Summary of flue gas denitration technology for coal-fired power plants

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Summary of flue gas denitration technology for coal-fired power plants

Wanpeng Yang *

School of North China Electric Power University, Baoding, China

*Corresponding author e-mail: 18266693938@163.com

Abstract. With the rapid development of the economy, nitrogen oxide pollution has become a problem that cannot be ignored. Therefore, it is necessary to strengthen the control of nitrogen oxides in coal-fired power plants. This paper introduces the current denitration technology overview, including the selective catalytic reduction (SCR), non-selective catalytic reduction (SCNR), SCR-SNCR mixed denitration technology, including acid absorption, Wet denitration technology such as lye absorption method, oxidation absorption method and activated carbon absorption method, as well as coal-fired flue gas combined desulfurization and denitration technology were introduced. The process principle and characteristics were briefly described, and the development direction of flue gas denitration technology was introduced. The outlook was made.Introduction Nitrogen oxides (NOx) is an atmospheric pollutant that combines with water in the air to promote the formation of acid rain. It also produces photochemical smog under certain conditions with other pollutants. It also participates in the destruction of the ozone layer and oxidation. Nitrogen will destroy the ozone layer in the high-temperature stratosphere and increase the incidence of skin cancer. Therefore, while building a power plant to meet social energy needs, it should strengthen the effective control of nitrogen oxide emissions from coal-fired power plants, reduce air pollution, and reduce the serious damage caused by nitrogen oxides emissions to human living environment. The emission of nitrogen oxides from power plants. Denitration technology is particularly important.

1. Overview of denitrification technology

At present, China's control methods for combustion are divided into three categories according to the processing sequence before and after combustion: pre-combustion, combustion, and post-combustion denitrification [1].

Denitrification before combustion is to reduce the nitrogen content of the fuel or to use a low-nitrogen fuel to reduce the amount of production. There are two main methods: hydrogenation and washing. The principle of hydrodenitrogenation is to selectively hydro-saturate olefins and aromatic hydrocarbons in raw coal, hydrogenolysis of non-hydrocarbon compounds such as sulfur, nitrogen and oxygen in raw coal, and to remove impurities such as metals and asphalt from raw coal [2]. Coal washing and coal preparation refer to the removal of ash, vermiculite, sulfur, nitrogen and other impurities contained in raw coal by washing out, and according to coal type, ash, calorific value and particle size, it is divided into different grades of coal to meet different scenarios. Demand. However, the technical requirements and costs of these two methods are relatively high and the practicality is not strong.

Denitrification in combustion refers to reducing the amount of production in the boiler by improving the combustion mode and production process during the combustion process, that is, low combustion technology. Commonly used denitration technologies in combustion mainly include low excess air combustion (LEA), air staged combustion, low burners, and flue gas recycling technologies.

Denitrification after combustion refers to the treatment of flue gas generated after combustion, that is, the denitration device is installed at the tail of the flue, and the method of reducing or adsorbing in the flue gas is also called flue gas denitration technology. Flue gas denitration technology is divided into wet denitrification and dry denitrification according to the form of reactants. It is the most effective method to reduce NOx emissions. Therefore, denitration after combustion is the most widely used denitration method in industrial applications.

1.1. Alkali absorption method

The alkaline solution absorbs NO_2 or a certain proportion of NO/NO_2 mixed gas has a good effect, and the NaOH can be used to absorb NOx to achieve the purpose of denitration. Common alkaline absorption liquids are alkali liquids formed by substances such as hydroxides (potassium, sodium, magnesium, etc.) and weak acid salts, such as soda ash, caustic soda, lime milk, ammonia water, and the like. The principle of the method is that lye reacts with NOx to form nitrate and nitrite, and the resulting salt can be recovered by evaporation and crystallization, but NO is hardly soluble in water and alkali, when the molar ratio of NO/NO_2 gas is high. At 0.5, NO can hardly be absorbed, so this method is only suitable for flue gas with high NO_2 content. For coal-fired boilers (NO accounts for more than 90% of total NOx), the method has low denitration efficiency. Therefore, it is not adopted.

