Effects of Temperature and Circulating Flue Gas Components on Combustion and NO_x Emissions Characteristics of Four Types Quasi-particles in Iron Ore Sintering Process

Hao ZHOU,* Pengnan MA, Ming CHENG, Mingxi ZHOU and Yawei LI

State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou, 310027 China.

(Received on March 15, 2018; accepted on May 24, 2018)

It's significant to deeply understand the combustion and NO_x yield characteristics of quasi-particles in flue gas recirculation sintering process. In present study, effects of temperature and different circulating flue gas components on the mass conversion rate and conversion of fuel-N to NO_x of quasi-particles were investigated in a vertical quartz tube reactor. Four types quasi-particles were considered according to the existing state of coke in granules: C type, P type, S type and S' type. The mass conversion rate of four types quasi-particles ranked in the order of C > P > S > S' at different temperature. It was found that D₁ model was most appropriate to describe the combustion characteristics of S, S' and P type while D₃ model was better than other models to describe the combustion characteristics of C type quasi-particles through the comparison of correlation coefficients calculated by different mechanism models. Effect of circulating flue gas components on the conversion of fuel-N to NO_x of quasi-particles was studied. O₂ has a positive impact on the conversion of fuel-N to NO_x for S, S' and C type but an inhibitory effect for P type quasi-particles. CO₂ and CO could decrease the conversion rate of fuel-N to NO_x for all types quasi-particles. Effect of H₂O(g) on the conversion rate of fuel-N to NO_x was different for four types quasi-particles. The conversion rate of fuel-N to NO_x firstly increases then decreases for S', S and C type quasi-particles while continuously increases for P type quasi-particles with increasing H₂O(g) content.

KEY WORDS: quasi-particles; iron ore sintering; flue gas recirculation; NO_x emissions.

1. Introduction

In 2016 China's crude steel production was 808 million tons, accounting for 49.6% of the world's total crude steel production.¹⁾ Iron ore sintering, a critical process for steel production, provides agglomeration for blast furnace. Raw materials used in iron ore sintering process are mainly iron ore, coke, fluxes, etc. The grain size of iron ore, coke breeze, fluxes is no more than 10 mm, 5 mm and 3 mm, respectively. Raw materials were uniformly mixed and then granulated in drums with required water addition to increase the average particle size.²⁾ The process of iron ore sintering is the major source of NO_x emissions, occupying about 40% of the total NO_x emissions in the iron and steel industry.³⁾ NO_x removal in iron ore sintering industry has already become a significant research topic with stricter environmental protection policy.

Different types quasi-particles were formed in the process of granulation. The distribution state of coke in quasi-particles was affected by the granulating process. -0.25 mm coke particles would be uniformly distributed in the adhering fine layer, +1 mm coke particles are mostly free

particles, and medium fine coke particles (plus 0.25 mm minus 1 mm) are located in the outside of adhering fine layer and easy to fall off.^{4,5)} Maeda⁶⁾ evaluated quantitatively the distribution of coke breeze in the quasi-particles and the effects of particle size of iron ore and coke breeze on granulation properties. It was found that conversion of fuel-N to NO_x could be decreased by mixing iron powder and coke breeze.⁷⁾ Hida⁸⁾ divided the quasi-particles into four types according to the existing state of coke in quasi-particles: S type - single coarse coke particle coated with fine iron ore powder, P type - pellet of well mixed fine coke and fine iron ore powder, C type - large iron ore particle coated with fine coke and fine iron ore powder, S' type - free coke particle. The four types quasi-particles were shown in Fig. 1. Ohno⁹⁾ investigated the combustion rate of P type quasi-particles considering void rate and liquid formation. Hou¹⁰⁾ showed that the combustion rate of C type quasi-particles was higher than that of P type quasi-particles. Kasai¹¹⁾ pointed out that the combustion rate and average conversion rate of NO of S' type quasi-particles both decreased with increasing particle size. Gan^{12,13)} studied the effect of different granulating methods on the combustion characteristics of quasi-particles and proposed that fuel pre-granulation technology is conducive to inhibiting the conversion of fuel-N to NO_x during iron ore sintering. Katayama¹⁴⁾ found that lime coating coke

* Corresponding author: E-mail: zhouhao@zju.edu.cn

DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2018-185>

Fig. 1. Schematic diagram of four types quasi-particles.

Fig. 2. Schematic diagram of the conventional iron ore sintering and sintering with flue gas recirculation.

could decrease NO_x because of the formation of CF melt on coke surface. Numerical model was widely used to study the combustion behavior of fuel in iron ore sintering. Ogi H⁽¹⁵⁾ studied the effect of coke breeze distribution on coke combustion rate using unreacted core model. Kasai⁽¹⁶⁾ conducted the combustion rate of P type and S type quasi-particles using unreacted core model.

