions were 16.245 million tons, of which 12.550 million tons of industrial nitrogen oxide emissions, Accounting for 77.0% of the national nitrogen oxide emissions (Li and Shi, 2016).

At present, Chinese people pay more and more attention on air pollution, and atmospheric environmental standards are constantly upgrading. In the electric power industry, the present standards are known as the most stringent standards of the history. Coal-fired boiler emissions targets are required to achieve the index of burning natural gas, NO_x < 50 mg/Nm³. This has been called "Ultra Clean Emission". Many power plants are working to upgrade the environmental facilities. Not only the power plants, but also, the steel industry, building materials industry (glass, cement etc.) and coking industry have to upgrade their environmental facilities. At present, the denitrification treatment technology of the flue gas containing nitrogen is mainly divided into two categories, namely the treatment technology based on the reduction and oxidation principle respectively. SCR technology, non-selective catalytic reduction (SNCR), and SNCR-SCR combined denitrification are the main technologies for flue gas denitrification based on the reduction principle (Tezanou et al., 2009). This kind of technology has the purification rate high, the movement is reliable, the secondary pollution is small and so on merits. But in general, such technology generally has the problems of equipment investment and operation

cost, catalyst deactivation, ammonia escape and so on, thus restricting its large-scale application to a certain extent (Ferrer and Víctor, 2007). Generally speaking, NO_x mainly includes NO, NO₂, N₂O₃, N₂O, N₂O₅ and so on, in which NO and NO₂, which cause acid rain, are dominant (Shi et al., 2016). The main difficulty is the problem of temperature and impurity. In sintering machine, for example, the flue gas temperature is commonly below 200 degrees, and SO₂ is often up to 1000 mg/Nm³, meanwhile the concentration of dust is quite high. In the case of coke oven, the flue gas temperature is commonly between 200-300 degrees, according to the production condition. If we used SCR to de NO_x, the catalyst can easily be jammed by tar or get poisoned by SO₂ and H₂O (Zheksenbaeva et al., 2015).

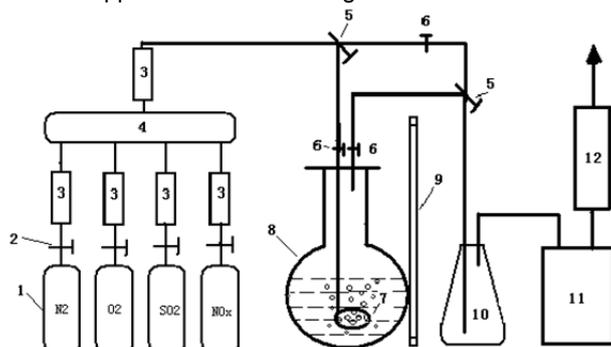
Advanced oxidation technology (AOPs), also known as the depth of oxidation technology, was first proposed in 1987 by Glaze (Glaze et al., 1987), refers to the reaction process has a large number of hydroxyl radicals involved in chemical oxidation technology. Through chemical or physical and chemical methods, the water pollutants directly mineralized into CO₂, H₂O and other inorganic substances. And the pollutants decomposed into low toxicity, easy biodegradation of small points of the material. AOPs are generally considered to be the use of the process of chemical activity generated by strong hydroxyl radicals (\cdot OH). Because of this technology has a high efficiency, thoroughness, a wide range of applications, no secondary pollution and other advantages, the technology has been more and more attention.

Denitration technology based on oxidation principle is applied to flue gas treatment, which is a kind of new method recently. As a main component of nitrogen oxides in flue gas, there are significant differences in the properties of NO and NO₂. NO₂ has a greater solubility in the water, and dissolved nitric acid and nitrous acid can be generated with the common desulfurization absorber (such as calcium oxide, etc.) reaction. The NO has minimal solubility in water, and can not react with the common alkaline absorbent. As the actual flue gas in industry, more than 90% of NO_x are NO. In order to achieve better denitrification efficiency, first we need to get the NO oxidation, and then use the appropriate process. NO can be oxidized to NO₂ by an oxidation technique and then absorbed by an alkaline absorbent. The method is not only a relatively small investment, but also easy to achieve the flue gas SO₂ and NO_x removal at same time. It will be a promising new technology of flue gas denitrification.

