Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268
e-ISSN: 2395-3454

Vol. 18 | No. 5 (Special Issue) | pp. 1621-1625 | 2019

Original Research Paper | Open Access

Research on Integrated Technology of Desulphurization, Denitration and Waste Heat Recovery of Coke Oven Flue Gas

Haiying Zhang* and Ahmed Jalal Khan Chowdhury**
*China University of Petroleum, Shandong, China
**Department of Marine Science, Kulliyyah of Science, International Islamic University, Malaysia

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 26-08-2019
Accepted: 25-10-2019

Key Words:
Coke oven flue gas
Desulphurization
Denitration
Heat recovery
Integrated technology

ABSTRACT

The main pollution components of coke oven flue gas are SO_2 and NOx. The SO_2 and NOx not only harm human health, but also cause serious environmental pollution. Combined with the new type of denitration catalyst, magnesium flue gas desulphurization process and radial heat pipe waste, heat boiler and other core patented technologies, this paper creatively put forward the integrated technology of coke oven flue gas desulphurization, denitration, and waste heat recovery and utilization. This method can fundamentally solve the problems of environmental pollution caused by coke oven flue gas emission and waste heat recovery and utilization in China. The denitration efficiency is always stable above 98%, which reflects the super-high denitration efficiency of catalyst. It not only has the remarkable economic efficiency, but also has huge social efficiency.

INTRODUCTION

SO_2, NOx, belongs to the main pollutant indexes in the coke oven flue gas. These kind of components will not only endanger human body health, but to create a resource-conserving and environment-friendly society in our country will also be affected by certain negative influence; and in order to minimize these negative effects, in this paper, the integration of coke oven flue gas desulphurization and denitration waste heat recycling technology is studied (Tang et al. 2017). Coking plant is specialized in metallurgical coke production and metallurgical coking products processing and recovery of professional factories. Among them, the mature magnesium oxide desulphurization technology is a kind of desulphurization technology second only to the calcium process in terms of maturity. The magnesium oxide desulphurization technology has been widely applied all over the world, among which more than 100 projects have been applied in Japan, and 95% of power stations in Taiwan use magnesium oxide (Wang et al. 2017). Abundant sources of raw materials in China's magnesium oxide reserves are very considerable, the amount of proven magnesium oxide reserves is about 16 billion-ton, accounting for about 80% of the world. Its resources are mainly distributed in Liaoning, Shandong, Sichuan, Hebei and other provinces, of which Liaoning accounts for 84.7%. Coke oven flue gas is mainly the waste gas produced after combustion of coke oven gas, and its main components include SO_2 and NO_x. In China, sulphur dioxide and nitrogen oxide are the main pollutants in the atmosphere, and they are important indicators to measure whether the atmosphere is polluted (Li et al. 2016).

The innovation of this paper lies in the integration and innovation of new denitrification catalyst, magnesium flue gas desulphurization process, radial heat pipe waste heat boiler and other core patented technologies and puts forward the solutions for coke oven flue gas desulphurization, denitrification and waste heat recovery and utilization.

PAST RESEARCH

The harm of SO_2 and NOx in the atmosphere of some towns discovered by Wei et al. (2016) is common and very serious. In June 2012, the ministry of environmental protection and the state administration for quality supervision, inspection and quarantine jointly issued the GB16171-2012 "coking chemical industry pollutant emission standard", which clearly stipulated the atmospheric pollutant emission standard for coking industry. A study found that Sinosteel Anshan Thermal Energy Research Institute Co. Ltd. and technicians from the Chinese Academy of Sciences integrated low-temperature SCR flue gas denitrification technology, magnesium flue gas desulphurization process and radial heat pipe waste heat boiler and other proprietary core technologies, and proposed a comprehensive solution for coke oven flue gas desulphurization, denitrification and waste heat recovery (Gamrat et al. 2017). A steel thermal energy research institute, investigated the development of waste heat recovery of coke oven flue

