ISSN: 2664-9640

Pollution control technology of NOX in municipal solid waste incineration process

Chao Wu*

Department of environmental science and Engineering, North China Electric Power University (Baoding), Baoding 071003, China

wcncepu@163.com

Abstract

With the accelerating process of urbanization,people's consumption level is rising,which leads to more and more serious environmental pollution problems.In particular,the domestic garbage in the city is growing at a double speed,which destroys the beautiful appearance of the city we depend on,hinders the sustainable development of the city,and runs counter to the green development advocated by the international community. Based on the current situation of municipal solid waste in China,the composition of flue gas in MSW incineration process is analyzed.Taking NOX as the key research object,several main NOX emission control technologies are described in detail,and their advantages and disadvantages are compared.Finally,the possibility of SNCR + PNCR denitrification technology applied to waste incineration plant is prospected.

Keywords

Waste incineration,Flue gas denitrification technology,SCR.

1. Introduction

In the 21st century,with the continuous advancement of the reform process,the population and economy are growing rapidly,especially the urban population is growing exponentially,which brings about increasingly serious urban pollution problems.In some areas,the amount of pollutants such as municipal solid waste even exceeds the environmental capacity of the city itself.The municipal solid waste (MSW) has a wide range of sources,various types and high moisture content, so at present,landfill,incineration,composting and other technologies are mainly used in China.However,landfill technology covers a large area and composting treatment only works on organic solid waste,so incineration technology is becoming the mainstream of municipal solid waste treatment process.

2. Composition of flue gas in waste incineration process

Incineration is to realize the reduction,harmlessness and recycling of domestic waste through thermal decomposition,combustion,melting and other reactions under suitable high temperature.Although the energy can be recycled in a small area.However,the flue gas from incineration contains solid particles,acid gases (such as NO_X and SO_X),heavy metals and organic compounds.China's existing waste incineration plants are backward in technology and management,and the incineration process is not open and transparent.As a result, some waste incineration plants cut corners in order to save costs and directly discharge flue gas if they fail to meet the standards.It causes secondary pollution to the environment[1].In particular,NO_X emissions will cause photochemical smog,acid rain and other phenomena,which will cause varying degrees of harm to human health and living environment.Therefore,reducing the content of NO_X in flue gas is of great significance for improving air quality and practicing the concept of green development.China's current national standards have made clear provisions on the emission of flue gas from incineration (see Table 1).

Table 1 Flue gas emission standard of incinerator

Contaminants	Company	National GB 18485-2014
Particulate matter	mg/m^3	20
HCl	mg/m^3	50
CO	mg/m^3	80
SO_X	mg/m^3	80
NO_X	mg/m^3	250
Hg and its compounds	mg/m^3	0.05
Cd and its compounds	mg/m^3	0.1
Pb and its compounds	mg/m^3	1.0
Dioxins	ng TEQ/m^3	0.1

At present,China's waste incineration flue gas treatment system generally uses a purification process as the main body, supplemented by no_Xremoval system and activated carbon jet adsorption.Among them, the flue gas denitrification technology mainly includes incinerator combustion control furnace temperature, flue gas reflux technology,SCR system,SNCR system and PNCR system.In particular, the combustion control furnace temperature and flue gas reflux technology can effectively reduce the original no_Xconcentration.SCR + SNCR system and SNCR + PNCR system are the main denitration processes used in domestic waste incineration power plants.

3. Commonly used NOX emission control technology in China

At present,the common methods of NO_X removal are denitration before combustion,during combustion and after combustion.Denitration before combustion is a special treatment to change the fuel with high nitrogen content into low ammonia.The disadvantage is that the cost is too high and it is not suitable for large-scale application.Denitration during combustion is to reduce NO_X emission by changing combustion methods and production processes, such as staged combustion and low nitrogen combustion,However,it will affect the combustion efficiency.Denitration after combustion is to remove NO_X from flue gas by some specific methods, including dry method and wet method. Among them, selective catalytic reduction (SCR) and selective non catalytic reduction (SNCR) have become the most widely used flue gas denitrification technologies due to their high removal efficiency.

