Improvement in Blast Furnace Reaction Efficiency Through the Use of Catalyst-doped Highly Reactive Coke

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Abstract

A method to produce coke in 'lump' form with high strength and reactivity through the addition of a catalyst was investigated in order to improve blast furnace reaction efficiency. Firstly, the addition of Ca compounds to coal before carbonization was found to considerably increase the reactivity of the coke at a low temperature range in the thermal reserve zone of a blast furnace and it was proved that the resultant coke decreases the thermal reserve zone temperature in a laboratory scale blast furnace simulator. Furthermore it was proved that strong, highly reactive 'lump' form coke could be produced by adding a Ca-rich non-caking coal and adjusting the coal blend composition. Based on this fundamental study, the Ca-rich coke was successfully produced in coke ovens on a commercial scale, both at Kimitsu and Muroran works, and the use of the Ca-rich coke in the Muroran No. 2 blast furnace was found to cause a decrease in the reducing agent rate by 10 kg/t-p. This technology, producing coke of high reactivity and strength through catalyst addition, is promising as a means of improving the reaction efficiency of a blast furnace.

1. Introduction

Developing technology to improve the reaction efficiency in the blast furnace ironmaking process is extremely important because it is expected that any improvement in reaction efficiency will help lower both the reducing agent ratio and the emission of carbon dioxide. As a means of improving blast furnace reaction efficiency, the use of highly reactive coke to lower the temperature of the thermal reserve zone and decrease the reducing agent ratio has been proposed by Naito et al.[1]. In this regard, it has been reported that the use of highly reactive nut coke improved the efficiency of reaction in an actual furnace[2] and lowered the temperature of the thermal reserve zone[3]. Thus, in order to further improve the in-furnace reaction efficiency, it is considered effective to increase the reactivity of ordinary lump coke. However, if lump coke is to be charged into the blast furnace, it must have not only high reactivity but also high cold strength (drum index).

Generally speaking, the drum index of coke declines markedly when the reactivity of coke is increased, for example, by adding non-caking or slightly-caking coal with a low coal rank to the coking

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coal. Because of this, high-strength, high-reactivity lump coke that can be used in an actual furnace has not been manufactured on a commercial basis. In the present study, therefore, we aimed to produce coke of high strength and high reactivity through the addition of a suitable catalyst and the adjustment of the coal-blending ratio whilst paying attention to the effect of the catalyst as the seed for increasing the chemical reactivity of coke and lowering the temperature at which coke begins to react.

What matters here is: 1) how to add the catalyst to coke; and 2) what catalyst to add. Two practical methods of catalyst addition can be considered: post-addition of catalyst to coke (**Fig. 1**) and pre-addition of catalyst to coke (**Fig. 2**). In the former method, a solution of catalyst is made to adhere to coke produced by carbonization of coal. In the latter method, a mixture of coal and catalyst is carbonized into coke in a coke oven. In a broad sense, adjusting the ash composition by selecting a suitable type of coal is included in this method. In the present study, we adopted the latter method.

Concerning the catalyst to be added, it has been reported that alkali metals, alkaline earth metals and transition metals are highly effective as catalysts for gasifying carbon into carbon dioxide[4, 5].
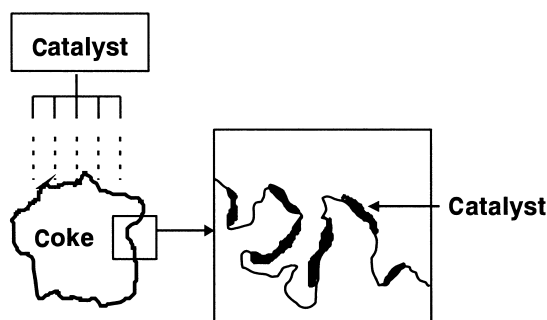

