



Research Article

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## A mathematical model and the corresponding software for combining selective catalytic reduction with regenerative heat exchange

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### ABSTRACT

*In order to achieve dual goals of waste heat recovery and nitrogen oxides (NO<sub>x</sub>) removal in fuel gas from High Temperature Air Combustion (HiTAC) furnaces and coal-fired boilers in power plants, the honeycombed Selective Catalytic Reduction (SCR) catalysts were implanted in the regenerative heat exchange system. Under the premise of ignoring the influence of catalytic reaction on the heat transfer process, the single channel one-dimensional mathematical model for catalytic reduction and regenerative heat exchange of NO was established at unsteady state, in which the adsorption and reaction of reactants obeyed the Eley-Rideal Mechanism. With governing equation dispersion via the finite-volume method and calculation program compiled based on C# language in Visual Studio 2010, a corresponding calculation software was developed. The preliminary analysis of simulation results validated the rationality of the model.*

**Keywords:** Heat exchange; HiTAC; Mathematical model; Regenerative SCR; Software.

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### INTRODUCTION

Recently, the massive increase in energy consumption has encouraged progressively deteriorating issues of energy shortage and environmental pollution. In order to conserve energy and reduce emissions, numerous advanced technologies including regenerative heat exchange [1] and SCR [2], two relatively mature technologies, have been developed. The former is widely applied to waste heat recovery in HiTAC[3] industrial furnaces, and the latter is widely used to remove NO<sub>x</sub> in coal-fired boilers of power plants. Both possess a high efficiency of above 80%. However, it tends to readily generate excess NO<sub>x</sub> in the case of high combustion temperature [4], oil fuel [5], and the complicated combustion surroundings in HiTAC furnaces. In power plants, high waste heat recovery efficiency needs huge heat transfer equipment, which occupies large area and also costs much money.

To treat the flue gas, the regenerators, a key part of regenerative heat exchanger technology, has a similar geometry with SCR catalysts after adopting honeycomb ceramics and the placement that allowed regenerators and catalysts to superimpose on each other was helpful for the displacement among cells. Therefore, two technologies were considered to be combined, that is, regenerators with suitable temperature regimes for SCR catalyst reactions (temperature windows) were replaced by catalysts in regenerative heat exchange system. NH<sub>3</sub> injected at proper position sufficiently mix with the flue gas, which made it possible to recover the waste heat and simultaneously reduce NO<sub>x</sub> emissions and equipment footprints. Figure 1 shows the principle of the coupled technology.

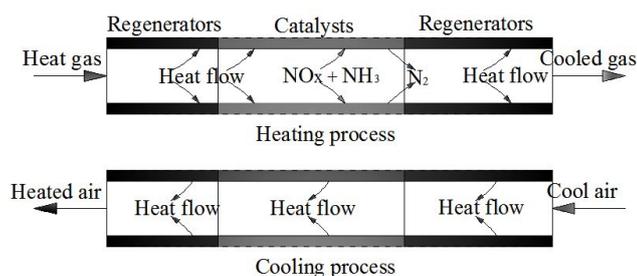


Figure 1. The Principle of the Coupled Technology

A considerable amount of research has been conducted during the last few decades seeking to better understand the details of heat exchange modes[6-7] and SCR denitration modes[8-9], and abundant computation experiences are accumulated. The compound mode which integrates governing equations of flow, heat and mass transfer, and catalytic reaction was established in this paper. The one-dimensional model was employed in view of the complicated cases and corresponding simulation software was programmed. The analysis of numerical results verified the rationality and practical value of the model.

### 1. COMBINED MODEL

A mathematical model concerning SCR denitration and regenerative heat exchange was proposed to preliminarily investigate the aforementioned combined technology. The model was expounded in detail hereinafter.

