Influence Study of Ammonia-Nitrogen Molar Ratio on SNCR Denitrification

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Abstract: The influences of different ammonia-nitrogen molar ratios (Normalized Stoichiometric Ratio, NSR) on the NOx emission concentration, ammonia escaping amount, and selective non-catalytic reduction (SNCR) denitrification efficiency were measured through a field test. The results show that with the increase of NSR, the NOx emission concentration changes little, the ammonia escaping amount is gradually increased, and the SNCR denitrification efficiency is basically kept stable after increasing firstly. In full consideration of the ultralow emission limit and reducing agent consumption, it is believed that 2.01 is the optimal NSR value under the test load.

1. Introduction
The selective non-catalytic reduction (SNCR) technology is a denitrification process [1-3] of generating N₂ and H₂O through the chemical reaction of reducing agent selectively with NOx (mainly NO and NO₂) without any need of catalyzer.

The SNCR denitrification reactions are seen in equations (1)-(3):

\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1) \]
\[ 4\text{NH}_3 + 2\text{NO} + 2\text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \quad (2) \]
\[ 8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \quad (3) \]

The injection system sprays the reducing agent (liquid ammonia, ammonium hydroxide, urea solution, etc.) in the specific temperature region in the furnace. The reducing agent will react with the NOx in the flue gas, and reduce the NOx into N₂, H₂O and CO₂, so as to realize the NOx removal.

The key factors influencing the SNCR denitrification efficiency are divided into two aspects: diffusion and reaction, namely, the mixing degree of reducing agent with flue gas, and whether the denitrification reaction is thorough[4]. On the one hand, the reducing agent sprayed into the furnace can sufficiently contact the NOx only when it is fully mixed with the flue gas, which can lay a foundation for the denitrification reaction; on the other hand, the range of reaction temperature, standing time of flue gas, type of reducing agent, NSR and additive are factors influencing whether the denitrification reaction is thorough[5], among which the temperature has the greatest influence on the SNCR reaction. To be specific, the SNCR denitrification reaction is slow at too low temperature, but...
when the temperature is too high, NH₃ will undergo oxidizing reaction to generate more NOx, thus reducing the denitrification rate[6]. Generally speaking, the proper reaction temperature of liquid ammonia and ammonium hydroxide is 871-1,038℃, and that of urea solution is 927-1,093℃.

Ammonia-nitrogen molar ratio (NSR) is another important factor influencing the SNCR denitrification effect. Theoretically speaking, 1 mol of NH₃ is needed to reduce 1 mol of NO, but the amount of NH₃ needed should be higher than 1 mol in practical situation because of reaction standing time, diffusion of reducing agent, etc. From the angle of reaction equilibrium, the reaction equilibrium constant remains unchanged at a certain temperature, so the equilibrium will move towards the right (reactions (1)-(3)) and the NO removal efficiency will be improved if the concentration of NH₃ is elevated; from the perspective of reaction dynamics, elevating the concentration of reactant will accelerate the reaction. Therefore, the NO removal efficiency will be improved within the same standing time. The denitrification efficiency will be improved to a certain extent with the increase of NSR. However, the operating cost and ammonia escaping amount will be increased under excessive amount of reducing agent. On this basis, determining the optimal NSR range through a test will reduce the ammonia escaping amount of the machine set while guaranteeing the up-to-standard emission, and relieve the scaling phenomenon of the air pre-heater.

With the SNCR denitrification system of a supercritical circulating fluidized bed boiler, ten groups of different NSR tests were implemented under basically unchanged conditions such as reaction temperature, standing time of flue gas, etc. The most suitable NSR value was selected by taking the denitrification efficiency and ammonia escaping amount as the criteria, so as to provide a data reference and adjustment basis for the economical and efficient SNCR operation.

2. Test

2.1 Profile of boiler equipment

The supercritical circulating fluidized bed combustion mode is adopted for the boiler of 2# machine set in one power generation company. This combustion mode is featured by intermediate reheating once, balanced ventilation and solid-state slagging, and the gas-solid separation is realized through a high-temperature steam-cooled cyclone separator. The water-cooling drum-type slag cooler is under M-type arrangement, the boiler is tightly sealed with a full steel frame suspension structure, and it is also synchronously installed with a flue gas denitrification device. The main technical parameters of the boiler are seen in Table 1.

| Item                                    | Maximum continuous rating of boiler | Nominal rating of boiler |
|-----------------------------------------|-------------------------------------|--------------------------|
| Superheated steam flow/tꞏh⁻¹             | 1241                                | 1182                     |
| Steam temperature at superheater outlet /℃ | 571.0                              | 571.0                    |
| Steam pressure at superheater outlet/MPa | 25.40                               | 25.33                    |
| Steam pressure at reheater inlet/MPa    | 5.95                                | 5.65                     |
| Steam temperature at reheater inlet/℃   | 359.0                               | 353.0                    |
| Steam pressure at reheater outlet/MPa   | 5.76                                | 5.47                     |
| Steam temperature at reheater outlet/℃  | 569.0                               | 569.0                    |
| Reheated steam flow/tꞏh⁻¹               | 1.35                                | 985                      |
| Feed-water temperature/℃               | 300.0                               | 297.0                    |
The properties of the design coal and check coal for the boiler are seen in Table 2.

