Reaction Behavior of Ca-loaded Highly Reactive Coke

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Usage of highly reactive coke in order to decrease the thermal reserve zone temperature in a blast furnace is considered promising to increase the reaction efficiency in the blast furnace and to decrease the reducing agent rate. In order to develop a new method to produce highly reactive coke by adding a Ca catalyst other than Ca-rich coal, in this paper, firstly the effects of Ca compounds pre-addition to coal on coke qualities were investigated. It was shown that carbonizing the mixture of coal and Ca compounds (CaO, CaCO3) greatly increased coke reactivity and that it was possible to produce Ca-loaded highly reactive coke with high coke strength by adding 3% of Ca compounds under such conditions as high strength coke was produced. Furthermore, the reaction behavior of Ca-loaded highly reactive coke when mixed with conventional coke in the presence of an alkali was investigated. It was shown that when a mixture of Ca-loaded highly reactive coke and conventional coke was heated in a reaction gas, Ca-loaded coke selectively and preferentially reacted. It was also confirmed that Ca acted as catalyst in the existence of K. This shows that the reactivity of Ca-loaded coke is higher than that of conventional coke in an actual blast furnace whereby coke reactivity is promoted by condensed alkali vapor.

KEY WORDS: coke; calcium; high reactivity; thermal reserve zone; alkali.

1. Introduction

Decreasing the reducing agent rate (the amount in kilograms of reducing agents such as coke and coal needed to produce 1000 kg of pig iron) in the blast furnace has become one of the most significant issues in the ironmaking process from the viewpoint of saving energy and fossil fuel resources.1,2) Some ideas have been proposed to decrease the reducing agent. Among them, a technological approach proposed by Naito et al. that dramatically improves the reaction efficiency in blast furnaces through the use of highly reactive coke is considered the most feasible and promising.1–6) The theory of this technology is as follows: Highly reactive coke starts to react with CO2 (solution loss reaction C+CO2=2CO) at a lower temperature, which lowers the temperature range of the thermal reserve zone in blast furnace. This decrease in temperature shifts the Wustite-iron reduction equilibrium gas concentration to a higher CO2/(CO2+CO) composition and increases the driving force for reduction expressed by the gap between the actual gas concentration and the Wustite-iron reduction equilibrium gas concentration. A key to the success of this technology is how to produce highly reactive coke in a commercial-scale plant. The authors have investigated methods to produce highly reactive coke with high strength that can be used in an actual blast furnace, through the use of the catalytic effect.5,6) There have been many studies on catalysts for CO2 gasification of coal and char. The order of catalytic activity and the mechanism of catalytic reactions of the alkaline metals such as Na, K and Li, the alkaline earth metals such as Ca and Ba, and the transition metals such as Fe and Ni have been thoroughly and extensively studied.7–18) There are considered to be two basic methods of loading the catalyst to the coke: (1) the ‘post-loading of catalyst to coke’ method,19) whereby the catalyst and/or catalyst solution is sprayed onto the coke after the coke is pushed out of a coke oven chamber, and (2) the ‘pre-loading of catalyst to coke’ method, where the catalyst is mixed with coal before the mixture is carbonized in a coke oven chamber. As for the pre-loading of an iron catalyst, the authors have succeeded in producing highly reactive iron coke with proper strength (DI15015 80.9, equivalent to 82.4 after CDQ) and high reactivity (JIS ReI 40) in a coke oven chamber on a commercial scale by carbonizing the mixture of coal and iron ore powder.20) As for the pre-loading of a Ca catalyst, we succeeded in producing strong, highly reactive ‘lump’ form coke in commercial scale coke ovens by adding a Ca-rich coal and adjusting the coal blend composition.5) Moreover, we confirmed that the use of the Ca-rich coke decreased the thermal reserve zone temperature in an adiabatic blast furnace simulator (BIS) and that the use of the Ca-rich coke in the Muroran No. 2 blast furnace for a long period caused a decrease in the reducing agent rate as well as the thermal reserve zone temperature in the blast furnace.5)

On the other hand, a new method to produce highly reactive coke by adding a Ca catalyst other than Ca-rich coal is expected since Ca-rich coal resources are limited. Moreover,
the effectiveness of Ca-loaded highly reactive coke has been proven in a commercial scale experiment, however, the fundamental reaction behavior of the coke is still unclear. It has not been shown that Ca-rich coke starts to react at a lower temperature range than conventional coke does when the mixture of Ca-rich coke and conventional coke are charged in a blast furnace. Although it is known that coke reactivity is promoted by condensed alkali vapor in an actual blast furnace, there have been no studies on the behavior of Ca-loaded highly reactive coke in the presence of alkali and the interaction of the catalytic activity of Ca and alkali is uncertain.