There are many researches focused on the methods of NO_x reduction in iron ore sintering. These methods to control NO_x contain selective catalytic reduction,⁽¹⁷⁾ selective non-catalytic reduction,⁽¹⁸⁾ flue gas recirculation,⁽¹⁹⁾ process parameter control,^(20,21) modification of fuel,⁽²²⁾ as well as biomass utilization, *etc.*^(23,24) Flue gas recirculation sintering is a potential method to reduce NO_x emissions. It has many advantages including decreasing fuel consumption and pollutant emissions, *etc.*⁽²⁵⁾ Figure 2 shows the conventional iron ore sintering process and flue gas recirculation sintering

process. Flue gas recirculation in iron ore sintering is a technique recycling part of the heating flue gas to the sinter bed. It's especially different in combustion atmosphere between conventional sintering and flue gas recirculation sintering process. The main gas components in flue gas recirculation sintering process were O₂, CO, CO₂, H₂O. The combustion of CO, providing heat for sintering process, affects the heat exchange between gas phase and solid phase in sinter zone. Coke combustion efficiency is influenced by O₂ and CO₂ concentration. Moreover, the content of steam affects the formation of over-wet zone since it influences the moisture content.⁽²⁵⁾ Chen⁽²²⁾ found the modification of coke in flue gas recirculation sintering process was conducive to decreasing the NO_x emissions. Fan and Chen^(26–28) determined appropriate circulating flue gas components concentration range by studying the effect of recirculating flue gas components on sintering parameters and coke combustion efficiency.

In conclusion, many researchers have investigated the combustion behavior of quasi-particles in conventional sintering conditions as well as the effect of flue gas recirculation on sinter quality, however there are little research about the effects of recirculating flue gas components on the combustion and NO_x emissions characteristics of different types quasi-particles. The present work may provide more fundamental understanding in optimizing the combustion behavior and decreasing pollutants emissions in iron ore sintering process.

In this study, a flow tube reactor was used to investigate the influence of temperature and recirculating flue gas components (O₂, CO₂, CO, H₂O) on the combustion and NO_x emissions characteristics of different types quasi-particles. The most appropriate models, which were used to describe the combustion characteristics of four types quasi-particles, were determined by calculating correlation coefficients between different mechanism models and time *t*. Then the influence mechanism of different circulating flue gas components on NO_x emissions characteristics of quasi-particles was revealed.

2. Experimental

2.1. Sample Preparation

The constitute and ratio of four types quasi-particles are listed in Table 1 according to the classification method by Hida.⁽⁸⁾ Coke and iron ore were screened to -0.25 mm and 2.0 – 2.8 mm, -0.25 mm for adhering fines and 2.0 – 2.8 mm for core particle. Limestone was sieved to -0.25 mm for adhering fines. The S type quasi-particles were made of 2 – 2.8 mm coarse coke particles adhering with -0.25 mm limestone and iron ore with the weight ratio of core to adhering layer being 3 to 1. The quasi-particles of P type were the mixture of -0.25 mm coke, limestone and iron ore with the weight ratio being 1: 0.5: 0.5. The C type quasi-particles had -0.25 mm coke and limestone adhering on nuclei particles of 2 – 2.8 mm iron ores. The quasi-particles of S' type were 2 – 2.8 mm single coke particles. The quasi-particles were prepared by an small experimental drum mixer. For S type quasi-particles, -0.25 mm limestone particles and iron ore particles were well mixed in the small experimental drum mixer first, 2 – 2.8 mm coke particles whose surfaces wetted with moderate moisture were mixed with them later. And similar for C type quasi-particles, -0.25 mm limestone

Table 1. Composition and mass ratio of four types quasi-particles.

Type	Core		Adhering layer			Weight ratio (core: adhering layer)
	species	size (mm)	species	size (mm)	ratio	
S	Coke	2–2.8	Limestone Iron ore	–0.25	1:1	3:1
P	–	–	Coke Limestone Iron ore	–0.25	1:0.5:0.5	–
C	Iron ore	2–2.8	Coke Limestone	–0.25	1:1	9:1
S'	Coke	2–2.8	–	–	–	1:0

Table 2. Chemical compositions of Raw materials (wt%).

Item	Fe	FeO	Al ₂ O ₃	SiO ₂	MgO	CaO	LOI1000
Iron ore	62.39	0.35	2.23	4.28	0.13	0.15	3.51
Limestone	0.36	0.1	0.98	2.23	0.48	53.40	42.00
Coke	1.07	0	4.32	6.11	0.04	0.62	86.85

Table 3. Ultimate and proximate analysis of coke.

Proximate analysis (%)					Ultimate analysis (%)				
M _{ad}	A _{ad}	V _{ad}	FC _{ad}	M _t	C _{ad}	H _{ad}	N _{ad}	S _{t,ad}	O _{ad}
1.12	13.42	1.61	83.85	12.02	83.26	/	1.10	0.71	0.39

particles and coke particles were well mixed in the small experimental drum mixer first, 2–2.8 mm iron ore particles whose surfaces wetted with moderate moisture were mixed with them later. For P type quasi-particles, –0.25 mm limestone particles, coke particles and iron ore particles with moderate water adding were well mixed in the small experimental drum mixer. As for S' type quasi-particles, they are 2–2.8 mm coarse coke particles only.

The diameters of all types quasi-particles used in tests were about 3 mm and the mass of different types quasi-particles used in tests was about 1 g. The mass fractions of coke were different in each quasi-particles, 5% for C type, 50% for P type, 75% for S type and 100% for S' type. The chemical compositions of raw materials and the ultimate and proximate analysis of coke were listed in **Tables 2** and **3**, respectively. All of the samples were dried in an oven at 378 K for 4 hours prior to the tests.