3.1. SCR Flue Gas Denitrification Technology

3.1.1 SCR overview

Selective catalytic reduction (SCR) is the most widely used flue gas denitrification technology in the world.In this method, NO_x is reduced to N_2 in a certain temperature range by using NH_3 as reducing agent under the action of catalyst, and almost no oxidation reaction of NH_3 and O_2 occurs. Thus, the selectivity of NH_3 is improved and the consumption of NH_3 is reduced.With the popularization of SCR technology, the improvement of SCR catalyst performance and the optimization of reaction operating conditions, SCR technology will become more and more mature.

3.1.2 SCR reaction principle

SCR denitrification is a method of selectively reducing NO_X to N_2 in the presence of catalyst.For fixed source denitrification, urea or ammonia is injected into flue gas at 280-420℃ to reduce

ISSN: 2664-9640

NO_X to N_2 and H_2O[2].The main reaction formula of selective reduction of NO_X by NH_3 is as follows:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$$

In the presence of SO_2 and H_2O, the following adverse reactions will also occur on the surface of SCR catalyst.

$$SO_2 + 1/2O_2 \rightarrow SO_3$$

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$$

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$(NH_4)_2SO_4$ and NH_4HSO_4 formed in the reaction are easy to contaminate the air preheater and cause great damage to the air preheater.

3.1.3 Influencing factors of SCR denitrification process

In the catalytic reaction, the reduction degree of nitrogen oxides depends on the catalyst used, reaction temperature, ammonia nitrogen ratio and contact time.

(1) Catalyst.Catalyst is an indispensable component in SCR denitrification system.SCR denitrification efficiency is directly affected by its structure, type, surface area and related parameters.There are many kinds of catalysts, and the suitable reaction temperature varies with different catalysts;The activity of most catalysts is greatly reduced at low temperature, which can not play a catalytic role, and the denitration effect is poor,Continuous operation can also cause catalyst damage.At high temperature, NH_3 is very likely to be oxidized and the content of nitrogen oxides is greatly increased.The better the denitrification efficiency is, the better the surface area of the catalyst is.Therefore, the catalyst should have higher activity and selectivity at lower temperature and certain temperature range.When the temperature fluctuates greatly, it has good thermal stability, wear resistance and long service life.

(2) Reaction temperature.The reaction temperature greatly affects the activity of catalyst and the rate of chemical reaction. Too low and too high reaction temperature is not conducive to the reaction.The type of catalyst and the composition of flue gas determine the optimal reaction temperature in SCR denitrification system.The optimum reaction temperature of metal oxide type catalyst is higher than that of non-metal oxide type catalyst and has a wider temperature range.Therefore, metal oxide catalysts are usually used.The optimum reaction temperature is 250℃ - 427℃, so the SCR system temperature is usually set at 280℃ - 420℃.

(3) Ammonia nitrogen ratio.Ammonia nitrogen molar ratio is a technical index to evaluate the economy of SCR process.Under the same denitrification efficiency, the higher the ammonia nitrogen molar ratio, the lower the economic efficiency.With the increase of ammonia nitrogen molar ratio, denitrification efficiency first increased and then decreased, and the maximum value was at the position of ammonia nitrogen molar ratio of 1.2.Therefore, in general, the molar ratio of ammonia to nitrogen is generally set in the range of 1.1-1.4.

(4) Contact time.Since any reaction takes time, it is necessary to ensure that the reducing agent of denitrification equipment has sufficient contact time in the flue gas within the appropriate temperature range to produce reduction reaction.In a certain range, the longer the contact time of reducing agent is, the better the denitrification effect is. Beyond this range, the denitrification rate will decrease, and the best contact time is 0.2S.

3.1.4 Catalysts for SCR denitration technology

From the principle of SCR denitration technology, the main requirements for SCR catalyst are: high activity, strong selectivity, good mechanical properties, strong anti-virus.At present, the most widely used SCR catalysts are honeycomb catalysts with TiO_2 ,which V_2O_5- WO_3 and V_2O_5-MoO_3 are added as active components.The catalyst has large specific surface area, high activity and small volume.The catalytic active substances are 50% - 70% more than other types.The selectivity of the regenerated catalyst was maintained.

