Effect of Coke Breeze Addition Timing on Sintering Operation

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(Received on January 25, 2013; accepted on May 9, 2013)

For the purpose of reducing specific coke breeze consumption, we examined the influence which the morphology of coke breeze and pseudo-particles structure have on sintering quality. As a means to control the morphology of coke breeze in pseudo-particles, we delayed the timing of coke breeze addition in granulation process of sintering materials. As a result, when we added more coke breeze in the latter stage of granulation, we noticed that granulating property as well as permeability were improved. Also, much of coke breeze stayed on the surface layer of pseudo-particles or in free particle, which led to improved quality and burn through speed (abbreviated as BTS).

When we added the entire charge of coke breeze in the latter stage, combustion quality of coke breeze was improved. However, conduction and accumulation of heat turned down, which resulted in deteriorating yield due to the exhaust heat loss.

Therefore, we searched for a ratio of the second-stage addition favorable for improving yield by making a higher raw material bed.

With the second-stage addition at 50%, we were able to build a higher raw material bed through improvement in sinter quality and permeability, while maintaining good BTS. As a result, expanded area in the sintering bed with temperature at 1 200°C or higher led to liquid phase growth, which finally enabled the reduction in coke breeze consumption without causing deterioration in both yield and shutter index.

KEY WORDS: coke breeze; the second-stage addition ratio; granulation; the morphology of a coke breeze; combustion quality; liquid phase ratio; yield.

1. Introduction

In the process of producing iron ore sinter, coke breeze is used as a caking additive, and it burns to generate CO₂ gas. Reduction of CO₂ emissions, accompanied with lower coke breeze consumption is the most urgent issue to tackle for the purpose of environmental protection.

There are many reports referring to combustion quality of coke breeze as well as its morphology in pseudo-particles which affects sinter quality. For instance, Sugahara et al.,1) suggested divided addition of coke breeze during granulation as a technique to strengthen the formation of pseudo-particles and prevent the deterioration of combustion quality. Sawamura et al.,2) introduced the divided coke breeze addition to No. 1 sintering plant of Kamaishi Works of Nippon Steel, and he reported that productivity was improved with a better combustion quality of coke breeze at the plant. Hida et al.,3) sorted pseudo-particles into three categories of Single (S), Composite (C) and Pellet (P) according to the morphology of coke breeze and he examined the amount of heat generation, burning velocity and CO/CO₂ gas concentration of each categorized item during sintering. And he concluded that the pseudo-particles with coke breeze as the core and fine iron ores adhered on the surface burned insufficiently.

Regarding relations between combustion quality and morphology of coke breeze in the pseudo-particles, Kasai et al.,4) compared the coke breeze with fine iron ores adhered on the surface and the stand-alone coke breeze, and he found that such a fine iron ores-adhered coke breeze performed significantly poorly as far as combustion quality was concerned. Kasai also reported that addition of calcium ferrite (abbreviated as CF) powders improved BTS. Oyama et al.,5) put “Coke Breeze and Limestone Coating Granulation Method” to practical use, in which the quality of sinter was improved by adhering both coke breeze and limestone on the adhesion layer of the pseudo-particles. He reported that critical factors were limestone and coke breeze coating time.

There are not many reports on the sinter quality focused on the pseudo-particle structure, such as Hida’s. We, therefore, examined how the pseudo-particle structure influences its sinterability in our experiments using pseudo-particles made with differentiated timings of coke breeze addition during the granulation. Furthermore, we tried to find measures to reduce coke breeze consumption by controlling its morphology.
2. Experimental Method

2.1. Experiment 1 (Impact Investigation of Coke Breeze Addition Timing (the Second-stage Addition) Exerted on Sinterability)

We used the following fine iron ores in the experiment: Pisolite ore (abbreviated as ①, ②), Maramamba type (③) and Brockman type (④) of hematite ore.

Additive materials were serpentine, limestone and silica stone.

Table 1 shows chemical composition of fine iron ores.

Table 2 shows blending ratio of raw materials (Coke breeze was the member of the outside).

Figure 1 shows the granulation method of sinter material in laboratory test of sinter material, Table 3 shows granulation conditions and Table 4 shows second-stage addition ratio of coke breeze. We performed the granulation using a drum mixer for batch experiments and mixed raw materials except the coke breeze to add in the second stage granulation after mixer charge in the first stage granulation for 30 seconds so that raw materials occupied ratio became 7.7 vol.%. We inserted a water supply nozzle in the mixer central part and added water to become water content 7.0 mass% and granulated it afterwards for 105 seconds. The second stage granulation added the coke breeze of the ratio to show in Table 4 in raw materials after the first stage granulation, and granulated it for 105 seconds. In addition, we used the return fine with the actual equipment, but this experiment did not use the return fine.