In this article, the removal of nitrogen oxides in low temperature flue gas was studied. The influence of various factors on the experimental results was investigated by H₂O₂/UV system. The influence of various factors on the experimental results was investigated by response surface methodology. The optimum process conditions were analysed. On this basis, kinetics study were carried out to explore the kinetics of flue gas denitrification under optimum conditions. The results are committed to the development a suitable advanced oxidation denitrification technology for metallurgical enterprises flue gas.

2. Materials and methods

Experimental apparatus is shown in figure 1.



1 Gas Cylinder; 2 Cylinder Valve; 3 Flowmeter; 4 Gas Cylinders; 5 Three-Way Valve; 6 Gas Valve; 7 Bubble Reactor; 8 Reactor; 9 UV Lamp; 10 Drying Bottle; 11 Flue Gas Analyzer; 12 Tail Gas Absorption Bottle

Figure 1: Sketch of the experimental process

The gas is generated from gas cylinders in the flue gas simulation system. It can be adjusted to the appropriate flow rate by means of a pressure reducing valve and a flow meter. The gas is mixed through the mixing tank and heated by evaporator, then entered to the gas pipe. UV light was put close to the reactor. It can irradiate the hydrogen peroxide solution in the reactor. The bubbler which has been used in water treatment commonly was used in the aeration head, completely sink in the solution. The inlet and outlet of the reactor were connected to the bypass. The flue gas was dried and the concentrations of N₂, O₂ and NO were

measured by KM-900 flue gas analyzer. Before starting the experiment, we opened the bypass system and closed the main gas path. After that we set the initial concentration of various gases in the flue gas, and use the flue gas analyzer to measure the initial concentration of O₂, N₂ and NO. After the start of the experiment, the reactor and UV lamp were put into the closed hood, avoiding exposure to sunlight and people. Then we opened the UV light, turned off the bypass system and switched to the main gas path. The gas can flow into the reactor, and the concentration can be measured. The removal rate is calculated according to the following formula.

$$\eta_{NO} = \frac{C_t - C_0}{C_0} \times 100\% \quad (1)$$

η_{NO} --NO removal rate, %;

C_t --NO export concentration, mg / m³;

C_0 --NO concentration, mg / m³;

According to equation (1), the denitration efficiency can be calculated.

3. Results and discussion

3.1 Effect of removal rate in different system

In order to compare the effect of UV irradiation on the removal of NO by H₂O₂, the removal rate of NO was investigated in H₂O₂ and H₂O₂ / UV systems.

The initial concentration of NO: 650mg/m³, the temperature of flue gas: 130°C, the power of UV lamp is 40w, the flow rate of flue gas is 850ml/min, the concentration of H₂O₂ is 5%, the temperature of solution is 55°C. The NO removal experiment was carried out by using H₂O₂ and H₂O₂ / UV systems separately. The experimental results are shown in Fig.2

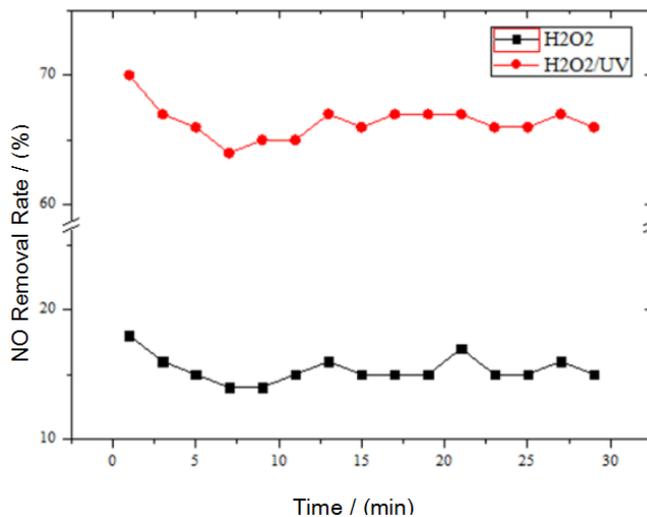


Figure 2: Removal rate of NO in different systems

The figure shows in the H₂O₂ solution, the removal rate of NO did not change significantly with the reaction time, and remained around 15%. In the H₂O₂ / UV system, the removal rate of NO is the much higher, and it does not change with the reaction time either, which is basically stable at about 67%. The results show that there is a significant synergistic effect between H₂O₂ and UV light.