gas from large domestic iron and steel enterprises. In view of the advantages and disadvantages of the axial heat pipe heat exchanger, it solved the problem on the premise of ensuring the technical advantages of axial heat pipe heat exchangers. The inherent shortcomings of the axial heat pipe heat exchanger, a radial heat pipe heat exchanger was developed. The researchers of heat energy in Sinosteel first put forward the use of eccentric radial heat pipe heat exchanger to recover the residual heat of coke oven flue gas in theory and verified it through engineering practice. Using eccentric radial heat pipe heat exchanger of waste heat recovery coke oven flue gas, scientifically designed the radial heat pipe eccentricity, increased the heat pipe working medium filling amount, to achieve a reasonable state of working medium, to improve the thermal efficiency of heat pipe heat exchanger, reduce overall project cost and raise the production efficiency; the energy-saving efficiency reached the international advanced level. Two patents have been applied for radial heat pipe heat exchanger (Gong et al. 2018).

MATERIALS AND METHODS

In this paper, the integrated technology of desulphurization and denitrification of coke oven flue gas and recovery and utilization of waste heat is integrated.

Scheme description: Coke oven flue gas treatment process (as shown in Fig. 1) consists of a coke oven, coke oven flue gas, denitrification reactor, heat pipe flue gas heat exchanger, booster fan, desulphurization tower, tower top tunnels, high temperature flue gas temperature ascending flue and chimney, draught fan and closed chimney discharge.

Firstly, the coke oven underground flue gas is extracted from the ground before entering the original gate valve. Electric regulating valve is set on the pipeline. The flue gas is extracted through the pipeline and then enters the denitrification reactor. After denitration, flue gas enters the flue gas waste heat recovery device, whose main function is to recover flue gas sensible heat to generate 0.6MPa saturated steam. After the hot flue gas is cooled by the waste heat recovery device, it is supercharged by the booster fan and enters into the wet desulphurization tower unit. After desulphurization, the flue gas is discharged through the tower top chimney. Denitration device before a by-pass line, and through small spare fan and diesel generator the flue gas will smoke into the underground tunnels. Its role is to short-term emergency start to send high-temperature flue gas when the desulphurization, denitration system fails or the power is cut Enter the underground flue, increase the temperature of the flue and chimney, and when the chimney has sufficient pumping power, turn off the backup fan and open the underground flue shutter.

Key Technologies in The Analysis Process

***Denitrification reactor*:** The selective catalytic reduction (SCR) method of denitration selected in this paper is the most mature and the most efficient method for denitration of tail gas at present. The principle of NO_x removal by selective catalytic reduction (SCR) is as follows: a certain amount of ammonia is added to the tail gas, and ammonia is used as the reducing agent to reduce NO_x to N_2 on the surface of the catalyst. The reaction equation is as follows:

