Numerical simulation of NO emission reduction in coke oven regenerator with synergistic SNCR/SCR process

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Abstract. According to the temperature gradient distribution characteristics of the regenerator of the coke oven, a method of synergistic the SNCR/SCR process inside the regenerator to achieve NO emission reduction was proposed in this work. Based on the verification of SNCR and SCR models, the NH_3/NO concentration field and the spatial distribution characteristics of NO in the process of SNCR, SCR, and SNCR+SCR were studied. The conclusion shows that the synergistic SNCR and SCR processes had achieved NO reduction by 64.3% and 37.1%, respectively. However, the increase in reaction temperature caused by the change of injection position resulted in a 0.4% decrease in SNCR+SCR compared to SNCR. It was also found that temperature dramatically influences the SNCR process and the reductant injection position. Limited by the structure of the regenerator and the catalyst coating area, the SCR process exhibited a low NO reduction ability. The SNCR+SCR process should focus on improving the efficiency of the SCR process.

1 Introduction

The coke produced by modern coke ovens plays an essential role in steel smelting. However, the high concentration of NO_x of 400~1000mg/m³ will be generated during the coke oven heating system[1]. At present, the pollutants emission standards for coke oven flue gas issued and implemented by the Chinese environmental protection department require that the NO_x in particular areas be less than 150mg/m³. It brings enormous environmental pressure to coking companies.

Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are popular post-treatment technologies applied to NO_x reduction[2, 3]. The mechanism is that the reducing agent (ammonia or urea) selectively reacts with NO_x to generate N₂ and H₂O. Because SCR exhibits a NO_x reduction effect of more than 90%, it is preferred by coking companies to apply it to flue gas treatment. The typical working temperature of the vanadium-based catalyst is 300~400°C. However, the coke oven flue gas at 180~230°C needs to be preheated before entering the SCR denitrification tower[4]. It leads to additional fuel consumption and produces secondary pollutants simultaneously. Many scholars have also developed low-temperature SCR catalysts. Because of the complex composition of the coke oven flue gas and the weakness of the SCR catalyst[5], it has not been effectively applied and implemented in the flue gas system. For SNCR, the effective reaction temperature is 850~1175°C, and operating parameters restrict the NO_x reduction efficiency. Some researchers have obtained 70~90% NO_x conversion efficiency through experiments or numerical simulations. Some companies have carried

out SNCR tests on the top of the regenerator to obtain an outlet NO_x concentration of 98mg/m³[6].

The hybrid SNCR-SCR technology can be used to optimize NO reduction and reduce costs. A higher reduction effect can be obtained than using SCR alone[7]. There are few reports on the hybrid SNCR-SCR technology. In order to solve the various problems faced by coking enterprises in the management of flue gas NO_x emissions, this research applied SNCR/SCR technology to the coke oven regenerator to achieve NO reduction according to the unique heating system characteristics of the coke oven. Based on the research on the flow and heat transfer characteristics of the coke oven regenerator[8], this work had studied the influence of SNCR, SCR, and hybrid SNCR+SCR on NO emission reduction in the transformed regenerator. We can obtain the relevant parameters and theoretical support for the synergy of SNCR/SCR and coke oven regenerator for NO emission reduction through this research.

2 Models and methods

2.1 Geometric model

In order to realize the cooperative SNCR/SCR process, this work was based on the traditional structure (Fig 1a), removing part of the checker bricks as the reductant injection space inside the coke oven regenerator. The process of atomization, heat absorption, decomposition, and diffusion of the urea solution occurred inside the "space". The modified new-type coke oven regenerator models for SNCR, SCR, and SNCR+SCR are shown in Fig 1 (b), (c), (d), respectively. The structure of the

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regenerator in the direction from the inlet to the outlet was the high-temperature heat storage section in the AB section, the temperature transition section in the BC section (that is, the reductant injection space), and the medium-low temperature heat storage section in the CE section. The SNCR reaction was realized after the urea solution was injected into "space". The SCR catalytic reaction occurred near the wall surface of the middle-low temperature section, and it is assumed that the wall surface of the flue gas channel in the CD section of Fig. 1(c) and Fig. 1(d) is uniformly coated with vanadium-based active components. In particular, for SNCR+SCR, the remaining NH_3 from the upstream SNCR reaction participated in the SCR reaction. The specific coupling process and the

required reaction temperature window determined the height of the reductant injection space. In addition, the reductant injection point corresponded to the center of each channel and was located at one-third of the height of the reductant injection space. The reducing agent was injected into the reductant injection space against the flow direction of the flue gas to enhance the mixing effect of the flue gas and the reducing agent. According to the space axis symmetry characteristics, a quarter of the three-dimensional coupled SNCR/SCR regenerator model was established for numerical calculation. Assuming that the total height of the regenerator was 2250mm. The structural size parameters of the transformed regenerator for different reaction models are shown in Table 1.

Fig.1 The structure of the regenerator and the SNCR/SCR process implementation method.

