Elimination Behaviors of NO_x in the Sintering Process with Flue Gas Recirculation

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A novel sintering process is proposed based on part of flue gas is reused by reintroducing the flue gas into sintering bed, which is of great significance to cleaner production of sinter because it can reduce significantly the emission of exhaust gas. The reaction behaviors of NO_x during flue gas recirculation (FGR) process are researched. The elimination behavior of NO_x in sinter zone is NO–CO reaction on the catalysis of sinter, and the degradation rate of NO_x reaches a maximum at 700°C. The NO_x formation supervenes with coke combustion in combustion zone. The NO_x formation decreases due to the significantly reduced O₂, increased CO₂, and increased NO of FGR gas. The combustion atmosphere is the key point on the NO_x elimination since the fuel-N decomposition intermediate products could transform to NO or reduce NO. Moreover, the NO-carbon reaction conducting in combustion zone contributes to the NO_x elimination further. Therefore, it can significantly reduce the NO_x emission of sintering process when the FGR technology is taken in the sintering process.

KEY WORDS: iron ore sintering; flue gas recirculation; sinter zone; combustion zone; reaction behavior.

1. Introduction

Reducing NO_x (mainly including NO and NO₂) emissions is of global interest due to the NO_x adverse effects on the environment and human health.¹⁾ NO_x can combine with VOCs to form ground-level ozone, particulate matter, and ultimately be oxidized to form NO₃[–]. Excess NO₃[–] is a key factor in environmental and ecological problems, like acidic deposition, degradation of drinking water *etc.* Anthropogenic NO_x emissions have greatly increased primarily due to increased fossil fuel combustion and vehicles in the Industrial Revolution.^{2,3)} The NO_x emissions from iron and steel industry approximately account for 6% of the total industrial emissions in China. Meanwhile, NO_x emissions from the sintering machine represent about 48% of all emission from iron and steel industry.^{4,5)} Thus it is very essential to reduce NO_x emissions from the sintering machine, which contributes to the cleaner production of sinter.

Recent and ongoing efforts aim at further reducing ambient NO_x concentrations globally, which mainly includes source control, process control and end of pipe technology.⁶⁾ Cho Guk Jin *et al.* research how to reduce NO_x emission in the source by using low nitrogen of coke in the sintering process;⁷⁾ the process control technology is generally described as adding some additives into the sintering mixture to inhibit NO_x generation, such as carbohydrate,⁸⁾ Ca–Fe oxides,⁹⁾ ammonia¹⁰⁾ and modified coke.¹¹⁾ The efficiency of source and process control is relatively lower since the species and amount of low nitrogen fuels and additives are

few choices. The end of pipe technologies including flue gas denitration and flue gas recirculation develop rapidly in recent years. Flue gas denitration is divided into three categories, like wet denox process, semi-dry denox process and dry denox process. The dry denox process dominates in the flue gas denitration technology since its efficiency is the highest, which can reach 80%–90%.^{12,13)} Due to the high gas flow rate and low NO_x concentration, it suffers high cost of investment/operation and low utilization of by-products. Therefore, the flue gas recirculation technology is proposed by the researchers aiming to reducing the exhaust gas emission and reusing waste heat in 20th century, which is developed based on a principle that parts of waste gases recycled into sintering bed. The application of flue gas recirculation in sintering process lead to a significant decrease in the emissions of pollutants, like producing 1 ton sinter will reduce 35%–45% dust, 20%–45% NO_x, 60%–70% dioxin, 25%–30% SO₂ and 40%–50% CO. In addition, the reuse of waste heat in circulating flue gas is favorable to reduce solid fuel consumption of 2–5 kg/t-sinter.^{14–17)}

However, the NO_x content of exhaust gas increases even though 20%–45% reductions in NO_x emissions in the case of FGR technology. The NO_x content in stack should be reduced to comply with the more and more stringent environmental regulations. Our researches attempt to reveal the reaction behavior of NO_x in sintering bed during the FGR process which is simulated by five zones defined based on the temperature and physical and chemical reactions, and then propose the mechanism or operating parameters that makes a contribution to further reduction in the NO_x content of exhaust gas in FGR sintering.

