Technical Report

Lime Coating Coke (LCC) for Reduction of Nitrogen Oxide Emissions in Iron Ore Sintering Plants

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Abstract

The lime coating coke method (LCC), where coke breeze is coated with CaO materials, has been developed to decrease the nitrogen oxide (NO_x) emission from iron ore sintering plants. The CaO coated on the coke surface melts with the iron ore existing around LCC in the sintering bed then produces calcium ferrites on the coke surface at about 1 200°C. The reduction of the NO_x is achieved by the calcium ferrites, which promotes the reduction of the NO_x and also increases the temperature of coke combustion. Further investigations were performed in order to improve the strength of the coating layer. The LCC plant has successfully been installed at Oita No. 2 Sintering Plant and a NO_x reduction of more than 15% has been obtained since April 2013.

1. Introduction

In the iron ore sintering processes, coke breeze and other types of bonding agents are used with iron ore and limestone. Previous studies have concluded that a large part of nitrogen oxides (NO_x) in gas emissions from the sintering process is derived from nitrogen components in the coke breeze, generally called Fuel NO.1,2) The steel industry emits 14% of the total NO₂ emissions from stationary sources in Japan, being a large source following the electric and ceramic industries.³⁾ Sintering plants are the largest NO_x emission sources in steelworks. Steelmakers have been working to reduce NO, emissions while enhancing the production capacity in line with the continuous high demand for steel. A general NO₂ reduction measure is introducing exhaust gas treatment equipment on the exhaust gas lines in sintering plants to denitrate formed NO₂. However, the total gas emissions need to be treated in the later stage in this method and thereby large-scale equipment needs to be additionally installed to handle a large quantity of gas. Increase in the operation cost due to expensive supplies is inevitable in this case in addition to investment in high-value equipment.

Other technologies to reduce NO_x emissions in sintering plants directly have been studied. A previous study has revealed that Fuel NO, which is derived from nitrogen contained in coke breeze, can be reduced by decreasing the oxygen content in the gas film formed

on the surface of coke breeze and coke combustion at higher temperatures is effective for NO_x reduction.⁴⁾ Examples are a technology to improve the permeability of packed beds of the raw materials in which quick lime is blended as an iron ore granulation binder and another technology to remove small (0.5 mm or smaller) coke breeze. However, although the former has been practically implemented, the effects are limited and the latter has not been put to practical use because removing small coke breeze is difficult.⁵⁾

In addition, a technology to form a coating layer of calcium ferrite (CF) on the surface of coke breeze has been highly valued in the basic study as it reduces NO_x emissions significantly.^{6–8)} However, the formed thick coating layer may prevent the coke breeze from reacting in this method, which may cause the coke breeze to lose its function as a bonding agent, which in turn may deteriorate the sinter productivity. In addition, it is difficult to design commercial plants that can control the height and components of coating layers accurately since such plants naturally process a large quantity of materials, so this method has not been put to practical utilization.

Nippon Steel Corporation focused on forming a coating layer on the surface of coke and developed lime coating coke (LCC)—a new coating technology to cover coke breeze with CaO materials.⁹⁾ This coating technology can reduce NO_x emissions while maintaining the function as a bonding agent and it was introduced into Oita No.2

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Sintering Plant. This report describes in detail the basic study of this LCC technology development and operation results at Oita No.2 Sintering Plant.

2. Basic Experiment

2.1 Function of coating layer composition on the surface of coke and NO_x emissions

Coke breeze 1.4 to 2.0 mm in size was mixed with quick lime and 0.25-mm or smaller iron ore fines (coating materials) to prepare several types of coated coke for which the composition and quantity of both materials varied. The coated coke was mixed with alumina balls that were used in place of sinter raw materials (e.g., iron ore and limestone) and the mixture was charged into a laboratory-scale pot shown in Fig. 1 to form a packed bed. The alumina balls are used to prevent the main raw material that forms a packed bed from reacting with the coating materials. This measure makes it possible to identify which substance is effective for NO₂ emissions reduction. The coated coke on the surface of the packed bed was burned for 90 seconds in an ignition furnace. The reaction was maintained at a constant negative suction pressure of 4.0 kPa and the experiment ended when the coke at the bottom of the packed bed had completely reacted. The coke reaction time was from the test start to when the oxygen content in exhaust gas reached 19.5%. The mean gas content during this period was regarded as a representative value under each test condition.

