Current situation and prospect of Denitration technology in nonferrous smelting industry

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Abstract. Air pollution control of the non-ferrous industry is mainly concentrated on the dust and SO₂ in the flue gas. NOx control has just started. The relevant standards and specifications are still constantly updated and improved, control technology is also learning from other industries on the basis of continuous exploration and innovation. Through analyzing the NOx emission characteristics and emission standard requirements of non-ferrous smelting industry, this paper points out the current situation and development trend of the non-ferrous smelting industry.

1. Introduction
In recent years, with the rapid development of non-ferrous industry in China, the situation of smoke control is becoming more and more serious. The smelting smoke of non-ferrous industry has the characteristics of high pollutant concentration, relatively small smoke volume and large fluctuation, which makes the comprehensive treatment of smelting smoke of non-ferrous industry more difficult.

2. NOx emission characteristics of non-ferrous industries
The relatively late start of air pollution control in non-ferrous industry, coupled with the variable conditions and complex composition of flue gas in non-ferrous industry, increases the difficulty of smoke control.

Air pollution control of the non-ferrous industry is mainly concentrated on the dust and SO₂ in the flue gas. NOx control has just started. The NOx monitoring has not yet been incorporated into the routine monitoring of nonferrous industry, so few people focu on NOx emission [1].The relevant standards and specifications are still constantly updated and improved, control technology is also learning from other industries on the basis of continuous exploration and innovation.

NOx emissions of non-ferrous metal smelting in China are mainly divided into three types, respectively from acid production tail gas, industrial furnace flue gas and noble metal workshop exhaust gas. For different processes, the concentration of NOx varies greatly from tens of mg/m³ to tens of thousands of mg/m³, and different methods should be adopted to treat it.

3. NOx emission standards of non-ferrous industry
China's earliest pollutant emission standards for non-ferrous industries, "Copper, Nickel and Cobalt Industrial Pollutant Emission Standard" (GB25467) and "Lead and Zinc Industrial Pollutant Emission Standard" (GB25466), were released and implemented in 2010, and no NOx emission concentration limit was stipulated in the standards.
In 2013, the Ministry of Environmental Protection revised and improved the "Lead and Zinc Industrial Pollutant Discharge Standard" (GB25466), formulated a revision of the standard, and added the NOx emission limit. In 2014, the Ministry of Environmental Protection revised and improved the Discharge Standard for Pollutants from the Copper, Nickel and Cobalt Industries (GB 25467), formulated a revision sheet to the standard, and added the NOx emission limit.

The emission limit of NOx concentration was stipulated in the Discharge Standard for Pollutants from the Industry of Tin, Antimony and Mercury (GB 30770) issued in 2014 and the Discharge Standard for Pollutants from the Industry of Recycled Copper, Aluminum, Lead and Zinc (GB 31574) issued in 2015. It can be seen that the state gradually attaches importance to the NOx emissions of the non-ferrous industry, and the management requirements of smelting flue gas in the non-ferrous industry are becoming more and more strict.

4. NOx emission type in nonferrous industry

4.1. Acid production flue gas
The NOx emission concentration in acid production gas of nonferrous smelting enterprises in China is generally less than 200mg/m3, which basically meets the NOx emission standard requirements of the industry. Therefore, there is almost no NOx treatment case reference.

Selective catalytic reduction (SCR) method has been successfully applied to remove NOx in acid production from smelting flue gas. SCR method has been applied to remove NOx from acid production from smelting flue gas in Budel Zink zinc plant in the Netherlands, with good results. SCR is used for denitration of flue gas from smelting acid production. The denitration reactor is placed before the first phase of conversion of acid production. At this time, the flue gas has been fully purified and the reaction temperature requirements are met by heating up of gas-gas heat exchanger. The designed NOx entry concentration is 200mg/m3, and the removal efficiency can reach 95%. The acid production system of a smelter in Japan was modified by SCR device, and the NOx entry concentration was designed to be 200mg/m3, and the removal efficiency could reach 95% [2].

The NOx content in the finished sulfuric acid can meet the requirements of the industrial sulfuric acid standard after the denitration method of smelting acid flue gas is adopted. In addition to the denitration of the acid making flue gas, the method of directly removing NOx in the finished sulfuric acid can also be adopted.

4.2. Furnace flue gas
The concentration of NOx in the flue gas of all kinds of furnace is generally tens to thousands of mg/m3. For flue gas denitration, the flue gas from the furnace can basically meet the requirements of SNCR denitration technology for the "temperature window". The flue gas is continuously reduced to 120~300℃ after the waste heat boiler and dust collection process. During this process, heavy metal oxide fumes contained in the flue gas will rapidly deactivate the SCR catalyst.

A domestic lead and zinc smelting enterprises design a set of SNCR urea denitration device processing lead smelting furnace bottom blowing nitrogen oxide in flue gas. Industrial test proved that NOx concentration can achieve special limit below 100 mg/m3 [3].