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Table 1. Chemical composition of raw materials and their percents in mixture/mass%.

Raw materials	TFe	SiO ₂	CaO	MgO	Al ₂ O ₃	FeO	LOI	Ratio
Iron ore fine	60.01	4.39	2.84	0.61	1.37	4.59	5.16	58.96
dolomite	0.32	0.41	31.66	21.38	0.01	0.06	45.56	2.48
limestone	0.22	0.88	55.21	0.25	0.24	0.06	42.88	3.16
burnt lime	0.30	3.61	69.3	1.33	0.68	0.06	24.39	1.50
Coke breeze	0.85	7.40	0.59	0.11	1.49	0.00	87.30	3.90
Return fine	57.06	5.14	9.47	1.84	1.70	6.64	0.77	30.00

Table 2. Proximate analysis and elemental analysis of coke breeze/mass%.

Fuel	Ad	Vdaf	FCad	S	N	H
Coke breeze	14.36	2.92	82.72	0.78	0.72	0.33

* Ad: ash content (dry basis); Vdaf: volatile matter content (dry ash-free basis); FCad: fixed carbon content (air dried basis).

2. Materials and Methods

2.1. Sintering Pot Test

2.1.1. Raw Material

Iron ore blending, fuels and fluxes (including dolomite, limestone, quicklime) were utilized to produce sinter with TFe 58.11%, SiO₂ 4.88%, basicity ($R = \text{CaO}/\text{SiO}_2$) 1.85 and MgO 1.60%. The chemical compositions of raw materials and their mass fractions are given in **Table 1**. The proximate analysis of coke breeze and chemical composition of its ash are shown in **Table 2**. The fixed carbon content was 82.72% while the nitrogen content was 0.72%.

2.1.2. Pot Tests Apparatus

The sintering tests were conducted in a laboratorial pot which was 100 mm in diameter and 700 mm in height. The schematic diagram of the sintering apparatus was shown in **Fig. 1**. Sintering tests include ore proportioning, mixing, granulation, ignition, sintering, cooling, sieving and quality testing of sinter. The operation methods were as below: The raw materials were mixed after ore proportioning. Then the mixture was charged into a drum mixer of 600 mm in diameter and 300 mm in length to granulate for 4 min at 15 r/min. The granulated mixture was then fed into the sintering pot after 0.5 kg sinters of 10–16 mm fed on the grate bars. The mixture was ignited with nature gas for 1.5 min at 1 050°C at the top of pot under the suction pressure of 5 kPa, and then kept heating at 950°C for 1 min. The mixture experienced a series of sintering reactions under an initial suction pressure of 10 kPa. Subsequently, cooling followed for 3 min at 5 kPa suction pressure. After sintering, the sinter indexes were measured and calculated, including *VSV* (vertical sintering velocity), *P* (productivity), *Y* (yield) and *TI* (tumble index). The sintering time was the total time from the ignition to the BTP (burn through point). The *VSV* was calculated by dividing initial height of sintering bed by sintering time. The *Y* stated the qualified rate of sinter, which was defined as the mass fraction of particles of >5 mm size. It was detected by the standard of JIS M8711-1977. The *P* was defined as the sinter production of per unit time and area, which revealed the production efficiency of

1-standard gas 2-shaft furnace 3-steam production 4-gas mixing room 5-sealer cover 6-hearth layer 7,9-flue gas analyzer 8-air gas

Fig. 1. Simulation of sintering process with flue gas recirculation.

sintering machine. The *TI* was measured according to the standard of ISO 3271-1975.

For simulating the process of FGR, a sealed cover was added on the top of sintering pot after igniting, and the circulating gas was introduced onto the surface of pot through the pipeline. The simulation system of FGR included gas blending system, steam generator and pre-heating furnace. The circulating flue gases pre-heated by the vertical furnace were simulated by mixing air and standard gases (including O₂, CO, CO₂, NO and Ar), and then joined with the steam to introduce into sintering bed. Moreover, the components and temperature of inlet gas were controlled by a gas analyzer. Besides, the compositions of flue gas were tested by another gas analytical instrument (MGA 5, MRU Corporation of Germany) during sintering process.