Square channels were adopted for catalysts and regenerators in simulation, and it was replaced by the equivalent sectional sizes cylinder. The model was built under these assumptions due to the complicated situation: (1), the inlet mixture gas parameters are constant; (2), the heat exchange process in all channels is the same; (3), the gas density is determined by its temperature; (4), both the gas thermal conductivity and the solid radial thermal conductivity are zero; (5), the catalytic reaction has no influence on the heat transfer process; (6), the temperature of catalytic reaction is the local solid temperature; and (7), the diffusion of gas components in the micropore is ignored. The model is as follows:

#### 1) Regenerative heat exchange model

##### 1. Gas phase mass balance:

$$\frac{\partial \rho_g}{\partial t} + \frac{\partial (\rho_g u_g)}{\partial z} = 0 \quad (1)$$

##### 2. Gas phase energy balance:

$$\frac{\partial (\rho_g c_{p,g} T_g)}{\partial t} + \frac{\partial (\rho_g u_g c_{p,g} T_g)}{\partial z} = \frac{h a_v (T_s - T_g)}{\varepsilon_g} \quad (2)$$

##### 3. Solid phase energy balance:

$$\frac{\partial (\rho_s c_{p,s} T_s)}{\partial t} = \frac{h a_v (T_g - T_s)}{1 - \varepsilon_g} \quad (3)$$

##### 4. Relationship between gas temperature and its density:

$$\rho_g = \frac{p_0}{R_g T_g} \quad (4)$$

Heat transfer coefficient was obtained from the reference [11]:

$$Nu = 4.364 + 13.18 \left( \frac{1000}{Gz} \right)^{-0.524} \exp \left( -\frac{60.2}{Gz} \right) \quad (5)$$

Where the subscripts g and s represent gas and solid, respectively;  $\rho$  is density;  $c_p$  is special heat capacity;  $T$  is temperature;  $t$  is time;  $u$  is velocity;  $u_0$  is standard state velocity;  $z$  is axial coordinate;  $d_{ei}$  is equivalent diameter;  $p_0$  is standard state pressure;  $\varepsilon_g$  is porosity of porous medium;  $D_i$  is diffusion coefficient;  $D_{i,N_2}$  is binary diffusion coefficient;  $R_g$  is gas constant;  $Nu$  is Nusselt number;  $Gz$  is Graetz number.

#### 2) SCR model

The majority of  $NO_x$  is NO in flue gas. When the concentration of  $O_2$  exceeds 1%, the main reaction is:



Adsorption and reaction of reactants follows Eley-Rideal mechanism.  $\text{NH}_3$  is firstly attached to the solid surface of catalyst in chemical adsorption, and desorption of  $\text{NH}_3$  is simultaneous. Then  $\text{NO}$  reacts with  $\text{NH}_3$  attached to the catalyst surface and finally products desorb and spread out. The governing equations are as follows:

1. NO mass balances in channel:

$$\frac{\partial C_{\text{NO}}}{\partial t} + \frac{\partial(u_g C_{\text{NO}})}{\partial z} = \frac{h_{\text{NO}} a_v (C_{\text{NO},f} - C_{\text{NO}})}{\varepsilon_g} \quad (7)$$

2.  $\text{NH}_3$  mass balances in channel:

$$\frac{\partial C_{\text{NH}_3}}{\partial t} + \frac{\partial(u_g C_{\text{NH}_3})}{\partial z} = \frac{h_{\text{NH}_3} a_v (C_{\text{NH}_3,f} - C_{\text{NH}_3})}{\varepsilon_g} \quad (8)$$

3. Solid phase mass balance:

$$\Omega \frac{\partial \theta_{\text{NH}_3}}{\partial t} = R_{\text{NH}_3,\text{ads}} - R_{\text{NH}_3,\text{des}} - R_{\text{NH}_3,\text{red}} \quad (9)$$

4. The adsorption rate of  $\text{NH}_3$  on the catalyst surface is assumed to be proportional to the  $\text{NH}_3$  concentration in the gas phase:

$$\frac{\partial C_{\text{NH}_3,f}}{\partial t} = \frac{h_{\text{NH}_3} a_v (C_{\text{NH}_3} - C_{\text{NH}_3,f})}{1 - \varepsilon_g} + R_{\text{NH}_3,\text{ads}} - R_{\text{NH}_3,\text{des}} \quad (10)$$

5. NO reaction in catalyst interface:

$$\frac{\partial C_{\text{NO},f}}{\partial t} = \frac{h_{\text{NO}} a_v (C_{\text{NO}} - C_{\text{NO},f})}{1 - \varepsilon_g} - R_{\text{NO},f} \quad (11)$$

Where:

$$C_i = \frac{T_0 y_i}{T_g V_m} \quad (12)$$

The NO reduction reaction is considered to be of first order with respect to each reactant:

$$R_{\text{NO}} = R_{\text{NH}_3} = k_{\text{red}} C_{\text{NO}} \theta_{\text{NH}_3} \Omega$$