Iron pellets were used as the hearth layer with its depth at 20 mm, and, on top of it, the raw material beds were formed for 380 mm in a test pot. The internal diameter of the pot was 300 mm, which are as shown in Fig. 2-1. Ignition time was 90 seconds, and, in order to exclude the influence of pseudo-particle’s size variation and to investigate only the influence of combustion quality of the coke breeze at the time of sintering, air flow rate was kept at 1.6 Nm3/min. Sintering time started from the ignition and ended when the temperature of the exhaust gas that we measured by the thermocouple that we set up right under the pot reached the maximum. In the experiment, we recorded temperature changes in the raw material bed, air flow rate, pressure and concentration of CO, CO2 and O2 in the exhaust gas.

Evaluation of granulation was expressed in Granule Index (GI),6) and evaluation of sinter quality was based on points such as sintering rate, gas analysis, heat diffusion pattern in raw material bed, yield and productivity.

Also, we examined morphology of coke breeze by the following methods.

(1) Carbon content in each pseudo-particles

Pseudo-particles were screened and separated into three

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Second-stage addition ratio of coke breeze (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>0</td>
</tr>
<tr>
<td>Case 2</td>
<td>50</td>
</tr>
<tr>
<td>Case 3</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 1. Granulation method in laboratory test.

Fig. 2. Appearance of sinter pot.
groups, i.e. +4.75 mm, 4.75–2.0 mm and –2.0 mm. Then we calculated carbon content in pseudo-particles as follows. Pseudo-particles were sintered in a high-frequency furnace, and CO2 in the exhaust gas was measured by infrared analysis according to JIS M8819. Quantity of carbon from coke breeze was calculated by subtracting limestone-originated carbon from total carbon content gauged. From the calculated carbon quantity of coke breeze and size distribution of pseudo-particles (+4.75 mm, 4.75–2.0 mm, –2.0 mm), we have calculated distribution of coke breeze per pseudo-particle.

(2) Morphology of coke breeze in each pseudo-particle

We first tried to examine morphology of coke breeze in all types of pseudo-particles according to tinge of color by visual inspection before sintering, but it did not work well. Therefore, we focused only on fine iron ore and coke breeze granulated under the conditions shown in Fig. 1 and Table 3.

Blending ratio of fine iron ores and coke breeze was 100:3.8. Raw pseudo-particles were screened by 1.0 mm and 4.75 mm. About 100 g of pseudo-particles with the size between 1.0 mm and 4.75 mm was sampled. Then we examined morphology of coke breeze in each pseudo-particle by visual inspection. Figure 3 shows categorization of pseudo-particles by the inspection. G1 was classified according to appearance of pseudo-particles, and G2, G3 and G4 were classified by breaking down an adhesion layer with tweezers after visual inspection.

2.2. Experiment 2 (Examination for Reducing Coke Breeze Consumption Through the Improvement of Combustion Quality)

Regarding the morphology of coke breeze in pseudo-particles, excessive quantity of coke breeze existing as stand-alone or in the adhesion layer of pseudo-particles caused yield deterioration because BTS was so fast that heat did not transfer through the sinter. Therefore we examined measures to improve yield without causing deterioration in the sinter productivity by making higher raw material bed.

We kept same conditions for blending and granulation referred in 2.1 except the ratio of coke breeze addition. Table 5 shows conditions of the experiment. The size of the pot was 300 mm in interior diameter and 800 mm in height as shown in Fig. 2-2. Heights of the raw material beds were 500 mm and 700 mm, and we kept the same distance between the surface of raw material beds and the burner by putting pellets at the bottom of the pot to adjust the height. The evaluation items were BTS, yield, productivity and Shutter Index (abbreviated as SI).

3. Results and Discussion

3.1. Experiment 1

Figure 4 shows how the coke breeze second-stage addition ratio (abbreviated as C.S.R) influenced Granulation Index (abbreviated as GI). With increasing C.S.R, GI improved. We analyzed that, since coke breeze inhibits the granulation under the weak liquid bridge, C.S.R contributed to the improved granulation.

Figure 5 shows the relation of coke breeze content by each split size for pseudo-particles and C.S.R. The distribution of coke breeze by size is shown in
Carbon content was highest in pseudo-particles with the size between 2.0 mm and 5.0 mm when C.S.R was zero. But the highest coke breeze content moved from coarser pseudo-particles to finer pseudo-particles as C.S.R increased. Since most of the coke breezes were less than 2 mm in size as shown in Table 6, we inferred that coke breeze remained stand-alone, free from other materials, or that coke breeze fell from pseudo-particles during screening.