In this paper, firstly the effects of Ca compounds pre-addition to coal on coke qualities were investigated. Secondly, the reaction behavior of the mixture of Ca-loaded highly reactive coke and conventional coke were investigated. Finally, the catalytic effect of Ca in the presence of an alkali was studied with thermogravimetric analysis.

2. Experimental

2.1. Evaluation of the Effect of Catalytic Ca Powder Addition on Coke Qualities

2.1.1. Caking Properties

Three types of coal (Table 1) were used in the test. Coals A and B are caking coals and coal C is a slightly caking coal. The catalytic Ca powder (CaO, CaCO3) or coke breeze were added to the coal at an addition rate of 2.5–7.5% or 1.0–5.0% respectively and the dilatation and fluidity were measured.

2.1.2. Carbonization Tests and Coke Quality Measurements

In Test 1, Ca catalysts were added to coal blend 1 (coal B 70%, coal C 30%, 80% < 3 mm, the moisture content 4%) at an addition rate of 2.5–7.5%. Then the prepared sample was charged in a galvanized steel box (420 mm wide, 600 mm long and 400 mm high) at a bulk density of 830 dry-kg/m³ and carbonized in an electrically heated test coke oven. In Test 2, CaO powder was added to coal blend 2 (coal A 30%, coal B 30%, coal C 40%, 85% < 3 mm, the moisture content 4%) at an addition rate of 3% and mixed in a mixer. Then the prepared sample was charged at a bulk density of 850 dry-kg/m³ and carbonized in the test coke oven. After the coke was quenched with nitrogen, the JIS drum index of coke (DI15015), the JIS coke reactivity index (JIS ReI), which stands for the chemical reaction rate of 10 g of 0.85–1.7 mm coke breeze with CO2 at 950°C, and the Coke Reactivity Index (CRI), which is expressed by the percentage of weight loss to the original coke mass (200 g of 20 mm coke) after reaction under CO2 at 1100°C for 2 hours were measured.

2.2. Evaluation Tests of Reaction Behavior of a Ca-loaded Highly Reactive Coke/Conventional Coke Mixture

Two kinds of coke samples (C1, C3) shown in Table 2 were used. C1 is a conventional coke used in a blast furnace and C3 is a Ca-loaded highly reactive coke (abbreviated hereafter as Ca-loaded coke) produced by carbonizing coal blends (low rank and slightly caking coal blending ratio 90%) to which CaO is pre-added by 3%. Coke samples (9–11 mm in size) were charged in the reaction tube of a large scale thermobalance as single or as mixture. The amount of charged sample was 200 g. In the mixed charge experiment, conventional coke and Ca-loaded coke were charged and separated with metal wire cage as shown in Fig. 1. Three tests were conducted: conventional coke (C1) alone, Ca-loaded coke (C3) alone and a mixture of C1 and C3. The sample was heated from room temperature at a heating rate of 10°C/min in an atmosphere of CO2/CO=50/50 (ηCO=50%) and weight change was recorded during the experiment. When the weight reached a desired value or the temperature reached 1200°C, heating was stopped and quenched in N2. Conventional coke and Ca-loaded coke were collected separately after the experiment. Coke strength

![Fig. 1. Mixed charge method of conventional coke and Ca-loaded coke in a large scale thermobalance.](image)

Table 1. Coal properties.

| Coal | Proximate Analysis | Petrographic Analysis |
|------|--------------------|----------------------|
|      | VM (%)  | Ash (%)  | Ruhr Dilatometry | Petrographic Analysis |
|      | (%) db   | (%) db   | Total Dilatation (%) | Mean Max Vit. Ref. (%) |
| A    | 21.1    | 9.4   | 127                | 2.63                 | 1.35               |
| B    | 23.8    | 9.0   | 119                | 2.92                 | 1.19               |
| C    | 35.8    | 9.2   | 32                 | 2.18                 | 0.73               |
after reaction was evaluated by $I_600^1$ (the percentage of coke mass retained on a sieve with 1.0 mm apertures to the mass of the reacted coke sample after 600 revolutions in an I-type drum tester).

