Abstract

JFE Steel Corporation developed a technology for injection of hydrogen-based gas fuel in sintering machines, "Super-SINTER™ (Secondary-fuel Injection Technology for Energy Reduction)", which makes it possible to greatly reduce CO2 emissions in the sintering process, and successfully applied this technology to a commercial sinter plant for the first time in the world. This equipment was put into commercial operation in December 2010~August 2011 at West Japan Works (Kurashiki District), and in July 2011, and has continued to perform smoothly up to the present. In ordinary sintering process, after coke breeze is mixed with iron ore and limestone, raw materials are charged and sintered in sintering machine. To product high strength and reducibility sintered ore, the temperature in the sintering bed is kept between 1,200 degrees and 1,400 degrees during sintering. In the temperature zone below 1,200 degrees, the strength of sintered ore decrease because raw materials are not melted enough. In the temperature zone over 1,400 degrees, the strength and reducibility decrease by increase of glassy silicate. With "Super-SINTER" technology, it is possible to extend the period in the optimum temperature by injecting a hydrogen-based gas fuel from the upper side of the charged raw materials as a partial substitute for coke breeze. As the result, the energy efficiency of the sintering process is greatly improved.

Key words: Sintering; Gas; Fuel; Injection.

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In recent years, the reduction of CO₂ emissions has become an urgent issue in the steel industry as countermeasure against global warming. Approximately 60% of the steel industry emissions are generated in the sintering and blast furnace processes. Therefore, the reduction of coke breeze ratio used in sintering machine (hereinafter, bonding agent ratio, BAR) and the carbonaceous materials ratio used in the blast furnace (hereinafter, reducing agent ratio, RAR) has been strongly required. It is widely known that the improvement of sinter strength and reducibility is an effective method for reducing BAR and RAR. In other words, if the sinter strength is improved, the generation ratio of return fine decrease and the BAR can be reduced. If the sinter reducibility is improved, it becomes possible to reduce RAR in the blast furnace. Accordingly, it is important to produce the high strength and high reducibility sinter for decrease in CO₂ emissions in ironmaking process.

The temperature in the sintering bed must be kept between 1,200°C and 1,400°C to produce high strength sinter. Generally when BAR increases, the sinter strength improves, because sinter mixtures are melted enough. If BAR increases excessively, the sinter strength decreases by the generation of glassy silicate with over melting. In the past, various technologies have been proposed, in order to improve the sinter yield without increasing BAR. For example, it was reported that the main exhaust gas recirculation system in sintering machines decreases the cooling rate with its sensible heat. In these previous reports, it was pointed the sinter productivity decrease with the lower O₂ concentration and higher humidity in the main exhaust gas. On the other hand, the preheated air injection methods were suggested. It is difficult to control the temperature zone over 1,200°C, because the preheating air temperature was low between 150°C and 450°C. It also deteriorated the permeability with the increase in actual velocity. Therefore each technology is not widely applied to sintering machines for above reasons.

Then the hydrogen-based gaseous fuel (hereinafter, gaseous fuel) injection technology was developed and applied successfully to sintering machines at Kurashiki No.2~4 sintering plants in JFE Steel Corporation. This technology enables to produce high strength sinter without increasing BAR by changing the heating/cooling rate in the sintering process.

The fundamental research was carried out at the laboratory scale to clarify the effect of gaseous fuel injection on the temperature distribution, pressure drop and the pore structure in the sinter cake. Operational tests were also performed at commercial plant to verify the principle of this technology.

2 CONCEPT OF THIS TECHNOLOGY

2.1 Control of Mineral Compositions in the Sinter

The major mineral composition of sinter is hematite. The others are silico ferrite calcium and aluminum (hereinafter, SFCA) texture excelling in strength and reducibility, and glassy silicate texture being inferior strength and reducibility. It is common knowledge that these mineral compositions influence sinter strength and reducibility. Figure 1 shows the schematic diagram of forming mineral composition in the sintering process. SFCA texture is formed above 1,200°C, however it decomposed into glassy silicate over 1,400°C. Based on fundamental research, authors found out that it’s effective for forming SFCA texture to control the holding time of temperature between 1,200°C and 1,400°C.
2.2 Control of Temperature in the Sintering Bed with Gaseous Fuel Injection

Increasing coke breeze rate is a conventional method to extend the holding time of temperature over 1,200°C. However, this method causes overheating and temperature exceeding 1,400°C. As a result, SFCA texture decomposed into glassy silicate texture, and then strength and reducibility may decrease by contraries. Therefore, the increase of coke breeze rate is not effective way to improve sinter strength and reducibility.

