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The Effects of Coke Parameters and Circulating Flue Gas Characteristics on NO_x Emission during Flue Gas Recirculation Sintering Process

Juntao Han ¹, Guofeng Lou ^{1,2,*}, Sizong Zhang ¹, Zhi Wen ^{1,2}, Xunliang Liu ^{1,2} and Jiada Liu ¹¹ School of Energy and Environmental Engineering, University of Science & Technology Beijing, Beijing 100083, China² Beijing Key Laboratory of Energy Saving and Emission Reduction for Metallurgical Industry, University of Science & Technology Beijing, Beijing 100083, China

* Correspondence: lgf@ustb.edu.cn

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Abstract: The new process of flue gas recirculation, which reduces coke consumption and reducing NO_x emissions, is now extensively used. Compared with traditional sintering, the characteristics of circulating flue gas and coke parameters significantly affect the combustion atmosphere and coke combustion efficiency. Based on the actual complex process of sintering machine, this study proposes a relatively comprehensive one-dimensional, unsteady mathematical model for flue gas recirculation research. The model encompasses NO_x pollutant generation and reduction, as well as SO₂ generation and adsorption. We focus on the effects of cyclic flue gas characteristics on the sintering-bed temperature and NO_x emissions, which are rarely studied, and provide a theoretical basis for NO_x emission reduction. Simulation results show that during sintering, the fuel NO_x is reduced by 50% and 10% when passing through the surface of coke particles and CO, respectively. During flue gas recirculation sintering, the increase in circulating gas O₂ content, temperature, and supply-gas volume cause increased combustion efficiency of coke, reducing atmosphere, and NO_x content in the circulating area; the temperature of the material layer also increases significantly and the sintering endpoint advances. During cyclic sintering, the small coke size and increased coke content increase the char-N release rate while promoting sufficient contact of NO_x with the coke surface. Consequently, the NO_x reduction rate increases. Compared with the conventional sintering, the designed flue gas recirculation condition saves 3.75% of coke consumption, i.e., for 1.2 kg of solid fuel per ton of sinter, the amount of flue gas treatment is reduced by 21.64% and NO_x emissions is reduced by 23.59%. Moreover, without changing the existing sintering equipment, sintering capacity increases by about 5.56%.

Keywords: numerical simulation; flue gas recirculation; coke combustion; NO_x emission

1. Introduction

Since NO_x is the root cause of photochemical smog and acid rain, it causes serious environmental and ecological problems. Relevant emission regulations are continuously being improved given the global significance of controlling NO_x emissions. Among these emissions, those from the steel industry account for about 6% of the overall emissions of all industries. Moreover, SO₂ and NO_x emissions during sintering account for 60% and 50% of the overall emissions of SO₂ and NO_x in steel production, respectively [1]. At present, new technologies for reducing NO_x emission during sintering mainly include flue gas recirculation sintering (FGRS), selective catalytic reduction [2], biomass fuel [3–6], gas injection [7], and parameter control [8,9].

In recent years, some scholars have experimentally studied the emission law of NO_x in iron-ore sintering, focusing on the effects of using biomass-fuel substitution (e.g., charcoal, burned straw, and sawdust), different types of coke particles, coke preform, and calcium ferrite and CeO₂ catalytic reduction on the overall emission of NO_x [10,11]. Some studies have focused on the effects of the flue gas concentration around coke particles on char-N conversion and NO_x reduction [12]. Over the past two decades, various FGRS schemes have been proposed to reduce pollutant emissions and improve energy efficiency. Chen et al. [13] improved the coke-combustion efficiency by flue gas recirculation to reduce NO_x emission, when using CeO₂ modified coke and flue gas recirculation for sintering pot simulation, and the NO_x reduction rate is 38.0%. Fan et al. [14,15] performed a sintering-pot test and found that flue gas recycling contributes partly to NO_x reduction in the sintering bed layer. SO₂ is absorbed and filtered by the mixed layer, CO is reused as fuel, and the production of iron ore per ton can reduce NO_x by 20%–45%, dioxins by 60%–70% and SO₂ by 20%–45% [16], which proves that flue gas recycling can effectively reduce pollutant emissions. Although some research on the mechanism of NO_x formation and reduction during sintering has been conducted, these processes are complicated, so further research is needed. However, many studies have focused on the combustion behavior and heat transfer in iron-ore sintering, particularly the influences of fuel ratio, gas supply, coke size, limestone particle size, and different exhaust-gas cycle schemes on sintering [17–20]. Some papers have reported mathematical models and key parameters for NO_x behavior in conventional sintering (CS) [21,22]. Few studies have been conducted on the numerical simulation of iron-ore FGRS, especially on the influence of operating parameters on NO_x emissions during actual FGRS. In flue gas recirculation, flue gas is mixed with air as the input condition, compared with CS, flue gas recirculation technology has the advantages of low solid-fuel consumption, NO_x re-reduction, and improved efficiency of flue gas treatment in the late stage. However, due to the different locations of the circulating region, varied sources of circulating gases, and the change in the bed layer structure during combustion, the main input parameters of flue gas circulation are changed. These parameters include O₂ content, gas supply, and circulating-gas temperature. Moreover, the combustion atmosphere is quite different from that of CS, the heat and mass transfer process between gas and solid phases, and the combustion efficiency of coke in the sintering area are affected significantly, as well as the release and reductive process of char-N.

In the present study, a one-dimensional unsteady mathematical model based on the heat transfer, mass transfer, and complex physical and chemical changes in iron-ore sintering [23,24] is established. The reliability of the mathematical model has been verified by sintering pot tests. The effects of key input conditions (i.e., O₂ content and gas temperature and gas supply of the recirculation hood) and coke parameters on bed temperature and contents of NO_x, O₂, and CO in flue gas during sintering were quantified. The effectiveness of FGRS in reducing solid-fuel consumption, flue gas treatment, and NO_x emissions is also discussed and compared with CS. The effects of the main operating parameters on NO_x emission during recirculation sintering is explored, and a theoretical basis for the optimization of flue gas recirculation is provided.