2.3. Evaluation Tests of the Reaction Behavior of Ca-Loaded Highly Reactive Coke in the Presence of an Alkali

2.3.1. Thermogravimetric Analysis

Two kinds of coke samples (C2, C3) shown in Table 2 were used. Sample C2 was produced by carbonizing coal blends (low rank and slightly caking coal blending ratio 70%) and the reactivity of C2 (CRI 41.6) is higher than that of usual blast furnace coke. Catalysts (K, Ca and Fe) were loaded to coke (150–300 μm) by an incipient wetness method,\(^{23}\) where a given amount of an aqueous solution of nitrate potassium, nitrate calcium and nitrate iron was delivered by drops to coke. The target ratio of loaded catalyst to coke was 1 mass%. Test conditions are shown in Table 3. In TGA2 and TGA4, K was loaded to coke C2 and C3. Ca is pre-loaded to coke C3 then interaction of the catalytic effect of Ca and K was tested in TGA4. In TGA5, TGA6 and TGA7, Fe, Fe+Ca and Fe+Ca+K were loaded to coke C2 respectively. The concentration of the loaded K, Ca and Fe in coke was +0.6–1.2%, +0.5–0.7% and +0.5–0.6% respectively, which was close to the target value. 10 mg of the sample was heated to 800°C in N₂ atmosphere at a heating rate of 50°C/min in a thermobalance (Shimazu TG-50). At that temperature N₂ was changed to a reaction gas (CO₂/CO=30/70 or 10/90). The sample was further heated to 1200°C in the reactant gas at a heating rate of 10°C/min and the changes in weight were recorded.

2.3.2. Large Scale Thermobalance Tests

Coke samples C1 and C3 (19–21 mm in size) were soaked in a 15% KOH aqueous solution for 30 minutes then dried. The K concentration in coke was increased from 0.055–0.095% (avg. 0.076%) to 1.3–1.6% (avg. 1.45%). The sample (200 g) was charged in the reaction tube of the large scale thermobalance and heated from room temperature to 1100°C at a heating rate of 20°C/min in N₂ atmosphere. At that temperature N₂ was changed to a reaction gas (CO₂/CO=20/80). When the weight reached the desired value (10%, 20% or 30% in weight loss percent), heating was stopped and quenched in N₂. The coke strength after reaction was evaluated by $I_600^1$ (the percentage of coke mass retained on a sieve with 1.0 mm apertures to the mass of the reacted coke sample after 600 revolutions in an I-type drum tester).

3. Results and Discussion

3.1. The Effect of Ca Compound Addition on Coke Qualities

3.1.1. The Effect of Ca Compound Addition on Caking Property

As shown in Fig. 2, the addition of Ca compound decreases the total dilatation and the total dilatation is inhibited more by the addition of CaO than CaCO₃. The reasons for the decrease in the total dilatation might be explained by a ‘physical’ and ‘chemical’ effect of additives. A ‘physical’ effect is one where a non-fusible ‘inert’ substance like coke breeze promotes gas leakage from the molten coal and hence inhibits dilatation. A ‘chemical’ effect is one where some chemical interaction between additives and coal inhibits dilatation. Assuming that the gas leakage from the molten coal strongly depends on the surface area of inert additives, the ‘physical’ effect of additives on the coal caking properties can be considered the same under the same surface area of additives. The relationship between the surface area of additives per unit mass of coal and the total dilatation is plotted in Fig. 3. It is clear that under the same surface area of additives, the dilatation inhibition by additives is in the order of CaO>CaCO₃, coke breeze. This suggests that CaO addition inhibits the dilatation for any reason other than...

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**Table 3.** Test condition in TGA test and catalyst concentration in coke.

| Coke                     | Catalyst concentration in coke (%) | Added catalyst (%) |
|--------------------------|-----------------------------------|--------------------|
|                          | K       | Fe   | Ca   | K       | Fe   | Ca   |
| TGA1 C2 (Highly reactive coke) No addition | 0.12 | 0.42 | 0.20 | 0.00 | 0.00 | 0.00 |
| TGA2 C2 (Highly reactive coke) K            | 0.73 | –    | –    | 0.61 | –    | –    |
| TGA3 C3 (Ca coke) Ca (pre-added)          | –     | –    | 0.89 | –     | –    | 0.69 |
| TGA4 C3 (Ca coke) Ca (pre-added)+K        | 0.71 | –    | 0.89 | 0.59 | –    | 0.69 |
| TGA5 C2 (Highly reactive coke) Fe           | –     | 0.92 | –    | –     | 0.50 | –    |
| TGA6 C2 (Highly reactive coke) Fe+Ca       | –     | 1.03 | 0.74 | –     | 0.61 | 0.54 |
| TGA7 C2 (Highly reactive coke) Fe+Ca+K     | 1.31 | 1.01 | 0.76 | 1.19 | 0.59 | 0.56 |
physical effect, which is a subject of further investigation.