Therefore, authors focused on phenomenon that the combustion position of gaseous fuel is different from coke breeze in the sintering bed. If these combustion points are controlled properly, it'll enable to extend the holding time of optimum temperature between 1,200°C and 1,400°C.

3 EXPERIMENTAL METHOD

3.1 Sintering Pot Test

Figure 2 shows the measurement method for the temperature distribution and pressure drop in the sintering bed. Transparent quartz glass pot (300 mm φ x 400 mm height) was used. After charging all sinter mixture (ca. 42 kg/charge) into the pot and igniting it, liquefied natural gas (hereinafter, LNG; CH₄/C₂H₆/C₃H₈ = 89/5/6 vol.%]) and air were injected from the top of sintering bed after 60 s from ignition. LNG was injected for all sintering time. The sintering test was performed at the constant suction pressure of 6.9 kPa and the hearth layer thickness of 20 mm. Video camera and infrared thermography were set in front of the glass pot and R type sheathed thermocouples (1.6 mm φ x 200 mm length) were used to compensate the temperature data acquired by thermography. The three thermocouples were inserted 150 mm into pot side holes, which were installed at intervals of 100 mm in height.
The blending ratio of limestone and silica sand were adjusted to obtain a SiO₂ content of 4.8 mass% and basicity (CaO/SiO₂) of 1.9 in the sinter, and return fine ratio was set at 20 mass%.

Table 1 shows the experimental conditions in the sintering pot test. In the conventional case, coke breeze ratio was set at 5.0 mass% of the all sinter mixture. In the LNG injection case, LNG concentration was set at 0.4 vol.% versus suction air. When LNG concentration was set at more than 1/10 of the lean flammable limit 4.8 vol.%, the improvement effects were saturated. Based on this preliminary evaluation and safe, LNG concentration was decided. When the LNG injected with coke breeze ratio of 5.0 mass%, the over melting was caused and the sinter strength was decreased. Therefore coke breeze ratio was set at 4.6 mass% to match equal combustion heat amount and avoid over melting. Here, the combustion heat of coke breeze is higher heating value of 27.1 MJ/kg measured according to JIS M8814 and LNG is lower heating value of 41.6 MJ/Nm³ measured according to JIS K2301. The average suction air volume was 1.5 m³/min measured with the orifice flowmeter.

In these tests, shatter strength was measured according to JIS M 8711 (Test method for determination of shatter strength of iron ore sinter). The degree of reduction (hereinafter, JIS-RI) was measured according to JIS M 8713 and reduction disintegration index (hereinafter, JIS-RDI) was measured according to JIS M 8720. The quantitative analysis of hematite, SFCA, magnetite and glassy silicate were performed by the powder X-ray diffraction method in the same way as previous reports.

The pressure drop in the sintering bed was measured based on the method proposed by Shibata et al. The pressure probes (stainless steel tube) were inserted 150mm into the pot side hole. The temperature was measured simultaneously to classify the sintering reaction states. Suction gas volume was set at 1.0 Nm³/min with orifice flowmeter installed above sinter pot. The thickness of burning-melting zone was approximately 30 mm. Therefore the pressure probes were also inserted at 200 mm height and 230 mm height position from the top of sintering bed.

Table 1: Experimental conditions in the sintering pot test

<table>
<thead>
<tr>
<th></th>
<th>Conventional method</th>
<th>LNG injection method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke (mass%)</td>
<td>5.0</td>
<td>4.6</td>
</tr>
<tr>
<td>LNG (vol.%)</td>
<td>0.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>
3.2 Sintering Test Using Hot Stage X-Ray CT Scanner

The pore structure have a major effect on the sinter quality and permeability in the sintering bed\(^\text{(11)}\), because the pores in the sinter cake are simultaneously structural defects and also function as air passages. In more detail, the pores over 5 mm improved the permeability in the sintering bed\(^\text{(11)}\) and the pores (1-5 mm) deteriorated sinter strength\(^\text{(9)}\). Although, there were various theories\(^\text{(12)}\) for the diameter of micro pores to improve JIS-RI, the diameter was defined under 1 mm in these studies. Therefore a sintering test was performed with a X-ray CT scanner\(^\text{(13)}\), which had been remodeled to enable the LNG injection to observe the changes in the pore structure in the sinter cake directly.

The X-ray tube voltage was 130 kV, the tube current was 200 mA, and it took 2.8 s to photograph one cross-sectional image. The resolution of the CT images was 1 mm. First, the sinter mixture was charged into carbon test pot (100 mm $\phi \times$ 100 mm height), and the suction gas volume was set at 0.2 Nm$^3$/min measured by the pitot tube flowmeter located under the pot. The LNG concentration was set at 0.4 vol.% (relative to the suction air volume) and then LNG was injected from upper side after 180 s from ignition. The other conditions were the same as previous report\(^\text{(13)}\).