Table 1. Structural dimensions of different reaction models.
Unit: (mm)

Parameters	SNCR	SCR	SNCR+SCR
H ₁	550	1150	550
H ₂	300	300	300
H ₃	1400	800	1400

2.2 Governing equation

The synergistic SNCR/SCR process followed the conservation of mass, momentum, and energy. Considering the special structure of the reductant injection space, the RNG $k-\varepsilon$ turbulence model was selected to deal with low Reynolds number and near-wall flow. The SIMPLE algorithm was used to solve the pressure-velocity coupling problem in the momentum equation. A second-order central difference scheme solved the convection and diffusion terms in the governing equations. The calculation criterion of the equation was 10^{-6} .

The Discrete Phase Modeling (DPM) was used to

calculate the heat and mass transfer caused by the reductant injection process. The droplet size distribution conformed to the Rosin-Rammler distribution. A solid cone atomizing nozzle was used to inject a urea-water solution (UWS).

The SNCR model, including the seven-step reduction kinetic mechanism proposed by Brouwer et al. [9] and the two-step urea decomposition scheme proposed by Rota et al. [10], was adopted in this study.

The chemical equation of the SCR catalytic reduction reaction considered in this work was as follows:

It has been reported that the rate expression in the SCR reaction kinetic model of the overall catalyst [5, 11]

was described by the following equation:

$$r_{\text{NO}} = k_{\text{NO}} C_{\text{NO}} \theta_{\text{NH}_3} \quad (2)$$

$$\theta_{\text{NH}_3} = \frac{K C_{\text{NH}_3}}{1 + K C_{\text{NH}_3}} \quad (3)$$

$$k_{\text{NO}} = A_{\text{NO}} e^{\frac{-E_{a,\text{NO}}}{RT}} \quad (4)$$

$$K = A_{ads} e^{\frac{\Delta H_{ads}}{RT}} \quad (5)$$

where k_{NO} is the intrinsic reaction rate constant and C_{NO} is the concentration of NO, θ_{NH_3} is the coverage of NH_3 on catalyst; K is the NH_3 adsorption equilibrium constant on catalyst; A_{NO} and $E_{a,NO}$ are the preexponential factor and activation energy in Arrhenius equation; A_{ads} and ΔH_{ads} are the preexponential factor and NH_3 adsorption heat in NH_3 adsorption equation.

The SCR reaction kinetic model parameters shown in Table 2 are obtained through experiments[12]. The experiments carried out in a benchtop reactor used a commercial VOx/TiO₂ catalyst, and the reaction temperature was between 320~400°C.

Table 2. Kinetic parameters of SCR reaction.

Parameter	Value	Unit
A_{NO}	3.17×10^6	s^{-1}
$E_{a,NO}$	50.38	kJ/mol
A_{ads}	2.55×10^{-10}	m^3/mol
ΔH_{ads}	153.23	kJ/mol

2.3 Solving conditions

The data for this work came from a JNK43-98D coke oven in a coking plant. The volume fraction of the main components of the flue gas before entering the chimney was measured: CO₂/0.206, O₂/0.054, H₂O/0.057, N₂/0.685, and the NOx concentration in the flue gas was 400mg/m³. The mass flow rate at the inlet of the established geometric model was 0.0075kg/s, and the outlet was the pressure boundary. The convective heat transfer coefficients of the walls at the entrance and exit of the regenerator were 16.4W/(m²·K) and 9.8W/(m²·K), respectively, and the remaining walls were adiabatic. The temperature and heat flux density at the fluid-solid interface was continuous.

On-site data collection was performed on the coke oven regenerator[8], and the relationship (6) of the inlet flue gas temperature at the top of the coke oven regenerator over time was obtained by fitting:

$$T_{in} = 1342.391 + 0.02294t \quad (6)$$

3 Results and discussion

3.1 Model verification

The SNCR field experimental data reported by Nguyen et al.[13] were used to verify the SNCR model. The simulation results are shown in Table 3 result in lower NH_3 slip than the test. In addition, the deviations of outlet temperature and NO concentrations were 2.8% and 2.2%, respectively. These deviations were within the allowable engineering range, indicating that the collaborative SNCR model was adequate.

Table 3. Comparison of outlet parameters between experimental and simulation results.

Parameters	Experiment	Simulation
Temperature (°C)	930±8	956 (2.8%) ^a
NO concentration (ppm)	45±6	46 (2.2%) ^a
NH_3 slip (ppm)	< 5	< 1

$$^a \text{Error(\%)} = \frac{\text{simulation-experiment}}{\text{experiment}} \times 100$$

The SCR reaction mechanism and related parameters proposed by Zheng et al.[3] were used to verify the validity of the model. Fig 3 depicts the simulation results in the temperature range of 320~400 °C, and the comparison of experimental data in the literature shows that the maximum deviation did not exceed 7.5%. Therefore, the established model was effective for simulating the SCR reaction process.

Fig. 2. Experimental and simulation results of NO conversion efficiency at different temperatures.