3.1.2. The Effect of Ca Compound Addition on Coke Quality

As shown in Fig. 4, the addition of Ca compound decreases DI$_{150}$ and CaO decreases DI$_{150}$ to a greater extent than CaCO$_3$ as CaO decreases total dilatation to a greater extent than CaCO$_3$. The more Ca compound is added, the more DI$_{150}$ decreases. The dilatation inhibition by Ca compound addition caused insufficient adhesion of coal particles, which resulted in a decrease in DI$_{150}$. As shown in Figs. 5(a) and 5(b), both CaO and CaCO$_3$ addition increases the JIS coke reactivity index and CRI to a great extent. This is due to the catalytic effect of Ca on the reaction between C and CO$_2$. It seems that the catalytic activity of CaO is greater than CaCO$_3$ in Fig. 5, however, as shown in Fig. 6, the catalytic activity of CaO and CaCO$_3$ is nearly the same when it is evaluated on the condition that the blending ratio of Ca is the same. Moreover, as the blending ratio of additives increases, the catalytic effect shows signs of leveling off. This suggests that an addition of a proper amount of catalyst could increase coke reactivity whilst minimizing the decrease in coke strength.

In Test 2, in order to produce Ca-loaded highly reactive coke with high coke strength (DI$_{150}$ $\geq$ 85) and high reactivity (CRI $\geq$ 50), the bulk density was increased (850 dry-kg/m$^3$), coal was crushed more finely (–3 mm 85%) and CaO was added by 3%. The reason why 3% addition
was chosen is that in the case of 3% addition, the decrease in coke strength is small as shown in Fig. 4 and on the other hand the increase in coke reactivity is large as shown in Fig. 5. As shown in Fig. 7, in Test 2, addition of 3% CaO to the 0% CaO condition, coke strength and reactivity changed from \( \text{DI}_{150\%}^150 \ 86.2, \ CRI \ 25 \) to \( \text{DI}_{150\%}^150 \ 85.5, \ CRI \ 60 \), which shows that the coke strength is kept as high as \( \text{DI}_{150\%}^150 \ 85 \) and the coke reactivity was increased to a great extent.

As described above, carbonizing the mixture of coal and Ca compounds (CaO, CaCO\(_3\)) greatly increases the coke reactivity. Although it decreases the coke strength (\( \text{DI}_{150\%}^150 \)) since Ca compounds inhibit the caking properties of coal, it is possible to produce Ca-loaded highly reactive coke with high coke strength by adding a small amount of Ca compounds under suitable conditions. On the other hand, in order to establish necessary basic technologies for producing highly reactive coke with high strength, it is necessary to quantify the effect of coal kinds, coal particle size, bulk density, catalyst type and the addition ratio of catalyst on coke strength and reactivity, which is a subject of further investigation. Ca-compounds are promising in that their catalytic effect greatly increases coke reactivity. We would give further consideration as to the optimum conditions for producing Ca-loaded highly reactive coke.

3.2. Reaction Behavior of a Ca-loaded Highly Reactive Coke/Conventional Coke Mixture

The reaction percentage of Ca-loaded highly reactive coke (abbreviated as Ca-loaded coke) and conventional coke in the mixed charge experiment is shown in Fig. 8 and the weight loss curve is shown in Fig. 9. Ca-loaded coke and the mixture of Ca-loaded coke and conventional coke start to lose weight at a lower temperature than conventional coke. It is clear that Ca-loaded coke reacts selectively and preferentially and conventional coke displays little reaction when the mixture of Ca-loaded coke and conventional coke is heated in a reaction gas.

In Fig. 10, the weight data for the conventional/Ca-loaded coke mixed charge tests was corrected by expressing the weight as a percentage of the amount of charged Ca-loaded coke (that is 100 g). In the temperature range lower than 1100°C where conventional coke shows little weight change, the corrected weight percentage of the mixture of Ca-loaded coke and conventional coke is close to the weight percentage of respective Ca-loaded coke charged as single. This shows that there are no interactions between Ca-loaded coke and conventional coke when Ca-loaded coke is mixed with conventional coke and that Ca-loaded coke selectively starts to react in a lower temperature range in the mixed layer of Ca-loaded coke and conventional coke.