In addition, the pore size distribution was measured with a mercury porosimeter. The samples were screened in 4.0~6.7 mm to fit on cell size, and measured 3 times with each condition.

3.3 Commercial Sintering Machine Test

In order to quantify the effects of this technology on the commercial sintering operation, the operational tests were conducted at Kurashiki No.4 sinter plant, based on the laboratory experimental results. Table 2 shows the experimental conditions in the operational test. The LNG injection volume was set at 250 Nm$^3$/h (0.5 Nm$^3$/t-s, combustion heat amount: 20 MJ/t-s). The bonding agent consumption was reduced from 53 kg/t-s to 50 kg/t-s (heat amount 80 MJ/t-s). Therefore, the reduced heat amount was approximately 4 times as large as injected LNG heat amount. The LNG was injected at the initial 1/3 length of the sintering machine, where the flame front existed in the upper layer. The sinter strength of the upper layer tends to be weaker than that of the lower layer.

The blending conditions for sinter mixture were held constant. The granulation moisture was set at 7.6 mass% and the bed height was set at 650 mm. The pallet speed was controlled so that BTP (burn through point; end point of sintering) were constant. One test campaign was performed for 4 days, and 5 test campaigns were conducted. Tumble strength as the index of sinter strength was measured according to JIS M 8712.

Moreover, R type sheathed thermocouples (3.2 mm$\phi$ x 1,000 mm length) were inserted 500 mm into the sintering bed through the holes installed in the sidewall. The effect of LNG injection method on the temperature distribution was quantified in the sintering machine.
4 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Effect of Gaseous Fuel Injection Method on Sintering Characteristics

Figure 3 shows a comparison of the combustion behavior, sinter productivity and quality between the conventional method and the LNG injection method in the middle layer of the sintering bed. The observation results confirmed that the red-hot region, in which the combustion/melting zone existed, was greatly expanded by the LNG injection method.

On the other hand, the sinter strength improved and the generation rate of return fine decreased remarkably, while the sintering time was almost the same. Although JIS-RI and JIS-RDI normally tended to be inversely related to sinter strength, also improved with the LNG injection method.

<table>
<thead>
<tr>
<th>Measure</th>
<th>Conventional method</th>
<th>LNG injection method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke (mass%)</td>
<td>5.0</td>
<td>4.6</td>
</tr>
<tr>
<td>LNG (vol.%)</td>
<td>0.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Red-hot region width (mm)</td>
<td>60</td>
<td>150</td>
</tr>
<tr>
<td>Sintering time (min.)</td>
<td>16.0</td>
<td>16.7</td>
</tr>
<tr>
<td>Sinter yield (%)</td>
<td>69.0</td>
<td>72.8 (+3.8)</td>
</tr>
<tr>
<td>Productivity (t/h・m²)</td>
<td>1.56</td>
<td>1.64 (+0.8)</td>
</tr>
<tr>
<td>Shatter index (%)</td>
<td>70.7</td>
<td>72.9 (+2.2)</td>
</tr>
<tr>
<td>JIS-RDI (mass%)</td>
<td>36.1</td>
<td>28.3 (-7.8)</td>
</tr>
<tr>
<td>JIS-RI (%)</td>
<td>64.5</td>
<td>70.4 (+5.9)</td>
</tr>
</tbody>
</table>

Figure 3: Comparison of the combustion behavior in the sintering bed, sinter productivity and quality between the conventional method and the LNG injection method.

4.2 Effect of Gaseous Fuel Injection Method on Temperature Distribution in the Sintering Bed

Figure 4 shows the effect of the gaseous fuel injection method on temperature distribution measured by the thermography in the sintering bed. In this figure, the temperature zone over 1,200°C was expanded in upper direction with the LNG injection. The combustion positions of the LNG and coke breeze were different in the direction of bed height, because the LNG was injected from the top of sintering bed and burned before reaching at the coke breeze combustion position with the temperature 650-750°C. Here this temperature was the ignition temperature of CH₄ composing approximately 90% of LNG. Therefore the temperature zone over 1,200°C...
was expanded in upper direction with the low cooling rate by the combustion positions difference.

Figure 5 shows the changes in the temperature distribution measured by the infrared thermography with the gaseous fuel injection method. From these results, the temperature zone over 1,200°C was narrow and the maximum temperature was over 1,400°C in the conventional method.