2.2. Experimental Apparatus and Operation Procedure

A laboratory-scale experimental rig was set up to investigate the effects of temperature and circulating flue gas components on the combustion and NO_x emissions characteristics of four types quasi-particles. **Figure 3** shows the schematic diagram of experimental system for quasi-particles combustion. The experimental system mainly consists of a vertical quartz tube reactor, a steam generator, a gas supply system, an electric balance and a gas analyzer. The quartz tube reactor was heated electrically and the temperature was controlled by a temperature controller with the accuracy of $\pm 1^\circ\text{C}$. The inner diameter and height of the quartz tube reactor are 60 mm and 500 mm, respectively. A platinum basket, in which about 1 g of quasi-particles

Fig. 3. Schematic diagram of the experimental rig for quasi-particles combustion.

located, was hanged by a platinum wire connected with the electric balance. A thermocouple was installed at the center of the reactor close to the location of the quasi-particles to control the reaction temperature accurately. The quasi-particles were put into the reactor quickly with the given temperature. The mass of quasi-particles was recorded by the electronic balance to calculate the mass conversion rate of quasi-particles in the combustion period. The electric balance used in this experiment was a METTLER TOLEDO AL204 with the sampling time of 1 s and the accuracy of 0.1 mg. The gas flow rates of N₂, O₂, CO₂ and CO were controlled by four ALICAT mass flow controllers (MFCs) with the accuracy of $\pm 0.5\%$. Furthermore, the flow rate of deionized water was controlled by a peristaltic pump calibrated in advance. The deionized water was carried by the supplied gas into the steam generator. In order to guarantee the complete evaporation of the deionized water, the temperature of the steam generator was set to 600°C. Meanwhile, O₂, N₂, CO, and CO₂ were also preheated in the steam generator before they were introduced into the reactor. It was time to end the experiment when the sample weight remained the same.

In order to study the effect of circulating flue gas components on NO_x emissions characteristics of different types quasi-particles, the inlet gas compositions (O₂+N₂, O₂+N₂+CO₂, O₂+N₂+CO, O₂+N₂+H₂O) were introduced into the reactor in the experiments. The total flow rate of the inlet gas was set to 5 NL/min to maintain the same boundary condition. The flue gas composition was measured by Testo 350 gas analyzer with the sampling time of 5 s. To investigate the influence of temperature on combustion characteristics of quasi-particles, the experiments were conducted at different temperature (1 073 K, 1 173 K, 1 273 K) with the gas atmosphere of O₂/N₂=21%/79%. In present work, 64 tests were designed to study the influence of circulating flue gas components on NO_x emissions characteristics of four types quasi-particles based on components and proportions of circulating flue gas of different flue gas recirculation ratio in sintering process.²⁵⁾ All of the circulating flue gas conditions were listed in **Table 4**, such as O₂ content in circulating flue gas varied from 12% to 21%, CO₂ from 3% to 12%, CO from 0.5% to 2%, and H₂O(g) from 5% to 20%.

Moreover, It should be mentioned that at least 3 parallel tests had been done for effect of temperature on conversion

Table 4. Gas components conditions in the experiments.

Factors	Circulating flue gas components (%)			
	O ₂	CO ₂	CO	H ₂ O(g)
O ₂ content	12, 15, 18, 21	0	0	0
CO ₂ content	21	3, 6, 9, 12	0	0
CO content	21	0	0.5, 1.0, 1.5, 2.0	0
H ₂ O(g) content	21	0	0	5, 10, 15, 20

The rest part of circulating flue gas was filled by N₂.

of fuel-N to NO_x of four types quasi-particles and similar results were obtained.

2.3. Analysis Method

NO_x formation mechanism includes thermal NO_x, prompt NO_x and fuel NO_x. The formation temperature of thermal NO_x is more than 1 800 K, however the highest temperature in sinter bed was only about 1 600 K. Therefore there was little thermal NO_x in iron ore sintering process.²⁹⁾ Prompt NO_x is mainly from the impact of N₂ molecules and CH radicals generated by the decomposition of fuel. The fuel generally used in iron ore sintering was coke, which contains low volatile matter content and high fixed carbon content. Hence the generation of prompt NO_x could be neglected. The NO_x in iron ore sintering is mainly from fuel NO_x.

In order to quantify the NO_x emissions in the process of quasi-particles combustion, the conversion rate of fuel-N to NO_x during quasi-particles combustion was calculated by following equation:

$$\eta = \frac{Q \times M_N}{60 \times 22.4 \times m_0 \times w_1 \times w_2} \times \int_{t_0}^{t_1} C(NO_x) \times 10^{-6} dt \times 100\% \quad (1)$$

where Q is total gas flow rate (L/min), t_0 and t_1 are the starting time and terminal time of NO_x calculation (s), $C(NO_x)$ is the NO_x concentration (ppm), t was time (s), M_N is the molar mass of nitrogen atoms (g/mol), m_0 is the initial mass of quasi-particles (g), w_1 is mass fraction of coke in quasi-particles (%), w_2 is the mass fraction of N_{ad} (%). 22.4 is molar volume of gas (L/mol).