2. Mathematical Model of Sintering

After the sinter is batched, mixed, granulated, charged, and ignited, sintering begins. Considering that the temperature in the width direction of the bed layer is substantially the same and the running speed is slow, the actual sintering can be regarded as a one-dimensional porous-medium transmission process. The transmission in the width and the running direction is ignored. In order to reveal the heat and mass transfer, multi-reaction coupling and NO_x emission mechanism of flue gas recirculation process. The model considers relatively complete homogeneous, heterogeneous reactions and changes in the structural parameters of the bed layer; it also considers convective heat transfer and heat conduction between gas–solid phases, radiation heat transfer between solid phases, and the modification of initial particle size distribution of raw materials to the overall reaction rate of the reaction submodel.

2.1. Governing Equations

The sintered layer includes solid-phase components of iron ore (Fe_2O_3 , Fe_3O_4 , and Fe), coke particles, return fines and flux agent (limestone, dolomite, and hydrated lime), and physical water and gas-phase components (O_2 , NO_x , CO_2 , CO , and H_2O [g]). The following list provides governing equations that describe heat transfer, mass transfer, and gas flow during iron ore sintering.

The conservation equations for the solid and gas phase components are as follows [25,26].

$$\frac{\partial((1-\varepsilon)\rho_s u_s \cdot Y_j)}{\partial x} + \frac{\partial((1-\varepsilon)\rho_s \cdot Y_j)}{\partial t} = -\sum_k \sum_j M_{j,k} R_{j,k}, \quad (1)$$

$$\frac{\partial(\varepsilon \rho_g u_g \cdot \gamma_i)}{\partial x} + \frac{\partial(\varepsilon \rho_g \cdot \gamma_i)}{\partial t} = \sum_k \sum_i M_{i,k} R_{i,k}. \quad (2)$$

The pressure drop in the sintered bed is iteratively calculated using the Ergun equation for given geometric parameters and gas flow rates. The momentum conservation equation is expressed as follows [27].

$$\frac{P}{\Delta H} = 323 \frac{\mu}{(\varsigma_j d_p)^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} u_g + 3.78 \frac{\rho_g}{\varsigma_j d_p} \frac{1-\varepsilon}{\varepsilon^3} u_g^2. \quad (3)$$

Solid phase and gas phase energy conservation are as follows [26,28].

$$\frac{\partial((1-\varepsilon)u_s \rho_s C_{ps} T_s)}{\partial x} + \frac{\partial((1-\varepsilon)\rho_s C_{ps} T_s)}{\partial t} = \frac{\partial}{\partial x} \left(\lambda_{s,total} \frac{\partial T_s}{\partial x} \right) + h_{conv} A_{ssa} (T_g - T_s) + \sum_k M_k R_k (\Delta H_k - C_{ps} T_s), \quad (4)$$

$$\frac{\partial(\varepsilon \rho_g C_{pg} u_g T_g)}{\partial x} + \frac{\partial(\varepsilon \rho_g C_{pg} T_g)}{\partial t} = \frac{\partial}{\partial x} \left(\varepsilon \lambda_g \frac{\partial T_g}{\partial x} \right) + h_{conv} A_{ssa} (T_s - T_g) + \sum_k M_k R_k C_{ps} T_s. \quad (5)$$

2.2. Main Reaction Models

Throughout the entire sintering process from charging ignition to unloading, each sinter layer undergoes heterogeneous reactions such as gasification and combustion of solid fuel, drying and volatilization, thermal decomposition of limestone, thermal dissociation of slaked lime, reduction of iron oxides, and mineral melting and consolidation.

2.2.1. Gasification and Combustion of Solid Fuel

Coke is the main solid fuel used in the iron ore sintering, the combustion process consists of several elementary reactions. Coke combustion is an important parameter that determines the maximum temperature and flame thickness in the sinter, and the reaction equation is shown as Equation (6). The unreacted shrinkage model is used to describe the combustion process of coke particles. The combustion rate depends on the mass transfer in the film boundary layer, chemical reaction, and ash diffusion process. The reaction rate is Equation (7) [29,30].

$$R_{\text{coke}} = \frac{n_c \cdot 4\pi r_c^2 C_{\text{O}_2}}{\frac{1}{\varepsilon k_c} + \frac{\varsigma_j d_p}{Sh \cdot D_{\text{CO}_2,eff}} + \frac{\delta}{\varepsilon_j e^{-B\delta} \cdot D_{\text{O}_2}}}, \quad (7)$$

where $k_c = 1.715 \cdot T_s \cdot \exp(-74830/R_g T_s)$, $Sh = 2 + 0.7\text{Re}^{0.7} \text{Sc}^{0.33}$, $\delta = r_0 - r_c$.

2.2.2. Evaporation and Condensation of Water

The water content of the sintered raw material after mixing is generally 8%–12%. Evaporation and condensation occur in the preheating drying zone and the excessive wet zone of the sintered layer. Moreover, the reaction equation is $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$. The evaporation of water is mainly controlled by the actual partial pressure of water vapor on the surface of the solid-phase material and the saturated water vapor pressure at that temperature. The evaporation and condensation rates are expressed as follows [24,25]:

$$\begin{aligned} R_{dry} &= \chi \cdot \beta_{\text{H}_2\text{O}} \cdot A_{ssa} / R_g T_g (P_{\text{H}_2\text{O}}^* - P_{\text{H}_2\text{O}}) \\ R_{conden} &= \beta_{\text{H}_2\text{O}} \cdot A_{ssa} / R_g T_g (P_{\text{H}_2\text{O}} - P_{\text{H}_2\text{O}}^*), \end{aligned} \quad (8)$$

where $\chi = \min(1, 1 - (1 - w)(1 - 1.796w + 1.0593w^2))$, and $P'_{\text{H}_2\text{O}} = \exp(25.541 - 5211/T_s)$.