The reason for these phenomena is that hydroxyl radical ($\cdot\text{OH}$) has strong oxidizing ability, which plays a very important role in the process of NO removal by oxidation. At the beginning of the experiment, the activity of H₂O₂ was strong, and the hydroxyl radical increased with the increase of time. However, after a certain period of time, the hydroxyl radical remained at a certain level, then kept a substantial increase. But the overall denitrification rate is not high, indicating that the effect is not satisfactory in H₂O₂ solution system. And under the irradiation of ultraviolet lamp, hydrogen peroxide solution will inspire a lot of hydroxyl radicals (Venkatadri, 1993). UV light and hydrogen peroxide cooperation mechanism can be expressed by (2):



The results show that the UV radicals have a strong catalytic effect on the oxidation and denitrification of hydrogen peroxide (Liu et al., 2010).

In order to further study the effect of UV lamp and hydrogen peroxide solution on the removal of NO in UV/H₂O₂ system, the effects of H₂O₂ concentration, H₂O₂ solution temperature, NO initial concentration, Fe ion catalyst concentration, flue gas flow and O₂ concentration on the removal rate of NO were investigated.

3.2 The interaction between factors

According to the single factor research result and the response surface method design principle carries on the experiment design (Zhao et al., 2014).

Table 1: Experimental Design Factors

	A	B	C	D	E	F
	H ₂ O ₂ concentration	NO concentration	O ₂ concentration	Temperature	Fe ²⁺	Flue gas flow rate
level /%		/mg/Nm ³	/%	/°C	molar ratio	/ml/min
-1	3	500	6	35	1/1500	600
0	6	650	8	45	3/1500	750
1	9	800	10	55	5/1500	900

The influence factors shown in the table were selected. These six factors corresponding to the elements of A-F in experimental design. In the table we can also see the high level and low level of factors we had chosen.

Based on the Box-Behnken in response surface methodology, the data were analyzed and the fitted by using different fitting methods. When the quadratic equation was used, the normal distribution of variance was close to one Line, indicating that the regression model with a good fit. The model p-value of 0.0001, is a significant model, the response of the regression equation is:

$$R = +67.35 + 11.75*A + 10.42*B + 1.59*C + 9.74*D - 13.03*E + 2.27*F - 1.78*AB + 18.07*AC + 0.69*AE - 6.19*AF + 15.40*BC - 2.42*BE - 2.38*BF + 7.31*CE - 3.03*CF + 2.07*DE - 6.19*EF - 9.45*A^2 + 2.38*E^2 \quad (3)$$

The p-value <0.05 of A, B, D, E, AC, BC, CE is a significant factor, and the regression equation of the reduced level code is as follows, still significant model.

$$R = 9.62*A + 6.72*B + 2.48*C + 6.24*D - 10.60*E + 1.75*F + 9.98*AC + 6.42*BC + 6.69*CE + 62.15 \quad (4)$$

Table 2: The variance significance test was performed after removal of non - significant factors

Source	Sum of Squares	df	Mean Square	F Value	p-value	Prob > F
Model	5207.43	9	578.6	7.14	< 0.0001	
A-A	1129.71	1	1129.71	13.94	0.0009	
B-B	282.22	1	282.22	3.48	0.0734	
C-C	133	1	133	1.64	0.2115	
D-D	213.41	1	213.41	2.63	0.1167	
E-E	2652.76	1	2652.76	32.73	< 0.0001	
F-F	72.18	1	72.18	0.89	0.354	
AC	220.84	1	220.84	2.72	0.1108	
BC	205.04	1	205.04	2.53	0.1238	
CE	716.63	1	716.63	8.84	0.0063	

According to the experimental analysis, it can be concluded that the influence of various factors on the experiment was: E>A>CE>B>AC>D>BC>C> F, ie Fe²⁺ catalyst>H₂O₂ concentration>NO initial concentration>H₂O₂ solution temperature>O₂ concentration>flue gas flow. Although the oxygen concentration has little effect of six factors, the interaction between the oxygen concentration and the initial concentration of hydrogen peroxide and the Fe²⁺ catalyst is obvious which is shown in figure 3. That is because of the Fe²⁺ forms a strong oxidized fenton reagent with the hydrogen peroxide, and the initial oxygen concentration has some influence on its oxidation.