3. Kinetic Analysis

3.1. Data Analysis

In the experiments with different temperature, the mass reduction of sample was considered to be mainly caused by the following chemical reactions.^{9,30)}

Sample mass conversion rate could be defined as follows:

$$x(t) = \frac{m_0 - m_t}{m_0 - m_\infty} \times 100\% \quad (2)$$

Table 5. Different reaction mechanism functions of $f(x)$ and $G(x)$.

code	Reaction model	Differential $f(x)$	Integrate $G(x)$
S _m	Shrinking core model	$m(1-x)^{\frac{m-1}{m}}$	$1-(1-x)^{\frac{1}{m}}$
R _{1/2}	$m=1/2$	$\frac{1}{2}(1-x)^{-1}$	$1-(1-x)^2$
R _{1/3}	$m=1/3$	$\frac{1}{3}(1-x)^{-2}$	$1-(1-x)^3$
R _{1/4}	$m=1/4$	$\frac{1}{4}(1-x)^{-3}$	$1-(1-x)^4$
R ₂	$m=2$	$2(1-x)^{\frac{1}{2}}$	$1-(1-x)^{\frac{1}{2}}$
R ₃	$m=3$	$3(1-x)^{\frac{2}{3}}$	$1-(1-x)^{\frac{1}{3}}$
D _m	Diffusion model		
D ₁	Dimensional diffusion	$\frac{1}{2}x^{-1}$	x_2
D ₂	Two-Dimensional diffusion	$[-\ln(1-x)]^{-1}$	$x + (1-x)\ln(1-x)$
D ₃	Three-Dimensional diffusion	$\frac{3}{2}(1-x)^{\frac{2}{3}} \left[1 - (1-x)^{\frac{1}{3}} \right]^{-1}$	$\left[1 - (1-x)^{\frac{1}{3}} \right]^2$

where $x(t)$ was the sample mass conversion rate (%), m_0 and m_∞ are the initial and final mass of the sample, respectively (g), and m_t is the mass of the sample at time t (g).

3.2. Mechanism Model

The product of two independent functions was used to present the reaction rate for gas-solid reaction. The reaction rate of quasi-particle could be expressed as follows:

$$\frac{dx}{dt} = kf(x) \quad (3)$$

where, k was the total reaction rate constant for quasi-particle combustion, $f(x)$ was proper mechanism model used to describe the reaction.

Equation (3) could be rewritten as:

$$\frac{dx}{f(x)} = kdt \quad (4)$$

Integrate Eq. (4), the conversion time was a constant for certain quasi-particle:

$$\int_0^{x_1} \frac{dx}{f(x)} = \int_0^{t_1} kdt = kt \quad (5)$$

$$G(x) = \int_0^{x_1} \frac{dx}{f(x)} \quad (6)$$

$$G(x) = kt \quad (7)$$

where $G(x)$ was the mechanism function, t was time (s).

The most suitable mechanism function could be obtained through the comparison of correlation coefficients between $G(x)$ and t using different models. The ordinary models and mechanism functions were listed in **Table 5**.

4. Results

4.1. Combustion Characteristics of Quasi-particles at Different Temperature

In order to explore the effect of reaction temperature on the combustion characteristics of quasi-particles, three temperature (1 073 K, 1 173 K, 1 273 K) were considered. The mass conversion rate of C type quasi-particles at different temperature was shown in Fig. 4(a). From this figure, it was found that the mass conversion rate of C type quasi-particles was larger with higher temperature. Although not shown, the other three types quasi-particles also showed the same tendency. The results obtained were in good agreement with those of other investigators.^{9,16)}

Figure 4(b) shows the mass conversion rates of four types quasi-particles at 1 273 K. It could be obtained that the mass conversion rates were high in the initial stage and then gradually slowed down. The mass conversion rate of four types quasi-particles ranked in the order of C>P>S>S'. Although not shown, this phenomenon could be observed at all temperature investigated.

The correlation coefficients of four types quasi-particles at different temperature were calculated to find the most appropriate mechanism function for quasi-particles com-

bustion. The calculated results were shown in Table 6. As shown in Table 6, D₁ model was the most appropriate model for S, S', and P type quasi-particles. Nevertheless, D₃ model was better than other models for C type quasi-particles.

To further investigate the relation between reaction rate of quasi-particles and temperature. The total reaction rate constants of four types quasi-particles at different temperature were derived using the most applicable mechanism function. Figure 5 shows the temperature dependence of apparent total reaction rate of four types quasi-particles at different temperature. The apparent total reaction rate constants of different types quasi-particles ranked in the order of C>P>S>S'. This result was agreed well with previous results in this work. The apparent total reaction rate constants of four types quasi-particles at different temperature were listed in Table 7.

The formation rate of NO_x was proportional with combustion rate of quasi-particles. Apparent total reaction rate constant of C type quasi-particles was greater than other three types quasi-particles. Therefore, NO_x could be decreased by reducing the ratio of C type quasi-particles in

Table 6. Correlation coefficients of four types quasi-particles at different temperature according to different mechanism models.