2.2.3. Thermal Decomposition of Limestone

Limestone is the main flux in the sintering process. The decomposition reaction of limestone occurs when the bed temperature increases to the decomposition temperature during sintering. The reaction equation and rate are modeled as Equations (9) and (10) [31].

$$R_{limist} = \frac{n_L \cdot 4\pi r_c^2 (C_{\text{CO}_2}^* - C_{\text{CO}_2})}{\frac{\zeta_j dp}{Sh \cdot D_{\text{CO}_2, eff}} + \frac{d_0 \cdot 2\delta}{d_c \varepsilon_j^{1.41} \cdot D_{\text{CO}_2}} + \left(\frac{d_0}{d_c}\right)^2 \frac{4.1868 K_{eq}}{k_c R_g T_s}}, \quad (10)$$

where $K_{eq} = 101325 \cdot \exp(7.0099 - 8202.5/T_s)$, $k_c = 1520 \cdot \exp(-20143.4/T_s)$, $C_{\text{CO}_2} = K_{eq} / (1000 R_g T_s)$.

2.2.4. Thermal Dissociation of Slaked Lime

Slaked lime is derived from quicklime (CaO) and physical water added in the sintering raw material, and the reaction releases considerable heat that can effectively raise the temperature of the mixture and improve the gas permeability of the layer. The reaction equation and rate are presented as Equations (11) and (12), respectively [32].

$$R_{diss} = 1.18 \times 10^{18} \exp\left(\frac{-280400}{R_g T_s}\right) \cdot (P^* \exp\left(\frac{-138500}{R_g T_s}\right) / R_g T_s) \cdot S_0 m_c, \quad (12)$$

where $S_0 = (8.3 \pm 1) \times 10^3 \text{ m}^2 \cdot \text{kg}^{-1}$, $p^* = 1.834 \times 10^8 \text{ atm}$.

2.2.5. Reduction of Iron Oxides

The mixture of the sintered bed contains iron oxide. Given the presence of a reducing atmosphere, the iron oxide is easily reduced by CO, and the influence on the temperature field and gas component distribution in the sintering bed must be considered. The present study considered three stages of iron oxide reduction, that is, Equation (13). The reaction rate at each stage was calculated using Equation (14) [33].

$$R_{reduc} = k_i \cdot (m_0^{1/3} - m_c^{1/3})^2 \cdot m_0^{1/3} \quad (i = 1, 2, 3), \quad (14)$$

where $k_1 = 1.32 \times 10^6 \exp\left(-\frac{114000}{R_g T_s}\right)$, $k_2 = 3.06 \times 10^5 \exp\left(-\frac{68600}{R_g T_s}\right)$, $k_3 = 1.91 \times 10^5 \exp\left(-\frac{66000}{R_g T_s}\right)$.

2.2.6. Melting and Consolidation of Minerals

Melting and consolidation of minerals are the main factors that affect the structure and particle morphology of the sintered bed. The transformation process can be described as “solid-phase material→molten liquid phase→solidified phase.” The initial temperature of the melting is related to the composition of the solid-phase mixture. The melting initiation temperature and melting rate are expressed as follows [25].

$$\begin{aligned} T_{m,ini} &= 1380 + 21.22Al_2O_3 + 3.35SiO_2 - 1.8flux \\ R_{melt} &= 0.001 \cdot (T_s - T_{m,ini}) \cdot \rho_s. \end{aligned} \quad (15)$$

2.3. NO_x Generation and Reduction Model

The particle size of solid fuel coke during iron-ore sintering is generally 0–5 mm, which is similar to that of coal powder in a fluidized bed but relatively different from that in a pulverized coal furnace. The flue gas produced by coke combustion stays longer in the pore and coke-surface powder than does that produced by pulverized coal combustion, and the former is more conducive to NO_x reduction. The temperature during sintering generally does not exceed 1400 °C, and thermal NO_x forms through N₂ oxidation in air at high temperature. When the temperature is lower than 1800 K, almost no thermal NO_x is generated. Therefore, the models considered in the FGRS include mostly fuel NO_x formation and reduction by coke particles and CO. Figure 1 shows the char-N conversion process during combustion.

Figure 1. Conversion of char-N during combustion.

2.3.1. Fuel NO_x Formation Model

The solid fuel in iron-ore sintering primarily comprises coke particles and a small amount of anthracite. The volatile content is generally 1%–2%, so the NO_x generated by volatiles is neglected and only char-N conversion is considered. After the coke particles begin to burn, char-N is oxidized to form NO_x. According to previous research, the reaction equation is Char-N+O₂→NO_x. The fuel NO_x formation rate adopts the following model [21,34].

$$R_{NO,f} = \varphi \frac{\eta Y_N M_{NO}}{M_N} R_c. \quad (16)$$

2.3.2. NO_x Reduction Model

During iron ore sintering, the N on the surface of the coke particles reacts with O₂ to form NO_x. The generated NO_x diffuses, and some are adsorbed on the surface of coke particles to react with their active groups. Combined with previous experiments [21,35,36] and simulation studies, the reaction of NO with coke particles at high temperature is the first-order reaction of NO. The reaction equation of coke particle with NO is Char-C+NO→N₂+C(O). The reaction rate of single coke particle with NO is as follows.

$$R_{NO,c} = \eta k_{NO,c} P_{NO} S_c, \quad (17)$$

where $k_{NO,c} = 0.0045 \times \exp(-144000/R_g T_s)$.

Previous studies have shown that during sintering, coke can react with NO in the combustion zone, and CaO, MgO, and metal oxide have a certain catalytic effect on the CO reduction of NO.

The reaction is $\text{NO} + \text{CO} \rightarrow 0.5\text{N}_2 + \text{CO}_2$. The experimental study shows that the reaction between CO and NO is a first-order reaction. To simplify the model, only the reaction between CO and NO on the coke-particle surface is considered, the overall reaction rate can be expressed as follows [37,38]:

$$R_{\text{NO,CO}} = 3.68 \times 10^7 \exp(-108889/RT) C_{\text{NO}} C_{\text{CO}}. \quad (18)$$

2.4. Model Key Parameters and Numerical Methods

The main parameters involved in the numerical simulation include structural and physical parameters. The structural parameters mainly include the bed shrinkage rate, bed porosity, and solid particle size change. The physical parameters mainly include thermophysical parameters, gas-phase effective diffusion coefficient, and solid-phase heat conduction and radiation. The values and calculation formulas of the parameters are shown in Table 1.

Table 1. Key parameters in the model.

