Reduction of CO₂ Emissions by Use of Pre-reduced Iron Ore as Sinter Raw Material

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In order to reduce CO₂ emissions at an ironmaking process, it is an effective measure to decrease a bonding agent rate at an iron ore sinter plant. In this study, effect of using a pre-reduced iron ore as a part of a sinter raw material on a sintering process was investigated mainly from a viewpoint of decreasing a bonding agent rate.

Two brands of pisolitic iron ores were reduced up to wustite at 1 173 K with reducing gas of which an oxidation degree was 55%. The pre-reduced iron ore was stable against reoxidation in the atmosphere and through a cyclic wet and dry treatment.

Two brands of pisolitic iron ores and a Marra Mamba iron ore were pre-reduced and then used in a sinter pot test. A use of the pre-reduced iron ore was effective in decreasing a bonding agent rate at a given productivity. The reoxidation heat of the pre-reduced iron ore was estimated to be less than the combustion heat of the bonding agent being saved by use of the pre-reduced iron ore. The reoxidation heat is more effective in the sintering process than the combustion heat. The decrease of the bonding agent resulted in reduction of NOx emissions.

A mass and heat balance shows that a use of a pre-reduced iron ore as a sinter raw material enables reduction of CO₂ emissions not only at an ironmaking process but also at a whole integrated steel works.

KEY WORDS: sinter plant; blast furnace gas; pre-reduced iron ore; coke breeze saving.

1. Introduction

The Japanese steel industry has already achieved the world’s top-level energy efficiency by making persistent efforts for energy saving. However, it essentially needs a large amount of energy and accounts for approximately 15% of total domestic CO₂ emissions. Technological innovation will be required to be developed in order to furthermore reduce CO₂ emissions with an urgent and crucial concern.

An iron ore sinter plant is a source of the second largest amount of CO₂ emissions next to a blast furnace at an integrated steel works. A technological development in the sintering process has improved an iron ore sinter quality such as strength and reducibility, which contributes to a decrease in a reducing agent rate of a blast furnace resulting in reduction of CO₂ emissions. There have been a number of technologies developed for saving energy at a sinter plant, but they have an insignificant effect on reduction of CO₂ emissions. It is indispensable to decrease bonding agent consumption which is a main source of CO₂ emissions at a sinter plant. In a test operation1 lowering a bonding agent rate was carried out and deteriorated a productivity of a sinter plant. It is considered difficult to achieve a large amount of reduction of CO₂ emissions through an operational improvement or by simple decrease in a bonding agent rate at a sinter plant.

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A use of a sinter raw material containing metallic iron or FeO such as steel scrap2,3) and mill scale4–7) was confirmed to be effective in decreasing a bonding agent rate at a sinter plant. It is because that the reoxidation heat of metallic iron and FeO substitutes for the combustion heat of a bonding agent. But it should be hard to apply this technology to all the iron ore sinter plants because the amount of steel scrap and mill scale available is limited.

It is possible that a use of a magnetite iron ore as a sinter raw material contributes for decreasing a bonding agent rate due to reoxidation heat of magnetite to hematite.8) But it is still in consideration if a use of a magnetite iron ore has a full effect in decreasing a bonding agent rate because magnetite possibly remains in an iron ore sinter without reoxidation.9,10)

In future, an iron ore of poor quality containing high combined water such as a pisolitic iron ore and a Marra Mamba iron ore will be more used as a sinter raw material because an iron ore resource of good quality becomes depleted. It will possibly increase a bonding agent rate in order to make up for decomposition heat of the increasing combined water.11)

To find a solution to these diverse future problems at a sinter plant, a novel process using a pre-reduced ore as a part of a sinter raw material and effectively exploiting blast furnace gas (BFG) of low calorific value is proposed and an effect of using a pre-reduced iron ore on a sintering process is studied in this report.
2. Process of Reducing an Iron Ore with BFG

A process flow of a proposed technology is schematically drawn in Fig. 1. A fine iron ore containing high combined water is charged into a fluidized bed reactor and reduced at 1 173 K with partial combustion gas of BFG. The fine iron ore is dehydrated and reduced up to wustite with the reducing gas of a low reducing ability of which an oxidation degree (OD) is 55%.