4.3. Precious metal workshop flue gas
The rare and precious metal workshop of non-ferrous smelter uses a large amount of nitric acid in the process of pickling, acid dissolution and leaching. NOx will be discharged with the discharge of nitric acid fog and other substances in the heating process. The concentration range is from thousands to tens of thousands of mg/m3, and it has the characteristics of intermittent emission.

At present, the NOx produced in rare and precious metal smelting workshop is generally treated by alkali absorption method, which has a low overall adsorption efficiency and no obvious effect [4,5].

In view of the intermittent and high concentration of NOx in rare and precious metal smelting industry, the dry adsorption process independently developed by the Mining and Metallurgical Group
was applied to the treatment of NOx in the precious metal workshop of Shaoguan Smelting Plant, replacing the original alkali absorption process of the plant, and achieved good results. The concentration of NOx dropped from tens of thousands of milligrams to below the emission standard. In recent years, the mining and metallurgy group has made improvements on the selection of adsorbent raw materials, further improving the absorption effect of NOx, while improving the mechanical strength of the adsorbent.

5. Denitrification technology

5.1. Traditional denitration technology

Traditional denitration technology is divided into two categories: dry method and wet method. Dry method includes catalytic reduction method, catalytic decomposition method, electron beam method and adsorption method. Wet method includes alkali absorption method, acid absorption method and other absorption method. The characteristics of several mainstream flue gas denitrification technologies are as follows:

1) Selective catalytic reduction method

NOx is selectively reduced to N\textsubscript{2} and H\textsubscript{2}O in a certain temperature range with appropriate catalysts (such as platinum, palladium, molybdenum, iron, etc.) and reducing gases (such as NH\textsubscript{3}, etc.). Its removal rate is more than 90%, and suitable for the treatment of large gas industrial furnace waste gas. The drawback is that the catalyst is expensive, the reducing agent is industrial raw material, and it is also a gas, which requires storage, transportation and equipment, and the excess NH\textsubscript{3} in the tail gas after treatment needs to be treated.

2) Non-selective catalytic reduction method

The flue gas containing NOx, under the action of a certain temperature and catalyst, reacts with the reducing agent, in which the nitrogen dioxide is reduced to nitrogen, and the reducing agent reacts with the oxygen in the gas to generate water and carbon dioxide. Reductants include hydrogen, methane, carbon monoxide, and low hydrocarbon compounds. When several different fuel gas are used as reducing agent, the ignition temperature is different, so the preheating temperature is also different. Because the size of the boiler has a great influence on the engine, it is often used as a supplementary treatment for low nitrogen combustion technology.

3) Adsorption method

Chemical adsorption is the use of manganese hydroxide, basic iron oxide and other substances as adsorbents to adsorb NOx. Physical adsorption is to use molecular sieve, silica gel, zeolite, activated carbon and polymer materials as adsorbent to adsorb NOx. The traditional adsorption method has the problem of limited adsorption efficiency.

4) Absorption method

Typically, NOx is adsorbed by lye solution to produce nitrite and nitric acid. The method can adsorb NO\textsubscript{2}, but the adsorption efficiency of NO is very low. In order to increase the absorption efficiency of NO, oxidant must be added to oxidize NO to NO\textsubscript{2}.

5.2. Combined desulfurization and denitration technology

Combined desulfurization and denitration technology refers to the combination of traditional desulfurization technology and denitration technology in a set of desulfurization and denitration equipment technology. In this kind of technology, the removal of SO\textsubscript{2} and NOx is carried out in series in a process, and the removal mechanism is similar to that of desulfurization and denitration alone [6].

5.3. Integrated technology of desulfurization and denitration

According to the characteristics of acid flue gas and furnace flue gas in non-ferrous smelting industry, the integration technology of desulfurization and denitration reflects its advantages, which is the development trend of denitration of flue gas in non-ferrous smelting industry. The integrated technology of desulfurization and denitration is based on the traditional flue gas desulfurization technology, which
can realize the simultaneous removal of SO₂ and NOₓ in the flue gas in one process. This technology not only has the advantages of traditional technology, but also has its own unique advantages. The integrated technology of desulfurization and denitration includes calcium adsorbent desulfurization and denitration method, electron beam method, pulse corona method, etc.

BGRIMM based on the dense coherent tower half dry flue gas desulfurization technology, to explore and analyze the valuable metals with a catalytic activity of catalytic oxidation of NO in flue gas and the synergistic effect in the process of absorbing SO₂ and high NOₓ, and then through the composition of desulfurization denitration by-products, morphology observation and analysis, reveals the internal mechanism of synergy denitration in desulfurization process, formed suitable for copper smelting gas system of half dry desulfurization denitration technology together, and have been applied in actual engineering.

6. Subtotal
In this paper, through analyzing the characteristics of the non-ferrous metallurgical industry of NOₓ emissions and emissions standards, points out the current status quo and development trend of non-ferrous smelting industry out of stock, flue gas desulfurization denitration integration technology based on the traditional flue gas desulfurization technology, collaborative denitration at the same time, the technology not only has the advantages of the traditional technology, also has its own unique advantages, and is especially suitable for non-ferrous smelting flue gas denitration.

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