

Integrated Desulfurization and Denitrification of Coke Oven and CDQ Flue Gas: Industrial-Scale Validation of Ultra-Low Emission Control

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Abstract: *Focusing on the collaborative treatment of coke oven and CDQ (coke dry quenching) flue gas, this study performed a quantitative assessment of desulfurization and denitrification loads based on actual on-site production parameters. A comprehensive set of control processes was accordingly designed and implemented. Industrial application data demonstrate that the treatment system consistently meets the ultra-low emission limits prescribed for coking operations, thereby validating the effectiveness and reliability of translating theoretical pollutant control models into engineering practice.*

Keywords: Coke oven flue gas; CDQ flue gas; collaborative desulfurization and denitrification; ultra-low emission; industrial validation.

1. INTRODUCTION

Shiheng Special Steel Group Co., Ltd. is an integrated steel-coke enterprise. Its subsidiary coking company has one coke oven, designed as a (40+41)-hole 5.5m regenerative stamping coke oven. The main product of the coking company is coke, with by-products including gas, crude benzene, tar, and ammonium sulfate. The annual designed production capacity of the plant is 750,000 tons of coke. To meet ultra-low emission environmental protection requirements, the coke oven flue gas treatment system is equipped with desulfurization and denitrification devices. The desulfurization process adopts the limestone-gypsum method, and the denitrification process uses SCR denitrification. After desulfurization and denitrification, the coke oven flue gas can achieve compliance emission. With the improvement of environmental protection standards, coke oven flue gas, CDQ dust removal flue gas, CDQ venting flue gas, and coke side dust removal flue gas all need to meet ultra-low emission standards, and the three indicators of SO₂, NO_x, and dust at the flue gas outlet must comply with local and national environmental protection ultra-low emission standards.

2. CURRENT SITUATION ANALYSIS

From November 1, 2022, Shandong Province implemented new environmental emission limits for atmospheric emissions, adopting ultra-low emissions with stricter requirements. According to the ultra-low emission limits, the SO₂ emission value of the coke oven machine and coke side dust removal flue gas shall not exceed 30mg/m³ (previously not exceeding 50mg/m³ before November 1, 2020), and the SO₂ emission value of CDQ ground dust removal shall not exceed 50mg/m³ (previously not exceeding 100mg/m³ before November 1, 2020). During the actual operation of coke side dust removal, the maximum SO₂ emission value is 600mg/m³ (intermittent, once every 20 minutes, discontinuous, maximum during coke pushing, lasting 3 minutes). During the actual operation of CDQ ground dust removal, the maximum SO₂ emission value is 500mg/m³ (intermittent, once every 20 minutes, discontinuous, maximum during coke pushing, lasting 3 minutes). In accordance with the atmospheric environmental emission limits in Shandong Province, it is necessary to study and implement treatment for CDQ dust removal flue gas, CDQ venting flue gas, and coke side dust removal flue gas.

The Ministry of Ecology and Environment issued the "Opinions on Promoting the Implementation of Ultra-Low Emissions in the Coking Industry" in January 2024. In accordance with this "Opinions", our coke oven flue gas desulfurization and denitrification system needs to add backup desulfurization and denitrification waste heat facilities to meet the shutdown maintenance needs of the in-use desulfurization and denitrification waste heat system.

3. GOVERNANCE PROCESS DESIGN

Through the analysis and research of data on coke oven flue gas, coke side dust removal flue gas, CDQ coke charging flue gas, and CDQ venting flue gas, combined with the existing coke oven desulfurization and denitrification process flow, we proposed an idea for the comprehensive treatment of the above flue gases in the coking company. Based on this idea, we designed a comprehensive desulfurization treatment process flow for coke oven flue gas, coke side dust removal flue gas, CDQ coke charging flue gas, and CDQ venting flue gas.

First, on the basis of the existing actual site and the coke oven flue gas desulfurization and denitrification waste heat system, a new set of coke oven flue gas desulfurization and denitrification waste heat device was added.