Type	Temperature	Correlation coefficient of different mechanism models							
		R _{1/2}	R _{1/3}	R _{1/4}	R ₂	R ₃	D ₁	D ₂	D ₃
S	1 073 K	0.922	0.850	0.789	0.995	0.982	0.991	0.973	0.897
	1 173 K	0.927	0.849	0.777	0.987	0.963	0.992	0.966	0.857
	1 273 K	0.915	0.825	0.739	0.989	0.967	0.998	0.976	0.865
S'	1 073 K	0.903	0.823	0.756	0.994	0.980	0.991	0.975	0.903
	1 173 K	0.908	0.828	0.758	0.993	0.974	0.993	0.978	0.892
	1 273 K	0.918	0.838	0.769	0.991	0.971	0.994	0.966	0.855
C	1 073 K	0.624	0.502	0.440	0.965	0.983	0.945	0.988	0.973
	1 173 K	0.482	0.370	0.318	0.899	0.941	0.835	0.917	0.980
	1 273 K	0.542	0.421	0.350	0.893	0.926	0.842	0.910	0.953
P	1 073 K	0.862	0.769	0.695	0.999	0.993	0.996	0.995	0.928
	1 173 K	0.823	0.695	0.599	0.995	0.988	0.997	0.995	0.925
	1 273 K	0.844	0.710	0.598	0.996	0.988	0.998	0.993	0.926

Fig. 4. Comparison of mass conversion rate of quasi-particles at different temperature: (a) The mass conversion rate of C type quasi-particles at different temperature. (b) Comparison of mass conversion rate of four types quasi-particles at 1 273 K.

Fig. 5. Temperature dependence of apparent total reaction rate constant of four types quasi-particles at different temperature.

Table 7. Apparent total reaction rate constant of four types quasi-particles at 1 073 K, 1 173 K, 1 273 K.

Temperature	S	S'	P	C
1 073 K	3.19E-04	3.06E-04	4.12E-04	0.00251
1 173 K	3.71E-04	3.28E-04	3.94E-04	0.00212
1 273 K	3.21E-04	3.18E-04	7.30E-04	0.00481

iron ore sintering process.

During quasi-particles combustion, reaction rate of four types quasi-particles was not constant. Reactivity index was adopted to further investigate the influence of different temperature on quasi-particles combustion. The reactivity index could be expressed as follows:

$$R_{0.5} = \frac{0.5}{\tau_{0.5}} \dots\dots\dots (8)$$

where, $\tau_{0.5}$ was the time needed for mass conversion rate achieving 50% (s).

Figure 6 shows the reactivity index of four types quasi-particles at different reaction temperature, it could be drawn that the reactivity index increases with increasing temperature. Temperature has a significant influence on reactivity index, especially for C type quasi-particles. For example, the reactivity index of C type quasi-particles at 1 273 K was 3.2 times greater than that at 1 073 K. The reactivity index of four types quasi-particles ranked in the order of $C > P > S > S'$ and the result was agreed well with previous results in this work.

4.2. Conversion of Fuel-N to NO_x of Quasi-particles at Different Temperature

As shown in **Fig. 7**, the conversion rate of fuel-N to NO_x decreases with higher temperature for C and P types quasi-particles but first decreases then increases for S and S' types quasi-particles. In other words, the conversion rate of fuel-N to NO_x changes slightly with the increasing temperature for S, S' and P type quasi-particles. However, the conversion rate of fuel-N to NO_x obviously decreases with increasing temperature for C type quasi-particles. For example, the conversion rate of fuel-N to NO_x decreases from 44.94% at 1 073 K to 19.58% at 1 273 K for C type quasi-particles.

4.3. Conversion of Fuel-N to NO_x of Quasi-particles Vary with Circulating Flue Gas Components

In the process of flue gas recirculation sintering, the main components of circulating flue gas were O₂, CO, CO₂, H₂O(g). The combustion of CO provides heat for iron ore sintering process and affects the heat front. O₂ and CO₂ affect the atmosphere of coke combustion. Moreover, the content of steam affects the formation of over-wet zone.²⁵⁾ A series of reactions, including coke combustion, Fe₂O₃ reduction and CaCO₃ decomposition and so on, affect the NO_x yield in the process of quasi-particles combustion. In present work, the effect of different circulating flue gas components on the NO_x emissions during quasi-particles combustion was investigated.

Fig. 6. Reactivity index of four types quasi-particles at different reaction temperature.

Fig. 7. Conversion of fuel-N to NO_x for four types quasi-particles at different temperature.

4.3.1. Conversion of Fuel-N to NO_x of Quasi-particles Vary with O₂ Concentration

As shown in **Fig. 8**, the conversion rate of fuel-N to NO_x increases with increasing O₂ concentration for C, S and S' type quasi-particles. However, the conversion rate of fuel-N to NO_x decreases with increasing O₂ concentration for P type quasi-particles.

The increasing O₂ concentration is conducive to conversion of fuel-N to NO_x for S, S' and C types quasi-particles due to the reactions of R5–R9.³¹⁾

4.3.2. Conversion of Fuel-N to NO_x of Quasi-particles Vary with CO Concentration

The effect of CO concentration on conversion of fuel-N to NO_x was shown in **Fig. 9**. With the concentration of CO increasing, the conversion rate of four types quasi-particles all decreased. CO has a great capacity to decrease NO_x

Fig. 8. Conversion of fuel-N to NO_x for four types quasi-particles varying with O₂ concentration.

Fig. 10. Conversion of fuel-N to NO_x for four types quasi-particles varying with CO₂ concentration.

Fig. 9. Conversion of fuel-N to NO_x for four types quasi-particles varying with CO concentration.

Fig. 11. Conversion of fuel-N to NO_x for four types quasi-particles varying with H₂O concentration.

emissions. For example, the conversion rate of fuel-N to NO_x of C type quasi-particles decreased from 27.18% to 10.28% when CO increased from 0.5% to 2%.