Key Parameter	Expression	Equation
Thermal property parameter	$\frac{1}{\rho_s} = \sum \frac{\gamma_i}{100\rho_{s,i}}$ $C_{pg} = \sum \gamma_i C_{pg,i}$ $\frac{1}{\lambda_g} = \sum \frac{\gamma_i}{100\lambda_{g,i}}$ $\frac{1}{\rho_s} = \sum \frac{\gamma_j}{100\rho_{s,j}}$ $C_{ps} = \sum \gamma_j C_{ps,j}$ $\frac{1}{\lambda_s} = \sum \frac{\gamma_j}{100\lambda_{s,j}}$	(19)
Gas-phase effective diffusion coefficient [39]	$D_{i,eff} = \frac{\varepsilon_{ash}}{\tau} D_i \cdot D_k / (D_i + D_k)$ $D_k = \frac{d_p}{3} \cdot \left(\frac{8R_g T_g}{\pi M_i} \right)^{0.5}$	(20)
Bed shrinkage [25]	$f_s = M_f^\omega \cdot f_{s,max}$ $f_{s,max} = 0.15$	(21)
Bed porosity [24]	$\varepsilon = \varepsilon_0 + \left(\frac{\varepsilon_0 - \varepsilon}{\varepsilon_0 - 0.07} + \frac{f_s}{1 - f_s} \right) (1 - \varepsilon_0) + \sum_{m=1}^2 \left(n_m \cdot \frac{\pi}{6} (d_0^3 - d_c^3) \right)$	(22)
Solid particle size change [26]	$d_p = \left[(1 - f_{ash}) F d_0^3 + f_{ash} d_0^3 \right]^{1/3}$	(23)
Gas–solid convection heat transfer	$h_{conv} = \lambda_g \cdot (1 + 1.5(1 - \varepsilon)) (2 + \text{Re}^{0.6} \text{Pr}^{0.333}) / \varepsilon d_p$	(24)
Solid-phase heat conduction and radiation [40]	$\lambda_{s,total} = (1 - \varepsilon) \lambda_s + 4\sigma \varepsilon d_p T_s^3$	(25)
Solid convection coefficient [41]	$h_{j2-j1} = 2 \sqrt{\frac{(1 - \varepsilon_{j1}) \lambda_s \rho_s C_{ps} + \varepsilon_{j1} \lambda_p C_p}{\pi((1 - \varepsilon_{j1}) T_s + \varepsilon_{j1} T_g)}} \frac{1 - \varepsilon_{j1}}{1 - \varepsilon_{j2}}$	(26)

The solution process of flow, heat, and mass transfer problems in this study is based on the C# programming language. First, the region is discretized, and the rectangular coordinates are established for the sintered layer. The top of the bed layer and the ignition furnace entrance point are the origins, and the mesh is divided. In accordance with the control volume of the node at a certain moment, the mass or energy balance is used to discretize the equation, and the tridiagonal matrix method is used to solve the problem. Considering that the nucleation model based on the kinetic reaction is used in calculating the reaction submodel, the grid space step size is $\Delta x = 2.5$ mm, and the time step size is $\Delta t = 0.5$ ms. In the solution process, the boundary conditions of the inlet are adjusted in accordance with the stage of the trolley.

2.5. Initial and Boundary Conditions

Using the developed model and calculation program, the sintering machine of a domestic steel plant is studied. The length of the sintering machine is 88.8 m, the sintering-bed thickness is 680 mm, the running speed is $2.5 \text{ m} \cdot \text{min}^{-1}$, and the flue gas of 1–5# and 20–23# bellows is extracted, sending to the 6–16# (i.e., 23 m–67 m) bellows for recycling. Figure 2 shows the FGRS process.

The actual production conditions of the sintering machine are set as the initial and boundary conditions of the calculation program. According to the characteristics of the sintering, the boundary conditions of the sintering simulation zone are divided into ignition, insulation and sintering zones.

In the ignition zone (0–4 m), the ignition temperature is 1150°C , the ignition fuel is coke oven gas, the suction air temperature is 30°C , the temperature in the insulation zone (4–9 m) is 450°C , and the inhalation component is air. The input gas temperature and gas composition in the cyclic sintering zone (23–67 m) will be listed in the simulation case. In the other sintering areas, the inhalation component is air and the inhalation air temperature is 30°C . Table 2 shows the mixing ratio and

chemical composition of the raw materials. As an important initial condition for the study, the initial temperature of the solid phase is set at 55 °C.

Figure 2. Flue gas recirculation sintering (FGRS).

Table 2. Proportion and chemical composition of raw materials for sintering (wt.%).

Solid Phases	Proportion	SiO ₂	Al ₂ O ₃	CaO	TFe	MnO	N	S	Moisture
Coal char	3.20	5.45	3.96	0.49	0.42	0.05	0.89	0	13.62
Iron ore fines	62.58	4.73	1.60	1.42	59.62	0.76	-	0.24	7.95
Returned fines	26.04	4.98	1.82	8.76	58.83	1.56	-	0.28	0.32
Limestone	4.15	1.89	0.57	52.91	0.11	1.07	-	0.02	5.2
Dolomite	2.56	0.74	0.38	31.47	0	20.65	-	0	3.67
Burnt-lime	1.47	1.09	0.34	52.66	0.08	0.47	-	0.04	-

Moreover, the pressure at the top of the sinter bed is considered to be 1.0 atm, the radiation heat transfer is neglected, the heat and mass losses at the outlet boundary are not considered, and the gradient of all parameters is set to zero. The mixture temperature is set to be equal to the gas temperature in the sinter bed.

3. Results and Discussion

The reliability of the model is verified by comparing the simulated values with the experimental one. First, the effects of circulating gas O₂ content, gas temperature and gas supply on NO_x emissions in flue gas are studied. Second, the influence of coke parameters on NO_x emissions is examined. Finally, the cycle conditions are designed using the CS calculation results, and the energy-saving and emission-reduction effects of the cyclic sintering compared with CS are calculated.