A use of the pre-reduced iron ore as a part of a sinter raw material gives a thermal advantage that heat supply for decomposition of combined water is not necessary and reoxidation heat of wustite is generated. As a result, it brings a decrease in consumption of a bonding agent, such as coke breeze and anthracite. Furthermore, a heat recovery system can generate steam and preheat BFG before the partial combustion.

3. Experimental Procedure

3.1. Small-scale Fundamental Experiment

First, fundamental reduction behavior of an iron ore containing high combined water was examined using reducing gas of high OD, which was assumed to be partial combustion gas of BFG. An experiment was conducted with a small-scale experimental reduction apparatus shown in Fig. 2. Two brands of pisolitic iron ores, Ore A and Ore B, were used and those composition is shown in Table 1. The ores were reduced at 1 173 K with reducing gas (CO:21%, CO2:25%, N2:54%) simulating BFG partial combustion gas. Effects of a brand and a particle size of an iron ore on reduction behavior were studied with this experiment.

3.2. Dehydration and Reduction of An Iron Ore for a Sinter Pot Test

Two brands of pisolitic iron ores used in the previous fundamental experiment and a Marra Mamba iron ore, Ore C, were dehydrated or pre-reduced prior to a sinter pot test with a reduction test equipment shown in Fig. 3. The composition of Ore C is shown in Table 1.

In case of a reduction test, an iron ore in a reaction tube was heated to a temperature between 1 123 K and 1 173 K under an atmosphere of nitrogen gas and then pre-reduced with reducing gas of mixture of CO/CO2 gas having the same OD as BFG partial oxidization gas. In case of a dehydration test, an iron ore in a reaction tube was heated to a temperature between 573 K–673 K under an atmosphere of nitrogen gas. These dehydrated or pre-reduced ores were then used in a sinter pot test. The ores were chemically analyzed and a reduction degree was calculated.

In order to confirm the reoxidizing tendency of the pre-reduced iron ore, an exposure test was conducted for four weeks under the atmosphere with or without a soak in water once a week. A change of the reduction degree of the ore was checked by a chemical analysis during the exposure test.

3.3. Sinter Pot Test

A sinter pot test was carried out using a pre-reduced iron ore or a dehydrated iron ore that was prepared with the reduction test equipment as a part of a sinter raw material. A sinter raw material of approximately 70 kg was granulated with a drum mixer having a diameter of 1 000 mm with addition of a certain amount of coke breeze. An amount of water added at granulation was 7.5% in weight of a sinter raw material. A granulated sinter raw material was charged into a pot of a cylindrical shape with a diameter of 300 mmø till a bed height of 600 mm. Then a granulated sinter raw

**Table 1. Chemical composition of iron ores.**

<table>
<thead>
<tr>
<th>Ore brand</th>
<th>Chemical composition [%]</th>
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<tbody>
<tr>
<td></td>
<td>CW</td>
</tr>
<tr>
<td>Pisolitic iron ore</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Marra Mamba iron ore</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>CW: Combined water</td>
<td></td>
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A sinter material was fired at a suction pressure of 15.0 kPa. A sinter cake produced with a sinter pot was repeatedly dropped five times from a height of 2 m, and then a ratio of weight of sinter particles having a size of at least 5 mm to the sinter cake weight was considered to be a yield. In addition, RI (Reducibility Index, JIS-M8713), RDI (Reduction Disintegration Index, JIS-M8720), and SI (Shatter Index, JIS-M8711) were measured to evaluate the quality of an iron ore sinter.

A sinter raw material was blended as shown in Table 2.

In a reference case without using a pre-reduced iron ore, Ore A, Ore B and Ore C were blended with a different amount of coke breeze addition. In case of using the pre-reduced or dehydrated Ore A, a half amount of Ore A used in a reference case was replaced with the pre-reduced or dehydrated Ore A and an amount of coke breeze addition varied from that of a reference case. In case of using the pre-reduced Ore B, a full amount of Ore B used in a reference case was replaced with the pre-reduced Ore B. Similarly, in case of using the pre-reduced or dehydrated Ore C, a full amount of Ore C used in a reference case was replaced with the pre-reduced or dehydrated Ore C. It is noted that the blending ratio stated here is based on the weight of ore before pre-reduction or dehydration. For the purpose of maximizing the effects of the pre-reduced iron ore, the entire amount of Ore A, Ore B, and Ore C were respectively replaced with the pre-reduced iron ores.

