NO\textsubscript{x} reduction in the sintering process

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Abstract: A new process, NO\textsubscript{x} reduction with recycling flue gas and modifying coke breeze, was proposed. The effects of modified coke breeze and recycled flue gas on NO\textsubscript{x} reduction were investigated by sinter pot tests. The results show that the NO\textsubscript{x} reduction rate is over 10wt\% in the sintering of modified coke breeze, the effects of the additives on NO\textsubscript{x} reduction are: CeO\textsubscript{2}>CaO>K\textsubscript{2}CO\textsubscript{3}. The NO\textsubscript{x} reduction rate increases with the amount of recycled flue gas, and is 22.35wt\% in the sintering with recycling 30vol\% of the flue gas. When 30vol\% of the flue gas is recycled into the sintering of CeO\textsubscript{2}, CaO, and K\textsubscript{2}CO\textsubscript{3} modified coke breeze, the NO\textsubscript{x} reduction rates are 36.10wt\%, 32.56wt\%, and 32.17wt\%, respectively.

Key words: nitrogen oxide; flue gas; coke breeze; cerium oxide; sintering

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1. Introduction

Annual total emissions of NO\textsubscript{x} are over ten million metric tons in China, which will increase yearly [1]. The minimization of NO\textsubscript{x} has been one of the main concerns because it can cause acid rain and photochemical fog. The amount of NO\textsubscript{x} produced in sintering, representing the major NO\textsubscript{x} emissions in the iron and steel industry, accounts for about 6wt\% of the total nationwide NO\textsubscript{x} emissions. The majority of sinter plants, in such developed countries as Japan and Germany, have adopted denitrification equipments to treat the flue gas; however, the flue gas without any post process is directly discharged into the air in China.

There are two methods for reducing the amount of NO\textsubscript{x} emitted from sinter plants. One method is the treatment of flue gas. The flue gas volume is large (about 100 m\textsuperscript{3}/(m\textsuperscript{2}·min)) and the absolute level of NO\textsubscript{x} is relatively low (about 200×10\textsuperscript{-6}-300×10\textsuperscript{-6}), making it difficult to apply this method. Moreover, the huge capital investment and high operational cost have reduced the competitiveness of this method. The other method is the NO\textsubscript{x} reduction technology, through controlling operational conditions or mixing sinter materials with some additives. For example, NO\textsubscript{x} emission can be reduced by treating the top sinter materials with microwaves before ignition [2], and it is also reduced by mixing sinter materials with fine limestone (<2.5 mm) [3] or some hydrocarbons (rice husk, sugar cane slag, sawdust, sugar, and flour) [4].

In sintering, over 90vol\% of NO\textsubscript{x} comes from the fuel, the rest is from iron ores and fluxes [4], so the selective use of fuel with low nitrogen content is a practical method for reducing NO\textsubscript{x} emission [5], although low-nitrogen fuel is limited. Some reports indicate that NO\textsubscript{x} emission in coke combustion is greatly affected by minerals in coke; active components (such as Na and Fe) make the conversion of fuel-N to NO\textsubscript{x} decrease, whereas, inert components (such as Ca) cause an increase in the NO\textsubscript{x} emission level [6-7]. In general, the mineral matter suppresses the conversion of fuel-N to NO\textsubscript{x} during coke combustion [8]. A new process, NO\textsubscript{x} reduction, by recycling flue gas and modifying coke breeze, is proposed [9]. It
is based on the principle of *in-situ* catalytic denitrification by modified coke breeze and NO\(_x\) reduction by recycling flue gas. In this process, the NO\(_x\) reduction includes: (i) *in-situ* catalytic denitrification of modified coke breeze; (ii) the reduction of NO\(_x\) in recycled flue gas by burning coke breeze and CO produced in coke breeze combustion; (iii) NO\(_x\) reduction by sinter ore. A comprehensive understanding of modified coke breeze and recycled flue gas on the formation and reduction of NO\(_x\) during sintering would be of great use for controlling NO\(_x\) emission. In this study, the sinter pot tests have been performed to investigate the effects of modified coke breeze and recycled flue gas on NO\(_x\) reduction.

### 2. Experimental

#### 2.1. Experimental materials

Sinter materials include iron ores (A, B, and C), fluxes (dolomite, limestone, and lime), and coke breeze. The chemical compositions of raw materials are shown in Table 1, and the particle size distributions of raw materials are shown in Table 2.