Next, as an index to evaluate NO_x emissions, the NO conversion rate (ηNO) that indicates the molar ratio of the NO_x emission amount to the nitrogen amount in the raw materials was calculated with Formula (1). It was assumed that the CO and CO_2 in the exhaust gas was derived from the ignition gas, coke breeze, and limestone (limestone was used in the experiments to be described in the following chapters) and that the NO_x in the exhaust gas was derived only from the coke breeze to calculate ηNO .

 $\eta \text{NO} = 100 \times \text{NO}_{x} / \{(\text{CO} + \text{CO}_{2}) \cdot \text{N}_{\text{COKE}} / (\text{C}_{\text{LPG}} + \text{C}_{\text{COKE}} + \text{C}_{\text{LS}})\} / 10000$ (1)

Where,

 η NO: NO_x conversion rate (%)

NO_x: NO_x concentration in exhaust gas (ppm)

CO: CO concentration in exhaust gas (%)

 CO_2 : CO_2 concentration in exhaust gas (%)

N_{COKE}: Nitrogen amount in raw materials from coke breeze (mol)





C_{LPG}: Carbon amount in ignition gas (mol)

 C_{COKE} : Carbon amount in raw materials from coke breeze (mol)

C_{1 s}: Carbon amount in raw materials from limestone (mol)

Figure 2 shows a function of the coating material composition and η NO. When only iron ore fines or CaO was used for coating, NO_x emissions reduction was limited. When CF was combinedly used (CF coating), the effect was remarkably high and the closer the coating material composition to the composition of active melt formation, the higher the effect. These results reveal that the NO_x emissions reduction effect is manifested via the formation of CF melt instead of the reaction of CaO itself.

2.2 Direct observation of melting behavior of CaO coating layers and surrounding iron ore

In actual sinter raw materials, coke breeze is surrounded by iron ore. The CaO materials themselves on the surface of coke breeze do not function to reduce NO_x emissions. However, it is regarded that CaO reacting with iron ore (main sinter raw material) forms CF melt that contributes to NO_x emissions reduction. An infrared heating furnace (hereinafter, gold image furnace or GI furnace) shown in **Fig. 3** was used to directly observe melting behavior occurring between coated coke and the surrounding iron ore fines at a constant temperature rise rate of 15°C/s up to 1400°C. One particle of coke breeze 2.0 mm in size or LCC was placed at the center of an alumina crucible with a diameter of 8 mm and this particle was surrounded by iron ore fines 0.5 to 1.0 mm in size to observe the melting behavior of the coating layer.



Fig. 2 η NO as a function of the quick lime ratio in the coating layer



Fig. 3 Gold image furnace used for evaluation of melting on the coke surface



Fig. 4 Pictures of coke and LCC surrounded by the iron ore heated up to 1300°C in the GI furnace

Figure 4 shows observation photographs of the GI furnace. The LCC was sound at 800°C. However, CF melt was formed at 1200°C by the chemical reaction between the CaO and iron ore fines. Moreover, the diffusion of the melt promoted the reaction, which increased the melt of the iron ore and LCC. Finally, melt was formed in a wide area and the coating layer completely melted to expose the coke breeze. On the other hand, in the case of coke breeze without adherent materials, melt formation near the coke was negligible even at 1 300°C. These results show that in the mixed raw materials containing iron ore as the main sinter material, even a coating layer consisting of only CaO can form CF melt including both materials quickly around 1 200°C.

2.3 Influence of coating CaO amount and lcc mixing time on NO conversion rate

The effects of coated coke on reducing NO_x emissions were evaluated in a series of sinter pot tests with general sinter raw materials including iron ore and limestone. Two types of coated coke were prepared: CaO coating (LCC) and mixed-powder coating of CaO and iron ore fines (CFCC). To understand the appropriate coating layer height and quantity, the blending ratio of the coating materials to the coke breeze was changed from 0 to 20 wt% (CaO/coke). Coke breeze is usually mixed and granulated with other raw materials in a drum mixer. However, the collapse of the coating layers in this process was of concern, so the time to mix CaO with other raw materials was changed from 20 to 300 seconds in accordance with the testing flow shown in **Fig. 5** to examine the influence of the mixing time on the NO_x emission amount.