4. Results and Discussions

4.1. Small-scale Fundamental Experiment

The results of the fundamental reduction experiment on a pisolithic iron ore with reducing gas of high OD is shown in Fig. 4. From the relationship between a reducing time and a reduction degree, both Ore A and Ore B reached a reduction degree of approximately 22–23% in 60 minutes from the beginning of the reaction. It was shown that the reducing rate of the ores depended on the ore brands but not on the ore particle size. In the EPMA analysis of the ore section magnetite and wustite were observed everywhere inside the ore. This phenomenon is considered to be due to the characteristic porous structure of a pisolithic iron ore which enables reducing gas to rapidly diffuse into the particles. Therefore, a pisolithic iron ore is considered to be suitable for the use since the ore particle can be evenly reduced inside with keeping the pores which may help reoxidation in the sintering process.

4.2. Preparation of a Pre-reduced Iron Ore for a Sinter Pot Test

Particle size distribution of a dehydrated or pre-reduced Ore A for a sinter pot test is shown in Fig. 5. Compared with the Ore A before processing, the particle becomes finer by dehydration and even finer by pre-reduction. From the viewpoint of the sintering process, disintegration of a particle is not preferable because it possibly causes a deterioration of sinter bed permeability. However, for the purpose of assess-
ing a total effect of using a processed ore on the sintering process including an effect of the disintegration, the processed ore was used as it is in a sinter pot test. The reduction degree of Ore A, Ore B and Ore C were all approximately 25%.

A result of a test on a reoxidation tendency of a pre-reduced ore B is shown in Fig. 6. The pre-reduced ore was not reoxidized probably because the reducing temperature of 1 173 K is high enough against reoxidation in the atmosphere. The pre-reduced ores can be stocked in an open-air yard without any difficulty.

4.3. Sinter Pot Test

The effect of using a pre-reduced or dehydrated Ore A on a yield, flame front speed (FFS) and productivity is shown in Figs. 7–9. FFS was calculated by dividing the bed height by the time taken for waste gas temperature to peak indicating burn-through. The yield of a test case with using a dehydrated Ore A was almost same as that of a reference case without using a dehydrated iron ore. There is little advantage of using a dehydrated ore though the decomposition heat of combined water is dispensable for the sintering process in the test case. But there was a marked improvement in the yield by using a pre-reduced Ore A at the same coke breeze rate as in the reference case. It can be seen that a thermal benefit can be derived from the reoxidation heat of a pre-reduced ore. The FFS was not different among the tests at a given coke breeze rate regardless of whether a processed ore is added or not. No disadvantage can be attributed to the pre-reduced iron ore addition in the range of this usage regarding the FFS. With respect to the productivity expressed through the product of yield and FFS, the test case with using a pre-reduced iron ore gave a higher productivity than the other cases at a given coke breeze rate. Compared with the reference case at the coke breeze rate of 4.3%, a coke breeze rate can decrease to around 3.7% in the test case with using the pre-reduced Ore A instead of 10% of a sinter raw material at the same productivity as in the reference case.

The effects of using the processed Ore B and Ore C on
productivity are respectively shown in Figs. 10–11. Similar to the effects of using processed Ore A, a coke breeze rate decreased due to the use of the pre-reduced ores at the same productivity as in the reference case. And there was little difference of productivity at a given coke breeze rate between the test case with addition of dehydrated Ore C and the reference case.

The effects of a pre-reduced iron ore on the decrease in a coke breeze rate are summarized in Table 3. The amount of coke breeze decreases in proportion to the amount of addition of pre-reduced iron ore, and there was no difference among those brands of ores. In addition, the amount of decrease of the coke breeze rate in the tests was 1.5 times more than that of the estimate that a quantity of combustion heat of coke breeze is equivalent to a quantity of reoxidation heat of a pre-reduced iron ore assuming that FeO of the ore become fully oxidized to Fe₂O₃. The reoxidation of a pre-reduced iron ore is considered to be more effective in supplying heat in a sintering process than the combustion of coke breeze.

The result of a sinter pot test is shown in Figs. 12–13 as the effect of a pre-reduced iron ore on reduction of NOx emissions in the exhaust gas. The reduction of NOx emissions was achieved by using a pre-reducing iron ore at the same productivity as in the reference case. It depends on a decrease of coke breeze rate because N in coke breeze is a main source of NOx emissions.

Table 3. Effects of pre-reduced ore on coke breeze saving.