$$NO_x + NH_3 + O_2 \rightarrow N_2 + H_2O$$

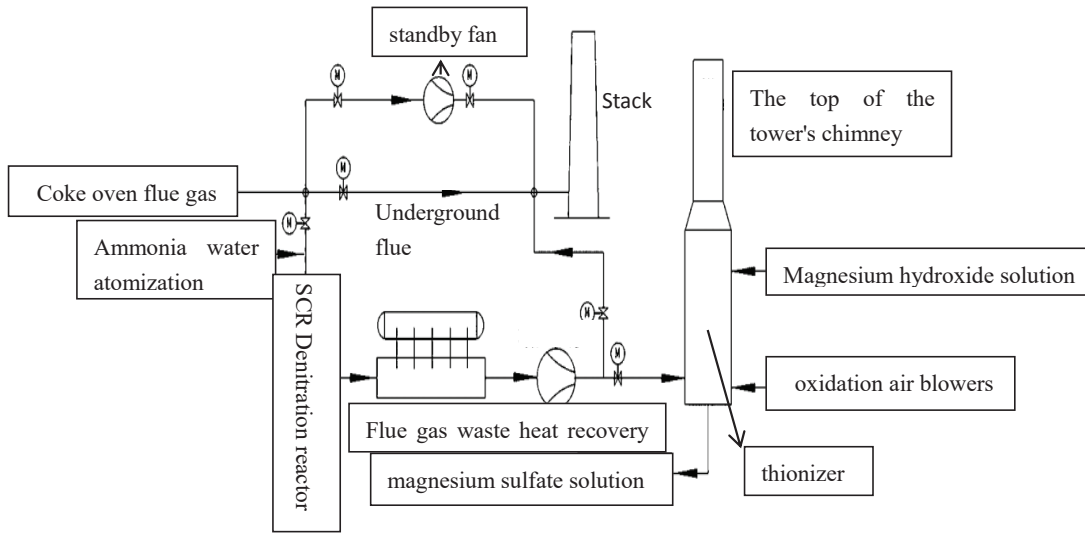

Fig. 1: Coke oven flue gas treatment process.

(1) Ammonia Source

In the denitrification reaction, ammonia source uses liquid ammonia or steam ammonia section to produce concentrated ammonia water with a concentration of 20%, which is introduced into the denitrification reaction system by pipeline, and then enters into the mixer to evenly mix with flue gas after controlling the flow through the regulating valve. NO_x sensors are set at the inlet and outlet of the denitrification reactor to monitor the concentration of NO_x at the inlet and outlet in real time and control the amount of ammonia addition according to the feedback signal.

(2) Denitration Catalyst

In the denitration process, the most important catalyst is the denitration catalyst, which is composed of ceramic honeycomb, metal oxide coating and active components. The oxide coating adheres to the outer surface of honeycomb ceramic evenly and firmly, and the active components are dispersed on the oxide coating.

It can be seen that the concentration of nitrogen oxide in flue gas fluctuates between 800 and 1200mg/m^3 during the operation of the experiment. The concentration of various substances in the flue gas at the outlet of butterfly valve was continuously monitored, in which NO_x, NO, SO_2, O_2 and NO_2 were about 1100, 720, 450, 190 and 10 mg/m^3, respectively. Periodic fluctuation occurs in the composition of coke oven flue gas every 15 minutes, which is generated by the coke oven operation system. After treatment with nitrate, the concentration of nitrogen oxide can be reduced to less than 20mg/m^3, and the denitration efficiency is up to 98%.

***Eccentric radial heat pipe heat exchanger*:** The conventional axial gravity heat pipe technology is adopted in the coke oven flue gas waste heat recovery device, mainly because the radial heat pipe heat exchanger technology effectively solves the problems of complicated structure of coke oven flue gas waste heat recovery heat pipe heat exchanger and large consumption of steel with a ton of steam output. It overcomes such problems as irreversible loss of total heat transfer area after axial heat pipe damage and significant reduction of heat transfer efficiency (Wenjie et al. 2016).

***Magnesium flue gas desulphurization*:** Wet desulphurization is adopted in this paper. According to the raw materials of desulphurization, it can be divided into limestone/lime method, ammonia method, sodium alkali method, sodium and calcium double alkali method, metal oxide method and basic aluminium sulphate method, among which limestone/lime method, sodium alkali method, sodium and calcium double alkali method and metal oxide method are relatively common (Buczynski et al. 2016). The biggest advantage of reliable operation of magnesium method for desulphurization compared with calcium method is that the system will not produce equipment fouling and clogging problem, which can ensure the safe and effective operation of the whole desulphurization system. At the same time, the pH value of magnesium method is controlled between 6.0 and 6.5, under which the equipment corrosion problem is also solved to a certain extent. In general, the safety performance of magnesium desulphurization in practical engineering is very strong.

The reaction equation of magnesium flue gas desulphurization is as follows:

1. Preparation of magnesium oxide slurry (curing)

   $MgO(solid) + H_2O \rightarrow Mg(OH)_2(serous)(size)$

   $Mg(OH)_2(serous) \rightarrow Mg^{2+} + 2OH^-$

2. SO_2 absorption (desulphurization)

   $SO_2(gas) + H_2O \rightarrow H_2SO_3$

   $H_2SO_3 \rightarrow H^+ + HSO_3^-$

   $HSO_3 - \rightarrow H^+ + SO_3^{2-}$

   $Mg^{2+} + SO_3^{2-} \rightarrow MgSO_3$

   $SO_2 + MgSO_3 + H_2O \rightarrow Mg(HSO_3)_2$

3. Neutralization and regeneration

   $Mg(HSO_3)_2 + Mg(OH)_2 \rightarrow 2MgSO_3 + 2H_2O$

4. Oxidation and neutralization of desulphurization products

   $MgSO_3 + 1/2O_2 \rightarrow MgSO_4$

   $Mg(HSO_3)_2 + O_2 \rightarrow Mg(HSO_4)_2$

   $Mg(HSO_4)_2 + Mg(OH)_2 \rightarrow 2MgSO_4 + 2H_2O$

RESULTS

The experiment was in normal operation and running for nearly 1200h in total. The coke oven flue gas emission standard values are shown in Table 1.

Denitration of coke oven flue gas: During the denitrification experiment, the concentration of nitrogen oxides in the inlet and outlet of the reactor and the denitrification efficiency showed that during the experiment, the concentration of nitrogen oxides in the flue gas fluctuated between 800 and 1200mg/m^3. After the denitrification treatment, the concentration of nitrogen oxides could be reduced to less than 20mg/m^3, and the denitrification efficiency was up to 98% (Tables 2 & 3).

1. The denitration efficiency is always stable above 98% (the measured NO content is within 10^{-6}, which can be understood as systematic error), close to 100%, reflecting the super-high denitration efficiency of the catalyst;

Table 1: Coke oven flue gas emission standards.

Standard content	SO_2 concentration	NOx concentration	Dust concentration
Common areas	<50mg/m^3	<500mg/m^3	<30mg/m^3
Special area	<30mg/m^3	<150mg/m^3	<15mg/m^3

Table 2: Denitrification efficiency of new catalysts.

	950h	1000h	1050h	1200h
Hydroxide concentration (mg/m^3)	800	1000	1200	1100
The denitration efficiency (%)	98.1	98.7	99.0	99.3

Table 3: Coke oven chimney outlet before and after the integrated project is put into operation.

Section	Pollutants	Pre-modification discharge Mass concentration /mg·m^{-3}	Modified discharge Mass concentration/mg·m^{-3}	Medium requirement index/ mg·m^{-3}
Denitration	NOx	220-400	37-90	≤ 150
The desulphurization	SO_2	23-42	5-8	≤ 30
Dust removal	dust	17-23	6-8	≤ 15

2. The maximum operating airspeed of the experiment was about 16000h^{-1}, about 4 times of the traditional denitration catalyst;
3. The catalyst bed resistance drops to around 300Pa, which is extremely low and can significantly reduce fan energy consumption;
4. The catalyst adopts modular design, which avoids the future engineering amplification problem to the greatest extent and is conducive to realizing engineering amplification.

Analysis of desulphurization effect of flue gas magnesium method: According to the experimental results, the high desulphurization efficiency of magnesium oxide is far greater than that of calcium-based desulphurizer in terms of chemical reactivity, and because the molecular weight of magnesium oxide is smaller than that of calcium carbonate and calcium oxide, the desulphurization efficiency of magnesium oxide is higher than that of calcium method under the same other conditions. In general, the desulphurization efficiency of magnesium oxide can reach 95% ~ 98%, while the desulphurization efficiency of limestone/gypsum method is only about 90% ~ 95%. Because magnesium oxide as a desulphurizer has its unique advantages, so in the absorption tower structure design, the size of circulating slurry volume, the overall scale of the system, the power of the equipment can be correspondingly small, the overall design of the desulphurization system investment costs can be reduced by 10%-20%. The price of magnesium oxide is higher than that of calcium oxide, but the amount of magnesium oxide required for removing the same SO_2 is 40% of that of calcium carbonate. The liquid-gas ratio is a very important factor in the consumption of power, such as water, electricity and steam. For limestone gypsum system, the liquid-gas ratio is generally above 15L/m^3, while the magnesium oxide is below 5L/m^3, so the magnesium oxide desulphurization process can save a large part of the cost. At the same time, the sale of by-products of magnesium oxide process can offset a large part of the cost.