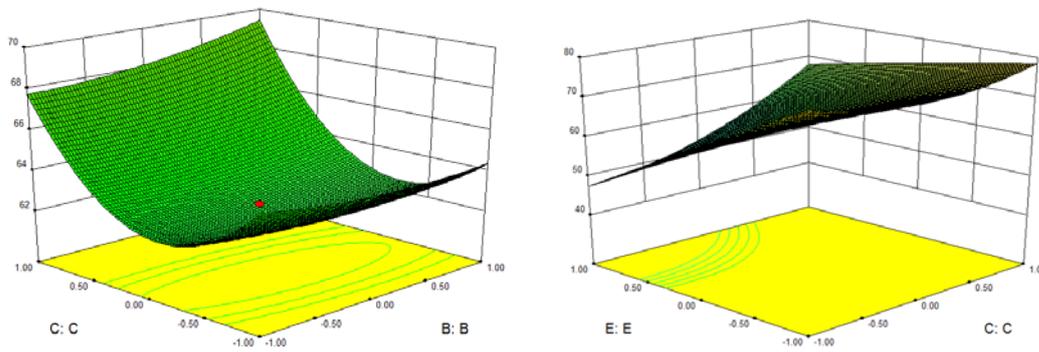


Figure 3: BC and CE factors interaction on NO removal efficiency

3.3 Determination of optimal denitrification conditions

According to the obtained factor regression equation, the regression equation is:

$$R = -10.10203 \cdot X_1 - 0.12647 \cdot X_2 - 27.68087 \cdot X_3 + 0.62404 \cdot X_4 - 28071.60614 \cdot X_5 + 0.011653 \cdot X_6 + 1.66373 \cdot X_1 X_3 + 0.021411 \cdot X_2 X_3 + 2513.87184 \cdot X_3 X_5 + 214.3005 \quad (5)$$

X1 - H₂O₂ concentration (%);

X2 - NO concentration (%);

X3 - O₂ concentration (%);

X4 - Temperature (°C);

X5 - Fe²⁺ catalyst molar ratio;

X6 - Flue gas flow (ml/min)

We can obtain the highest NO removal efficiency through the optimal solution of the equation. The highest removal efficiency of NO is 89.91%, the optimum conditions are as follow: concentration of H₂O₂ is 8.89%, the NO concentration is 775.65mg/Nm³, the O₂ concentration was 7.16% and the temperature was 54.36°C, the molar ratio of H₂O₂ and catalyst was 6.28E-4, the flue gas flow rate was 897.84ml / min.

3.4 Reaction kinetics study

The reaction order is an extremely important dynamic parameter, which is essential to establish the rate equation of the reaction (Gagliano et al., 2016). There are usually four methods for determining the order of reactions: integration, differentiation, half-life, and the ratio of reactants (Turner, 1977). In this study, the half-life method was used to calculate the reaction order of H₂O₂/UV system.

The results of linear fitting of $\ln T_{1/2} - \ln C_t$ with the best efficiency are as follows:

$$y = -0.98057x + 6.68719, R^2 = 0.98736 \quad (7)$$

It can be seen that the oxidation half-life logarithm $\ln T_{1/2}$ and the corresponding outlet concentration logarithm $\ln C_t$ linearly correlate significantly in the oxidation process of H₂O₂/UV system under the optimal conditions. So we can calculate the slope of the line $K = -0.98057 = 1 - n$ (BarrazaBurgos et al., 2015). The reaction order must be an integer, so that $n = 2$. Therefore, under the optimum conditions, the apparent reaction order of oxidation of NO in H₂O₂ / UV system is 2.

4. Conclusions

This article shows that under laboratory condition, simulated flue gas system and used hydrogen peroxide(H₂O₂) solution to conduct de-NO_x experiment, as well as investigated influence of many factors on the de-NO_x efficiency and arrived at a optimal de-NO_x system. At the same the machanisms were analysed. And on this basis, the reseach on dynamics and thermodynamics were carried on to explore the dynamics and thermodynamics theory of this de-NO_x system.

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nitric oxide removal efficiency well. The impact of various factors on the results for Fe catalyst descending> H₂O₂ concentration> NO initial concentration> H₂O₂ solution temperature> O₂ concentration> flue gas flow. Under optimum conditions the theoretical NO removal efficiency reached up to 89.91%.

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