1.2. Acid absorption method

Since the solubility of NO and NO_2 in nitric acid is much greater than in water (for example, the solubility of NO in 12% nitric acid is 12 times greater than that in water), dilute nitric acid absorption is used to increase NOX removal rate. The technology is widely used. As the concentration of nitric acid increases, the absorption efficiency increases remarkably. However, considering the practical application and cost of the industry, the concentration of nitric acid used in actual operation is generally controlled within the range of 15% to 20%. The denitration efficiency of the pickling method is affected by factors such as absorption temperature and pressure. Studies have shown that the operating temperature is 10-20 °C in practical applications, and the operating conditions are high pressure conditions. High-pressure conditions also mean that more energy is needed to achieveOxidation absorption method

The principle of the oxidation absorption method is to use a strong oxidizing agent to oxidize the poorly soluble NO in the flue gas to NO_2 which is easily soluble in water or soluble in the lye, and then denitrate by using the absorbing alkali solution. The strong oxidant is divided into a vapor phase oxidant and a liquid phase oxidant, the vapor phase oxidant includes Cl_2, ClO_2, O_3, etc., and the liquid phase oxidant includes $KMnO_4$, $NaClO_2$, NaClO, H_2O_2, $KBrO_3$, K_2CrO_7, $HClO_3$, Na_2CrO_4 and the like. Currently more common are O_3 oxidation and H_2O_2 oxidation.

1.3. Activated carbon absorption method

Activated carbon is a black powder or granular amorphous carbon which has a porous structure and is therefore widely used as a good adsorbent material. Activated carbon absorption denitration technology also uses activated carbon to adsorb NOx in flue gas, and activated carbon can also oxidize NO to $N0_2$ [3]. In the practical application of activated carbon absorption denitration technology, ammonia can be added for improvement, research shows that the denitrification rate of this improved method can reach 50% to 80% [4]. The factors affecting the denitration technology of activated carbon absorption method are mainly the porosity and specific surface area of activated carbon itself. Due to the presence of $S0_2$ in the flue gas, it affects the absorption of NOx by activated carbon [5]. Activated carbon absorption denitration technology has no secondary pollution and activated carbon can be recycled. The disadvantage of the activated carbon absorption denitration technology is that the adsorption equipment is huge.

1.4. Reduction absorption method

The principle of the reduction absorption method is to reduce the NOx to N_2 by using a reducing agent in the liquid to achieve the purpose of denitration. Common reducing agents are $CO(NH_2)_2$, $(NH_4)_2SO_3$, etc., and the main reaction formulas are shown in formula (1) and formula (2) [6].

$$NO + NO_2 + CO(NH)_2 \rightarrow 2N_2 + 2H_2O + 2CO \quad (1)$$

$$NO + NO_2 + 3(NH4)_2SO_3 \rightarrow 2N_2 + (NH_4)_2SO_4 \quad (2)$$

The denitration rate of the reduction absorption method is generally 40% to 60% . When $(NH_4)_2SO_3$ is a reducing agent, the product $(NH_4)_2SO_4$ after flue gas denitration can be recycled. It can be seen from formula (2) that the molar ratio of $NO:NO_2$ is 1:1, so the method is applicable to flue gas with NO/NO_2 less than 0.5. Therefore, the method is not suitable for flue gas denitration of coal-fired boilers.

2. Dry denitration technology

Dry denitration refers to the reduction of NOx into N_2 which is not harmful to the environment in the gas phase by means of reducing agents or high-energy electron beams, microwaves, etc., or conversion to nitrate for recycling. Dry denitration techniques include selective catalytic reduction (SCR), non-selective catalytic reduction (SCNR), and SCR-SNCR mixed denitration.

2.1. Selective Catalytic Reduction (SCR)

SCR technology is currently the most widely used flue gas denitration technology in commercial applications. The technology was invented by Eegelhard in the United States and patented in 1959, and Japan was the first to industrialize the method in the 1970s [7]. SCR refers to a process of reducing NO in flue gas to N_2 and water with a reducing agent NH_3 in the presence of O_2 and a heterogeneous catalyst at a temperature maintained in the range of 220-450 °C. This process is called selectivity because the reducing agent NH_3 preferentially reacts with NO in the flue gas rather than by oxygen in the flue gas [8]. The SCR denitration technology reaction process is as follows.

Main reaction:

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \quad (3)$$

$$2NO_2 + O_2 + 4NH_3 \rightarrow 2N_2 + 6H_2O \quad (4)$$

$$2NO + 2O_2 + 4NH_3 \rightarrow 3N_2 + 6H_2O \quad (5)$$

Side effects:

$$2SO_2 + O_2 \rightarrow 2SO_3 \quad (6)$$

In the application process of SCR technology, the preparation and production of catalyst is one of the most important parts, and its catalytic performance directly affects the overall denitration effect of the SCR system. For SCR denitration systems, the choice of catalyst is key. Considering the factors of economy, operation and maintenance, the catalyst is required to have high activity, good sulfur resistance and water resistance, long life, good economy and no secondary pollution. A large number of studies have been carried out on SCR catalysts by domestic and foreign scholars. The commonly used catalysts are vanadium-based catalysts such as V_2O_5/TiO_2, V_2O_5-WO_3/TiO_2, etc., with NH_3 as a reducing agent.