Through investigation, it is understood that there are mainly three types of domestic coke oven flue gas desulfurization processes: first, wet desulfurization (limestone-gypsum method, currently used in our company's coking and sintering); second, semi-dry desulfurization (mainly two types: CFB circulating fluidized bed desulfurization and SDA rotating spray desulfurization; our company's power plant 220 boiler uses the SDA desulfurization method); third, dry desulfurization (mainly sodium-based desulfurizer desulfurization and calcium-based desulfurizer desulfurization). The flue gas denitrification process all adopts SCR low-temperature denitrification process, with ammonia sprayed into the flue for denitrification.

The flue gas desulfurization process currently used in our coking company is the wet desulfurization process. Based on several years of operational experience, we have conducted a comprehensive comparative analysis of these three types of desulfurization and denitrification processes. The wet desulfurization process has the following advantages: First, its operating cost is lower than that of semi-dry and dry desulfurization processes; second, its desulfurization efficiency is higher than that of semi-dry and dry desulfurization processes, making it more suitable for coking flue gas desulfurization conditions with high sulfur content; third, the desulfurization by-product is gypsum, and our group company has a micro-powder workshop that can internally consume and use it. The filter press water generated from desulfurization can be transported to our company's sewage treatment plant for treatment, with no adverse impact on the external environment. Moreover, the wet desulfurization process complies with the policy requirements for coking desulfurization process flow in national environmental protection policies. After comparative analysis, we still chose the wet desulfurization process, and for the denitrification process, we selected the mature SCR low-temperature denitrification process flow.

The newly added desulfurization, denitrification and waste heat system (System 2#) is constructed in accordance with the requirements of ultra-low emission standards. The processing capacity of the entire system has a certain margin even under 100% maximum operating conditions. The fan has a reserved capacity of approximately 20%, with the maximum air volume designed at 324,000 Nm³/h, the total pressure at 9500 Pa, and the fan motor power at 2000 Kw. The interface of this renovation project was completed on February 28, 2022, and it was put into 168-hour trial operation. After operation testing, the emission concentrations of NO_x, SO₂ and soot at the coking oven flue gas outlet can all meet the ultra-low emission standard requirements. The inlet nitrogen oxides are 560-600 mg/m³, and the outlet nitrogen oxides are approximately 50 mg/m³; the ammonia slip rate is 0.5 ppm; the inlet SO₂ content is 180-200 mg/m³, the outlet SO₂ content is 12-15 mg/m³, the outlet soot content is around 1.5mg/m³, the maximum flue gas flow rate is 250,000 m³/h, and the system operates stably. The original desulfurization, denitrification and waste heat device (System 1#) serves as a backup system for coking oven flue gas treatment.

While constructing the new desulfurization, denitrification, and waste heat system, the ground dust removal system for the coke dry quenching (CDQ) and the coke side dust removal system were also retrofitted, introducing the CDQ coke charging flue gas into the coke side dust removal system. This retrofitting is based on the fact that coke oven coke pushing and CDQ coke charging do not occur simultaneously; therefore, the air volume of the coke side dust removal fan can meet the dust removal requirements for both coke oven coke pushing and CDQ coke charging. Subsequently, the flue gas after coke side dust removal (including coke oven coke pushing flue gas and CDQ coke charging flue gas) is introduced into the desulfurization tower of the coke oven's 1# desulfurization system for desulfurization treatment. After desulfurization, ultra-low SO₂ emissions are achieved. After the retrofitting, the coke side dust removal and the desulfurization of CDQ coke charging dust removal flue gas operate stably and normally, with the outlet SO₂ content at 10 mg/m³ and the outlet dust content at approximately 3 mg/m³, meeting the ultra-low emission standard requirements.

The third control measure is to introduce the CDQ vent flue gas into the coke oven flue gas desulfurization system for treatment. Since the CDQ vent flue gas has high sulfur and dust contents, it is first dedusted by two parallel single dust collectors to reduce the dust content of the flue gas. Then, it is pressurized by a fan and sent to the newly constructed coke oven flue gas desulfurization tower (2# system) for desulfurization treatment, achieving the requirement of ultra-low SO₂ emission compliance. During the retrofitting, a backup treatment route was also designed for the CDQ vent flue gas. Under normal circumstances, the vent flue gas enters the newly constructed coke oven flue gas desulfurization tower (2# system) for desulfurization treatment; during the maintenance of the 2# system, it is introduced into the backup route, i.e., into the 1# desulfurization tower for desulfurization treatment. Valves are designed on both pipelines for mutual switching during maintenance.