<table>
<thead>
<tr>
<th>Ore brand</th>
<th>Ratio of prereduced ore added to the sinter raw materials [%]</th>
<th>Coke breeze saving [%]</th>
<th>Amount of coke breeze saved per unit weight of FeO [kg-coke/kg-FeO]</th>
<th>Estimate in an actual sinter plant [kg/t-sinter cake]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore A</td>
<td>10.0</td>
<td>▼ 0.6 (4.3→3.7%)</td>
<td>▼ 0.4</td>
<td>0.12</td>
</tr>
<tr>
<td>Ore B</td>
<td>20.0</td>
<td>▼ 1.1 (4.3→3.2%)</td>
<td>▼ 0.8</td>
<td>0.10</td>
</tr>
<tr>
<td>Ore C</td>
<td>12.9</td>
<td>▼ 0.7 (4.3→3.6%)</td>
<td>▼ 0.5</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Estimate of coke breeze saving: calculated under the assumption that a quantity of combustion heat of coke breeze is equivalent to a quantity of reoxidation heat of a pre-reduced iron ore when FeO of the ore become fully oxidized to Fe₂O₃.
The quality of the iron ore sinter such as RI, RDI and SI produced in the sinter pot test with the pre-reduced iron Ore B is shown in Figs. 14–16. In a test case of using the pre-reduced Ore B as 20% of a sinter raw material there was no negative effect on the quality of produced iron ore sinter at the same productivity as in the reference case.

The results of the sinter pot test shown in Figs. 17–18 indicate the productivity and NOx emissions when ore A, ore B and ore C were all pre-reduced and used as a sinter raw material. A large amount of pre-reduced iron ore usage enables a considerable decrease of both a coke breeze rate and NOx emissions, and a stable sintering process without a flameout even at a so low coke breeze rate as to extinguish a coke breeze burning in a sinter raw material without using a pre-reduced iron ore. Moreover, at the same productivity as in the reference case, NOx emissions could be reduced by half according to a significant decrease in coke breeze. In the past research, it has been reported that productivity of a sinter plant drastically diminished when the ratio of added metallic iron or raw materials containing FeO was increased. Nevertheless, it is confirmed that this technology of using a pre-reduced iron ore as a part of a sinter raw material enables us to acquire the decrease of a bonding agent rate and NOx emissions without a deterioration of productivity.

The result of the sinter pot test using a large amount of pre-reduced iron ore is in detail shown in Table 4 compared to a result of the reference sinter pot test. In the sinter pot test reoxidation heat of a pre-reduced iron ore was equivalent to a combustion heat amount of coke breeze replace by the pre-reduce iron ore. Disintegration of an iron ore particle occurred by pre-reduction. It results in a decrease in a quasi-particle size and increase in a finer particle amount, which
caused permeability deterioration of a sinter raw material bed. The permeability expressed with JPU before ignition significantly deteriorated especially in case of using a large amount of a pre-reduced iron ore. A mean density of a charged sinter raw material in a sinter pot increased by replacing coke breeze to a pre-reduced iron ore because coke breeze has a lower density than pre-reduced iron ore. In addition, reoxidation of a pre-reduced iron ore doesn’t bring any new void in a sinter bed through a sintering process though combustion of coke breeze brings new ones because a space occupied by coke breeze remain as a void after combustion of the coke breeze. As a result, FFS fell markedly by use of a large amount of a pre-reduced iron ore. However, the yield was then considerably improved on the other hand. Consequently, the productivity remained approximately the same in both conditions. Moreover, coke breeze consumption decreased by such a large amount that the NOx content in the exhaust gas drastically diminished. Regarding the quality of the iron ore sinter, an extremely characteristic trend was revealed that RDI was largely deteriorated, while RI was slightly improved despite lowered porosity. In addition, the benefits to SI improved significantly in correlation with the rise in the yield. On the other hand, no significant difference in the FeO content in the iron ore sinter could be found compared to the reference case, so it was verified that the FeO in the pre-reduced iron ore was reoxidized in the sintering process.