<table>
<thead>
<tr>
<th>Coke 5.0mass% (Conventional method)</th>
<th>Coke 4.6mass% and LNG 0.4vol.% (LNG injection method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Video</td>
<td>Thermography</td>
</tr>
</tbody>
</table>

Figure 4: Effect of the gaseous fuel injection method on temperature distribution measured by the thermography in the sintering bed.

In contrast, the maximum temperature decreased, but the temperature zone over 1,200°C was greatly expanded with the gaseous fuel injection method. Moreover the holding time over 1,200°C measured by the thermocouples was extended from 144 s to 376 s at 200 mm height from the top of sintering bed. Moreover it was confirmed that the gaseous fuel burned above the coke breeze combustion position with the temperature 650-750°C in Figure 5.

Figure 5: Changes in the temperature distribution measured by the infrared thermography with the gaseous fuel injection method.
4.3 Effect of Gaseous Fuel Injection on Pore Structure in Sintering Bed

A sintering test using the hot stage X-ray CT scanner was performed to clarify the effects of gaseous fuel injection on pore structure in the sintering bed. Figure 6 shows the comparison of X-ray CT image in the sinter cake between the conventional method and the LNG injection method. In this figure, the solid parts are shown in white and pores in black. From these results, the pore over 5 mm increased and the pore (1-5 mm) decreased by the LNG injection method in comparison with the conventional method. The extension of the holding time over 1,200°C increased liquid phase rate of the SFCA. As a result, the increase in liquid phase ratio promoted the combination of pores (1-5 mm) and improved the sinter strength.\(^9\)

Figure 7 shows the change in the pore size distribution measured by the mercury porosimeter with LNG injection method. From this figure, with the LNG injection method, the sinter contained a large number of micro pores under 1 µm in comparison with the conventional method. As shown in Figure 5, the BAR was decreased with the LNG injection method and the maximum temperature decreased. As a result, the iron ore self-densification\(^{14}\) was depressed and a large number of micro pores under 1 µm remained in unmelted ores with the LNG injection method. Therefore JIS-RI was improved with a larger number of micro pores under 1 mm remained in unmelted ores by the LNG injection method\(^{12}\).
4.4 Effect of Gaseous Fuel Injection on Permeability

After 500 s from ignition, the pressure drop reached its maximum value and its difference was remarkable between the conventional method and the LNG injection method. Therefore the pressure drops of both conditions were compared to investigate the effect of the gaseous fuel injection method after 500 s from ignition. The sintering bed was classified into 4 zones (sinter cake zone, melting zone, combustion zone, wet zone) and the thickness of each zone was determined with the temperature distribution based on the method proposed by Shibata et al.\(^{(10)}\).

Figure 8 shows the changes of pressure drop in each zone by the LNG injection method at 500 s after ignition. In this figure, no remarkable difference was observed in the wet zone with the both methods. The LNG injection method decreased the pressure drop in the combustion/melting zone by 32% in comparison with the conventional method. As a result, the LNG injection method decreased the pressure drop in the whole sintering bed by 15% in comparison with the conventional method.

As described section 4.3, the LNG injection method extended the holding time over 1,200°C and increase the liquid phase ratio\(^{(15)}\). As a result, the increase in liquid phase ratio promoted the combination of pores (1-5 mm) and increased the penetrated pores over 5 mm as air passages. Therefore the pressure drop decreased in the combustion/melting zone\(^{(11)}\).

4.5 Effect of Gaseous Fuel Injection on Formation of Mineral Texture

Figure 9 shows the change of mineral composition with LNG injection method in the sintering pot test. From these results, LNG injection method increased the SFCA ratio by 1.6 times in the sinter and decreased in the glassy silicate ratio.

The LNG injection method extended the holding time between 1,200°C and 1,400°C in the sintering bed from 144 s to 376 s. This extension of holding time in the proper temperature zone depressed the decomposing SFCA texture into glassy silicate texture. As a result, the SFCA ratio increased and the glassy silicate ratio decreased with the LNG injection method.

Kissin et al.\(^{(8)}\) reported that the SFCA texture was excellent strength and reducibility,
and the glassy silicate texture was inferior in these two properties. Therefore the increase in the SFCA ratio and the decrease in the glassy silicate ratio were part of reason that the LNG injection method improved sinter strength and reducibility.