3.1.5 Advantages and disadvantages of SCR denitration technology

SCR denitrification process has high removal efficiency of NO_x, less secondary pollution, mature technology and wide application, but it has high investment cost and high operation cost.Although SCR process has high denitrification efficiency, there are still some problems, such as ammonia escape and follow-up problems, catalyst wear, low load operation, flow field uniformity and waste catalyst treatment.Especially for the treatment of waste catalyst, regeneration technology should be adopted for the deactivated catalyst as far as possible. If it is unable to be regenerated, it should be treated innocuously to prevent secondary pollution.

3.1.6 Process flow of SCR denitration technology

Generally speaking, SCR process is divided into five systems, which are ammonia storage, ammonia mixing, ammonia injection, reaction tower (catalyst system), flue and control system.The storage pressure of anhydrous liquid ammonia depends on the temperature of the tank (for example, the pressure at 20℃ is 1MPa).Ammonia mixing is to pass the liquid ammonia through the steam and hot water in the evaporator,It is transported to ammonia evaporation tank by vacuum evaporation.Air with a certain proportion of ammonia is pumped into the ammonia and air mixer through a blower.Ammonia injection is that the diluted ammonia gas is injected into the flue grid through the nozzle in the injection system and mixed with the original flue gas.

3.1.7 Application of SCR denitration technology

In order to prolong the service life of catalyst, SCR system is often arranged at the back end of bag filter.In order to enhance the stability of SCR system, the flue gas at 150℃ at the outlet of bag filter is usually heated to above 170℃ by flue gas reheat system, and then it enters SCR system for denitrification.Compared with coal-fired power plants,MSW incineration process have small flue gas emission and low combustion heat value.Low temperature SCR denitration technology can reduce the construction and operation costs.The reaction temperature is 230-450 ℃, the application temperature is 320-400 ℃, and the denitration efficiency is 70% - 90%, which is far higher than the denitration efficiency of traditional process[3].

3.2. SNCR flue gas denitrification technology

3.2.1 SNCR Overview

Selective non-catalytic reduction (SNCR) refers to the reduction of nitrogen oxides in flue gas to harmless nitrogen and water by injecting some reducing agents containing amino groups in the temperature range suitable for denitrification without catalyst.In this technology, the furnace is used as the reactor, and ammonia, urea or hydrazine are used as reducing agents to reduce NO_x.The denitration efficiency of SNCR flue gas denitrification technology is generally 30% - 80%, which is greatly affected by the boiler structure and size.The reducing agent only reacts with NO_x in flue gas, and generally does not react with oxygen.SNCR system mainly includes SNCR ammonia injection system, tank farm, pressure pump and its control system, spray system, distribution and regulation system and mixing system.Due to the low cost of SNCR.The transformation is convenient and suitable for collaborative application of other technologies.

3.2.2 SNCR reaction principle

ISSN: 2664-9640

The reaction mechanism of SNCR is very complex, which is still not fully understood. The following is a brief description.Since no catalyst is used in this process, it is necessary to inject urea or amino compounds into the first or second flue of incinerator under specific ambient temperature. The reducing agent reacts with NO_X in flue gas to generate N_2 and H_2O. the main reactions are as follows:

$$(NH_4)_2CO + 2NO + 1/2O_2 \rightarrow 2N_2 + 3H_2O$$

$$2NH_3 + 2NO + 1/2O_2 \rightarrow 2N_2 + 3H_2O$$

3.2.3 Influencing factors of SNCR denitrification process

There are many factors that affect the denitrification efficiency in the practical application of SNCR method

(1) Selection of injection point of reducing agent.The injection point of reducing agent must ensure that the reducing agent enters the appropriate reaction temperature range in the furnace.If the reaction temperature is too low, the NH_3 reaction is not enough, which will easily lead to NH_3 leakage.If the reaction temperature is too high, NH_3 is easily oxidized to NO_X, which just offsets the removal effect of NH_3. Therefore, it is necessary to strictly control the temperature. In actual production, 850-1150℃ is often used[4].