2.2. Selective Catalytic Reduction (SNCR)

Non-selective catalytic reduction denitrification (SNCR) is a process in which a reducing agent such as NH_3 or urea is sprayed into the furnace to selectively react with NOx without using a catalyst, so that a reducing agent must be added in a high temperature region. The reducing agent is sprayed into the furnace at a temperature of 900 to 1200 °C, and the reducing agent is rapidly thermally decomposed into NH_3 and reacted with NO_2 in the flue gas to form N_2 . The method is based on a furnace as a reactor [9], wherein the main reaction of reducing NH_2 by using NH_3 or urea as a reducing agent is:

1) NH3 as a reducing agent:

$$4NO + O_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O \tag{7}$$

$$2NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \tag{8}$$

2) Urea as a reducing agent:

$$CO(NH_2)_2 + 2HO_2 \rightarrow 2CO_2 + 2N_2 + 2H_2O \tag{9}$$

$$4NO + O_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O \tag{10}$$

The chemical reaction efficiency of SNCR reduction of NO depends on the temperature of the flue gas, the residence time at high temperature, the type and amount of ammonia-containing compound, ie, the injection of reducing agent, the mixing efficiency and the content of NOx [10]. In general, the SNCR denitration efficiency can reach 25% to 40% for large coal-fired units and 80% for small units. As one of the most widely used denitration technologies, SNCR has the following advantages: less investment, no catalyst, simple equipment modification, short cycle, reliable operation and simple operation. However, there are some problems in practical applications [11]: the utilization rate of ammonia in the process is not high, and it is easy to form excessive ammonia leakage; the amount of ammonia consumed is large; the greenhouse gas N_2O is formed; it is greater than 800 °C before the boiler superheater The injection of the low temperature urea solution into the furnace location will inevitably affect the continued combustion of the hot coal, causing problems of increased fly ash and unburned carbon.

2.3. SNCR-SCR mixed denitration

SNCR-SCR mixed flue gas denitration technology is not a simple combination of SCR process and SNCR process. It is a new process developed by combining the characteristics of SCR technology and SNCR technology investment. Brain et al. [12] suggested that the SNCR-SCR combination technology can achieve 90% NOx removal rate, and the NH_3 leakage rate is only 0.0003%. The SNCR-SCR mixed denitration process combines the injection of the reducing agent of the SNCR process into the furnace technology and the catalytic reaction of the SCR process with the escape ammonia to further remove NOx. The mixed denitration process uses urea as the absorbent, which is an effective combination of a special SNCR process in the furnace and a simple back-end SCR denitration reactor.

The main reaction process of the SNCR-SCR mixed denitration process is as follows:

$$CO(NH_2)_2 + 2HO_2 \rightarrow 2CO_2 + 2N_2 + 2H_2O \tag{11}$$

$$CO(NH_2)_2 + HO_2 \rightarrow CO_2 + 2NH_3 \tag{12}$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \tag{13}$$

$$4NO + O_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O \quad (14)$$

$$2NO_2 + O_2 + 4NH_3 \rightarrow 2N_2 + 6H_2O \quad (15)$$

Compared with the single SCR process and SNCR process, the main improvement of the hybrid SNCR-SCR process is the elimination of the complex AIG (ammonia injection) system with SCR set in the flue. It has the following advantages: high denitration efficiency and SCR The denitration efficiency of the method; the reaction tower has small volume and strong space adaptability; the system pressure drop is small, the operating cost is reduced; the corrosion hazard is reduced; urea can be conveniently used as a denitration reducing agent; and the generation of N_2O is reduced.

3. Conclusion

At present, the research on flue gas denitration technology at home and abroad has made great progress. At present, China's coal-fired boilers use more dry denitration technologies. Among them, SCR denitration technology has many application examples, but SCR denitration technology has high operating cost and is difficult to process after catalyst deactivation. Therefore, the development direction of SCR denitration technology is developed. A catalyst that is low temperature, is not susceptible to SO_2 poisoning, and develops a technology that facilitates catalyst disassembly. The denitrification rate of SNCR technology is not high and the ammonia slip is higher than SCR technology. The development direction is to improve the furnace distributor, combined with low nitrogen combustion technology or SCR denitration technology. The wet denitration technology has a simple process, is easy to operate, has low operating cost, can be recycled, and can achieve the purpose of desulfurization and denitrification integration. Coal-fired flue gas combined desulfurization and denitrification technology has become a research hotspot in the field of environmental protection, and is the development direction of desulfurization and denitrification research in the future.

In summary, China has adopted more denitrification technologies, but it is necessary to comprehensively consider the characteristics of different coal-fired power plants to select appropriate denitration technology, and draw on foreign advanced denitration technology, combined with the actual situation of China's coal-fired power plants, and jointly promote The development of China's denitrification industry reduces NOx emissions.

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