The adsorption rate of  $\text{NH}_3$  on the catalyst surface is assumed :

$$R_{\text{NH}_3,\text{ads}} = k_{\text{ads}} C_{\text{NH}_3} (1 - \theta_{\text{NH}_3}) \Omega$$

while the rate of desorption is assumed to be proportional to the concentration of the adsorbed species:

$$R_{\text{NH}_3,\text{des}} = k_{\text{des}} C_{\text{NH}_3} \theta_{\text{NH}_3} \Omega$$

An Arrhenius type dependence of the kinetic constants  $k$  is assumed

$$k_{\text{red}} = A_{\text{red}} \exp(-E_{\text{red}}/RT_s)$$

$$k_{\text{ads}} = A_{\text{ads}} \exp(-E_{\text{ads}}/RT_s)$$

$$k_{\text{des}} = A_{\text{des}} \exp(-E_{\text{des}}/RT_s)$$

$$\text{Where, } E_{\text{des}} = E_{\text{des}}^0 (1 - \beta \theta_{\text{NH}_3})$$

Mass transfer coefficient:

$$h_i = \frac{\text{Sh} \rho_g D_i}{d_{ei}} \quad (13)$$

Here the diffusion coefficient of  $i$  equals the binary diffusion coefficient of  $i$ :

$$D_i = D_{i,\text{N}_2} = \frac{4.36 \times 10^{-5} T^{1.5}}{p_0 (V_i^{1/3} + V_{\text{N}_2}^{1/3})^2} \left( \frac{1}{M_i} + \frac{1}{M_{\text{N}_2}} \right)^{1/2} \quad (14)$$

Here, the subscripts ads, des, and red stand for adsorption, desorption, and reduction respectively,  $i$  represents component,  $f$  represents value at the gas-solid interface.  $C_i$  is mole concentration of reactants,  $R_i$  reactive rate,  $y_i$  volume fraction,  $V_m$  molar volume,  $A$  pre-exponential factor,  $E$  activation energy,  $\theta_i$  surface coverage,  $\beta$  parameter for the surface coverage dependence,  $\Omega$  catalyst capacity,  $k$  reaction rate constant,  $R$  universal gas constant,  $V_i$

molecular diffusion volume,  $M_i$  molecular mass.

Boundary conditions:

Heating process:  $T(0, t) = T_{\text{fg, in}}, y_i(0, t) = y_{i, \text{in}}, (nt_{\text{sw}} < t < (n+1)t_{\text{sw}})$ ;

Cooling process:  $T(z_1, t) = T_{\text{a, in}}, y_i(0, t) = y_{i, \text{in}}, ((n+1)t_{\text{sw}} < t < (n+2)t_{\text{sw}})$ .

Here  $T_{\text{fg, in}}$  is inlet flue gas temperature,  $z_1$  overall length of channel,  $T_{\text{a, in}}$  inlet air temperature,  $y_{i, \text{in}}$  inlet volume fraction,  $t_{\text{sw}}$  switching time,  $n=1, 2, 3, \dots$

The finite volume method is adopted to calculate the model; meanwhile, the independence of the grids has been proved.

Heat recovery efficiency is described by

$$x_Q = \frac{\bar{W}_{\text{a, out}} \bar{T}_{\text{a, out}} - W_{\text{a, in}} T_{\text{a, in}}}{W_{\text{m, in}} T_{\text{m, in}}} \quad (15)$$

Where:  $W = \rho c_p u$ ,  $\bar{W}_{\text{a, out}} = \frac{1}{t_{\text{sw}}} \int_0^{t_{\text{sw}}} W_{\text{a, out}}(t) dt$ ,  $\bar{T}_{\text{a, out}} = \frac{1}{t_{\text{sw}}} \int_0^{t_{\text{sw}}} T_{\text{a, out}}(t) dt$

Denitrification performance was evaluated by the conversion of NO (denitrification efficiency). As the temperature of gas changed instantaneously, volume percentage was employed for calculation.