Effect of CO on the conversion of fuel-N to NO_x was attributed to two aspects. On one hand, CO reacts with NO directly through R10 to decrease the conversion of fuel-N to NO_x. On the other hand, CO can reduce the NO yield through reactions with char (R11 and R12).³²⁾

4.3.3. Conversion of Fuel-N to NO_x of Quasi-particles Vary with CO₂ Concentration

To investigate the effect of CO₂ on NO_x yield during quasi-particles combustion, a mixed gas components of CO₂, O₂, N₂ were adopted. N₂ was used to adjust the concentration of CO₂. As shown in Fig. 10, the conversion rate of fuel-N to NO_x of four types quasi-particles all decreased with increasing CO₂ concentration.

The results shown in Fig. 10 were consistent with previous investigation.^{32,33)} The increasing CO₂ concentration promotes the production of CO through R13. CO could

either react with NO directly or react with char indirectly to decrease the conversion of fuel-N to NO_x and hence suppressing the NO_x yield (R10–R12).

4.3.4. Conversion of Fuel-N to NO_x of Quasi-particles Vary with H₂O Concentration

As shown in Fig. 11, the conversion rate of fuel-N to NO_x increases with the increasing H₂O(g) content for P type quasi-particles. Nevertheless, the conversion rate of fuel-N to NO_x firstly increases then decreases with increasing H₂O(g) content for S', S and C type quasi-particles.

The increasing H₂O(g) content decreases combustion temperature,²⁸⁾ which is conducive to NO_x yield. Effect of H₂O(g) on the conversion of fuel-N to NO_x mainly depends on decreasing the sintering bed temperature²⁸⁾ and enhancing the reducing atmosphere.³³⁾ With the excessive H₂O(g) content, the enhanced reducing atmosphere through R14 plays a major role. The conversion rate of fuel-N to NO_x decreases owing to the NO_x reduced by CO and H₂ (R10 and R15).³⁴⁾

5. Discussion

5.1. Effect of Temperature on Combustion Characteristics of Quasi-particles

The results obtained from Fig. 4(b) were agreed with Ohno⁹⁾ who found that quasi-particles with smaller coke proportion made the combustion reaction rate larger. The mass fraction of coke was only 5% for C type quasi-particles, much less than other three types quasi-particles. The combustion rate of C type quasi-particles could be greatly influenced by temperature compared with other three types quasi-particles.

Kasai¹¹⁾ found that the combustion rate of quasi-particles decreased with increasing particle size. Diameters of coke particles for C and P type quasi-particles were ~ 0.25 mm, smaller than that in S and S' type quasi-particles in present experiment hence higher mass conversion rate of C and P type than S and S' type quasi-particles. Moreover, there were significant effects of adhering layer on coke combustion. The reactions between coke and limestone or hematite (R3 and R4) can decrease the mass of quasi-particles. Close contact of hematite and limestone with coke will accelerate those reactions to lower the ignition temperature.^{30,35–37)} Therefore the mass conversion rate of S' type quasi-particles which have no adhering layer was the lowest.

5.2. Effect of Temperature on Conversion of Fuel-N to NOx of Quasi-particles

It could be seen from Fig. 7 that conversion rate of fuel-N to NOx for C type quasi-particles decreases more obvious than other three types quasi-particles with increasing temperature.

The rising temperature enhances the adsorption capacity of char to NO and increases the heterogeneous reduction reaction rate constant between char and NO. Moreover, the rising temperature accelerates the combustion speed and decreases the O₂ concentration at the surface of coke, causing the decrease of conversion rate of fuel-N to NOx for C type quasi-particles.^{38,39)} Apart from that, coke particles with the diameter of ~ 0.25 mm and mass fraction of 5% for C type quasi-particles result in combustion rate greatly influenced by temperature. For other three types quasi-particles, mass fraction of coke is higher (50% for P type, 75% for S type, 100% for S') and relative influence is not so obvious. Additionally, the loose distribution of coke on the surface of C type quasi-particles leads to burning more intensively with higher temperature compared with S and P type quasi-particles. S' type quasi-particles were coarse coke particles and conditions for contact with O₂ were worse than C type quasi-particles, although decrease of O₂ concentration also occurred on the surface of S' type quasi-particles.

Taking the factors mentioned above into comprehensive consideration, C type quasi-particles were affected by temperature more obviously than other three types quasi-particles.

5.3. Effect of O₂ Concentration on Conversion of Fuel-N to NOx of Quasi-particles

Effect of O₂ concentration on the conversion rate of fuel-N to NOx is very complex. On one hand, the increase of O₂ content is conducive to the production of NOx. On

the other hand, the increase of O₂ content will promote the heterogeneous reduction reaction between NOx and char.⁴⁰⁾

For S' and S types quasi-particles, the combustion occurs on the surface of 2–2.8 mm coke slowly. For C type quasi-particles, coke fraction is just 5%. Therefore, oxidizing atmosphere may occur in the combustion process for S, S' and C types quasi-particles.

The increasing O₂ concentration occupies more carbon active sites, reducing the carbon active sites where happens heterogeneous reduction reaction between char and NO. In addition, the formation of oxidizing atmosphere is unfavorable for reduction reaction.⁴¹⁾

However, Coke particles with diameter of ~ 0.25 mm and fraction of 50% were uniformly distributed in P type quasi-particles resulting in faster O₂ consumption and more generation of CO hence a stronger reductive atmosphere compared with the other three types quasi-particles. The effect of NOx reduced by char and CO, which was promoted by O₂, plays a major role for P type quasi-particles.

