The Integration technology of desulfurization, denitration and heat recovery from coke oven flue gas

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Abstract: The main components of coke oven flue gas were SO₂, NOₓ etc. SO₂ and NOₓ were not only harmful to human health, but also seriously polluted the environment. The stricter “Standard for Discharge of Pollutants from coking chemical industry” was introduced. An integration settlement scheme of flue gas desulfurization, denitration and waste heat recovery was put forward. The proprietary core technologies, such as denitration, COG desulfurization and radial heat pipe boiler were researched. The integration settlement scheme can solve the problems of polluting the environment and waste heat without recovery, which had not only significant economic benefits, but also huge social benefits.

1. Introduction
Coking plant was a special plant of production coke and processing coke products. Flue gas of coke oven was exhaust gas after combustion, whose harmful gas components were mainly SO₂, NOₓ etc. Pollutants had the characteristic of organization and continuous emission, so coking industry was one of the more serious pollution of industry.

New “Standard for Discharge of Pollutants from coking chemical industry” clearly defined standards for the discharge of atmospheric pollutants in coking industry. With the very stringent standard and the increasingly tight energy supply more advanced, economic, reasonable coke oven flue gas processing method was needed.

2. Integration settlement scheme
A new integration settlement scheme of flue gas desulfurization, denitration and waste heat recovery was put forward. The flue gas treatment process was Coke Oven Gas desulfurization, combustion, flue gas denitration, radial heat pipe boiler, booster fan and chimney. Its core technologies were denitration and radial heat pipe boiler.

2.1. COG desulfurization before combustion
COG desulfurization methods in large coking plants were mainly wet desulfurization. The principle was the reaction of desulfurization catalyst and H₂S in alkaline solution[1]. Elemental sulfur was precipitated with air regeneration. Desulfurization before chemicals and desulfurization after chemicals were two main methods of wet desulfurization in the coking plant. The former was that COG from the condensation blast firstly processed desulfurization with ammonia, and followed chemicals[2].
method eliminated the corrosion of $H_2S$ on subsequent equipment, but generally $H_2S$ concentration decreased to 200 mg/m$^3$, which need additional second desulfurization equipment to achieve delivery standard.

The latter was that COG from the condensation blast firstly processed chemicals with $Na_2CO_3$, and followed desulfurization[3]. The method had heavy corrosive on subsequent equipments and need at the same time consumed a large amount of $Na_2CO_3$ in order to guarantee the alkalinity index. But the method had high desulfurization, up to the requirements of 20mg/m$^3$, without additional second desulfurization device.

2.2. Denitrification reactor

At present the common denitration methods [4~5] were selective non catalytic reduction (SNCR), oxidation absorption method and selective catalytic reduction (SCR) etc. Selective catalytic reduction (SCR) was currently the most mature and efficient method for exhaust gas denitrification. The principle of SCR for NOx removal was that on catalyst surface NOx was reduced to $N_2$ with ammonia added in exhaust gas, the reaction equation follows.

$$4NOx + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

Ammonia water or gas containing a certain concentration of ammonia was introduced to denitrification reaction with pipe. It flowed into the mixer and uniformly mixed with flue gas. The sensors were respectively arranged at the reactor inlet and outlet for on-line real time monitoring NOx concentration controlling the amount of ammonia according to the feedback signal.

The denitrification catalyst was very important in the denitrification process. A new denitration catalyst was developed. The catalyst used the whole coating structure with ceramic honeycomb, which was composed by the ceramic honeycomb, metal oxide coating and active component. Metal oxide coating uniformly and firmly attached to the outer surface of the ceramic honeycomb, then active component was dispersed on the oxide coating. The catalyst was a very suitable monolithic catalyst for flue gas denitration, which had advantages of high airspeed operation, low resistance, good selectivity, low ammonia leak rate, wide temperature range and small thermal expansion coefficient.

When NOx concentrations was very high at the entrance high accuracy NOx removal also can achieve, and even the concentration of NOx can be less than 150mg/m$^3$. If the emission standards is further upgraded, the catalyst and reaction device does not have to alter. If the amount of ammonia slightly increases, then the NOx concentration in the exhaust gas is less than the specified limit.

Denitration industry test was done in a coking plant, whose experimental device was shown in Figure 1.
Without denitration treatment, continuous monitoring concentration of NOx, NO2, SO2, O2 and NO respectively was 1100 mg/m^3, 720 mg/m^3, 450 mg/m^3, 190 mg/m^3 and 10 mg/m^3 or so at the outlet of butterfly valve, the cyclical fluctuations of gas composition every 15 minutes was produced by coke oven operation system, as shown in Figure 2.

From Figure 3 we can see when a certain amount of ammonia was pumped, NOx concentration was 30ppm, which was accord with the national standards. Up to now, the experiment has been running for almost 1000 hours, the following conclusions were obtained from comprehensive denitrification experimental results.

- The denitration efficiency reached stably more than 99% (measured NO content was several ppm, which can be understood as systematic error), closed to 100%. The denitrification efficiency of the catalyst was super high, as shown in Figure 4;
- The experimental operation airspeed was about 16000 h^-1, which was 4 times that of traditional denitration catalyst;
- The pressure drop in catalyst bed was about 100 Pa and can significantly reduce the energy consumption of the fan;
- Modular design of catalyst can avoid farthest future engineering amplification problem and was beneficial to the realization of engineering amplification.

2.3. Radial heat pipe heat-exchanger
The conventional axial heat pipe was applied to heat recovery from coke oven flue gas. It had advantages of efficient superconductor equipment, excellent isothermal homeothermia, excellent unidirectional thermal-transfer characteristics, good environmental adaptability and avoid dew point corrosion, but disadvantages of complex structure, huge equipment, easy tube explosion, damageing irreversibility and relatively high equipment cost.
In view of the advantages and disadvantages of the axial and heat pipe a new radial heat pipe heat-exchanger was designed.

- The eccentric radial heat pipe heat-exchanger had some advantages of eccentricity scientifically designed and heat pipe working medium increased to achieve a reasonable state of working medium, improve the thermal efficiency of heat pipe heat-exchanger, reduce overall project cost and raise the production efficiency, whose energy-saving efficiency reached the international advanced level.

- According to the existing problem of the axial heat pipe heat-exchanger at home and abroad, the technology effectively resolved problems such as complex structure, big steel consumption to steam production, irreversible loss and low thermal efficiency after damaging for the axial heat pipe heat-exchanger.

Eccentric radial heat pipe developed was successfully applied to 4.3m coke oven in a domestic company coking plant. The key equipment operation was stable and steam production capacity can meet the requirements, air had not blocking phenomenon, whose pressure control was good in the bottom of the furnace flue.

Per ton coke can produce saturated steam 68.8 kg, namely 0.19 GJ/t, in the same period the radial heat pipe consumed only 1.29kW/t.

3. Conclusions
Denitrification catalyst had advantages of high efficiency and operation airspeed, low pressure drop. Modular design of catalyst can avoid farthest future engineering amplification problem and was beneficial to the realization of engineering amplification.

New radial heat pipe heat-exchanger effectively resolved problems such as complex structure, big steel consumption to steam production, irreversible loss and low thermal efficiency after damaging for the axial heat pipe heat-exchanger.

The scheme can solve the problems of polluting the environment and waste heat without recovery, which had not only significant economic benefits, but also huge social benefits.

4. References
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