2.1.3. Determination of Concentrations of Re-circulated Gases

The components of circulating flue gas were calculated based on the principles that exhaust gas emission rule and mass balance. The principles included:

① Q_{cir} (gas required as using flue gas recirculation process) was determined according to the equation ($C_{\text{cir}} \cdot Q_{\text{cir}} = Q_{\text{air}} \cdot C_{\text{air}}$). Q_{air} (gas required as using conventional sintering process) was ascertained by tests while the C_{air} (the heat capacity of air) and C_{cir} (the heat capacity of circulating flue gas) were known physical quantities which were related to the properties of gas. If the amount of circulating flue gas couldn't reach the Q_{cir} , the short part is made up with hot cooling gas. ② The consumption of O₂ and production of CO₂ and H₂O(g) during FGR sintering were calculated according to carbon, H₂O, FeO and carbonate contents of sintering mixture. ③ The phenomenon that CO in inlet gas was combusted completely was assumed during FGR sintering process. The gas temperature is controlled by regulating the hot cooling gas if it is lower than 250°C.

A multiple linear equation set is proposed and solved according to the principle that mentioned above, of which the solution presents the compositions and temperature of circulating flue gas under the conditions of different propor-

Table 3. Properties of circulating flue gas of different technologies.

Sintering condition	Recirculation ratio/vol%	Circulating flue gas composition/vol%					Circulating flue gas temperature/°C
		O ₂	CO ₂	CO	H ₂ O	NO _x	
Conventional	0	21.00	0	0	0	0	Room temperature
FGR	20	18.42	1.74	0.19	2.40	0.0100	250
	25	17.55	2.28	0.23	3.14	0.0180	
	30	16.57	2.87	0.28	3.96	0.0256	
	35	15.43	3.52	0.33	4.86	0.0345

Fig. 2. Schematic diagram of sinter zone simulation.

tions. **Table 3** shows the components and temperature of circulating flue gas.

Compared to conventional process, with the increase of FGR ratio, CO_x and steam contents were increased while O₂ content was reduced. The O₂ content was 15.43 vol% as well as the steam content was increased to 4.86 vol% when the FGR ratio was 35 vol%. And the temperature of circulating flue gas increased from room temperature to 250°C.

2.2. Electric Furnace Test

2.2.1. Experimental Apparatus

The sintering bed were divided five zones based on the temperature and physical and chemical reactions in order to simulate the sintering process, sinter zone, combustion zone, drying-preheating zone, over-wet zone and green mixture zone vertically. When flue gas was circulated to sintering bed, it passed through the five zones successively. In this paper, the reaction behaviors of NO_x in circulating flue gas during the sintering process were mainly studied in sinter and combustion zones since NO_x hardly got changed in the sub-layer. The reaction behaviors of NO_x during the sinter zone and combustion zone were investigated in a quartz fixed bed reactor which was 10 mm in diameter and 50 mm in height, and the schematic diagram of the sintering apparatus was shown in **Fig. 2**. The experimental apparatus includes gas atmosphere simulation, heat pattern simulation

and exhaust gas monitoring.

The experiments proceeded as follows: 40 g sinter (used to simulate sinter zone) or granulated mixture dried in advance (used to simulate combustion zone) of 5–8 mm were charged into the charging cup; the granulate mixture came from the granulation while the sinter sample was the final product of sinter pot test. When taking sinter zone simulation test, the sinter zone temperature (500–900°C) was as the same as the set pre-heat temperature since no much heat released from sinter samples. However, as much heat released by coke combustion in combustion zone, the pre-heat temperature was set relatively lower than the maximum temperature of combustion zone. The temperatures of combustion zone (1 100–1 300°C) were achieved by setting the pre-heat temperature according to the curve which is fitted based on a series of experiments on the relationship between temperature of sinter bed and setting temperature of electric furnace. At the same time, a special content standard gases (O₂, CO, CO₂, NO and Ar) were introduced into the quartz tube and passed through the charging cup after mixing. And the gas velocity kept a constant at 18 m/min. The compositions in outlet gas were detected by gas analyzer along with the heating period. The gas analyzer named as MGA5 was intelligent infrared multigas analyzer. On the basis of NDIR technology, MGA5 can measure multigas such as O₂, CO, CO₂, NO, NO₂, NO_x, SO₂ and C_xH_y.