| Item                              | Design coal | Check coal 1 | Check coal 2 |
|-----------------------------------|-------------|--------------|--------------|
| Carbon of as-received basis/%     | 36.61       | 32.57        | 33.00        |
| Hydrogen of as-received basis/%   | 2.26        | 2.10         | 2.29         |
| Oxygen of as-received basis/%     | 6.72        | 6.72         | 7.63         |
| Nitrogen of as-received basis/%   | 0.65        | 0.56         | 0.59         |
| Sulfur of as-received basis/%     | 2.06        | 1.99         | 2.09         |
| Total moisture/%                  | 6.50        | 8.00         | 9.87         |
| Air-dried moisture/%              | 1.67        | 2.17         | 1.11         |
| As-received base ash content/%    | 45.20       | 48.06        | 44.53        |
| Dry ash-free base volatiles/%     | 35.91       | 40.43        | 40.28        |
| Lower heating value of as-received basis /kJ·kg⁻¹ | 13800       | 11770        | 12790        |
| Hardgrove grindability index      | 76          | 92           | /            |

2.2. Profile of denitrification device

2.2.1. Technology introduction

According to the technological process, the denitrification system of this machine set mainly consists of urea dissolution system, urea solution storage and transport system, dilution water system, urea solution dilution, measurement and dispensing system, and urea solution injection system.

2.2.1.1 Urea dissolution and storage system

The urea particles in bags were poured into an underground hopper after manual bag opening, transported into a urea dissolution tank through a bucket elevator, then mixed with demineralized water in the urea dissolution tank, and heated to prepare the urea solution with mass concentration of 50%. To fully dissolve the urea particles, a top-entering agitator was arranged in the urea dissolution tank. The urea solution was transported to the urea solution storage tank via a urea solution circulating pump.

2.2.1.2 Urea solution dilution and measurement system

Before being sprayed into the boiler, the urea solution was mixed and diluted with dilution water, and its mass concentration should not be greater than 20% after dilution. A static mixer was used as the dilution mixer, and the source of dilution water was demineralized water. Two dilution pumps were set on two boilers, where one boiler was in operation and the other was for standby application. The urea solution measurement and dispensing device could accurately measure and control the flow quantity of urea solution transported into the furnace. Each boiler was set with one set of measurement and dispensing device to control the flow quantity in the urea solution injector as well as the atomization pressure and pressure of cooling air. The mass concentration of urea solution was controlled within 10% before the reducing agent was sprayed into the furnace.
2.2.1.3 Urea solution injection system
Under different boiler loads, the reducing agent was sprayed into the injection region where the flue gas temperature was within the optimal reaction interval. The position of injection region and spray gun setting were determined through the accurate simulation results of temperature field in the furnace, flue gas flow field, reducing agent jet flow field, and chemical reaction process. According to the operating requirements, one machine set should be divided into 4 injection regions in this SNCR project, where 3 spray guns were placed in each injection region, each SNCR spray gun was designed with an actuator (insertion depth: adjustable within 0-0.2 m), and the arrangement of spray guns was guided by the SNCR process simulation to reach the maximization of the denitrification efficiency.

2.2.2. Design parameters
The design parameters of flue gas at the inlet of the flue gas denitrification device are seen in Table 3.

| Item                                                                 | Value          |
|----------------------------------------------------------------------|----------------|
| Wet flue gas (standard state) amount at SNCR inlet/m³·h⁻¹            | 1122110        |
| H₂O/Vol%                                                             | 7.66           |
| O₂/Vol%                                                              | 2.99           |
| N₂/Vol%                                                              | 73.34          |
| CO₂/Vol%                                                             | 15.06          |
| NOx (6% O₂, standard state, dry basis) at SNCR inlet/mg·m⁻³           | 150            |
| NOx (6% O₂, standard state, dry basis) at SNCR outlet/mg·m⁻³          | 35             |
| Ammonia escaping amount/µL·L⁻¹                                       | 5              |

2.3. Test instruments and equipment
The main test instruments included Laoying 3012H automatic soot/gas tester, TESTO370 flue gas analyzer, Thermal410P ammonia analyzer, Greyline Doppler ultrasonic flowmeter and FLUKE51 digital thermometer.