The result of our visual inspection of each single pseudo-particle showed that coke breeze in the state of G1 and G2 increased in return for the decrease in G3 and G4 as C.S.R increased.

This tendency matched Hida’s report which searched morphology of coke breeze in the actual production line and analyzed that the formation of C type pseudo-particles (equivalent to our G2) increased from about 20 mass% in ordinary granulation procedure to about 40 mass% in two separate pseudo-particles with coke breeze in granulation.

When coke breeze was added in the second stage after the primary granulation, as Oyama also suggested, number of coke breeze in the state of stand alone or in the adhesion layer of pseudo-particles increased because of its nature to inhibit granulation.

As shown in Fig. 7, the improved granulation after increased C.S.R led to lower pressure drop and BTS became faster. From this, it was revealed that permeability at the time of the sintering was improved when we increased the C.S.R. The average concentrations of CO gas, CO₂ gas and O₂ gas in the exhaust gas during the laboratory test are shown in Table 7. With the increase in C.S.R, O₂ concentration dropped and CO₂ concentration rose. Compared to the emission from general sintering plant, CO concentration and O₂ concentration were lower and CO₂ concentration went higher. As shown in Table 8, yield was the lowest with Case 3, and higher productivity was achieved as C.S.R rose.

We examined how morphology of coke breeze dictates sinter quality, referring to reports in the past as well.

As shown in Fig. 8, the temperature of the exhaust gas and highest temperature (Highest temperature; The mean of the high of the temperature in each six places of raw material bed that we measured by a thermocouple that we established in a sinter pot to show in Fig. 2.)

### Table 6. Carbon content was highest in pseudo-particles with the size between 2.0 mm and 5.0 mm when C.S.R was zero. But the highest coke breeze content moved from coarser pseudo-particles to finer pseudo-particles as C.S.R increased. Since most of the coke breezes were less than 2 mm in size as shown in Table 6, we inferred that coke breeze remained stand-alone, free from other materials, or that coke breeze fell from pseudo-particles during screening.

<table>
<thead>
<tr>
<th>Particle size (mm)</th>
<th>0.125</th>
<th>0.25</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>5.0</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accumulation ratio (mass%)</td>
<td>16.2</td>
<td>30.8</td>
<td>45.9</td>
<td>61.1</td>
<td>80.3</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

### Table 7. Mean gas composition results of the exhaust gas.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>O₂ (Vol.%)</th>
<th>CO₂ (Vol.%)</th>
<th>CO (Vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case1</td>
<td>8.3</td>
<td>17.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Case2</td>
<td>7.1</td>
<td>18.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Case3</td>
<td>5.8</td>
<td>20.2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

### Table 8. Influence of the coke breeze second-stage addition ratio on yield and productivity.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Yield (mass%)</th>
<th>Productivity (t/d/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case1</td>
<td>65.3</td>
<td>1.30</td>
</tr>
<tr>
<td>Case2</td>
<td>65.8</td>
<td>1.37</td>
</tr>
<tr>
<td>Case3</td>
<td>64.2</td>
<td>1.38</td>
</tr>
</tbody>
</table>
er BTS, higher sintering temperature and higher CO and CO₂ concentration in the exhaust gas. It also accounted for Kasai’s⁴ report that BTS was accelerated when the surface of coke breeze becomes bare after melted adhesion layer came off from G3.

Also, Table 7 suggests that, though coke breeze burnt efficiently with increased CO₂ concentration in the exhaust gas, yield was down with insufficient sintering heat and time. We attribute it to insufficiently functioning of adhesion layer of pseudo-particles for insulation⁸ and prevention of heat diffusion,⁴ which caused the rise in temperature of the exhaust gas and the drop in temperature of raw material bed as shown Fig. 8.

From the above, we concluded that we can control the morphology of coke breeze and the formation of pseudo-particles by understanding granulation process and adjusting C.S.R. As a result we should be able to control the combustion quality of coke breeze.

3.2. Experiment 2

Figure 9 shows relations between BTS and yield. Comparison of Case A and Case B shows that, when C.S.R was 50 mass%, we were able to maintain similar BTS with increased heights and similar yield with coke breeze reduction. On the other hand, yield dropped with Case B, C and D when we reduced quantities of coke breeze. In Fig. 10, productivity was improved from 0.89 t/d/m² to 1.16 t/d/m², and SI remained similar in Case A and B. In Case D, compared with Case A, BTS was increased, but both productivity and SI were aggravated due to yield deterioration.