Moreover, it was estimated that calcium ferrite has been formed inside P type quasi-particles, resulting in the decrease of conversion rate of fuel-N to NOx with increasing O₂ concentration. For S type quasi-particles, existence of adhering layer hinders the radiation effect and temperature inside S type quasi-particles may be lower than 1 273 K. For S' type quasi-particles, on one hand, coke size was 10 times larger than P type quasi-particles; on the other hand, conditions for contact with O₂ are worse than P type quasi-particles. Therefore, temperature inside S' type quasi-particles may be lower than the generation temperature of calcium ferrite. Coke fraction is only 5% for C type quasi-particles, limited heat was produced and temperature inside which may be lower than formation temperature of calcium ferrite, although diameter of coke was ~ 0.25 mm and evenly distributed on the surface of quasi-particles. Coke particles with diameter of ~ 0.25 mm and mass fraction of 50% are evenly distributed in P type quasi-particles. They burned more intensively with increasing O₂ concentration, temperature inside P type quasi-particles may have been raised above 1 273 K and the calcium ferrite may have been formed.⁴²⁾ Conversion rate of fuel-N to NOx could be decreased by calcium ferrite effectively. More calcium ferrite may be generated with increasing O₂ concentration, resulting in the decrease of conversion rate of fuel-N to NOx for P type quasi-particles.

5.4. Recommendations on Decreasing NOx Emissions in Iron Ore Sintering

Effect of circulating flue gas components on iron ore sintering process has been researched by many scholars.^{25,43)} The suitable O₂ concentration in circulating flue gas is greater than 15% considering the combustion speed and combustion efficiency. The post-combustion of CO improves the sinter indexes, therefore it's conducive to sintering process. In order to avoid the decrease of combustion efficiency, the CO₂ concentration should be lower than 6%. The appropriate H₂O(g) concentration is no higher than 8% considering the width of over-wet zone.

The above experimental results exhibits that the conversion rate of fuel-N to NOx of C type quasi-particles was higher than that of other types quasi-particles in different flue gas atmosphere. Hence, NOx emissions could

be reduced by decreasing the proportion of C type quasi-particles and improving the proportion of other types quasi-particles. Controlling the fuel existing state in granules is a useful method for reducing NO_x emissions during iron ore sintering process. Fuel pre-granulation technology has been considered as an effective measure to reduce NO_x emission.^{12–14)} The structure of granule was divided into inner layer consisting of coke, limestone and iron ore and outer layer composing of limestone and iron ore. Fuel combusts in a low O₂ concentration due to the restriction of in-diffusion of O₂, which is detrimental for NO_x yield. Furthermore, NO_x was reduced by reacting with CO during the out-diffusion process. Compared with conventional granulation process, fuel pre-granulation is a more promising method to reduce NO_x emissions. Moreover, NO_x could be further reduced by coupling fuel pre-granulation with flue gas recirculation technology.

6. Conclusions

Experimental investigation of the conversion of fuel-N to NO_x for four types quasi-particles under different circulating flue gas components and the mass conversion rate of four types quasi-particles at different temperatures was conducted in a vertical quartz tube reactor. The following conclusions were drawn:

(1) The mass conversion rate of four types quasi-particles was larger with higher temperature and ranked in the order of C>P>S>S' at all temperature investigated.

(2) Through calculating the correlation coefficient between different mechanism models G(x) and t, it was found that D₁ model was the most appropriate model to describe the combustion behavior of S, S' and P type quasi-particles and D₃ model was better than other models to describe the combustion behavior of C type quasi-particles. The apparent total reaction rate constant of four types quasi-particles ranked in the order of C>P>S>S'.

(3) The conversion rate of fuel-N to NO_x increases with increasing O₂ concentration for S, S' and C type quasi-particles due to the oxidation of char-N. However, the conversion rate of fuel-N to NO_x decreases with the increasing O₂ concentration for P type quasi-particles due to two competing reactions: NO_x reduction in the surface of coke and the oxidation of char-N. The conversion rate of fuel-N to NO_x of four types quasi-particles all decreased with the increasing CO₂ and CO concentration. Effect of H₂O(g) content on the conversion rate of fuel-N to NO_x for four types quasi-particles was different. For S', S and C type quasi-particles, the conversion rate of fuel-N to NO_x firstly increases and then decreases with the increasing H₂O (g) content. However, the conversion rate of fuel-N to NO_x increases with the increasing H₂O(g) content for P type quasi-particles.

Acknowledgements

This work was supported by the Zhejiang Provincial Commonweal Project (2017C31062).