(2) Stay time.Under the same conditions, the longer the residence time of reducing agent, the better denitrification effect is. During this time, the mixing of reducing agent such as NH_3 or urea with flue gas, evaporation of water, decomposition of reducing agent and reduction of no_xmust be completed. The general required time is 0.5s.Because of the serious stratification phenomenon, it can not be proved by experiments,However, the high-speed injection can not only make the mixture uniform, reduce the residual NO_X by about 30%, but also make the fuel fully burn and improve the decomposition rate.

(3) Appropriate ammonia nitrogen molar ratio.In a certain range, the reduction rate of NO_x increases with the increase of the mole ratio of ammonia to nitrogen, but the reduction effect is not obvious with the increase of the molar ratio of ammonia to nitrogen. On the contrary, it will produce large ammonia escape and cause ash deposition corrosion in flue gas.

(4) The mixing degree of reducing agent and oxygen.According to the reaction principle, O_2 in flue gas is a necessary condition for SNCR denitrification, and the concentration of O_2 has a great influence on the temperature range and denitration efficiency of SNCR.With the increase of O_2 concentration, the reaction temperature and denitrification rate decreased.

(5) The initial no_Xconcentration level.The initial content of no_xalso affected the reduction efficiency.The reduction of reactant concentration leads to the decrease of reaction power.Under the condition of lower reactant concentration, the optimal temperature decreases, so the reaction efficiency also decreases. There is a critical concentration of NO_x. If the initial concentration of NO_x is less than the critical value, the ammonia nitrogen ratio will be increased in any case,At the same time, if the initial concentration of NO_x is too high, the reaction temperature will be lower.

3.2.4 Advantages and disadvantages of SNCR denitrification technology

Compared with SCR process, SNCR process does not need catalyst, has the advantages of simple system, low initial investment, small resistance, small occupation area and less secondary pollution.However, due to the large amount of reducing agent such as urea, the leakage of ammonia gas is also large, and the reaction temperature is high, it is difficult to control, and the removal efficiency is not high, only 30% - 50%.

For aste incinerator with a daily treatment capacity of 400-500t, when the injection amount of urea water in the furnace is 200-400L/h, the flue gas temperature will decrease by about 5-10℃, because of the heat absorption of urea water and the increase of steam quantity in flue gas, the steam evaporation capacity will be reduced by about 200L[5].

ISSN: 2664-9640

3.3. PNCR flue gas denitrification technology

PNCR, which is also known as polymer selective denitration, is a new technology for flue gas denitrification in China. It uses the principle of pneumatic conveying to transport powdery polymer denitration agent from the storage bin by means of negative pressure and positive pressure. The denitration agent is transported to the best reaction temperature zone (usually 700-900 ℃) in the furnace by fan. Under high temperature, the chemical bond between amino and polymer is broken, amount of ammonia containing free radicals are released, which reacts with NO_X in flue gas to realize denitration[6].

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$4NO_2 + 2NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$$

The PNCR system mainly includes denitration agent storage system, denitration agent transportation and supply system, denitrification agent metering and distribution system, compressed air system, dust collection system, furnace front injection system, instrument and instrument electrical system.

The process flow of PNCR process is simple, the installation cycle is short, the denitration agent is solid powder, transportation and storage are safe and convenient.The cost of denitrification agent is the same as that of SNCR process, but the annual water consumption of PNCR method is 1500 tons less than that of SNCR process, and the denitration rate is as high as 90%.

3.4. Combined denitrification technology

Due to the advantages and disadvantages of each technology in different aspects, in order to improve the denitrification efficiency, the two technologies are often combined.Among them, SCR + SNCR denitration is a process that is widely used in China's no_Xultra-low emission projects. Part of NO_X is removed in the furnace by SNCR system, and then denitration is further carried out by SCR system. The combined mode has stable operation and high reliability.It is widely used in waste incineration plants.Some MSW incineration plants have adopted SNCR + PNCR denitrification, but from the production practice results, the stability is not as good as SNCR + SCR.