![Figure 9: Change of mineral composition by LNG injection method in the sintering pot test.](image)

**4.6 Effect on Operational Condition at Kurashiki No.4 Sinter Plant with Gaseous Fuel Injection**

At first, the effect of the gaseous fuel injection on the temperature distribution was evaluated at Kurashiki No.4 sinter plant. Figure 10 (a) shows the temperature distribution in the upper layer, while (b) shows that in the lower layer. As shown in Figure 10 (a), although the upper layer tends to get low heat, the holding time over 1,200°C was extended from 135 s to 290 s without the maximum temperature rising by the LNG injection method. Although the lower layer tends to overheat, Figure 10 (b) shows that the maximum temperature decreased from 1,410°C to 1,346°C with the LNG injection method. The decrease of the maximum temperature was caused by the decrease of bonding agent consumption in 3.1 kg/t-s. Therefore the sinter strength at the upper weak layer was improved by the LNG injection and the decrease of bonding agent consumption.

The temperature distribution with the LNG injection method was considered to be the 'low-temperature sintering process' (15), in which the maximum temperature was not greatly increased and the holding time over 1,200°C was extended.

Figure 11 shows the changes in the operational result and quality between LNG injection method and conventional method. In this figure, the shatter strength increased by approximately 0.9% with the same sinter production in the LNG injection method. Therefore, the bonding agent consumption was reduced with this increase in the sinter strength. Bonding agent consumption was reduced by 3.1 kg/t-s and CO₂ emissions were reduced by a maximum of approximately 170kton/year at Kurashiki No.2〜4 sinter plants.
Figure 10: Effects of LNG injection on the temperature in the sintering machine at Kurashiki No.4 Sinter Plant.

Figure 11: Effects of LNG injection on sintering operation and quality at Kurashiki No.4 sinter plant.

Table 3 shows the comparison of heat balance and sinter quality at Kurashiki No.4 sinter plant. In the calculation for the heat balance, the heat inputs consisted of combustion heat of coke oven gas in the ignition furnace, combustion heat of coke breeze and LNG. From this table, the unit heat consumption decreased by approximately 60 MJ/t-s with the LNG injection method in comparison with the conventional method. Here, combustion heat of coke oven gas was 17.6 MJ/Nm³, coke breeze was 27.1 MJ/kg and LNG was 41.6 MJ/Nm³. However the unit heat
consumption decreased with the LNG injection method, it was possible to improve by 0.9% in shatter strength in comparison with the all coke method at the same sinter production.

The several times of operational tests were carried out at the commercial sintering machine and confirmed the principle of this technology.

Table 3: Effects of LNG injection on the temperature in the sintering machine at Kurashiki No.4 sinter plant

<table>
<thead>
<tr>
<th>Heat input</th>
<th>Conventional method</th>
<th>LNG injection method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion heat of Coke-oven gas</td>
<td>39</td>
<td>39</td>
</tr>
<tr>
<td>Combustion heat of coke breeze</td>
<td>1505</td>
<td>1420</td>
</tr>
<tr>
<td>Combustion heat of LNG</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>Total (MJ/t-s)</td>
<td>1544</td>
<td>1481</td>
</tr>
</tbody>
</table>

5 CONCLUSION

A fundamental study was carried out in the laboratory experiment to confirm the effect of the gaseous fuel injection technology on the temperature distribution, the sinter texture, pressure drop and the pore structure in the sinter cake. The effects of this technology were also quantified by performing operational tests at the commercial plant.

The following conclusions were obtained as a result of this research.

- The temperature zone between 1,200°C and 1,400°C was expanded in upper direction without increasing the maximum temperature in the sintering bed with the gaseous fuel injection method, because the gaseous fuel was injected from top of sintering bed and burned before reach at the coke breeze combustion position with the temperature 650-750°C;
- the increase in SFCA ratio and decrease in glassy silicate ratio were caused with the extension of holding time between 1,200°C and 1,400°C in the sintering bed with the gaseous fuel injection method. The increase in SFCA ratio and the decrease in the glassy silicate ratio were part of reason that the LNG injection technology improved sinter strength and reducibility;
- the gaseous fuel injection technology promoted the pore (1-5 mm) combination and the pore over 5 mm growth by increasing the liquid phase ratio. As a result, the decrease in the number of pores (1-5mm) improved sinter strength and the increase in the number of penetrated pores over 5 mm improved permeability in the sintering bed;
- the bonding agent ratio was decreased with the gaseous fuel injection method and the maximum temperature decreased in the sintering bed. As a result, the iron ore self-densification was depressed and the large number of micro pores under 1 µm remained in the unmelted ores with the gaseous fuel injection method. This also improved reducibility;
- the gaseous fuel injection technology enabled to produce the high strength and high reducibility sinter while maintaining the same level of sinter production at commercial sinter plant. Moreover it has achieved to decrease bonding agent consumption by 3.1 kg/t-s and reduce CO₂ emissions by a maximum of approximately 170 kton/year at Kurashiki No.2~4 sinter plants.
REFERENCES