REFERENCES

- World Metals: Global crude steel production in 2016 return to growth, <http://www.worldmetals.com.cn/viscms/xingyeyawen3686/240285.jhtml>, (accessed 2017-12-09).
- Z. Liu: Ph.D. thesis, Zhejiang University, (2015), <http://www.cnki.net/>, (accessed 2018-02-15).
- D. Liu, Y. Wei and L. Yang: *Environ. Eng.*, **30** (2012), 118.
- C. E. Loo: *Ironmaking Steelmaking*, **18** (1991), 33.
- C. S. Teo, R. A. Mikka and C. E. Loo: *ISIJ Int.*, **32** (1992), 1047.
- T. Maeda, R. Kikuchi, K. Ohno, M. Shimizu and K. Kunitomo: *ISIJ Int.*, **53** (2013), 1503.
- E. Kasai, T. Sugiyama and Y. Omori: *Tetsu-to-Hagané*, **80** (1994), 282.
- Y. Hida, M. Sasaki, T. Enokido, Y. Umezue, T. Iida and S. Uno: *Tetsu-to-Hagané*, **68** (1982), 400.
- K. Ohno, K. Noda, K. Nishioka, T. Maeda and M. Shimizu: *ISIJ Int.*, **53** (2013), 1588.
- P. Hou, S. Choi, E. Choi and H. Kang: *Ironmaking Steelmaking*, **38** (2011), 379.
- E. Kasai, S. Wu, T. Sugiyama, S. Inaba and Y. Omori: *Tetsu-to-Hagané*, **78** (1992), 1005.
- M. Gan, X. Fan, W. Lv, X. Chen, Z. Ji, T. Jiang, Z. Yu and Y. Zhou: *Powder Technol.*, **301** (2016), 478.
- M. Gan, X. Fan, Z. Ji, X. Chen, T. Jiang and Z. Yu: *Ironmaking Steelmaking*, **41** (2014), 430.
- K. Katayama and S. Kasama: *ISIJ Int.*, **56** (2016), 1563.
- H. Ogi, T. Maeda, K. I. Ohno and K. Kunitomo: *ISIJ Int.*, **55** (2015), 2550.
- E. Kasai and Y. Omori: *Tetsu-to-Hagané*, **72** (1986), 1537.
- M. Goemans, P. Clarysse, J. Joannès, P. D. Clercq, S. Lenaerts, K. Matthys and K. Boels: *Chemosphere*, **54** (2004), 1357.
- S. Wei, S. Wang and R. Zhou: *Environ. Eng.*, **32** (2014), 95.
- X. Fan, Z. Yu, M. Gan, X. Chen and Y. Huang: *Ironmaking Steelmaking*, **43** (2016), 403.
- H. Zhou, M. Cheng, M. Zhou, Z. Liu, R. Liu and K. Cen: *Appl. Therm. Eng.*, **94** (2016), 786.
- H. Zhou, Z. Liu, M. Cheng, M. Zhou and R. Liu: *Energy Fuel.*, **29** (2015), 974.
- Y. Chen, Z. Guo and Z. Wang: *ISIJ Int.*, **48** (2008), 1517.
- M. Gan, X. Fan, Z. Ji, T. Jiang, X. Chen, Z. Yu, G. Li and L. Yin: *Ironmaking Steelmaking*, **42** (2015), 27.
- G. Jha and S. Soren: *Renew. Sustain. Energy Rev.*, **80** (2017), 399.
- X. Fan, Z. Yu, M. Gan, X. Chen, T. Jiang and H. Wen: *ISIJ Int.*, **54** (2014), 2541.
- X. Fan, Z. Yu, M. Gan, W. Li and Z. Ji: *J. Iron Steel Res. Int.*, **20** (2013), 1.
- X. Fan, Z. Yu, M. Gan, X. Chen and Z. Ji: *J. Cent. South Univ.*, **21** (2014), 2391.
- X. Chen, Y. Huang, M. Gan, X. Fan, Z. Yu and L. Yuan: *J. Iron Steel Res. Int.*, **22** (2015), 1107.
- S. C. Hill and L. D. Smoot: *Prog. Energy Combust. Sci.*, **26** (2000), 417.
- Y. Tobu, M. Nakano, T. Nakagawa and T. Nagasaka: *ISIJ Int.*, **53** (2013), 1594.
- G. G. D. Soete, E. Croiset and J. R. Richard: *Combust. Flame*, **117** (1999), 140.
- K. Zhao, A. D. Jensen and P. Glarborg: *Energy Fuel.*, **28** (2014), 4684.
- H. Zhou, Y. Li, N. Li, R. Qiu and K. Cen: *Energy Fuel.*, **31** (2017), 7157.
- S. Li, X. Wei and X. Guo: *Energy Fuel.*, **26** (2012), 4277.
- Y. Kashiwaya, M. Kanbe and K. Ishii: *ISIJ Int.*, **46** (2006), 1610.
- S. Ueda, K. Yanagiya, K. Watanabe, T. Murakami, R. Inoue and T. Ariyama: *ISIJ Int.*, **49** (2009), 827.
- K. Watanabe, S. Ueda, R. Inoue and T. Ariyama: *ISIJ Int.*, **50** (2010), 524.
- K. M. Thomas: *Fuel*, **76** (1997), 457.
- J. P. Spinti and D. W. Pershing: *Combust. Flame*, **135** (2003), 299.
- Z. Zhao, W. Li and B. Li: *J. China Univ. Min. Technol.*, **30** (2001), 484.
- X. Zhang: Ph.D. thesis, Zhejiang University, (2012), <http://www.cnki.net/>, (accessed 2017-02-15).
- Y. Oba, H. Konishi, H. Ono, H. Kawabata and E. Takeuchi: *Tetsu-to-Hagané*, **103** (2017), 299.
- H. Zhang, M. Rao, Z. Fan, Y. Zhang, G. Li and T. Jiang: *ISIJ Int.*, **52** (2012), 2139.