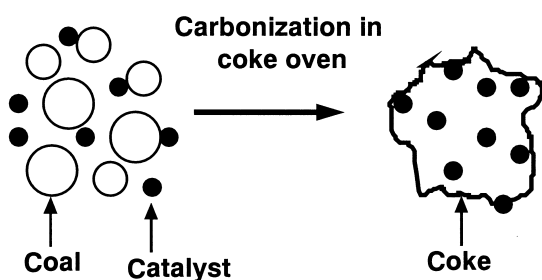**Fig. 1   Post-addition of catalyst to coke method**

Fig. 2   Pre-addition of catalyst to coke method

However, with respect to the contribution of catalysts in improving the reactivity of metallurgical coke in the blast furnace's thermal reserve zone, there is very little quantitative data. Since alkalis cause scaffolding on the blast furnace wall, it is undesirable to increase the amount of alkalis in coke. When the catalyst pre-addition method is to be used, it is also undesirable to use iron (Fe) as a transition metal catalyst since it causes a substance with a low melting point (fayalite) to be produced because FeO reacts with SiO_2—the principal constituent of the silica brick used for the walls of a coke oven. Therefore, as our catalysts, it was decided to adopt alkaline earth metals which are used as auxiliary raw materials for blast furnaces and which are contained in coal ash.

This paper initially describes the results of preliminary studies in which various types of alkaline earth metals were added to coke by the above method and those elements that significantly improved the coke reactivity were identified. The preliminary studies showed that calcium (Ca) was especially effective in improving the reactivity of coke. Therefore, as a technique to manufacture highly reactive coke by catalyst addition, a study was conducted for the production of high-strength, high-reactivity lump coke from coal with exceptionally high Ca concentration using an experimental coke oven and an actual coke oven. The results of this study shall also be described. A discussion follows relating to the results of the use of Ca-rich, high-reactivity coke in Hokkai Iron & Coke Muroran Works' No. 2 BF.

2. Basic Study on Technology for Manufacturing High-Strength, High-Reactivity Lump Coke by Catalyst Addition

2.1 Experimental procedure

2.1.1 Properties of coals and additives

In the present experiment, four types of coals were used (**Table 1**). Coals A and B are caking coals commonly used in the production of metallurgical coke, and coal C is a slightly-caking coal with low rank and low fluidity. Ca-rich coal is a non-caking coal showing no fluidity. It is characteristic in that its ash contains a large proportion of calcium. In addition, in order to study the effects of the addition of various alkaline earth metals on the reactivity of coke, five different chemical compounds were used ($SrCO_3$, $CaCO_3$, $MgCO_3$, CaO and MgO).

2.1.2 Carbonization tests

(1) Carbonization of coals with compounds added

In order to study the effect of the addition of the above compounds on the reactivity of coke, samples were prepared of mixtures of coals and one of the compounds. One blended coal (grain size after pulverization: 3 mm or less accounting for 80%), made up of 70% of coal B and 30% of coal C, was used as the reference coal sample. Each sample was added and mixed with a prescribed amount

Table 1   Characterization data for the coals used

Coal	Proximate analysis (mass % db)		Total dilatation (vol %)	Maximum fluidity (log MF/ddpm)	Mean reflectance (%)	Major ash component (%)							
	VM	Ash				P_2O_5	K_2O	Na_2O	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
A	20.7	9.8	99	2.56	1.42	0.74	1.12	0.83	59.99	26.66	4.20	1.42	0.59
B	23.8	8.8	103	2.93	1.28	0.45	1.07	0.75	56.40	31.48	3.70	0.87	0.59
C	35.7	9.1	32	2.08	0.79	0.41	1.14	0.51	62.98	23.83	4.99	1.52	0.76
Ca-rich	37.4	5.3	0	-	0.61	0.08	0.13	1.47	21.23	9.18	6.07	45.99	1.34

Table 2　Blending composition of the coals

Coal	Test						
	1	2	3	4	5	6	7
A				20	20	20	20
B	70	90	80	50	50	50	50
C	30			30	25	20	15
Ca-rich		10	20		5	10	15

(2.5% to 7.5%) of one of the compounds. Each of the samples was, after adjustment of its moisture content to 4%, put into a charging can made of galvanized sheet (charging density: 830 dry, kg-coal/m³) and carbonized in a test coke oven of electric heater type (width: 420 mm, length: 600 mm, height: 400 mm)[6].

