

Experimental Study on NH₃ Oxidation Law

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Abstract: NO_x is one of the major air pollutants produced by power station boilers and has severe harm to mankind health and environment. Effective control of NO_x generation and discharge has become an imperative task. This paper studied the oxidation law of SNCR reductor NH₃ under different atmosphere through the developed thermal horizontal reaction tube experiment platform, which is of great significance to the determination of SNCR reductor spraying position.

Keywords NO_x; NH₃; SNCR; Denitration; Thermal horizontal reaction tube; Experiment

INTRODUCTION

China will make greater efforts to control NO_x emission and proactively develop efficient and low cost denitration technology so as to meet with greater environmental protection demand. Power station boilers and industrial boilers, as the main fire coal equipment, will the focus of NO_x emission control [1]. At present, NO_x control technologies applied to power station boilers are mainly low NO_x combustion technology and De-NO_x technology. The air fractional combustion belongs to the former while SNCR belongs to the latter [2-3]. SNCR reaction process is the mutually competitive reaction process of NO being restored and reductor being oxidized. When the reductor is sprayed into the area with appropriate temperature, the denitration reaction of NO being restored occurs; but when it's sprayed into the area with high temperature, the reductor oxidation reaction starts taking the lead. At this time, plenty of reductors will be oxidized. At the same time, the O₂ concentration in the actual smoke is also an important factor for the reductor being oxidized [4-5]. This paper is of great importance to confirming the SNCR reductor spraying position.

EXPERIMENT SYSTEMS

The experiment platform is thermal horizontal reaction tube experiment platform which allows experiment in a larger temperature scope. The highest experiment temperature can reach 1,100 °C. The experiment systems are mainly composed of such parts as horizontal tube electric heating furnace, quartz glass reactor, valve system and smoke components analysis system, etc. In the experiment, NH₃ is taken into the reactor through N₂ by the mass flowmeter; the three routes of gas including O₂, CO₂

and N₂ enters the gas bottle for full mix through the mass flowmeter, and then flow into the reactor on the other end. The two routes of gas react with each other inside the reaction tube after being preheated, and then enter the smoke analysis system at the reactor exit.

Horizontal Electric Heater

The horizontal electric heater mainly consists of silicon carbide tube, resistance wires, fire-resistant layer, insulation layer and metal steel sleeve. The heater has the inner diameter of 40mm, and its full length is 1.1m. Its temperature is controlled through using the three-stage program method. The heating element is the electric resistant wire, and the maximum heating temperature is up to 1100°C. Three temperature measurement thermocouple attachments are inserted into the heater to monitor the temperature of heater.

Quartz Glass Reactor

The processing material of reactor is the quartz glass, which can withstand the high temperature of 1100°C. The structure of reactor is shown in Figure 1:

The ground joint is used for the connection between the central jet nozzle and reaction section. In the test, the sealing at the ground joint is good, so there is no gas leakage even at high temperature. The central jet nozzle has the outer diameter of 14mm, with the opening at one end and sealing at the other end. At the opening end, the pipe is narrowed until the outer diameter is 6mm; at the bubbling place of the sealing end, eight holes with the diameter of 0.8mm are opened in the pipe walls along the circumferential direction; NH₃ is injected into the reaction tube from these holes. All of these are designed to facilitate the connection of gas lines.

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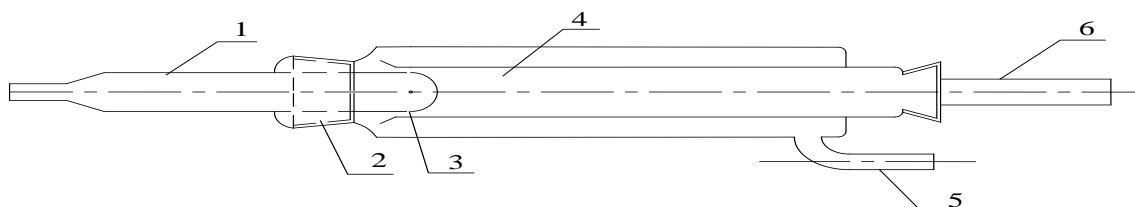


Figure 1. Structure Diagram of Quartz Reactor.