Figure 11 shows the strength (\( \text{I}^{600\%} \)) of conventional coke and Ca-loaded coke before and after reaction in the mixed charge experiment. The \( \text{I}^{600\%} \) of conventional coke after reaction is close to that prior to the reaction, however the \( \text{I}^{600\%} \) of Ca-loaded coke after the reaction is smaller than that pri-
or to the reaction. This shows that Ca-loaded coke reacts selectively and becomes weak, while conventional coke is protected. Fine coke powder which generates from weak highly reactive coke after reaction is considered to be consumed in a reaction with CO$_2$ in a blast furnace and not to negatively affect blast furnace operation, however, how to use highly reactive coke in a blast furnace (e.g. amount of charge, burden distribution) is a subject of further investigation.

3.3. Reaction Behavior of Ca-loaded Highly Reactive Coke in the Presence of an Alkali

3.3.1. Evaluation of the Reaction Behavior of Ca-loaded Highly Reactive Coke in the Presence of an Alkali Using Thermogravimetric Analysis

The weight loss curves (CO$_2$/CO=30/70 and CO$_2$/CO=10/90) during thermogravimetric (TG) testing for Ca and K loaded coke are shown in Fig. 12 and the weight loss percentage at 1050°C (CO$_2$/CO=30/70) and 1200°C (CO$_2$/CO=10/90) in the TG test are shown in Fig. 13. The weight loss of Ca+K-loaded coke is larger than that of Ca-loaded coke and K-loaded coke in both the lower temperature range (1050°C) and the higher temperature range (1200°C). It is clear that Ca acts as a catalyst in the presence of K. In this study, Ca and K shows synergetic catalytic activity, that is a subject to be studied.

The weight loss curve (CO$_2$/CO=30/70 and CO$_2$/CO=10/90) for the thermogravimetric (TG) tests for Fe, Ca and K loaded coke are shown in Fig. 14 and the weight loss percentage at 1000°C (CO$_2$/CO=30/70) and 1200°C (CO$_2$/CO=10/90) during the TG tests are shown in Fig. 15. The weight loss is in the order of Fe+Ca+K-loaded coke >
Fe+Ca-loaded coke > Fe-loaded coke and it is clear that Ca acts as a catalyst in the coexistence of Fe and K as in a blast furnace.

3.3.2. Evaluation of the Reaction Behavior of Ca-loaded Highly Reactive Coke in the Presence of an Alkali Using a Large Scale Thermobalance Test

The weight loss curve after the reaction gas was changed to CO₂/CO=20/80 is shown in Fig. 16. Alkali (K) addition increases the weight loss of conventional coke and Ca-loaded coke. In the presence of an alkali the weight loss of Ca-loaded coke is higher than that of conventional coke. This shows that the reactivity of Ca-loaded coke is higher than that of conventional coke. This reactivity is promoted by condensed alkali vapor.
Figure 17 shows the relationship between the reaction percentage and strength after reaction for normal coke and Ca-loaded coke. Strength decreases as the reaction percentage increases. At a certain reaction percentage the strength of K-loaded coke is higher than that of coke without K. It has been reported that the strength of the catalyst post-loaded coke could be close to or greater than that of the catalyst no-addition coke.25) It is shown in the study that the post-loading of K to Ca pre-loaded coke increases the post-reaction strength. This is considered because the reaction mode of the coke became close to the uniform reaction due to lower temperature reaction, which resulted in a small radial gradient of the reaction rate.

4. Conclusion

In order to develop a method to produce Ca-loaded highly reactive coke, the effects of Ca compounds pre-addition to coal on coke qualities were investigated. Moreover, the reaction behavior of Ca-loaded highly reactive coke when mixed with conventional coke and in the presence of an alkali was investigated. The major findings from this study are as follows: (1) Carbonizing the mixture of coal and Ca compounds (CaO, CaCO3) increases the coke reactivity greatly. Although it decreases the coke strength (DI 15015) since the Ca compounds inhibit the caking properties of coal, it is possible to produce Ca-loaded highly reactive coke with high coke strength by adding 3% of Ca compounds under such conditions as high strength coke was produced. (2) When the mixture of Ca-loaded highly reactive coke and conventional coke is heated in a reaction gas, Ca-loaded coke reacts selectively and preferentially in a lower temperature range and the conventional coke is protected from being weak. (3) The reactivity of Ca-loaded coke is higher than that of conventional coke in the existence of K as in an actual blast furnace. The post-loading of K to the conventional coke and the Ca-loaded coke increases the post-reaction strength of both cokes at a certain reaction percentage.

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