In Fig. 11, duration of temperature at 1200°C and over and the highest temperature in raw material bed in each case are shown. Case A showed the highest temperature, and Case B, Case C and Case D went lower. On the other hand, the longest duration with the temperature at 1200°C and over was with Case B.

By analyzing the heat pattern in the raw material bed, we calculated the liquid phase ratio, and then examined its relation with yield. The calculation of the liquid phase was done as follows:

1. The liquid phase occurs from composition of the eutectic point of a system CaO–Fe₂O₃ shown in Fig. 12.
2. Dissolution quantity per unit time and surface area of Fe₂O₃ was calculated by following formula.¹⁰
   \[ k_{eff} = \exp \left(2.035 - 113.1 \times 10^3 / R \times T \right) \text{[g/(cm²·sec)]} \]
   \[ \ast R \text{ (gas constant)} = 8.314 \text{ [JK}^{-1} \text{ mol}^{-1}] \]
3. Dissolution quantity of CaO was calculated from the dissolution quantity of Fe₂O₃ which we calculated in (2), assuming that the formed liquid was composed of CaO–2Fe₂O₃.
4. We calculated the accumulated dissolution quantity from the dissolution quantity of Fe₂O₃ and CaO in each temperature and time in (2) and (3), and then calculated Fe₂O₃ content \( \alpha \) in a liquid phase.
5. We assumed Fe₂O₃ content \( \beta \) in a liquid phase in each temperature out from the liquidus of phase diagram CaO–Fe₂O₃ in Fig. 12, assumed that the dissolution ends when it became \( \alpha > \beta \), and then calculated a liquid phase ratio from the accumulated dissolution quantity of Fe₂O₃ and CaO at that time.
6. We calculated liquid phase ratios for temperatures in six places of raw material bed in the sinter pot mea-
sured by thermocouple shown in Fig. 2, and assumed the mean of the six as the representing liquid phase ratio.

Figure 13 shows relationship between the highest temperature and liquid phase ratio. Figure 14 shows relationship between heat index and liquid phase ratio (heat index= \( \int_{t_1}^{t_2} T(t)dt \); Time which became 1 200 °C while the temperature in sintering bed was rising or falling). From this, liquid phase ratio has stronger correlation with heat index than that of highest temperature. In the calculation method of the liquid phase, we calculated a liquid phase ratio for the temperature in raw material bed every time and assumed the sum a liquid phase ratio and increased a concept at not only the temperature but also time. As a result, we concluded that heat index and liquid phase ratio had better correlation. Case A and Case B, though the latter was lower in coke breeze addition by 0.5 mass%, the increased height by 200 mm with Case B led to the increase in heat index, and the liquid phase ratio of the both cases became close. Figure 15 shows the relation between liquid phase ratio and yield. The yield rose as straight as a line until the liquid phase reached 29 mass%, and peaked out then. We assumed that it will fall according to aeration aggravation if the yield became fixed and became more than it above a certain liquid phase rate (near 29%).

Control on C.S.R will improve permeability and combustion quality and make raw material bed higher, which will result in reduction in coke breeze consumption without deteriorating yield and SI.

4. Conclusions

In our laboratory experiment, we controlled the coke breeze second-stage addition ratio (abbreviated as C.S.R), made pseudo-particles with different morphology of coke breeze and examined how such changes in the morphology influenced on the combustion quality. Further, we examined the possibility of reducing consumption of coke breeze.

And the following are what we have found through our experiment.

(1) We confirmed by the visual observation that we had been able to change the morphology of coke breeze in pseudo-particles. As a result, it was found that when we raised C.S.R, it became clear that most of coke breezes stayed in adhesion layer of pseudo-particles or in stand-alone.

(2) We found out in the pot test that BTS became faster due to the improved combustion quality of coke breezes in the adhesion layer of pseudo-particles, which was the result of the increased contacts of coke breezes with the air.

(3) When we raised C.S.R, both granulation and permeability were improved. Also, most of coke breeze stayed in adhesion layer or in stand-alone, which resulted in improved combustion quality and higher BTS.

(4) With C.S.R at 100 mass%, both heat conductivity to raw material bed and heat accumulation dropped in exchange for improved combustion quality, which led to yield deterioration. Temperature of the exhaust gas also increased.

(5) In the case of C.S.R at 50 mass%, improvement in permeability and combustion quality enabled production of sinter with higher raw material bed while maintaining BTS. As a result, we confirmed the possibility to reduce the consumption of coke breeze without causing deterioration in yield and SI.

REFERENCES