1. Central jet nozzle 2. Ground joint 3. Gas orifice
4. Reaction section 5. Simulated flue gas inlet 6. Reactor outlet

In order to make the reaction gas to reach the specific temperature before the chemical reaction in the reaction section, the reaction section is designed as the casing structure. The simulated flue gas composed of N_2 , O_2 and CO_2 enters the reactor through the simulated flue gas inlet 5, and then it is fully heated through turning back in the casing annulus. After that, it reaches the bubble jet ejection hole at the top of central jet nozzle and mixes and reacts with NH_3 ejected from the holes. As the gas flow from the central jet nozzle is small, there is no necessity to prepare a longer pre-heating section to reach the predetermined reaction temperature. The tube diameter of reaction section cannot be too big; if the diameter is too big, the mixture effect is not good and the temperature at the cross section is not even. But if the diameter is too small, the “tube diameter effect” will be generated, and the time of gas staying in the reaction section will become shorter. On the basis of comprehensively considering flow, stay time and mixture and other factors, the inner diameter of 18mm is the best choice for the reaction section.

Before the test, the temperature field calibration of reactor is conducted; the temperatures of 400 °C, 600 °C, 800 °C and 1000 °C are set respectively on the heater for temperature measurement. It can be seen from the measurement results that, in the sections of 20~75cm away from the heater outlet, the thermostatic property is more ideal, and the temperature in the section of less than 20cm away from the heater outlet drops relatively quickly. So, the section with the length of 55cm which is 20~75cm away from the heater outlet is taken as the constant temperature section of reaction. The NH_3 nozzle is designed at the place 75cm away from the electric heater outlet, where NH_3 and the simulated flue gas begin to mix and react.

Gas Distribution System

The gas distribution system mainly consists of gas cylinder, pressure reducing valve, gas flow control cabinet, and mixing tank and gas pipelines. The gas path is divided into two parts: one is NH_3 , which goes through the gas flow control cabinet and is carried by N_2 to enter the central jet nozzle of the quartz reactor; the other is N_2 , O_2 and CO_2 , which first go through the gas flow control cabinet and enter the mixing tank for full mixture and then enter the reactor to react with NH_3 .

Flue Gas Composition Analysis System

In the test, for the concentration of NH_3 , NO , CO_2 and other gases, the GASMET (DX-4000) portable FTIR multi-component gas analyzer is used for online measurement. The concentration of O_2 is measured through the zirconia detector installed in the sampling pump. The gases after the reaction are pumped by the sampling pump and then enter the flue gas analyzer for measurement of components. Based on the principle of Fourier Transform Infrared Analysis, FTIR is used for online measurement through direct sampling; the measuring time is between 1 second and 5 minutes, and the error range is 2% of calibrated span.

EXPERIMENT ANALYSIS

The smoke components produced by boiler combustion are relatively complicated and contain more CO_2 and O_2 . The reaction process of sprayed reductor and NO_x is first the process of NH_3 and smoke mix but NH_3 oxidation laws are for different smoke components. The experiment studied different NH_3 oxidation laws for different components so as to provide reference for choosing spraying positions in SNCR engineering application. The working condition arrangement of the experiment is shown in Table 1.

The NO mole fraction at the reactor exit increases with temperature. NO concentration maintains the same first and then rapidly rises. Just as working condition 1, 2 and 3 show, when the temperature is lower than 900 °C, NO concentration is basically 0ppm; when the temperature is higher than 900 °C, NO concentration will go up quickly; working condition 4, 5 and 6 share similar relations. However, NO concentration almost doesn't change when it's lower than 800 °C. When the temperature goes beyond 800 °C, NO concentration is apparently enhanced. When O_2 and CO_2 concentration maintain the same, NO concentration increases with increase in initial concentration of NH_3 . If compared among working condition 1, 2 and 3, when the initial concentration of NH_3 increases to 1,200 from 300ppm, the maximum generation amount of NO rises to 112ppm from 71ppm at the temperature level of 1,100 °C. When the initial concentration of NH_3

maintains constant, the higher the O₂ concentration, the more the generated NO and the lower the starting temperature for NH₃ being oxidized into NO. The initial NH₃ concentration under working 3 and working 6 is 1,200ppm. When O₂ volume fraction is 15% (working condition 6), NO concentration starts

rising increasingly at the temperature of 800°C and increases to 180ppm when the temperature is 1,100°C. When O₂ volume fraction is 4% (working condition 4), the maximum generation amount of NO under the experiment condition is 112ppm. It means that O₂ can promote the oxidation reaction of NH₃.