(2) Carbonization of coals blended with Ca-rich coal

　Next, in order to study the effect of the addition of Ca-rich coal on the strength and reactivity of coke, the coal samples were pulverized (size 3 mm or less accounting for 85%), mixed as shown in **Table 2**, and after adjustment of their moisture contents to 3%, charged into the experimental coke oven (charging density: 850 dry, kg-coal/m³) for carbonization.

2.1.3 Coke quality evaluation test

　The coke obtained by carbonization was first quenched in a nitrogen atmosphere and then subjected to a drop test by a shatter tester[7] to measure its strength (drum index DI^{150}_{15} [7]). In order to decrease the temperature of the blast furnace thermal reserve zone, it is important to lower the temperature at which the reaction of coke begins to take place. Therefore, the reactivity of coke was evaluated using the JIS reactivity index[7] (R_eI: Reactivity Index) for the initial reaction rate at 950℃. In addition, nut coke reactivity was measured (CRI: percentage of weight loss after 2 hours of reaction at 1,100℃ in a CO_2 atmosphere) and coke strength after reaction (CSR)[8]. Furthermore, in addition to the above industrial evaluation methods, a thermo-balance was used to measure the reaction rates of cokes obtained from blended coals 1 and 6. Using coke samples obtained by crushing coke into sizes in the range 150 to 300 μ m, their reaction rates were measured in terms of the rate at which 10% weight loss is reached. In this measurement, the reaction temperature was in the range 1,000℃ to 1,150℃ and the CO_2:CO ratio was varied from 100:0 to 50:50 to 20:80.

2.2 Experimental results and discussion

2.2.1 Effect of alkaline earth metal addition on coke quality

　Fig. 3 shows the relationship between the rate of alkaline earth metal addition and the JIS coke reactivity index. It can be seen from the figure that of the alkaline earth metals used as catalysts, Sr is the
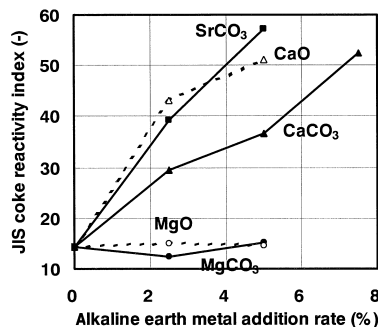
most active, followed by Ca and Mg in that order and that both CaO and $CaCO_3$ demonstrate good catalytic activity. The amount of Sr originally contained in coal is very small and there are no inexpensive Sr compounds that the iron and steel industry can use abundantly. With regard to Ca, by contrast, large quantities of limestone and calcium oxide have already been used as auxiliary raw materials for steelmaking. Besides, appreciable proportions of Ca are contained in coal too. Bearing all of this in mind, Ca is considered a promising catalyst for increasing the reactivity of coke.

2.2.2 Effect of Ca-rich coal addition on coke quality

　Table 3 shows the measurement results obtained with blended coals 1-3. It can be seen from the table that the addition of Ca-rich coal increases the JIS reactivity index of coke markedly. **Fig. 4** shows the relationship between the Ca-rich coal blending ratio, JIS reactivity index and CRI. As shown, when coal C is replaced with Ca-rich coal, the JIS reactivity index and CRI increase noticeably. This is considered attributable to the catalytic action of Ca. On the other hand, it can be seen from **Fig. 5** that when coal C is replaced with

Table 3　Effect of Ca-rich coal addition on coke quality

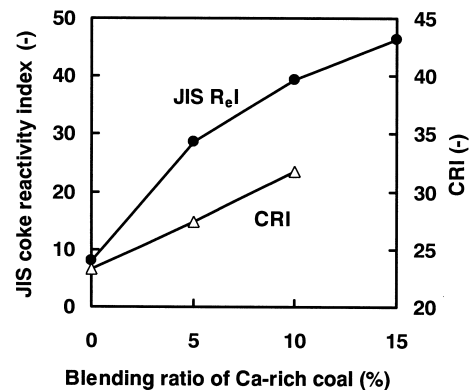|	Ca-rich coal (%)	DI^{150}_{15}	CRI	CSR	JIS R_eI
Test 1	0	84.5	23.3	66.8	6.6
Test 2	10	84.0	24.8	68.0	39.0
Test 3	20	81.8	33.2	58.6	41.8