The process flow diagram after retrofitting is as follows:

Coke oven flue gas, coke side dust removal flue gas, CDQ coke charging flue gas, CDQ vent flue gas

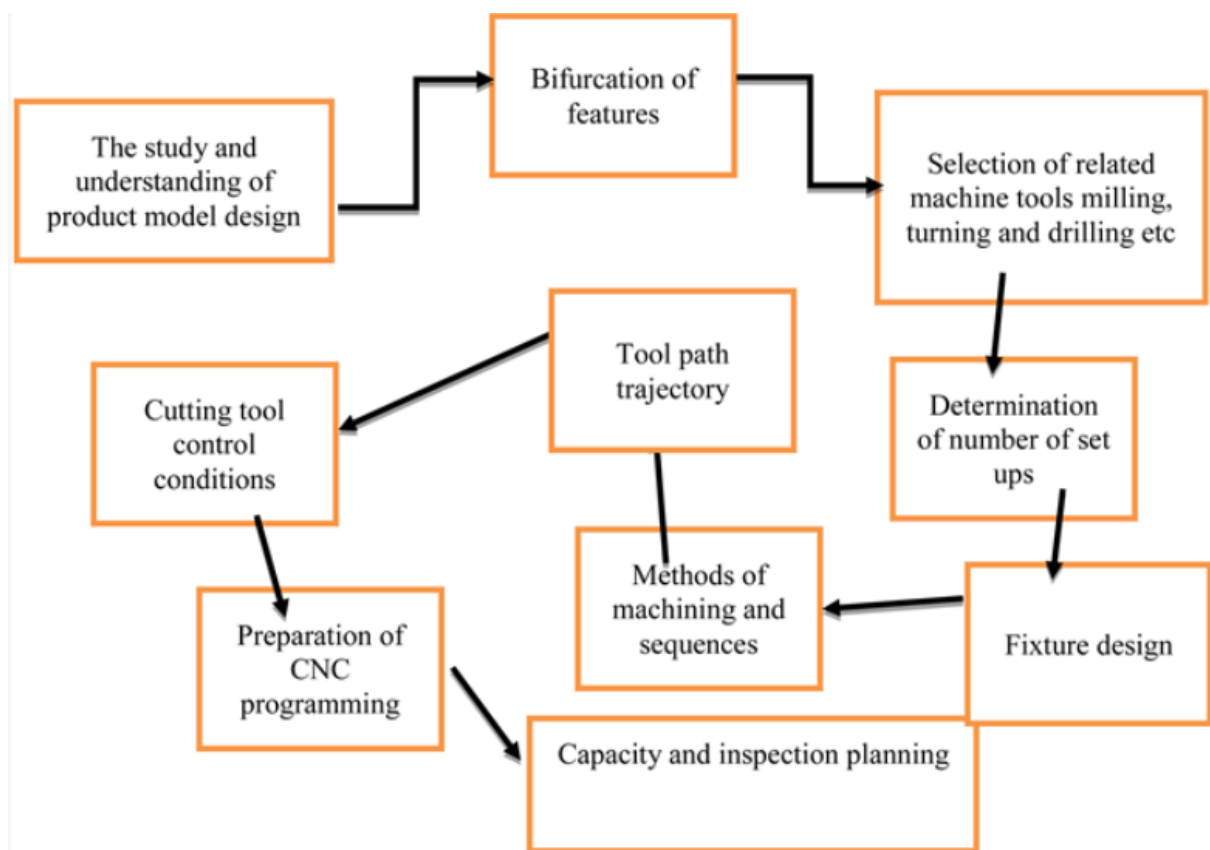


Figure 1: Comprehensive Control Process Flow Diagram

4. OPERATION MODE

During normal production, coke oven flue gas is mainly treated by the 2# desulfurization and denitrification system. If the 2# desulfurization and denitrification system needs to be shut down for maintenance, the coke oven flue gas is switched to the 1# desulfurization and denitrification system for treatment. When switching between the two sets of desulfurization, denitrification and waste heat systems, gradually close valve 9# while gradually opening valve 13#. Based on the negative pressure conditions at the inlets of the two denitrification units and in conjunction with the coke oven suction requirements, the opening degrees of the two electric valves are controlled in real-time on-site, and the fan speed is adjusted to achieve online switching between the two systems. After the maintenance of the 2# desulfurization and denitrification system is completed, the coke oven flue gas is switched back from the 1# system to the 2# system for treatment.

Before switching between the two sets of desulfurization, denitrification and waste heat systems, it is necessary to cut off the coke side dust removal flue gas and CDQ coke charging flue gas from the 1# desulfurization tower and

discharge them through the original chimney of the coke side dust removal station. At the same time, cut off the CDQ venting flue gas from the 2# desulfurization tower and switch it to the coke side dust removal system for discharge.

To meet the ultra-low emission standard requirements, powdered desulfurizer needs to be injected at the inlet of the coke side dust collector to desulfurize the coke pushing flue gas, coke charging flue gas and CDQ venting flue gas. The desulfurizer we selected is a powdered calcium-based desulfurizer, which is white, with $\text{Ca}(\text{OH})_2$ content $\geq 85\%$, moisture content $\leq 2\%$, particle size distribution: 325-mesh sieve Passing rate $\geq 85\%$, 200 mesh pass rate 100%, bulk density 0.40-0.65g/ml, and BET specific surface area $\geq 40 \text{ m}^2/\text{g}$. Attention should be paid to moisture prevention during desulfurizer storage; the desulfurizer should be covered and sealed with plastic sheeting, and after each use, it should be wrapped with plastic sheeting in a timely manner to prevent moisture absorption and deterioration, which would affect the desulfurization effect.