3.1. Model Verification

To verify the accuracy of the model used, through the sintering pot experiments, the temperature of the layer from the bottom to the top at 225 mm and 525 mm are measured. A portable MRU flue gas analyzer was used to measure the variation of the main components (O₂, CO₂, and CO) in flue gas, as also described in previous work [23,24]. Using the simulation system, the initial and boundary conditions of the simulation are set to the experimental conditions of the sintering pot. Ignoring the heat and mass losses at the exit boundary, the gradient of all parameters is considered to be zero. The comparison curves between calculated and measured temperatures at typical bed layers of sintering machine are shown in Figure 3. The calculated results of O₂, CO₂, and CO in flue gas and the measured results is shown in Figure 4.

Figure 3 shows that the calculated value of the model is basically consistent with the test value, but the rapid heating points of the measuring points differ from the simulated values. The main

reason is the positional shift of the thermocouple caused by the melting and pumping action of the bed layer in the sintering pot experiment. Figure 4 shows that after ignition and heat preservation, i.e., from 200 s to 1400 s, the O_2 , CO_2 , and CO contents in the sintering state stabilize until the end of sintering, which is also called the steady-state sintering stage. A difference between the calculated and experimental flue gas composition is observed near the endpoint of sintering, and the calculation process is slightly faster than the sintering pot experiment. This finding is probably due to the fact that the coke size assumption in the coke-combustion model is based on the average size of coke within each particle-size range, which differs from the fact.

Figure 3. Comparisons between simulated and measured data of bed-layer temperature.

Figure 4. Comparison of simulated and measured values of the main components of flue gas.

Considering that sintering-pot experiment previously does not measure NO_x content, to further verify the reliability of the NO_x model, the initial and boundary conditions of the simulation system are set to the experimental conditions of Gan et al. [6] The simulated values of NO_x formation, reduction, and overall emissions in the FGRS are shown in Figure 5.

Figure 5. Comparison of NOx simulated and measured results.

The calculation results show that the fuel NOx production in the steady-state sintering stage is about 685 ppm, and that the fuel NOx is derived primarily from char-N, in which NOx accounts for more than 90%. This value is related to the nitrogen content of the fuel, bed-layer temperature, and O₂ content, which are crucial to the NOx emissions. Thermal NOx is almost negligible because thermal NOx can be produced only when the temperature exceeds 1800 K and lasts for a certain time. Moreover, Figure 5 shows that the reduction of NOx by coke particles is about 354 ppm, accounting for about 51.6% of the overall formation. The main reason is that the reduction of NOx on the surface of coke particles is relatively strong during NOx diffusion. In addition, the CO generated on the coke surface during combustion partially diffuses into the coke pores and oxidized to form CO₂ in the reaction layer, and the other part is reduced with NOx around the coke particles. The amount of NOx reduced by CO is about 56 ppm, so the reduction of NOx by CO during sintering is obvious.

To compare the calculations and experimental results, the maximum bed-layer temperature (MaxT; °C), flame front speed (FFS; mm/min), and steady-state flue gas composition values during sintering are summarized in Table 3. During sintering, the melting and crystallization states of the materials are usually characterized by MaxT, and the sintering yield and utilization factor are characterized by FFS. Table 3 shows that the relative errors of the key parameters and flue gas components in sintering are less than 4%, which indicates that the established model can well reflect the actual process.

Table 3. Comparison of simulation and measured results.

Parameter	MaxT (°C) X = 225 mm	MaxT (°C) X = 525 mm	FFS (mm·min ⁻¹)	SSWGC			
				NOx (ppm)	CO (vol.%)	CO ₂ (vol.%)	O ₂ (vol.%)
Simulated	1385.05	1295.75	25.64	274.7	1.49	11.65	10.86
Measured	1346.35	1304.28	26.56	268.1	1.46	11.58	11.15
Relative error	2.94%	0.67%	3.59%	2.40%	2.01%	0.60%	2.67%

3.2. Effect of Circulating Flue Gas Characteristics on NOx Emissions

In FGRS, part of the flue gas in the sintering bed is reused, which is of great significance for the clean production of sinter because of the recovery of flue gas waste heat, the reduction of energy consumption, and decrease in the overall flue gas and NOx emissions. Given that the physical and chemical changes in flue gas recirculation are affected by the flue gas conditions in the recirculation hood, the effects of the circulating gas O₂ content, temperature, and gas supply on NOx emissions in flue gas are studied. Table 4 shows the simulation conditions determined according to the single factor principle. The parameter value range basically covers the practical production process of cyclic

sintering. Notably, the circulation area is calculated according to the CS simulation results and the designed circulation scheme. The NO_x content in the inhaled flue gas in the recirculation hood region is calculated to be 82 ppm, and during the single-factor analysis, the inhaled flue gas NO_x concentration is considered to be unchanged.

Table 4. Simulation case.

Case	O ₂ Content (vol.%)	Temperature (°C)	Gas Supply (Nm·s ⁻¹)
GasO ₂ -*	17, 19, 21	200	0.6
GasV-*	19	200	0.5, 0.6, 0.7
GasT-*	19	100, 200, 300	0.6

3.2.1. Circulating Gas O₂ Content

The burning rate of coke in the sintered bed layer depends mostly on the O₂ content around the coke particles in the combustion zone, so the O₂ content of the circulating flue gas has a significant influence on NO_x emission in sintering. With the remaining parameters unchanged, the variation curves of bed temperature and NO_x, O₂, and CO contents in flue gas under various cyclic gas O₂ contents (17 vol.%, 19 vol.%, and 21 vol.%) are simulated, as shown in Figure 6.

Figure 6. Effects of circulating gas O₂ content on the NO_x, CO and O₂ contents in flue gas and layer temperature.

According to Figure 6a,b, with increased O₂ content of the circulating flue gas from 17 vol.% to 21 vol.%, the rapid heating point of the circulating zone is advanced, and less distance to the bottom of the sintering bed layer means faster temperature increase. Considering the heat storage of the layer, a closer MaxT to the bottom of the layer means more obvious. The highest temperature of the layer affects the melting state and is a key factor affecting the sinter quality.