Figure 6 shows the effect of the blending quick lime ratio to the total sinter mixture on η NO. Coating coke breeze with quick lime is more effective for reducing NO_x emissions than blending quick lime in raw materials of sintered ore in the conventional method. It has been confirmed that in general raw materials of sintered ore mainly consisting of iron ore, CaO coating (LCC) can reduce NO_x emissions and that the effect is saturated when CaO/coke is 10% or more. **Figure 7** shows the influence of the time to mix the coke breeze and LCC on η NO. By decreasing the mixing time of LCC, NO_x decreased. At a mixing time of 20 seconds, η NO decreases by 5.2% corresponding to the NO_x decreasing rate of 17.6%. In the case of coke breeze, no NO_x emissions reduction is seen as a result



Fig. 5 Procedure for the sintering pot tests



Fig. 6 η NO as a function of the CaO blending ratio to the sinter mixture



Fig. 7 η NO as a function of mixing time between LCC and other sinter material

of the reduced mixing time.

Secondly, a mixture of coke breeze or LCC with other raw mate-

rials was sampled to analyze the elements near the coke (**Fig. 8**). When the LCC mixing time was 300 seconds, an iron ore layer was formed on the surface of the coke while the CaO coating layer on the surface of the LCC collapsed. In the case of a shorter mixing time of 20 seconds, the CaO coating layer was retained on the entire surface of the coke. These results show that in a shorter mixing time of the LCC and other raw materials, the coating layer remains sound, which obtains the effect of NO_x emissions reduction.

Thirdly, changes in the sinter productivity as a result of LCC utilization were examined. The coke reactivity is an important factor that affects the sintering speed and the temperature profile of the sintering bed and they in turn affect the productivity.¹⁰⁾ The oxygen utilization ratio per unit air volume (ηO_2) and coke reactivity (ηC) were calculated with the following formulas as related indexes.

$$\eta O_2 = (21 - O_2)/21 \tag{2}$$

$$C = (CO + CO) \times V \times 1000/22.4$$
(4)

$$C_{in} = C_{COKE} + C_{LPG} + C_{LS}$$
(5)

Where,

 $\mathrm{C}_{\mathrm{out}}\!:$ Total carbon amount reacted (mol)

C_{in}: Total carbon amount in raw mixture (mol)

 C_{COKE} : Carbon amount from coke breeze (mol)

 C_{LPG} : Carbon amount from ignition gas (mol)

C_{LS}: Carbon amount from limestone (mol)

CO: CO concentration in exhaust gas (%)

CO₂: CO₂ concentration in exhaust gas (%)

V: Total exhaust gas volume (Nm³)

Table 1 lists the reactivity index and productivity. The shorter the mixing time of the coke or LCC with other raw materials, the



Fig. 8 Elemental analysis results of coke and LCC mixed with other sinter materials

Table 1	Coke reactivit	v and sinter	productivity
rabic r	Conc reactivit	y and since	productivity

Coke type	Coke	Coke	LCC
Mixing (s)	300	20	20
ηO ₂ (-)	0.36	0.43	0.42
ηC (-)	0.82	0.92	0.92
Productivity (t/d/m ²)	34.1	38.9	40.9

higher the ηO_2 and ηC , which means that the reaction rate and volume of the coke were improved. In the case of LCC, exposure of the coke due to the melting coating layer at high temperatures, which was seen in the GI furnace test, may have improved the reactivity, which in turn may have improved the sinter productivity.

3. LCC Process Design and Commercial Plant Operation Results

Figure 9 shows how LCC reduces NO_x emissions at a sintering plant. Kasai et al. considered that CF compounds accelerate NO_x reduction by CO and that CF coating increases the reaction temperature of coke breeze, which reduces NO_x emissions.^{6,7} For LCC, the reaction may be employed between the main raw material (iron ore) and CaO (coating) to form a large quantity of CF on the surface of the coke and may achieve selective reaction at high temperatures as a result of the melting coating layer, which may form a reaction field that produces a NO_x emissions reduction effect similar to that of CF coating.

In addition, LCC does not require iron raw materials as coating materials unlike CF coating and thereby does not require excessive coating materials. Therefore, the risk of insufficient reaction of coke that is of concern in the utilization of coated coke can be reduced. To improve coke breeze reactivity, it is effective to form a thin adherent layer of iron ore on the surface of coke breeze. However, such method allows the coke to be exposed at all times and thereby the reaction of the coke becomes active at low temperatures in an early stage of the reaction, which increases NO₂ emissions. That is to say, controlling the adherent layer height of iron ore cannot reduce NO_x emissions and cannot improve the coke reactivity at the same time. Such reduction and improvement can be achieved by forming a coating layer with high meltability at high temperatures around 1200°C like LCC that suppresses the reaction at low temperatures and improves the reaction at high temperatures at the same time.