Because the reaction products of magnesium desulphurization are magnesium sulphite and magnesium sulphate, the comprehensive utilization value is very high. On the one hand, all magnesium sulphate is generated through forced oxidation, and then it is concentrated and purified to produce magnesium heptahydrate for sale. On the other hand, it can also be directly calcined to generate sulphur dioxide gas with high purity to produce sulphuric acid. In the common wet desulphurization process without secondary pollution, there is inevitably the problem of secondary pollution. For the magnesium oxide desulphurization technology, the subsequent treatment in the test is more perfect, which can not only concentrate the crystal of hydrated magnesium sulphate 7, but also regenerate the magnesium oxide, recover SO2 to produce dilute sulphuric acid, and solve the problem of secondary pollution.

CONCLUSION

The new type of denitrification catalyst has super high denitrification efficiency, super high operating airspeed and very low bed resistance drop. Modular design avoids the problem of future engineering amplification to the greatest extent and is beneficial to realize engineering amplification. The self-developed radial heat pipe type waste heat boiler has been verified by engineering experiments, which can reduce

the complexity of the overall equipment manufacturing, further reduce the equipment cost, reduce the steel consumption of tons of steam output, and greatly improve the economic benefits of the heat exchanger (Jin et al. 2018). It overcomes the loss of total heat transfer area after the axial heat pipe is damaged. At the same time, all the advantages of axial heat pipe heat exchanger are maintained to a great extent. Magnesium flue gas desulphurization process has the advantages of simple absorption liquid circulation system, stable process operation, simple maintenance, small occupation area, no need to discharge wastewater, and small system resistance, high desulphurization efficiency (≥ 95%), quick and easy start-up and exit operation, high by-product utilization value. The method proposed in this study can fundamentally solve the current domestic coke oven flue gas emission pollution of the environment and waste heat not been recycled. It not only has significant economic benefits, but also has great social benefits.

REFERENCES

Buczynski, R., Weber, R., Kim, R. and Schwöppe, P. 2016. One-dimensional model of heat-recovery, non-recovery coke ovens. Part ii: coking-bed sub-model. Fuel, 181: S0016236116001083.

Gamrat S., Cheng, X., Wang, Z., Ma, C. and Qin, Y. 2017. Investigation on Fe-Co binary metal oxides supported on activated semi-coke for NO reduction by CO. Applied Catalysis B Environmental, 201: 36-651.

Gong, Z., Wu, W., Zhao, Z. and Li, B. 2018. Combination of catalytic combustion and catalytic denitration on semi-coke with Fe_2O_3 and CeO_2. Catalysis Today, 318: 59-65.

Jin, Y., Xia, J., Dong, C., Jiang, W. and Li, J. 2018. Evolution of sulfur species on titanium ore modified activated coke during flue gas desulphurization. Energy & Fuels, 32(8): 8623-8630.

Li, Y., Wang, X. and Jie, T. 2016. Modeling of integrated processes for coking flue gas desulphurization and denitrification based on RBFNN. In: 2016 IEEE/ACIS 15th International Conference on Computer and Information Science (ICIS), pp. 1-6.

Tang, Z., Zhimin, H. E., Ebrahim, Guo, D., Zhao, Z. and Xing, X. et al. 2017. Desulphurization and denitration integrative process for coke oven flue gas using dual ammonia solution: from laboratory to industrial test. CIESC Journal.

Wang, L., Cheng, X., Wang, Z., Zhang, X. and Ma, C. 2017. NO reduction by CO over iron-based catalysts supported by activated semi-coke. Canadian Journal of Chemical Engineering, 95(3).

Wei, F.H., Zhou, Y., Jie, W. and Wang, T. 2016. 3d simulation of sintering flue gas desulphurization and denitration in a bubbling gas absorbing tower. Powder Technology, 314: S0032591016306350.

Wenjie, F. U., Tong, C., Mingming, X. U., Hao, J. and Zhao, R. 2016. Study on denitration technology of coal char reduction method. Journal of Hebei University of Science & Technology, 37(3).