According to Figure 6c, with increased circulating flue gas oxygen content from 17 vol.% to 21 vol.%, the flame-propagation speed increases, the sintering endpoint advances, the CO content

decreases, and the combustion consumption of O_2 increases. At this time, sufficient gas supply of circulating gas is likely to cause overburning. Figure 6d shows that the flue gas recirculation zone (23–67 m) is significantly higher than that in CS. Thus, when the O_2 content in the circulating flue gas is 17 vol.%, the NO_x emission level is about 309 ppm, whereas when the O_2 content in the circulating flue gas is 21 vol.%, the NO_x content increases to 357 ppm (about 15.5% higher than that under the 17 vol.% O_2 operating condition). The main reason is that with increased O_2 content and coke-combustion efficiency, the char-N release rate increases and the circulating flue gas O_2 content increases to promote the secondary combustion of CO. Moreover, the reducing atmosphere is weakened, resulting in higher NO_x emission level. If the O_2 content of the circulating flue gas is low, the adsorption of free oxygen by char-N decreases, the rate of NO_x formation is reduced, and part of NO_x is reductively decomposed through homogeneous and heterogeneous reactions.

3.2.2. Circulating Gas Temperature

The flue gas recycling can make full use of flue gas sensible heat, reduce solid fuel consumption, and conducive to environmental protection. However, the location of the selected flue gas is different, the flue gas temperature is very different, the flue gas temperature affects the quality of the sintered ore, when the flue gas temperature is too low, which will affect the fuel combustion inside the sintered layer, increasing the temperature of the circulating gas easily causes the exhaust pipe to be exhausted. the variation curves of bed temperature and NO_x , O_2 , and CO contents in flue gas under various cyclic gas temperature (100 °C, 200 °C, and 300 °C) are simulated, as shown in Figure 7.

Figure 7. Effects of circulating gas temperature on the NO_x , CO and O_2 contents in flue gas and layer temperature.

Figure 7a,b show that the rapid heating point of the sintering bed at $x = 550$ mm is almost unaffected because the heating process has been completed before entry into the flue gas recirculation zone. With increased temperature of the circulating flue gas from 100 °C to 300 °C, the maximum temperature of the bed layer is obviously improved and the heat storage of the bed layer is enhanced, which can

improve the quality of the sintered ore. Figure 7c,d show that the O_2 content in the circulation region is lower than that of conventional sintering, which may cause sintering delay. However, increased circulating gas temperature promotes flame-propagation speed, further increasing the consumption of O_2 , the burning rate of coke, and the release rate of NO_x . With increased temperature of circulating flue gas from $100\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$, O_2 concentration in the circulating area decreases from 12.4 vol.% to 10.8 vol.%, and NO_x emission increases from 313 ppm to 351 ppm, an increase of about 12.1%.

Notably, the increase in circulating flue gas temperature promotes coke combustion and NO_x production rate. Conversely, the increase in combustion rate increases O_2 consumption, and the resulting oxygen-poor atmosphere is conducive to NO_x reduction. In addition, the flue gas inhaled in the circulation area contains a certain concentration of NO_x , which increases the partial pressure of NO_x in the circulation area and promotes the reduction of NO_x .

3.2.3. Circulating Gas Supply

Sintering may actually be induced by the excessive wet belt moving down, so the flame front approaches the bottom of the layer. The thinner wet belt leads to larger porosity and particle size of the sintered layer; thus, gas flow capacity is enhanced. Consequently, the gas volume through the sintered layer changes. Therefore, the amount of circulating gas supply is closely related to the sintering process and NO_x emission levels. The curves of the sintering bed temperature and the NO_x , O_2 , and CO contents in flue gas under various circulating gas velocities (0.5 , 0.6 , and $0.7\text{ Nm}\cdot\text{s}^{-1}$) are simulated, as shown in Figure 8.

Figure 8. Effects of circulating gas supply on the NO_x , CO , and O_2 contents in flue gas and layer temperature.

Figure 8a,b shows the significant influence of circulating flue gas supply on bed temperature and NO_x emission. With increased circulating flue gas supply, the rapid heating point is advanced, and less distance to the bottom of the bed means earlier rapid heating point. In other words, the gas supply can improve the combustion efficiency of coke; however, in the actual production process, the increase

in gas supply increases the O_2 flux and combustion efficiency. At the same time, the increase in gas supply enhances the convective cooling effect of the sinter layer and increases the heat loss caused by combustion.

Figure 8c,d shows that with increased circulating-gas supply, the O_2 content in the flue gas recirculation area decreases from 11.9 vol.% to 10.3 vol.%, the NO_x content increases from 303 ppm to 358 ppm, the emission level increases by 18.2%, the flame-propagation speed is accelerated, the sintering endpoint is advanced, and the NO_x content decreases rapidly. Evidently, with increased circulating-gas supply, the coke combustion efficiency increases and the char-N release rate increases. At the same time, the consumption of O_2 increases, the O_2 content in circulating flue gas decreases, the content of CO increases, and the reducing atmosphere is enhanced, which are conducive to NO_x reduction and decreased NO_x emissions. In addition, the high material layer temperature is beneficial to the formation of a liquid phase and promotes the transformation of NO_x to N_2 .

3.3. Effect of Coke Particle Size and Coke Rate on NO_x Emissions

Different coke particle sizes cause differences in porosity and specific surface area, thereby affecting the concentration of gas phase components and gas-flow resistance in the pores of coke particles. Coke provides the energy required for sintering, and the coke rate affects the decomposition of the flux and the formation of the liquid phase. The effects of coke particle size and content on flue gas recirculation and overall NO_x emissions are discussed below. Table 5 shows the simulated conditions determined according to the single factor principle. During analysis, we consider that the inhaled NO_x content in the flue gas circulation area does not change.

Table 5. Simulation case.

Case	Coke Size (mm)	Coke Rate (%)	O_2 Content (vol.%)	Temperature ($^{\circ}C$)	Gas Supply ($Nm \cdot s^{-1}$)
size-*	1.5, 1.7, 1.9	3.2	19	200	0.6
rate-*	1.7	3.0, 3.2, 3.4	19	200	0.6

3.3.1. Coke Particle Size

With decreased particle size of a single coke, the effective reaction area of the combustion interface decreases, and the combustion efficiency remarkably decreases. However, for coke combustion per unit mass, the refinement of coke particles can increase the total surface area, thereby increasing the combustion rate and promoting full contact between NO_x and the coke surface. The effects of coke particle with equivalent diameters of 1.5, 1.7, and 1.9 mm on NO_x , O_2 , and CO emissions in flue gas and MaxT are simulated, as shown in Figure 9.