2.2.2. Experimental Conditions

Unlike the conventional air condition,¹⁸⁾ the gas compositions of introducing gas were controlled according to the atmosphere conditions in **Table 4**, which was the simulation of sintering atmosphere in the case of FGR process. The temperature of sinter zone varied from 500 to 900°C with an atmosphere of 0.4%CO, 16%O₂ 4%CO₂ and 345 ppm NO when studying the influence of temperature factor on NO–CO reaction; while the influence of CO content was revealed by changing its content with 16%O₂, 4%CO₂ and 345 ppm NO under 700°C. However, the factors on reaction behavior of NO in combustion zone covered temperature, O₂ and (O₂+CO₂) since the fuel combustion player a leading role in combustion zone, which is closely related to the NO_x generation. The effect of combustion zone temperature on NO_x generation with or without NO_x was researched by varying the temperature from 1 100 to 1 300°C. Another important factor on combustion zone was atmosphere, which performed as the changes of O₂ and CO₂ contents. Firstly just changed O₂ content in the range of 25%–10% under 1 300°C, then adjusted the CO₂ content from 0 to 11% under the precondition of (%O₂+%CO₂=21%). All the rest of gas flow was made up with Ar.

3. Results

3.1. Reaction Behavior of NO in Sinter Zone

3.1.1. Effect of Sinter Temperature on NO–CO Reaction

Figure 3 shows the effect of sinter temperature on NO–CO reaction in sinter zone. NO_x content in outlet gas hardly changed when sinter temperature was 500°C or lower. While it significantly decreased in the range of 600°C to 700°C. Moreover, NO_x content in the outlet gas maintained the lowest level when the temperature was 700°C. NO_x

Table 4. Experimental conditions of electric furnace tests.

	Factors	Temp.*/ °C	CO/%	O ₂ /%	CO ₂ /%	NO/ppm	Ar
Sinter zone	Temp.	500	0.4	16	4	345	Rest
		600	0.4	16	4	345	Rest
		700	0.4	16	4	345	Rest
		800	0.4	16	4	345	Rest
		900	0.4	16	4	345	Rest
	CO	700	0	16	4	345	Rest
		700	0.4	16	4	345	Rest
		700	0.8	16	4	345	Rest
		700	1.2	16	4	345	Rest
		700	1.2	16	4	345	Rest
Combustion zone	Temp.	1 100	0	21	0	0	Rest
		1 200	0	21	0	0	Rest
		1 300	0	21	0	0	Rest
		1 100	0	21	0	345	Rest
		1 200	0	21	0	345	Rest
		1 300	0	21	0	345	Rest
	O ₂	1 300	0	25	0	0	Rest
		1 300	0	21	0	0	Rest
		1 300	0	17	0	0	Rest
		1 300	0	13	0	0	Rest
		1 300	0	10	0	0	Rest
		1 300	0	21	0	0	Rest
	O ₂ +CO ₂	1 300	0	17	4	0	Rest
		1 300	0	13	8	0	Rest
		1 300	0	10	11	0	Rest
		1 300	0	10	11	0	Rest

Temp.*: temperature.

Fig. 3. Influence of sinter temperature on reaction behavior of NOx in sinter zone.

Fig. 4. Relationship of CO and NOx in sinter zone under different temperature.

Fig. 5. Influence of CO content on reaction behavior of NO in sinter zone.

content in the outlet gas decreased in initial phase and then increased to the same content in circulating flue gas when the sinter temperature continued to rise to 800–900°C. In a word, the NO–CO reaction in sinter zone proceeded fastest at 700°C. The NO oxidation to NO₂ was easily found out; however, NO₂ content in outlet gas was decreased after the first increase under a low temperature condition. And NO₂ content in outlet gas decreased with the increase of temperature.