4. Comparative analysis of four denitration technologies

For a comprehensive comparison of various technologies, see Table 2.

Table 2 Comprehensive comparison of Denitration Technology

Denitration Process	SCR	SNCR	PNCR	SCR+SNCR	SNCR+PNCR
Catalyzer	use	nothing	nothing	use	nothing
Steam	use	nothing	nothing	use	nothing
Temperature range / ℃	170-240	850-1050	800-900	-	-
Investment cost	high	low	moderate	high	moderate
Running cost	high	low	moderate	high	moderate
Stability	strong	strong	difference	-	-
Ammoniae scape	low	high	high	-	-
Denitration efficiency/%	＞90	40-60	＞90	＞90	＞90

For a 500t/d MSW incineration system, the main steam consumption is about 0.95t/h for every 10℃ increase of flue gas temperature at the outlet of bag filter, accounting for nearly 2% of the total. If the flue gas temperature is increased from 150℃ to 320℃, the required main steam will reach 16.15t/h, which means that 33% of the main steam will be lost, which will greatly increase the production energy consumption and reduce the operation efficiency of the garbage power plant.Therefore, this high temperature SCR denitration process is not suitable for waste incineration plant[7].

Compared with SCR technology alone, SCR + SNCR can not only improve the denitration efficiency, but also reduce ammonia escape, which can significantly improve the flue gas purification effect.Therefore, SCR + SNCR combined denitrification technology can be used in economically developed areas with high emission requirements.However, with the increase of catalyst service time, the performance gradually decreases, and the investment cost of the whole system is high.It is not suitable for areas with low garbage subsidy costs.When SCR + SNCR combined technology is adopted in waste incineration plant, in order to reduce energy input and operation cost, it is necessary to reduce the required temperature of flue gas at the outlet of bag filter as far as possible, and select the catalyst whose active temperature is as close as possible to the outlet temperature of dust remover.

5. Conclusion

At present, some domestic waste incineration plants are still conservative in concept and still stay in the past understanding of flue gas denitrification in coal-fired power plants. However, due to the different fuels in these two plants, the denitration technology must be different.From the perspective of producers, the denitrification efficiency of SNCR + PNCR method is no less than SCR + SNCR method, and the NO_X emission limit is 100mg/m^3.The investment and operation cost is low and the floor space is small[8], which can achieve green emission and reduce expenditure at the same time.However, the system failure rate is high, and the ammonia escape problem is serious. In order to popularize the technology to various waste incineration plants, it is necessary to further study these two problems.

References

[1]Xiumei Tan.Problems and treatment measures of municipal solid waste incineration in China.Environment and development,2018,30(07):229-230.

[2]Yan Qin,Jundong Li.Present situation and development of flue gas denitrification technology.Sulfur and phosphorus design and powder engineering,2021,(02):37-39+42+6.

[3]Shuqin Wang,Lifeng Liu,Weiliang Cheng.Application progress of low temperature SCR denitration catalytic technology.Energy and environment,2021,(02):65-69.

[4] Guanghua Liu.Technical and economic comparison of flue gas denitrification process schemes in thermal power plants.Mining equipment,2021,(02):50-51.

[5]Ziang Mi.NoX removal technology from flue gas of municipal solid waste incineration.Guangdong chemical industry,2013,40(17):147-148.

[6]Jialin Liu,Bingwei Li,Mingyu Li.Application of polymer denitration in waste incinerator.Energy conservation and environmental protection,2021,(04):104-106.

[7]Hongxing Hu,Chongjun Lin,Jincheng Lu.Study on the application of Denitration Process in waste incinerator.Energy saving,2020,39(11):102-103.

[8]Jin Yang,Zhigang Xiang,Xinhua Li.Application of SNCR + PNCR process in flue gas denitrification of coal-fired hot blast stoveGuangdong chemical industry,2020,47(06):182-184.