<table>
<thead>
<tr>
<th>Table 1. Chemical compositions of raw materials</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
<td>Fe(_{total})</td>
</tr>
<tr>
<td>A</td>
<td>59.19</td>
</tr>
<tr>
<td>B</td>
<td>64.37</td>
</tr>
<tr>
<td>C</td>
<td>68.12</td>
</tr>
<tr>
<td>Dolomite</td>
<td>—</td>
</tr>
<tr>
<td>Limestone</td>
<td>—</td>
</tr>
<tr>
<td>Lime</td>
<td>—</td>
</tr>
<tr>
<td>Coke breeze</td>
<td>0.47</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Particle size distributions of raw materials</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
<td>8</td>
</tr>
<tr>
<td>B</td>
<td>2.93</td>
</tr>
<tr>
<td>C</td>
<td>1.40</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0</td>
</tr>
<tr>
<td>Limestone</td>
<td>0</td>
</tr>
<tr>
<td>Lime</td>
<td>0</td>
</tr>
<tr>
<td>Coke breeze</td>
<td>0</td>
</tr>
</tbody>
</table>

The proximate and ultimate analysis of coke breeze is shown in Table 3. The coke breeze was modified by CeO\(_2\), CaO, and K\(_2\)CO\(_3\), respectively. To introduce CeO\(_2\), the CeO\(_2\) powder was first sieved to the size between 47 and 74 \(\mu\)m, and then it was added into water to make a certain concentration of CeO\(_2\) emulsion at a stirring rate of 20 r/min. The coke breeze sample was added into this CeO\(_2\) emulsion, and subsequently the CeO\(_2\) particles were adsorbed and distributed on the surface or in the pore of the coke breeze by the adsorption capacity of the coke breeze itself. Water was eliminated by evaporation, and the impregnated samples were fully dried at 110°C for 6 h before use. The coke breeze samples loaded with CaO or K\(_2\)CO\(_3\) can be obtained in the same way. The loading amounts of CeO\(_2\), CaO, and K\(_2\)CO\(_3\) are all 2.0wt%.

<table>
<thead>
<tr>
<th>Table 3. Proximate and ultimate analysis of coke breeze (air-dry basis)</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate analysis</strong></td>
<td>M</td>
</tr>
<tr>
<td>S(_i)</td>
<td>0.39</td>
</tr>
<tr>
<td><strong>Ultimate analysis</strong></td>
<td>C</td>
</tr>
<tr>
<td>S(_i)</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Note: * By difference.

#### 2.2. Experimental apparatus

As illustrated in Fig. 1, the apparatus consists of a flue gas recirculation section, a pressure test section, a sinter pot (200 mm in diameter, 750 mm in height), and an online gas analysis section. The amount of sinter materials for each test run is always 40.0 kg. About 2 min after ignition, the NO\(_i\) gas, simulated as the recycled flue gas, was introduced to the top surface of the sinter ore via a gas scatter, therefore, the NO\(_i\) gas and air flowed through the sintering bed un-
under the suction pressure.

2.3. Experimental method

Iron ore fines, fluxes, and coke breeze were mixed with water (7.0wt%) in a mixing drum to form granules for 3 min, and then the granules were evenly laid into the sinter pot. The addition of coke (4.2wt%), SiO2 content (4.4wt%), and basicity (CaO/SiO2=1.9) were kept constant for each run. The ignition temperature was 1100±50°C, ignition time 1.5 min, and ignition suction 6 kPa. The sintering suction was 10 kPa and the sintered ore was cooled for 15 min after the sintering ended. The composition of the flue gas was monitored by an online gas analyzer, KM9106 flue gas analyzer (Kane Ltd. Co., England), for the concentrations of CO, O2, NO, NO2, and NOx(NOx=NO+NO2), whereas, the concentration of CO2 was calculated by the O2 concentration. The precision for CO, NO, and NO2 was 1×10^-6, whereas, the precision for O2 was 0.1vol%. The temperature of the flue gas was measured by a Pt-Rh type thermocouple.

![Schematic diagram of the sinter pot tests.](image)

Fig. 1. Schematic diagram of the sinter pot tests.

The NOx in sintering is dominantly NO; the NO2 is lower than 10×10^-6. The NOx, CO, CO2, and O2 concentrations and the flue gas temperature in the sintering are shown in Fig. 2. The NOx concentration increases from 0 to 37×10^-6, whereas, the O2 concentration decreases from 20.9vol% to 12vol% during ignition. After ignition, the NO2 concentration increases rapidly to 110×10^-6, and keeps a slight increasing trend till the NO2 concentration reaches the maximum value of 152×10^-6 at 18.5 min. The O2 concentration fluctuates around 16vol% during the process, and the variation trend of O2 is opposite to that of NOx, which lasts till 3 min before the burn-through point. Then the NOx concentration drops down to zero and the O2 concentration rapidly rises up to the O2 level in air, and the temperature of the flue gas increases to the maximum value at the same time, indicating the end of sintering.