2.4. NOx concentration test
The NOx and O₂ tests were conducted using the flue gas analyzer under the load of 330 MW. Flue gas sampling points (8×3 points) were laid at the inlet of the air preheater. The flue gas was guided out of the gas flue through stainless steel pipes, washed with water to remove dust, dehumidified, cooled, and finally let into the flue gas analyzer. Under the feed and returning conditions of reducing agent (urea), the NOx and O₂ contents in the flue gas sample acquired point by point were analyzed. The NOx concentrations on the cross sections at inlet and outlet of the reactor, and the denitrification efficiency are calculated through the equations (4)-(6):

\[
NO_{\text{reduced agent returned}} = NO_{\text{in, O}_2, \text{ act}} \times 2.05 \times \frac{100}{95} \times \frac{21 - 6}{21 - O_{2, \text{act}}} \tag{4}
\]

\[
NO_{\text{reduced agent fed}} = NO_{\text{in, O}_2, \text{ act}} \times 2.05 \times \frac{100}{95} \times \frac{21 - 6}{21 - O_{2, \text{act}}} \tag{5}
\]

\[
\eta = \frac{NO_{\text{reduced agent fed}} - NO_{\text{reduced agent returned}}}{NO_{\text{reduced agent fed}}} \times 100 \tag{6}
\]

where: NOx, reducing agent returned —— NOx concentration when the reducing agent is returned, mg/m³,
2.5. NH3 escape concentration test

According to the NOx concentration distribution of flue gas on the section, 8 representative points were selected as NH3 sampling points. The ammonia escape samples were acquired through the chemical solution method in accordance with the American EPA CTM-027 standard, and the acquired flow quantity of dry flue gas and O2 concentration were recorded, based on which the dry NH3 concentrations in the flue gas at different sampling points were calculated.

3. Results and discussion

The test results are displayed in Figure 1.

As seen in Figure 1, the denitrification efficiency firstly presented an obvious increasing trend and then gradually became steady with the increase of NSR, and it was increased evidently under NSR=1.02-2.01, from 45.5% to 67.3%. When the NSR became greater than 2.01 and increased to 3.25, the denitrification efficiency was slightly degraded, but it was still kept at 65%. The possible reason was that the use amount of the reducing agent in the system was increased with the NSR, which contributed to the further denitrification reaction. However, as the NSR was further increased, the NOx concentration was continuously decreased, and thus the reaction was gradually slowed down, and the denitrification efficiency was reduced.

The NOx emission concentration was declining with the increase of NSR, but the reduction amplitude was not obvious. Under NSR=1.02, 2.01 and 3.25, the NOx emission concentrations were 22.7mg/m3, 19.0mg/m3 and 14.7mg/m3, respectively, all of which were lower than the ultralow emission limit.

The ammonia escaping amount was apparently increased after the NSR was greater than 2.01, especially when the NSR=2.78, 3.05 and 3.25, the ammonia escaping amounts were 8.02 mg/m3, 9.12
mg/m³ and 8.97 mg/m³, respectively, all of which exceeded the limit value of ammonia escaping amount suggested in DL/T 296-2011 Guide for Flue Gas Denitrification Technology in Thermal Power Plant.

4. Conclusion
NSR is a key factor influencing the SNCR denitrification efficiency. The dual requirements for reducing agent consumption and up-to-standard emission limit should be both considered in the actual operation. The optimal NSR should be determined through a test to ensure high denitrification efficiency and low ammonia escaping amount. It was verified through ten groups of tests in this study that NSR=2.01 was a proper value by measuring the denitrification system efficiency, ammonia escaping amount and NOx emission concentration. In addition, the load change may result in the change of the optimal NSR. The test mode and analysis method adopted in this test can provide a reference for the operating adjustment of the machine set.

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References:
[1] Jiang J D, Lin C, Zhang Y, Yu J, Zhang Z X. Numerical simulation of influence of technological operation parameters on SNCR denitrification performance of flue gas [J]. Proceedings of the CSEE, 2018,38(02):383-389+668.
[2] Zeng Y, Zhou J H. Key SNCR parameters of circulating fluidized bed boiler and engineering application [J]. Industrial Boiler, 2016(05):36-38.
[3] Bi D G, Zhang Z X, Zhang J, Yue P J. Experimental study of ammonia spraying combine SNCR deep denitrification in primary combustion zone of pulverized coal boiler [J]. Journal of Engineering for Thermal Energy and Power, 2017,32(08):89-93+150.
[4] Gong Y X, Su T X, Ma L Q, Chen F Q. Ammonia escape in boiler SNCR system and its impact on air preheater [J]. Energy and Energy Conservation, 2017(10):93-94.
[5] Wu Y Y, Zhang G X, Wang J Q, Chi Z H. Application of SNCR in medium temperature separator-type circulating fluidized bed boiler [J]. Power System Engineering, 2014,30(01):27-29+32.
[6] Zhao K, Kang L S, Guan H Y, Li S Y. Research status of SNCR denitrification technology in circulating fluidized bed boiler [J]. Energy Conservation Technology, 2017,35(06):514-519.