NO conversion is calculated by

$$x_{\text{NO}} = \frac{y_{\text{NO, in}} - \bar{y}_{\text{NO, out}}}{y_{\text{NO, in}}} \quad (16)$$

Where:  $\bar{y}_{\text{NO, out}} = \frac{1}{t_{\text{sw}}} \int_0^{t_{\text{sw}}} y_{\text{NO, out}}(t) dt$

Space velocity is defined by

$$SV = \frac{F_0}{V_{\text{ca}}} \quad (17)$$

Where,  $\bar{\quad}$  represents time-weighted averaged,  $W$  is water equivalent,  $y_{\text{NO, out}}$  outlet NO concentration,  $F_0$  standard flow conditions of gas mixture,  $V_{\text{ca}}$  the volume of catalyst,  $z_1$  the length of catalyst channel.

## 2. SIMULATION SOFTWARE

### 2.1 COMPUTATION PROCEDURES

This program was written in C# language based on the Visual Studio 2010 platform. Heat exchange computation at unsteady state unidirectionally affected the catalytic computation due to the fact that the effect of catalytic reaction on heat exchange process was ignored. Therefore, the computation procedure was simplified as follows:

- 1) The discrete equations obtained from governing equation were iteratively computed from initialization. The results included flue gas temperature, velocity fields and solid temperature field. Residuals needed to satisfy the convergence requirement before the process reached the next time step size. When periodic steady state was reached, the relevant data of gas and solid was substituted into the catalytic discrete equations.
- 2) SCR catalytic discrete equations were iteratively computed and the next time step size started when the residuals satisfied the new criterion for convergence of iteration.
- 3) The computation finished when the time period was reached.

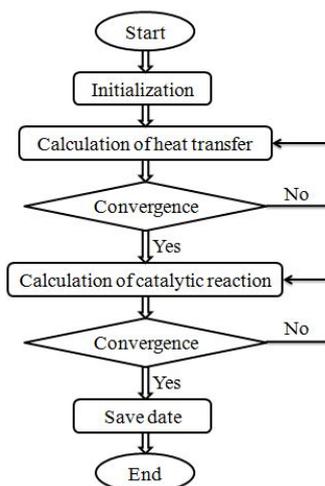


Figure 2. The Computation Procedure

## 2.2 INTRODUCTION OF SOFTWARE

The software consisted of four modules: 1, parameter collection and transmission module: gather the data on the user interface and assign them to the software; 2, heat exchange computation module: obtain data at different times by iterative calculation; 3, catalytic reaction module: calculate the SCR reaction concentration field; 4, results collection and save module: collect the data calculated and save it into the EXCEL files.

The factors which affect the regenerative heat exchanger can be various, and users can modify the relevant parameters according to the actual calculation or directly change it in program.

Regenerative heat exchange parameter interface was depicted in figure 3:

Information of materials		Internal diameter		Compositions of flue gas	
Length of catalysts	0.6	Internal diameter	0.005	N2	0.9
Length of regenerators	0.2	External diameter	0.006	O2	0.05
Density of catalysts	2500	Length of the side	0.075	H2O	0.05
Density of regenerators	2730				
Cp of catalysts	900				
Cp of regenerators	1200				
Computational conditions		Calculating scale			
Space velocity of flue gas	5000	Step size in time	0.01		
Initial temperature	30	Step size in length	0.001		
Inlet flue gas temperature	350				
Inlet air temperature	30				
Switching time	45				

Figure 3. Input Port of Heat Transfer Simulation Computation

SCR denitrification parameter interface was displayed in figure 4:

Figure 4. Input Port of Denitration Simulation Computation

### 3 SOFTWARE VALIDATIONS

#### 3.1 SIMULATION CONDITIONS

The physical model was established via referring to the relevant experiments [12]. Conventional honeycomb catalysts  $V_2O_5-WO_3(MoO_3)/TiO_2$  and honeycomb regenerators  $Al_2O_3$  were adopted in the simulation. The inner and outer boundary equivalent diameters of square channel were 5 and 6mm, respectively. The flue gas firstly flowed through catalysts and then flowed through the regenerators. The catalyst duct length and regenerator duct length were 0.6m and 0.2m, respectively. The density and special heat capacity of two materials were listed in table 1, and the catalytic reaction parameters could be found in table 2. The flue gas consisted of 5% v/v  $O_2$ , 5% v/v  $H_2O$ ,  $NO$ , and  $NH_3$ . The balance gas is  $N_2$ . The volume flow of the mixture equaled that of the air available for cool gas in the

system. Unless intentionally noted, the space velocity  $SV=5000h^{-1}$ , flue gas temperature  $T_{fg,in}=350^{\circ}C$ ;  $NO$  and  $NH_3$

concentration  $y_{NO,in}=y_{NH_3,in}=400ppm$ ; switching time  $t_{sw}=45s$ .