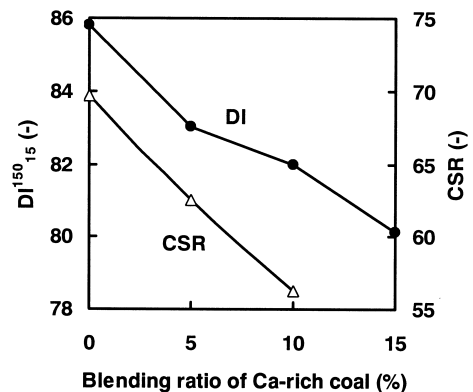**Fig. 4　Effect of the blending ratio of Ca-rich coal on the JIS coke reactivity index and CRI**

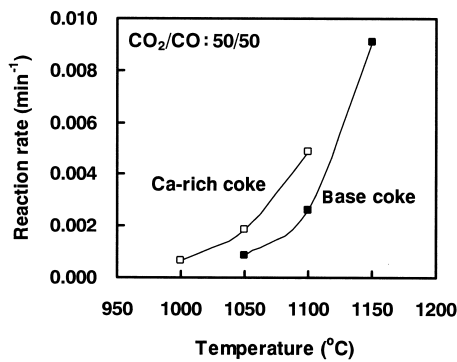**Fig. 5　Effect of the blending ratio of Ca-rich coal on DI^{150}_{15} and CSR**

Fig. 3　Relationship between the addition rate of the alkaline earth metal and the JIS coke reactivity index

Fig. 6 Relationship between reaction temperature and rate (CO_2/CO: 50/50)

Ca-rich coal, the DI^{150}_{15} and CSR significantly decrease in proportion to the blending ratio of Ca-rich coal.

An example of the relationship between the reaction temperature and the reaction rate measured by a thermo-balance is shown in **Fig. 6**. In this figure, the JIS reactivity index of the base coke (obtained from blended coal 1) and Ca-rich coke (obtained from blended coal 6) is 6.6 and 39.4, respectively. In a 50:50 atmosphere of CO_2:CO, which is close to the gas composition in the blast furnace's thermal reserve zone, the reaction rate of Ca-rich coke is more than twice that of the base coke and the Ca-rich coke reaction rate is comparatively high even at low reaction temperatures. Thus, Ca-rich coke is considered suitable for lowering the temperature of the blast furnace's thermal reserve zone.

3. High-Reactivity, Ca-Rich Coke Manufacturing Test using Actual Coke Oven at Nippon Steel Chemical Kimitsu Works

When it comes to manufacturing Ca-rich coke in an actual coke oven, it is necessary to replace non- or slightly-caking coal with caking coal in order to compensate for the decline in coke strength due to the addition of Ca-rich coal which is a non-caking coal. Generally speaking, when non- or slightly-caking coal is replaced with caking coal, it causes the reactivity of coke to decline too. Therefore, it is necessary to study the possibility of manufacturing a high-strength, high-reactivity lump coke that has a high JIS reactivity index and a DI^{150}_{15} value comparable to that of ordinary lump coke by means of a suitable combination of the addition of Ca-rich coal and adjustment of the coal blending ratio (i.e., increasing the proportion of caking

coal). Various coal combinations were therefore tested to find coal blending conditions that would make it possible to manufacture a coke having a DI^{150}_{15} and CSR comparable to those of the base coke and JIS reactivity index higher than that of the base coke.