The basic study described in the previous chapter has confirmed that retaining the CaO coating layers until the materials are charged into sintering plants is important. In the application of the LCC technology to a commercial sintering plant, collapse of coating layers was of concern compared to the basic study, so additional study was performed to form strong coating layers. In this process study, a pre-hydration process of quick lime for coating and a granulation process using a pelletizer (hereinafter "PP") after the coating process were evaluated in laboratory tests. Dry LCC was treated for 300 seconds with a rotating and tapping shaker. To evaluate the coating



Fig. 9 Image of how LCC reacts in the iron ore sintering bed



Fig. 10 Change in -0.25 mm fine ratio of the dried LCC by pre-hydration of quick lime and PP granulation



Fig. 11 NO_x concentration as a function of the LCC fine ratio with or without pelletizing of LCC

layer strength, the percentage of particles 0.25 mm in size or smaller was used.

Pre-hydrated quick lime (H-QL) and normal quick lime (QL) were used and LCC was sampled at each of the outlet of a coating mixer and following PP outlet and the LCC fines were sieved into particles 0.25 mm or smaller. **Figure 10** shows the -0.25-mm-LCC fine ratio. The pre-hydration of the quick lime (coating material) and the granulation with the PP decreases the -0.25-mm-LCC fine ratio, which shows that these operations contribute to enhancing the LCC coating strength. Quick lime turns to highly adhesive Ca(OH)₂ as a result of the hydration reaction. For both H-QL and QL, it is likely that Ca(OH)₂ exists in the mixer. The pre-hydration can complete the hydration reaction without fail, which may form a high-strength coating layer on the weak adhesive coke breeze.

The LCC processed with the PP was subjected to a pot test to evaluate NO_x emissions reduction effects. Figure 11 shows the function of the -0.25-mm LCC fine ratio and NO_x concentration. The lower the LCC fine ratio, the lower the NO_x concentration. These results show that the installation of a PP and the pre-hydration of quick lime work to enhance the coating strength, which serves to further reduce NO_x concentration.

Based on the results of the prior study, the LCC process was introduced into Oita No.2 Sintering Plant with a sintering area of 660 m². The operation began in April 2013. **Figure 12** illustrates the LCC process flow. The LCC production line consists of a hydrating mixer in which pre-hydrated quick lime is produced, a mixer that coats coke with the hydrated lime, and a PP for enhancing the coating strength. This process can utilize all of the coke breeze to LCC.

LCC is charged from the second drum mixer via a conveyor to reduce the time during which it is in contact with iron ore and other sinter raw materials. **Figure 13** shows the NO₂ concentration and



Fig. 12 LCC process schematic diagram installed to Oita No.2 Sintering Plant



other main operation results in sinter production using LCC. During the evaluation period, all contents of coke breeze of 50 kg/t-sinter except anthracite and other carbon materials among the bonding agents were processed on the LCC line. Immediately after the start of LCC utilization, the NO_x concentration clearly decreased. The NO_x emissions reduction effect is stable as the concentration has decreased by approximately 28 ppm and the emissions by 15% or more. In addition, in the operation using LCC, the product yield was improved by 1.1% and the productivity by 0.6 t/d/m². These improvements are likely attributed to the improved coke reactivity.

4. Conclusion

Nippon Steel succeeded in developing the technology to coat coke breeze with CaO—Lime coating coke (LCC)—that can reduce NO_x emissions in exhaust gas in the iron ore sintering processes directly.

In the LCC process, a CaO coating layer is formed on the surface of coke breeze. The technology can reduce NO_x emissions by using a spontaneous melting reaction with the surrounding iron ore fines to accelerate the NO_x reduction by CF compounds and achieve selective coke combustion at high temperatures. In addition, the selection of Ca(OH)₂ as a material coated on the surface of coke, which is highly adhesive, allows a coating layer that is practically

strong to be formed evenly on the surface of weak-adhesive coke.

In developing the LCC process at Oita No.2 Sintering Plant, the process was studied focusing on the suppression of coating layer collapse. The first LCC process was introduced into Oita No.2 Sintering Plant. The LCC production line consists of a quick lime pre-hydration mixer, a coating mixer, and a PP. LCC is charged from the outlet of the second mixer for sinter raw material granulation. This process has made it possible to charge LCC with sufficient height of the coating layer into the sintering machine at commercial large-scale sintering plants. The process has been operating without serious problems with its function and equipment since the operation start in April 2013, reducing NO_x emissions by 15% or more stably.

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