Table 1 Physical Properties of the Material

Parameters	Catalysts [13]	Regenerators [14]
Special heat capacity/ $J\ kg^{-1}\cdot\ k^{-1}$	900	2730
density/ $kg\cdot\ m^{-3}$	2500	1200

Table 2 Kinetic Parameters of Ccatalysts

Kinetic parameters	values
$A_{red}/s^{-1}$	$3.23\times 10^5$
$E_{red}/J\cdot\ mol^{-1}$	77500
$A_{ads}/m^3\cdot\ mol^{-1}\cdot\ s^{-1}$	0.887
$E_{ads}/J\cdot\ mol^{-1}$	9540
$A_{des}/s^{-1}$	$2.43\times 10^5$
$E_{des}^0/J\cdot\ mol^{-1}$	113970
$\beta$	0.163
$\sigma$	1.0

$\Omega/\text{mol}\cdot\text{m}^3$	130
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## RESULTS

### 3.2.1 ANALYSIS OF HEAT TRANSFER

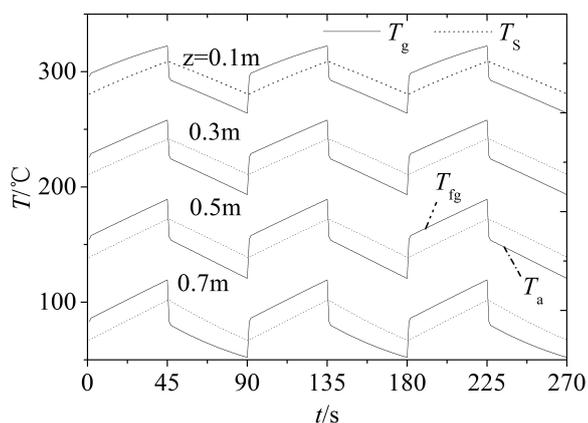


Figure 5. Change of Temperature at Different Locations

As can be seen from figure 5, temperature of gas and solid in different position periodically fluctuates with time. Solid temperature is lower than flue gas temperature when flue gas flows and higher than air temperature when air flows, which coincides with the actual situation of regenerative heat exchange. In addition, air temperature in catalyst layer is lower than flue gas temperature at the same position, which indicates that catalysts have an extremely good heat storage capacity and their material is suitable as a regenerative material.

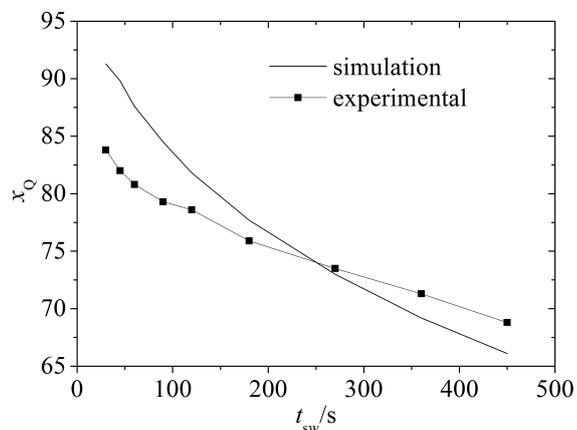
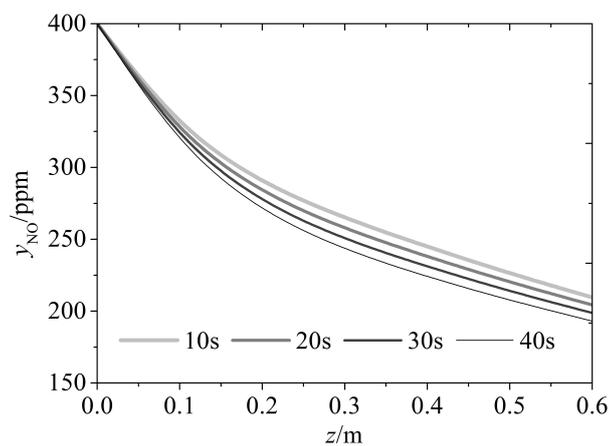
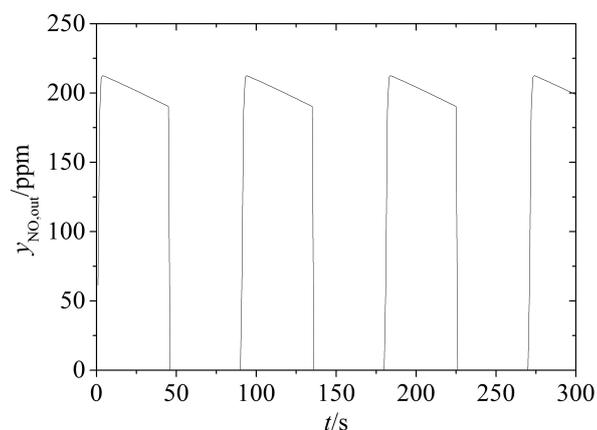