Figure 9a,b shows that with the refinement of coke particles, the number of coke particles per unit mass increases, the comprehensive combustion rate increases, and MaxT increases. Moreover, less distance to the bottom of the bed means a thicker high temperature zone and increased sinter strength. At the same time, O_2 consumption increases, O_2 content decreases from 11.3% to 9.7%, the inhibition of coke combustion is enhanced, the reducing atmosphere is enhanced, and the finished product rate is reduced. Thus, the O_2 content in the circulating hood should be kept close to air as much as possible.

Figure 9c,d shows that with decreased coke particle size, NO_x emission increases from 318 ppm to 360 ppm, an increase of about 13.2%. When the coke particle size is 1.5 mm, the comprehensive coke combustion rate increases, and the char-N release rate in the flue gas recirculation zone increases. Conversely, the coke surface area per unit mass increases such that the coke particles can make full contact with NO_x and thus promote the reduction of NO_x by coke particle and CO. At this time, the reduction rate is about 61.4%, which is conducive to reducing NO_x emissions. However, in the actual production process, considering the control of production costs, achieving superfine coke is impossible. At present, the equivalent particle size of coke for sintering is controlled at 1.5–2.0 mm. Screening of coke with smaller particle size is beneficial to the actual production process of flue gas recirculation, which is beneficial to the reduction of NO_x emissions.

Figure 9. Effects of coke size on NOx, CO, and O_2 contents in flue gas and MaxT.

3.3.2. Coke Rate

As a sintering fuel, coke content promotes flux decomposition and sintering liquid-phase formation. Fuel carbon and fuel nitrogen are the main sources of NOx release during sintering. To study the effects of coke rate on the temperature of the sinter bed layer and NOx emissions, the curves of NOx, O_2 , and CO contents in flue gas and MaxT (Maximum temperature) are simulated under the conditions of various coke contents (3.0%, 3.2%, and 3.4%), as shown in Figure 10.

Figure 10a,b shows that increased coke content increases the average temperature of the layer, and less distance to the bottom of the sintered bed layer means a higher MaxT. Consequently, the quality of the sintered ore is improved. With increased coke content, more heat is generated, the flame-propagation speed increases, and the vertical sintering speed increases, so the sintering endpoint is advanced. The increase in solid fuel increases the O_2 consumption, decreases the O_2 content in the circulation region from 11.5% to 9.9%, and enhances the reducing atmosphere.

Figure 10c,d shows that with increased coke rate, the NOx content increases from 306 ppm to 369 ppm, which is an increase of about 20.6%, and the reduction rate is 62.1%. The oxidation reaction of coke particles and O_2 and the reduction of coke particles and NOx are all strengthened, i.e., the amount of NOx formed and reduced increases with increased coke content. At the same time, the increase in coke content can increase the coke burning rate and increase the vertical sintering speed such that the sintering endpoint is reached in advance and the NOx content rapidly drops earlier. In summary, increased coke content means increased char-N, NOx emissions, and reduction rate of coke particle and CO.

Figure 10. Effect of coke rate on NO_x, CO, O₂ content in flue gas and MaxT (Maximum temperature).

3.4. Analysis of Energy-Saving and Emission-Reduction Features of FGRS

Conventional sintering has the problems of difficulty in utilizing waste heat and high cost of flue gas treatment. From the perspective of economy and technology, FGRS is advantageous over CS because FGRS can effectively use the flue gas heat to replace the chemical heat of solid fuel. Consequently, the amount of solid fuel, Char-N incorporation, and the amount of flue gas treatment are reduced. The efficiency of denitrification treatment is also improved, yielding significant economic benefits. According to the simulation results of CS, according to the cycle sintering design (i.e., the flue gas of the #1–#5 and #20–#23 bellows is sent to the #6–#16 bellows), the air leakage rate is calculated at 30%. Then, the flue gas composition and state of circulation area are calculated based on the exhaust emission law, as shown in Table 6.

Table 6. Simulation case.

Case	O ₂ Content (vol.%)	Temperature (°C)	Gas Supply (Nm·s ^{−1})	Coke Rate (%)	NO _x (ppm)
CS	21	30	0.437	3.2	0
FGRS	18.06	226	0.5465	3.08	104

3.4.1. Comparison of Flue Gas Recirculation Sintering and Conventional Sintering

We take a domestic 650 t/h sintering machine as the research object for flue gas circulation sintering. Given that the sensible heat and latent heat of the circulating flue gas are fully utilized, the coke content in sintering raw materials can be reduced appropriately. According to the simulation results, with decreased coke rate of sintering raw material from 3.2% to 3.08% in flue gas recirculation, the sintering endpoint temperature (defined in this study as the temperature at each thickness of the point layer $x = 30$ mm) is basically the same as the CS endpoint temperature. At this time,

the temperature of the material layer and the O₂, CO, and NO_x contents in the flue gas of cyclic sintering and CS are nearly unchanged. The content simulation results are shown in Figure 11.

Figure 11a shows that when the conventionally sintered coke content is 3.2%, the maximum temperature of each bed layer is the same as that of the recirculated sintered coke content of 3.08%. Outside the flue gas recirculation zone, the rapid heating point of the bed layer is slightly delayed because the coke content in this area is lower than that in CS, and the generated heat is slightly lower than that in CS. In the flue gas recirculation area, given the utilization of flue gas waste heat, less distance to the bottom of the layer means faster temperature increase in the layer, increased vertical sintering speed, and increased sinter output per unit time.

Figure 11b shows that decreased coke content before recirculated flue gas entry into the circulating region means lower char-N content and release rate of NO_x lower. When entering the flue gas recirculation region, the O₂ content in the flue gas is lower, the release rate of char-N is faster, and the inhalation flue gas contains some NO_x. Thus, the NO_x emission level in the circulating sintering zone is high.

Figure 11. Comparison of sinter bed temperature and flue gas composition of FGRS and CS cases.