As the above study on sinter temperature, the reduction efficiency of NO was the most significant under 700°C while it was negligible except initial phase under 900°C. **Figure 4** shows the relationship of CO and NOx in sinter zone under 700°C and 900°C. When the sinter temperature was 700°C, CO and NOx contents in outlet gas were decreased along with the reaction time increasing. However, CO content in outlet gas decreased to null sharp while NOx content in outlet gas increased rapidly after the first decrease when the sinter temperature was 900°C. At the same time, NO was easily oxidized to form NO₂ in the existence of O₂. NO₂ content in outlet gas under 900°C was less than its under 700°C since NO oxidation was exothermic reaction.

3.1.2. Effect of CO Content

Figure 5 shows the effect of CO content in circulating

flue gas on reaction behavior of NO in sinter zone when the sinter temperature was 700°C. NO in circulating flue gas was reduced with the existence of CO under the catalysis of sinter in sinter zone. In addition, NO content in outlet gas was decreased with increasing of CO content in circulating flue gas. The degradation rate of NO was defined as $(NO_{inlet} - NO_{outlet}) / NO_{inlet}$, which increased with the raise of CO content. While it was similar when CO content increased from 0.8 vol% to 1.2 vol% since NO degradation depended on the content and activity of catalyst in sinter zone, such as Fe–Ca oxide.

3.2. Reaction Behavior of NO in Combustion Zone

3.2.1. Effect of the Temperature of Combustion Zone

In order to reveal the effect of NO in FGR gas on NO generation in different combustion zone, three combustion zone with different maximum temperature was set (their heat patterns were given in Fig. 6). Figure 7 shows the reaction behavior of NO in these three combustion zones. With the increase of the temperature of combustion zone, the burning velocity of fuel was increased as well as NOx content in outlet gas under the air condition. When 345 ppm NO existed in the gas atmosphere, the fuel combustion barely changed. However, the total NO emissions with the existence of 345 ppm NO were less than the sum of the NO

Fig. 6. Heat pattern of 25 mm distance away from the top of sample bed under different maximum temperature.

Fig. 7. Influence of temperature on reaction behavior of NO in combustion zone.

generations under air condition and NO content of inlet gas. It means the existence of NO inhibits the NOx generation from fuel combustion; meanwhile, the NO elimination in NO–Carbon reaction is significant. Moreover, the NO–Carbon reaction is enhanced with the temperature increasing.

3.2.2. Effect of Combustion Atmosphere

Figure 8 shows the effect of O₂ content in circulating flue gas on COx and NOx emissions at 1 300°C. With the decrease of O₂ content in circulating flue gas, CO₂ content in outlet gas reduced while CO content increased gradually. Meanwhile, the burning velocity decreased when O₂ content decreased. It indicated that the decrease of O₂ in circulating flue gas resulted in a decrease in the fuel combustion efficiency (combustion ratio $CO_2 / (CO + CO_2)$). At the same time, the total NO emissions and peak in outlet gas were both decreased gradually with the decrease of O₂ in circulating flue gas.

The fuel combustion behavior is also affected with the presence of CO₂ as low O₂ content in combustion zone. The oxygen content ($CO_2 + 0.5CO + O_2$) in outlet combustion gas should be 21 vol% since there are no decarbonations, oxide reductions or air leakage in combustion tests. Figure 9 shows the effect of CO₂ content in circulating flue gas on NO emissions of outlet gas. With the increase of CO₂ content and decrease of O₂ content, the burning velocity of coke deceased and NO content in outlet gas significantly reduced. NO content in outlet gas was decreased from 829 ppm to 649 ppm when CO₂ content in circulating flue gas increased from 0 vol% to 4 vol%.

Fig. 8. Influences of O₂ content on fuel combustion and NOx emission (under 1 300°C).