Figure 6. Change of Heat Recovery Efficiency with Switching Time



(a)



(b)

Figure 7. Change of NO Concentration

As can be seen from the figure 6, the simulation values of heat recovery efficiency and the experimental values[12] of similar materials gradually decrease with switching time prolonging, which demonstrates that both have the same observable change tendencies despite the presence of deviation from material property difference and model simplification. The reason is that the longer switching time is, the smaller the temperature differences between gas and solid are, which indicates that catalysts have a fairly desirable heat storage-release property and the developed catalyst material is a suitable storage material.

### 3.2.2 CHANGE OF NO CONCENTRATION

Figure 7 a reveals that NO concentration around inlet decreases axially and rapidly due to the fact that the temperature is high and catalytic reaction proceeds strongly. Therefore, the denitrification efficiency is relatively high. Nevertheless, reaction intensity weakens in the low temperature area in downstream and the concentration profile changes gently. In Figure 7 b, a periodic change of outlet NO concentration with time is observed, and each period has a linear decrease. Period variety is resulted from change of gas flow direction. When the flue gas flows, the temperature gradually increases and the denitration reaction strengthens, leading to linear decrease of outlet NO concentration.

### 3.2.3 EFFECT OF SPACE VELOCITY ON NO CONVERSION

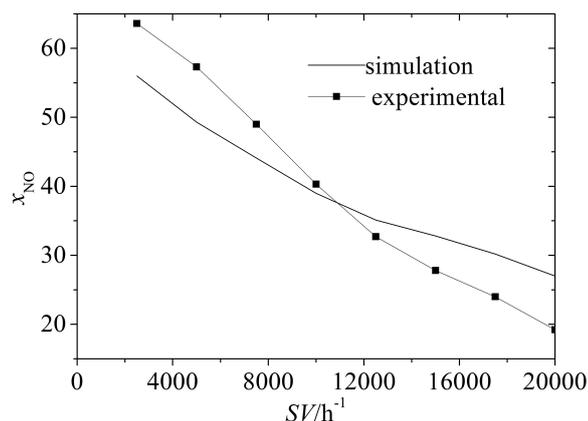


Figure 8. Change of NO Conversion with SV

Figure 8 shows that simulation and experimental denitration efficiency [12] presents a linear decrease with the increase of space velocity. That is because the increase in space velocity results in the increase of corresponding gas velocity. The reactant residence time in catalyst shortens and thus reactant effective reaction time becomes shorter, which leads to the decrease of denitration efficiency.

In a word, these analysis results, in a manner, could be verified by relevant experiments conducted by us, in which a  $V_2O_5-WO_3(MoO_3)/TiO_2$  catalyst was used. The model can predict the project and has a certain reference value.

## CONCLUSION

In order to obtain dual goals of waste heat recovery and nitrogen oxides ( $NO_x$ ) removal, the one-dimensional mathematical model combining selective catalytic reduction with regenerative heat exchanger was established. Compiled in C# language, the simple simulation software was developed. The simulation calculation was performed according to the related parameters and its physical properties of  $V_2O_5-WO_3(MoO_3)/TiO_2$  catalyst in the literature, which was widely applied in coal-fired power plant boilers. The results indicated that catalysts had a fairly desirable heat storage-release property. NO concentration axially decreased rapidly and then remained almost unchanged. The outlet NO concentration periodically changed with time and there existed a linearly decreased segment in each period. The denitrification efficiency decreased with space velocity increasing. Compared with the experiment results, the model possessed a certain rationality, which could lay a foundation for the model optimization in the future.

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