The by-product after desulfurization is a mixture of calcium sulfate and calcium sulfite, which is mixed with dust ash and discharged together. Our group company has a dedicated dust ash treatment workshop, and the dust ash containing calcium sulfate and calcium sulfite is sent to the dust ash treatment workshop for processing and recycling.

Spraying desulfurizer is a key task to ensure the achievement of ultra-low emissions, and special operational control measures and requirements have been formulated for this purpose:

(1) Start injecting desulfurizer at the inlet of the dust collector 12 hours before switching, aiming to allow the desulfurizer powder to uniformly and fully adhere to the surface of the filter bags (or filter cartridges), improve desulfurization efficiency, and ensure the desulfurization effect.

(2) Practice has verified that injecting 40 kg of desulfurizing agent per coke outlet can meet the desulfurization effect requirements, and minor adjustments can be made according to the emission indicators of the chimney at the outlet of the dust removal station.

(3) The backflushing and ash cleaning cycle of the coke side ground dust removal station is adjusted from 24 hours/time to 12 hours/time, with the monitoring of the dust collector pressure difference not exceeding 1000Pa as the standard. The ash discharge frequency is adjusted along with the cleaning cycle to ensure that the material level of the dust ash silo meets the requirements without ash accumulation.

By adopting the above control measures, the SO_2 index at the outlet of the coke side ground dust removal station can be controlled within 30mg/m³, meeting the ultra-low emission standard requirements.

5. CONCLUSION

Facing the increasingly strict environmental protection situation, combined with the actual situation of our enterprise, through in-depth analysis, research and treatment, we have finally enabled the coke oven flue gas, coke oven coke outlet flue gas, CDQ coke charging flue gas, and CDQ venting flue gas to meet the ultra-low emission standard requirements. Moreover, this comprehensive treatment and transformation has made full use of existing equipment and facilities, avoided the repeated construction of desulfurization facilities, and saved the group company more than 15 million yuan in investment. This transformation practice has accumulated valuable practical experience for solving similar problems in the future and has also achieved certain environmental and social benefits.

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