3.3. Effects of Flue Gas Recirculation on the NO_x Reduction

Table 5 shows the comparison of sinter indexes between convention and FGR. The sintering indexes were better than that of the conventional sintering in the case of FGR with less than 30 vol% recirculation ratio. However, they got significantly worse when FGR ratio increased to 35 vol%. The appropriate recirculation ratio should be better no more than 30 vol%. With the increase of FGR ratio, the waste gas emissions reduced gradually. It had a very good implementation for exhaust gas emissions reduction under a higher FGR ratio; however, it results in a decrease in sintering indexes by the significantly reduced O₂ content of the FGR gas. Thus, the sintering indexes and exhaust gas emissions reduction should be considered simultaneously in the application of FGR technology.

Figure 10 shows the flow diagram of sintering process with FGR, which is EOS-like lay out. The concept of this technique is to recycle a part of the mixed waste gas from

Fig. 9. Influences of CO₂ content on fuel combustion (under 1300°C).

Table 5. Comparison of sinter indexes between convention and FGR.

Sintering condition	Recirculation ratio/vol%	VSV/mm·min ⁻¹	Y/%	TI/%	P/t·m ⁻² ·h ⁻¹
Conventional	0	26.67	69.24	52.70	1.69
	20	28.94	69.91	53.00	1.90
FGR	25	27.76	69.30	53.00	1.82
	30	26.76	68.20	51.75	1.70
	35	23.45	67.90	47.95	1.48

the whole strand back to the entire surface of the strand. The FGR rate of the sintering waste gas is 30%, corresponding to a 16.57 vol% O₂, 2.87 vol% CO₂, 0.28 vol% CO, 3.96 vol% H₂O(g) and 256 ppm NO in the wet gas/air mixture in the hood. The effects of FGR on the emissions reduction of NO_x were shown in **Table 6**. Compared with the conventional sintering process, 30% reduction in gas flow was achieved in the case of 30 vol% FGR ratio. Otherwise, the nitrogen conversion rate of the FGR was 37.28%, which was significantly lower than that of the conventional sintering process of 58.09%. However, the NO_x content in exhaust gas increased from 579 mg/m³ to 741 mg/m³, which leads to 10.91% reduction in the NO_x emission.

4. Discussions

4.1. Elimination Mechanism of NO_x in Sinter Zone

During the FGR process, NO_x content in circulating flue gas will be reduced because of the existence of reduction agents in sinter zone, such as CO. At the same time, NO and CO gas in circulating flue gas will be oxidized. The reaction behaviors of NO and CO in sinter zone mainly include the following equations:

Figure 11 shows the relationship of lnK_p-T. The lnK_p-T curves of (R1), (R2) and (R3) with the increase of temperature. When the temperature increases from 500°C to 1100°C, the lnK_{R1} (reaction equilibrium constant of (R1)) varies from 24 to 10. It can explain the existence of NO₂ in

Table 6. Effects of FGR on the emissions reduction of exhaust gas.

Waste gas	Conventional sintering	FGR sintering	Reduction rate/%
Flow/Nm ³ ·h ⁻¹	22.36	15.65	30.00
Nitrogen conversion rate/%	58.09	37.28	35.82
*NO _x emission/mg·Nm ⁻³	579	741	10.91

* Mass of NO_x emission (mg) is calculated as NO₂ Molecular mass (46 g/mol).

Fig. 10. Flow diagram of sintering process with flue gas recirculation.

 Fig. 11. $\ln K_p$ -T curve of reaction in sinter zone.

sinter zone and NO_2 content decreased with the increase of sinter temperature. However, the $\ln K_{R2}$ and $\ln K_{R3}$ are significantly decreased with the temperature increasing. When the sinter temperature is higher than 1194 K (921°C), the K_{R2} performs as $K_{R2} < 1$. It means (R2) (the NO reduction reaction in sinter zone) almost does not exist when the temperature is higher than 921°C since the ΔG of (R2) is greater than zero under this condition. However, the degree of (R3) reduces but the reaction (R3) direction doesn't change with the increase of sinter temperature since the $K_{R3} >> 1$.