3.2 Synergistic SNCR

The Y=0~1800mm interval on the Z=30mm plane was selected as the investigation surface, and the injection surface was located at Y=1500mm. The NH_3 concentration field distribution in Fig. 3(a) shows that the NH_3 produced by the decomposition of the urea solution was mainly concentrated in the area below the injection surface and flowed to the exit direction along with the flue gas. Affected by the distribution and number of injection points, NH_3 was unevenly distributed in the pores of the middle and low-temperature sections. It caused part of NO to be unable to contact and react with NH_3 on the side of the outer channel. The study also found that NO and NH_3 had concentration peaks in the reductant injection space. It was because the speed difference between the injection flow and the smoke caused the injected reducing agent to fail to develop in the lateral direction and was bound by the mainstream smoke. The low NH_3 concentration between injection points resulted in high NO concentration, which in turn formed a concentration peak.

Fig 3. NH₃/NO concentration field and NO concentration distribution along the Y direction in the SNCR process.

In Fig. 3(b), the curve of NO change along the Y direction shows that the SNCR reaction mainly occurred in the space of Y=1600mm~1300mm, and NO decreased from 380.2 mg/m³ to 142.7mg/m³ during this process. On the injection surface Y=1500mm (blue dotted line), the NO concentration was 304.5mg/m³. It was caused by the upward diffusion of a small part of NH₃. The central reaction zone achieved 64.3% NO reduction, of which 40.5% occurred below the injection surface.

3.3 Synergistic SCR

According to the SCR structure model, the Y=0~1200mm interval on the Z=30mm plane was selected as the investigation surface, and the injection surface was located at Y=800mm. The reducing agent was injected into the reductant injection space to provide NH₃ for the SCR reaction. Fig 4(a) depicts the NH₃ concentration distribution after the reductant was injected into the reductant injection space and mixed with flue gas. NH₃ had good distribution in the cross-section, and part of the NH₃ diffused upward along the side of the wall. However, the NO concentration distribution indicated that the SCR catalytic reaction occurred in a small area near the wall.

Fig 4. NH₃/NO concentration field and NO concentration distribution along the Y direction in the SNCR process.

In Fig. 4(b), the NO concentration curve shows that the active catalyst started to occur at the Y=500mm position, indicating that the temperature at this position was lower than 400°C. In the range of Y=500mm~0mm, the NO concentration decreased from 396.2mg/m³ to 252.4mg/m³, achieving a 37.1% NO reduction. Compared with the effect of traditional SCR application, the NO reduction of this model was lower. It was mainly because the structural size of the grid brick pores of the regenerator was more significant than that of the industrial honeycomb channels, which resulted in the NO/NH₃ in the center was not in contact with the catalytic layer. In addition, the SCR catalytic area limited NO reduction.

3.4 Synergistic SNCR+SCR

The geometric model and process parameters of SNCR+SCR were the same as those of SNCR. In particular, the injection surface Y=1650mm was set to study the influence of different injection positions on the SNCR process. The NH₃ concentration shown in Fig 5(a) is mainly concentrated in the middle and upper part of the reductant injection space, which corresponded to the change in NO concentration. It may be because the

injection position was too high, and part of the reducing agent diffused into the high-temperature section. On the other hand, the high ambient temperature led to the simultaneous reaction of NO reduction and NH₃ oxidation in the SNCR process. Therefore, there was little remaining NH₃ that can escape from the outlet.

Fig 5. NH₃/NO concentration field and NO concentration distribution along the Y direction in the SNCR process.

In the space of Y=1800mm~1300mm, the NO concentration was reduced from 398.6mg/m³ to 144.1 mg/m³, achieving 63.9% NO reduction, which was 0.4% lower than the synergistic SNCR. It was because the injection position was too high, and the NH₃ oxidation rate was increased. Furthermore, in the range of Y=500mm~0mm, the NO near the active catalytic layer did not change significantly. The NH₃ concentration monitored at the outlet was 5.1mg/m³. It showed that a large amount of NH₃ was consumed in the SNCR process, and only a small amount of NH₃ remains, which was challenging to be used in the reaction in the SCR catalytic zone. It was greatly affected by the catalytic area and flow channels.

4 Conclusion

Numerical simulations were used to reduce NO by synergizing SNCR, SCR, and SNCR+SCR inside the coke oven regenerator. Synergistic SNCR and SCR achieved NO reduction by 64.3% and 37.1%, respectively. However, due to the increased reaction temperature caused by the variation of the injection position, the SNCR+SCR was 0.4% lower than the synergistic SNCR. The SNCR process mainly reacted in a limited space. It was susceptible to temperature, and the injected reducing agent should be controlled within a suitable space range. The SCR reaction was mainly limited by the regenerator structure and catalyst coating area. Without changing the structure, SNCR can get a higher NO reduction than SNCR+SCR. Moreover, SNCR+SCR should improve SCR efficiency, which will be discussed in-depth in the subsequent work.

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