The heat pattern in the bed during the sinter pot test under the above two conditions is shown in Fig. 19. T1, T2 and T3 indicate temperatures observed with a thermocouple set at 450 mm, 300 mm and 100 mm respectively from a bottom of a sinter raw material bed. There was little difference in temperature trends of T1 and T2 between the test case with the pre-reduced iron ore addition and the reference case. However, there was a unique temperature trend of T3 in the test case. The T3 temperature increased later, stayed longer at a high temperature and decreased more slowly than in the reference case. The previously mentioned phenomena of significantly higher RDI is presumed to be due to the fact that a sinter raw material in a lower bed was melted at a higher temperature and cooled more slowly in the sintering process compared to the reference case. It is also presumed that the reoxidation of the pre-reduced iron ore affects the sintering process such as a composition and an amount of melt and solid phase constitution.

5. Application to an Actual Plant

In case of introducing this technology to an integrated steel works with a hot metal production scale of 4 million tons/year, a conceptional flow design and evaluation of the material balance are shown in Fig. 20. If pre-reduced iron ore produced by processing 0.6 million tons/year of an iron ore containing high combined water such as ore A corresponding to 10% of a sinter raw material is added as a part of a sinter raw material, it is possible to annually save 40 000 tons of coke breeze at the same productivity and the same quality of an iron ore sinter as in the case that a pre-reduced iron ore isn’t used. An amount of BFG used in the pre-reduction process is 1 140 Nm³/t-ore and approximately corresponds to 700 million Nm³/y, which is around 5% of the annual amount of BFG from a blast furnace of 4 million tons in annual productivity. This amount of BFG usage will not become an obstacle to introducing this technology to an integrated steel works in viewpoint of the overall energy balance.
The results of this technology on reduction of CO₂ emissions are shown in Fig. 21. A CO₂ emission factor of power by an electric power company of 0.367 kg-CO₂/kWh was assumed. The coke breeze saving of 40,000 tons/year is equivalent to the reduction of CO₂ emissions of 120,000 tons/year at the sinter plant. This full benefit can be acquired if BFG is excess and the excess amount is more than a necessary amount for pre-reducing iron ore. On the other hand, if BFG is fully used and diverted from a power plant into a pre-reduction process, the equal amount of power must be supplied by an electric power company. However, the CO₂ emission factor of power by an electric power company is so lower than that of power generated by a private or cooperative power plant. The difference between the coke breeze saving and the purchased electricity brings the reduction of CO₂ emissions of 50,000 tons-CO₂/year.

6. Conclusion

In order to solve a facing problem of reduction of CO₂ emissions and deterioration of iron ore quality, we propose a process that uses a pre-reduced iron ore as a sinter raw material. The pre-reduced iron ore is produced from a poor quality iron ore containing high combined water by pre-reduction in an atmosphere of BFG partial combustion gas. And the effects of using pre-reduced iron ore on the sintering process was investigated by conducting sinter pot tests using a pre-reduced iron ore as a part of the sinter raw material. The followings were confirmed.

(1) The fundamental experiment reducing an iron ore containing high combined water was conducted with low reducibility gas similar to BFG partial combustion gas at 1173 K using a small-scale experimental apparatus. The degree of reduction became 22–23%. In addition, a reducing rate was found to be affected by an iron ore brand but almost independent of the particle size of the iron ore.

(2) When dehydrating or pre-reducing an iron ore at 1173 K, the iron ore particle disintegrated on dehydration, and progressively more disintegrated on pre-reduction. The pre-reduced iron ore never reoxidized under the atmosphere.

(3) According to the results of the sinter pot test conducted using the pre-reduced iron ore as a part of the sinter raw material, the reoxidation heat of FeO in the pre-reduced iron ore can be so effectively utilized to decrease coke breeze consumption at a given productivity. The amount of decrease in coke breeze consumption was in proportion to the amount of increase in a pre-reduced iron ore added. In addition, no difference among the ore brands was identified. Also, NOx emissions in the exhaust gas were able to be reduced along with the decrease in coke breeze consumption.

(4) As long as the rate of pre-reduced iron ore added did not exceed 20%, there was little effect of the addition of pre-reduced iron ore on the quality of the iron ore sinter at a given productivity. On the other hand, when a large quantity of pre-reduced iron ore was added to 53% of a sinter raw material, RI and SI improved while RDI worsened.

(5) The amount of coke breeze consumption in a sinter plant decreases by 40,000 tons/year according to substitution of pre-reduced iron ore for 10% of a sinter raw material in an integrated steel works with a hot metal production of 4 million tons/year, which contributes to reduction of CO₂ emissions between 50,000 and 120,000 tons-CO₂/year.

REFERENCES