The NO reduction at the surface of sinter contains two parts: one is Fe in sinter, which is produced by the reduction of Fe_2O_3 by CO, acts as a reduction agent for deoxidizing NO to N_2 ; the other is NO is deoxidized to N_2 directly by CO with the catalysis of metal oxides in sinter. **Figure 12** shows the influence of stuffing agents on NO-CO reaction. According to the research result, an increase in NOx reduction rate occurred obviously with the increase of CO content in FGR gas over sinter agent. However, NO-CO reaction hardly conducted over silica or null agent even if CO content in FGR gas was 1.2 vol%. Therefore, the sinter plays a role as catalysis of NO-CO reaction during the FGR process.

4.2. Elimination Mechanism of NOx in Combustion Zone

NOx formations come from volatile-N and char-N oxidation in the fuel combustion process. However, 70%–90% nitrogen elements of fuel are separated out in volatiles over 1000°C . The nitrogen-containing intermediates in the combustion of volatile-N include NH_3 and HCN , which participates in the NOx reduction homogeneously or heterogeneously.^{19,20)} The nitrogen in fuel will be split into nitrogen-containing intermediates (NH_i and HCN) more under a low O_2 partial pressure. At the same time, the NOx content in FGR gas will be decreased further because of the existence of reducing agents in sintering bed, such as CO and C. The reaction in combustion zone mainly covered following equations besides (R1), (R2) and (R3), and the thermodynamic equations curves in combustion zone are shown in **Fig. 13**.

Fig. 12. Influence of stuffing agents on NO-CO reaction.

Fig. 13. Diagram of thermodynamic equations in combustion zone.

As observed from **Fig. 13**, the combustion behavior of coke in combustion zone mainly conducts as (R3), (R6), (R7) and (R8). (R6) plays the most important role in the coke combustion and it might be affected hardly by the temperature since the ΔG^0 -T curve of (R6) is paralleled with coordinate axis. (R7) and (8) are easily found out in combustion zone over 1000°C , which results in an increase in CO content. Moreover, much more CO will generate over fuel surface as the significantly reduced O_2 and increased CO_2 contents of FGR gas. It contributes to NOx elimination in NO-CO reaction.

Besides NO-CO reaction, the NO-carbon reactions will be found out easily in combustion zone. The products of NO-carbon reaction are generally found to be N_2 , CO and CO_2 . The heterogeneous reactions of NO with carbon surface have been well recognized as the most important processes of reducing NO in the combustion zone. The NO-carbon reaction is made up of several processes.²¹⁾ The first step is the chemisorptions of NO on carbon which occurs along with the formation of carbon-oxygen complexes. N_2 is the only product in this temperature range:

It has been suggested that the O atom of NO molecule is held to the surface, which means that NO is adsorbed in O-down orientation. The oxygen complexes were then postulated as the sites for physical adsorption. NO adsorption

Fig. 14. Cross-section drawn of sintering pot.

also occurs in a N-down orientation to form N-containing complexes C(N). The reaction (R9), if applied to the higher temperature regime, could be split into two steps:

Desorption of C(O) to form CO is an important step for all practical oxidizing carbon gasification processes, and must be present in the mechanistic model:

The route to CO₂ formation was proposed to follows:

4.3. Behavior of NO in the Sintering Process

Figure 14 shows reaction behaviors of NO_x in each zone of sintering machine. As the above study preserved, NO of FGR gas is reduced to produce N₂ in the way of NO–CO reaction in sinter zone, meanwhile, it is also oxidized to form NO₂. Most of CO of FGR gas takes post-combustion under a high temperature. The NO_x formation supervenes with coke combustion in combustion zone. Almost all of fuel-N is decomposed to generate intermediate products, including N, CN, HCN and NH_i compounds. On one hand, these intermediate products could be transformed to NO if there are some oxy-compounds like O, O₂ and OH *etc.* On the other hand, they can react with NO to form N₂. The combustion atmosphere is the key point on the NO_x elimination in combustion zone. Moreover, the NO–CO and NO–Carbon reactions conduct drastically in combustion zone, which contributes to the NO_x elimination further.

5. Conclusion

(1) The flue gas recirculation sintering process is proposed based on part of flue gas is reused by reintroducing

the flue gas into sintering bed, which is of great significance to cleaner production of sinter because it can reduce significantly the emission of exhaust gas as well as pollutants emission.