Table 1. Initial Concentration of Reactant Gas under Different Working Conditions

	NH3 Volume Fraction (%)	O2 Volume Fraction (%)	CO2 Volume Fraction (%)	N2 Volume Fraction (%)
Working Condition 1	0.03	4	15	80.97
Working Condition 2	0.06	4	15	80.94
Working Condition 3	0.12	4	15	80.88
Working Condition 4	0.03	15	4	80.97
Working Condition 5	0.06	15	4	80.94
Working Condition 6	0.12	15	4	80.88

Under all working conditions, NH₃ concentration maintains the same at the beginning, then rapidly declines and then tends to be 0 and keeps stable. When the initial concentration of NH₃ is fixed, the greater the O₂ volume fraction is, the faster the reduction of NH₃ concentration is. At the same time, the temperature of NH₃ being oxidized is lowered so it's with the temperature of NH₃ being close to zero. Just as the table shows, under working condition 3, when the temperature is lower than 800°C, there's no big change in NH₃ concentration while it rapidly decreases when the temperature goes higher. It is reduced to 0ppmm when the temperature is 1,050°C. Yet, under working condition 6, NH₃ concentration begins showing obvious changes when the temperature is lower than 700°C and it borders on 0 when the temperature is 1,000°C.

In order to demonstrate the relationship between NO concentration generated by NH₃ oxidation and initial concentration of NH₃ in a quantitative way, the rate of NH₃ conversion to NO is defined as follows:

$$\beta = \frac{\text{NO mole fraction at the electric furnace exit}}{\text{NH}_3 \text{ initial mole fraction}} \quad (1)$$

After treatment of the experiment data, the conversion rate under all working conditions is 0 when the temperature is from 600 to 700°C. The conversion rate under all working conditions increases as the temperature goes up. Under the same O₂ and CO₂ concentration and temperature conditions, the conversion rate β decreases as the NH₃ initial concentration increases. For example, under working 1, 2 and 3, when the temperature is 1,100°C, the conversion rate β is reduced to 0.093 under the initial NH₃ concentration of 1,200ppm from 0.254 with the initial NH₃ concentration of 300ppm. Likewise, the working condition 4, 5 and 6 share similar relations.

When the initial NH₃ concentration remains the same, the conversion rate β increases because the O₂ concentration rises. For instance, under working condition 1 and 4, when O₂ initial concentration is 4%, the maximum value of the conversion rate β is 0.254 at the temperature of 1,100°C. Under working condition 4, the O₂ initial concentration turns into 15%. At this time, the conversion rate at the temperature of 1,100°C expands to 0.343.

It can be noted that O₂ concentration and temperature are two major factors which drives NH₃ oxidation. Hence, in the practical application of SNCR, the reductor needs to be sprayed into the appropriate temperature interval and the O₂ concentration in the sprayed area should be proper as well.

CONCLUSION

Experiment studies for NH₃ oxidation laws under different atmosphere and temperature are conducted on the thermal horizontal reaction tube experiment platform. At the same time, brief introduction to experiment systems and methods is made as well. The following conclusions can be reached after the analysis of experiment results:

- 1) No obvious NH₃ oxidation phenomenon occurs when the temperature is relatively low (600~700°C); when the temperature goes higher than 800°C or 900°C, the oxidation gradually becomes apparent and NH₃ concentration slowly decreases while NO concentration goes opposite. When the temperature is about 1,000°C, NH₃ is almost completely oxidized. In terms of engineering, then the spraying position is chosen, the smoke temperature in that position shouldn't be too low; otherwise, much ammonia will be lost.
- 2) The higher the NH₃ initial concentration, the more the NO generated by NH₃ oxidation; the higher

the O₂ concentration, the more the generated NO and the lower the initial temperature for NH₃ being oxidized into NO.

3) When the initial O₂, CO₂ concentration and temperature remain constant, the conversion rate β declines as NH₃ initial concentration ascends; when NH₃ initial concentration maintains the same, the conversion rate β increases as O₂ concentration goes up.

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