After ignition, the coke breeze in sinter materials burned and the combustion zone gradually moved down to the bottom of the sintering bed under the suction pressure. Therefore, the NOx produced in the combustion zone could only be reduced by coke breeze or CO formed during coke breeze combustion, which took place in or below the combustion zone. Coke had an important effect on NOx reduction [10]. The NOx concentration was low due to the thicker layer of coke below the combustion zone at the early stage of sintering. However, the NOx concentration gradually increases with sintering time, which is related to the steady decrease of the coke layer. Moreover, the increase of thickness in the combustion zone is another factor. The concentration of CO in the flue gas is about 1.0vol%-2.0vol%, which indicates that the chemical energy of coke breeze is not fully taken advantage of. Therefore, the energy efficiency can be improved by reducing CO emission in flue gas.

![Emissions of NOx and O2 during sintering.](image)

Fig. 2. Emissions of NOx and O2 during sintering.

3.2. Effect of modified coke breeze on NOx reduction

In the sintering of modified coke breeze, the NOx emissions are shown in Fig. 3. Apparently, the NOx emissions are lower than those of the base run. In the run of CaO modified coke breeze, the NOx concentration is 30×10^-6, lower than that of the base run, suggesting that CaO added in coke breeze, functions to inhibit the conversion of fuel-N to NOx. When the coke breeze modified by CeO2 is used for fuel, the
NO\textsubscript{x} concentration is $40 \times 10^{-6}$ lower than that of the base run, which is related with the redox property of CeO\textsubscript{2} [11] and the catalytic effect of CeO\textsubscript{2} on NO\textsubscript{x} reduction. The NO\textsubscript{x} concentration is low at the early stage and is high at a later stage, with K\textsubscript{2}CO\textsubscript{3} modified coke breeze being used as fuel, it may be affected by the catalytic combustion support and gasification effects of K\textsubscript{2}CO\textsubscript{3} [12].

The NO\textsubscript{x} emission is almost the same as that of the base run. The concentration of NO\textsubscript{x} emission is slightly higher than that of the base run when 30vol% of the flue gas is recycled into the sintering. The NO\textsubscript{x} concentration becomes apparently higher in the run of recycling 50vol% of the flue gas, indicating partial NO\textsubscript{x} in the flue gas is not reduced. In practical sintering, the initial concentration of O\textsubscript{2} decreases with increasing the amount of the recycled flue gas, resulting in a slower sintering speed and lower sinter productivity, therefore, the amount of the recycled flue gas should be not more than 30vol% of the total amount of the flue gas.

3.3. Effect of recycled flue gas on NO\textsubscript{x} reduction

When the flue gas is recycled into the sintering, the NO\textsubscript{x} reduction rates are shown in Fig. 6. The NO\textsubscript{x} reduction rates are 10.9wt%, 22.4wt%, and 29.0wt%, respectively, in the sintering with recycling 10vol%, 30vol%, and 50vol% of the flue gas, respectively. The NO\textsubscript{x} in the recycled flue gas passes through the sinter bed, the NO\textsubscript{x} elimination reactions not only occur in or below the combustion zone, but also in the sintered ore zone. In or below the combustion zone, the NO\textsubscript{x} reduction is the same as that in the base run. In the sintered ore zone, NO\textsubscript{x} will react with FeO and be reduced to N\textsubscript{2}, it has been demonstrated that the sintered ore has a positive effect on NO\textsubscript{x} reduction reactions [14].

3.4. Effects of recycled flue gas and modified coke breeze on NO\textsubscript{x} reduction

In the sintering of modified coke breeze with recycling 30vol% of the flue gas, the NO\textsubscript{x} emissions are shown in Fig. 7. The concentrations of the NO\textsubscript{x} emis-
sion are apparently lower than those of the base run. The existence of CeO$_2$ and CaO not only has some depressing effects on the formation of NO$_x$ in coke breeze combustion, but also has some promoting effect on the reduction of NO$_x$ in the recycled flue gas, whereas, the existence of K$_2$CO$_3$ has some positive effects on the gasification reaction, and the NO$_x$ reduction is mainly due to the increase of CO concentration.

The NO$_x$ reduction rates are shown in Fig. 8. The NO$_x$ reduction rate is 22.35wt% in sintering with recycling 30vol% of the flue gas. When 30vol%, 50vol% of the flue gas are recycled into the sinter, the NO$_x$ reduction rates are 10.89wt%, 22.35wt%, and 29.02wt%, respectively.

(3) NO$_x$ reduction is over 30wt% in the sintering of modified coke breeze with recycling 30vol% of the flue gas.

4. Conclusions

(1) The NO$_x$ emission is reduced in the sintering of modified coke breeze, the order of NO$_x$ reduction is: CeO$_2$>CaO>K$_2$CO$_3$.

(2) The NO$_x$ reduction rate increases with the amount of recycled flue gas. When 10vol%, 30vol%, and 50vol% of the flue gas are recycled into the sinter, the NO$_x$ reduction rates are 10.89wt%, 22.35wt%, and 29.02wt%, respectively.

(3) NO$_x$ reduction is over 30wt% in the sintering of modified coke breeze with recycling 30vol% of the flue gas.

References


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