(2) The elimination behavior of NO_x in sinter zone is in the way of NO–CO catalysis reaction, and the degradation rate of NO_x reaches a maximum at 700°C. The NO_x formation supervenes with coke combustion in combustion zone. The NO_x formation decreases due to the significantly reduced O₂, increased CO₂, and increased NO of FGR gas. The combustion atmosphere is the key point on the NO_x elimination since the fuel-N decomposition intermediate products could transform to NO or reduce NO. Moreover, the NO–CO and NO-carbon reactions conducting in combustion zone contributes to the NO_x elimination further.

(3) The elimination behavior of NO_x during flue gas recirculation sintering process can propose the mechanism or operating parameters that how to reduce the NO_x emission in sintering process which makes a contribution to the further NO_x reduction of exhaust gas in FGR sintering.

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REFERENCES

- 1) J. N. Galloway, F. Dentener, D. Capone, C. Cleveland, P. Green, E. Holland, D. Karl, A. Michaels, J. Porter, A. Townsend and C. Vörösmarty: *Biogeochemistry*, **70** (2004), 153.
- 2) J. D. Felix, E.-M. Elliott and S.-L. Shaw: *Environ. Sci. Technol.*, **46** (2012), 3528.
- 3) Y. N. Bai: *Safety Environ. Eng.*, **2** (2006), 52 (in Chinese).
- 4) T. Y. Zhu: Technology of Sintering Flue gGas cleaning; Chemical Industry Press, Beijing, China, (2009), 1 (in Chinese).
- 5) L. L. Fang: Master Thesis. Shandong University, Jinan, Shandong Province, (2007), 13 (in Chinese).
- 6) Y. G. Chen, Z. Wang and Z. C. Guo: *Acta Scientiae Circumstantiae*, **28** (2008), 1720 (in Chinese).
- 7) C. G. Jin, H. G. Su and L. J. Nam: Korean Patent, 20020040506(A), 2002-05-30.
- 8) C. L. Mo, C. S. Teo, I. Hamilton and J. Morriso: *ISIJ Int.*, **37** (1997), 350.
- 9) K. Morioka, S. Inaba, M. Shimizu, K. Ano and T. Sugiyama: *ISIJ Int.*, **40** (2000), 280.
- 10) X. G. Bi, J. Y. Liao, W. Xiong, G. F. Zhou and Z. H. Feng: *J. Wuhan Univ. Sci. Technol.*, **5** (2008), 449 (in Chinese).
- 11) Y. G. Chen, Z. Wang and Z. C. Guo: *Acta Scientiae Circumstantiae*, **28** (2008), 1727 (in Chinese).
- 12) M. Gan: PhD Dissertation, Central South University, Changsha, Hunan Province, (2012), 12 (in Chinese).
- 13) T. Terris and B. Hsiaotao: *Environ. Sci. Technol.*, **43** (2009), 5049.
- 14) S. Ikehara, J. Sakuragi, S. Kubo and Y. Terada: *Nippon Steel Tech. Rep. (Japan)*, **70** (1996), 55.
- 15) N. Menad, H. Tayibi, F. G. Carcedo and A. Hernandez: *J. Cleaner Product.*, **14** (2006), 740.
- 16) A. Fleischander, C. Aichingerz and E. Zwitta: *China Metall.*, **18** (2008), 41.
- 17) X. H. Fan, Z. Y. Yu, M. Gan, W. Q. Li and Z. Y. Ji: *J. Iron Steel Res. Int.*, **20** (2013), 1.
- 18) E. Kasai, S. L. Wu, T. Sugiyama, S. Inaba and Y. Omori: *Tetsu-to-Hagane*, **78** (1992), 1005.
- 19) C. P. Finimore: *Combust. Flame*, **26** (1976), 249.
- 20) M. Shelef: *Cham. Rev.*, **95** (1995), 209.
- 21) K. Hauff, U. Tuttlies, G. Eigenberger and U. Nieken: *Ind. Eng. Chem. Res.*, **52** (2013), 8399.