3.4.2. Energy-Saving and Emission-Reduction Feature Analyses

- (1) **Coke energy saving:** For FGRS, the sensible heat and latent heat of the circulating flue gas can be fully utilized. Simulation results show that the coke content of the sintering raw material under the flue gas circulation sintering condition is reduced from 3.2% to 3.08%, i.e., 3.75% coke consumption is saved. Thus, the new process can be considered to appropriately reduce the solid fuel consumption, and its value is 1.2 kg/t sinter. If the sintering machine capacity is calculated according to the output of 650 t/h and an annual running time of 8000 h, the annual savings of coke powder is 6.24×10^6 kg, equivalent to 6061.5 tons of standard coal (conversion coefficient of 0.9714).
- (2) **NO_x emission reduction:** In the new process design, flue gas in the #6–#16 bellows is used as the flue gas used for circulation according to the air leakage rate of 30%. The total amount of CS flue gas is $108.8 \text{ Nm}^3 \cdot \text{h}^{-1}$, and the total flue gas of circulation sintering $122.4 \text{ Nm}^3 \cdot \text{h}^{-1}$, in which the circulating flue gas is $37.1 \text{ Nm}^3 \cdot \text{h}^{-1}$, i.e., the flue gas treatment volume is reduced by 21.64%. The calculation results of conventional and cyclic sintering flue gas volume and simulation results of NO_x content in flue gas reveal that the new sinter production unit can reduce NO_x emissions by 23.59%.
- (3) **Capacity increase:** Simulation results show that the endpoint of the FGRS is about 5 m ahead, i.e., the sintering cycle time is shortened. Thus, the sintering capacity can be increased by about 5.56% without changing the existing sintering equipment.

4. Conclusions

- (1) To study the flue gas recirculation, a relatively comprehensive one-dimensional unsteady mathematical model is proposed, which includes most of the main reactions during sintering and emission models of pollutants NO_x and SO₂. On this basis, the effects of flue gas characteristics and coke parameters on sinter-bed temperature, as well as the NO_x, O₂, and CO contents in flue gas, are investigated. Compared with CS, the energy-saving and emission-reduction effects of flue gas recycling are discussed.
- (2) With decreased O₂ content in circulating gas, coke combustion is inhibited, MaxT is significantly reduced, sintering is delayed, and NO_x emission is significantly reduced. With increased circulating gas temperature, the high-temperature zone thickness increases, MaxT significantly increases, and O₂ consumption increases. Consequently, the reducing atmosphere is enhanced and NO_x emission increases. With increased circulating gas supply, flame-propagation speed increases, MaxT remains unchanged, O₂ consumption increases, and NO_x concentration in flue gas increases. Thus, coke-combustion efficiency increases, O₂ consumption increases, char-N release rate increases, and O₂ content in flue gas decreases. Moreover, the reducing atmosphere is enhanced and the NO_x reduction by coke particle and CO is promoted, which are favorable for NO_x emission reduction.
- (3) Changing the coke particle size and rate during flue gas recycling has an important effect on the bed layer temperature and NO_x emissions. However, smaller coke particle size and increased coke rate result in significantly increased MaxT, increased O₂ consumption, sufficient contact of NO_x with the coke surface, and increased reducing atmosphere. Consequently, the NO_x reduction rate increases.
- (4) On the basis of the research object, the designed flue gas recirculation can save 3.75% of coke consumption, i.e., 1.2 kg solid fuel consumption per ton sinter can be reduced, the flue gas treatment capacity can decrease by 21.64%, and the sinter production unit can reduce NO_x emission by 23.59%. Sintering capacity also increases by about 5.56% without changing the existing sintering equipment.

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Nomenclature

A_{ssa}	the specific surface area of the solid phase particles, $m^2 \cdot m^{-3}$
C_{ps}, C_{pg}	specific heat capacity of solid and gas phase, $J \cdot kg^{-1} K^{-1}$
C_{NO}, C_{CO}	molar concentrations of NO and CO, $mol \cdot m^{-3}$
$D_{i, eff}$	effective gas diffusion coefficient, $m^2 \cdot s^{-1}$
d_p	equivalent particle size of solid phase, m
h_{conv}	convection coefficient, $W \cdot m^{-2} K^{-1}$
$h_{j1, j2}$	convection among solid phases, $W \cdot m^{-2} K^{-1}$
ΔH	chemical reaction heat, $kJ \cdot kg^{-1}$
K_{eq}	reaction equilibrium constant, -
$k_{NO, c}, k_{NO, CO}$	reaction rate constant, $kg \cdot cm^{-2} s^{-1} Pa^{-1}$
m_0, m_c	mass density of the initial particle and un-reacted part, $kg \cdot m^{-3}$
M_{NO}, M_N	molecular weights of NO and N, $kg \cdot kmol^{-1}$
P_{NO}	partial pressure of NO in the air, Pa
$R_{NO, f}$	release rate of fuel NO _x , $kg \cdot s^{-1} m^{-3}$

$R_{NO,c}, R_{NO,CO}$	reduction rate of NOx by coke particles and CO, $\text{kg}\cdot\text{s}^{-1}\text{m}^{-3}$
R_c	fixed carbon release rate, $\text{kg}\cdot\text{s}^{-1}\text{m}^{-3}$
Sh	particle Sherwood number, -
S_c	coke internal surface area, m^2
T_s, T_g	the temperature of the solid and gas phases, K
γ_i, Y_j	solid and gas phase mass fraction, -
u_s, u_g	solid phase velocity and gas velocity, $\text{m}\cdot\text{s}^{-1}$
n_c	particle number density, $\text{l}\cdot\text{m}^{-3}$
r_c	radius of unreacted part, m
Greeks	
β	mass transfer coefficient, $\text{m}\cdot\text{s}^{-1}$
ε	solid-phases porosity, -
f_{ash}	proportion of ash mass to total ash mass at the end of reaction, -
ρ_s, ρ_g	solid and gas phase density, $\text{kg}\cdot\text{m}^{-3}$
μ	gas dynamic viscosity, $\text{kg}\cdot\text{m}^{-1}\text{s}^{-1}$
ς	shape factor, -
$\lambda_{s, total}$	comprehensive thermal conductivity of porous media, $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$
λ_g	gas phase mixture thermal conductivity, $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$
κ	incomplete combustion coefficient, -
ξ	correction factor, -
δ	ash layer thickness, m
η	effective factor, -

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