On the basis of the results of the above tests, we carried out a high-strength, high-reactivity lump coke manufacturing test using an actual coke oven at the Kimitsu Works of Nippon Steel Chemical under these coal blending conditions: Ca-rich coal blending ratio 5% to 7% and non-and slightly-caking coal ratio 19% to 29 % (44% for the base coke). The test results are summarized in **Table 4**. Concerning the coke quality, it was confirmed that it would be possible to manufacture a coke of the desired qualities (in terms of DI^{150}_{15} and JIS reactivity index) by using a suitable Ca-rich coal blending ratio and non-or slightly-caking coal ratio.

4. Manufacturing and Practical Use of Ca-Rich, High-Reactivity Coke at Hokkai Iron & Coke Muroran Works

4.1 Prolonged production of Ca-rich, high-reactivity coke using coke oven at Hokkai Iron & Coke Muroran Works

Using an actual coke oven at Hokkai Iron & Coke Muroran Works, Ca-rich, high-reactivity coke was manufactured in the period between June and September, 2002 without interruption. The coal blending ratio used in the coke production is shown in Table 4. The slightly-caking coal (SCC) ratio was not varied much from that for the base coke. Instead, a coal of high total dilatation was selectively used to increase the total dilatation of the blended coal. The maximum Ca-rich coal blending ratio was 8%, with the SCC ratio fixed at 45%. The whole of the Ca-rich coke that was manufactured was used in a blast furnace as described later. The principal properties of the Ca-rich coke manufactured at Hokkai Iron & Coke Muroran Works are summarized in Table 4. As shown, a coke was manufactured that is comparable in DI^{150}_{15} and superior in JIS reactivity index to the base coke for a period of more than two months without interruption.

Fig. 7 shows the relationship between DI^{150}_{15} and the JIS reactivity index of cokes manufactured in actual coke ovens. It can be seen from the figure that Ca-rich coke comparable in DI^{150}_{15} but superior in JIS reactivity index to the base coke could be manufactured by controlling the addition of Ca-rich coal and the coal blending ratio.

4.2 Evaluation of reduction properties of Ca-rich, high-reactivity coke using adiabatic blast furnace simulator

Before starting a usage test of the Ca-rich, high-reactivity coke in an actual blast furnace, the effect of the coke was studied on the reduction behavior of sinter using an adiabatic blast furnace reaction

Table 4 Coal blending composition, coal properties and coke quality in producing the Ca-rich coke in a commercial scale coke oven

|		Kimitsu		Muroran	
		Base	Ca-rich	Base	Ca-rich
Coal blend	Ca-rich coal (%)	0	5-7	0	8
	SCC* ratio (%) (incl. Ca-rich coal)	44	19-29	42	45
Coal property	VM (mass % db)	28.5	26.1-27.3	27.6	28.7
	Ash (mass % db)	9.0	8.6-8.7	9.2	8.9
	Total dilatation (vol %) (calc.)	56	69-76	49	81
	Maximum fluidity (log MF/ddpm) (calc.)	2.18	2.12-2.15	1.74	2.30
Coke quality	DI^{150}_{15} (-)	85.5	85.6-86.2	85.0	84.9
	CSR (-)	55.0	54.7-63.0	61.7	60.6
	JIS R_eI (-)	15.8	33.3-39.4	15.1	45.9

* SCC: slightly-caking coal
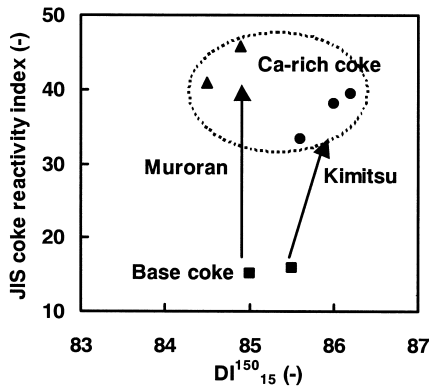
Fig. 7 Relationship between DI$^{150}_{15}$ and the JIS coke reactivity index

simulator [1, 9]. In the simulative experiment, the base coke (JIS R_eI: 15.8) and Ca-rich, high-reactivity coke (Ca-rich coal ratio: 5%, JIS R_eI: 33.8) that were manufactured by a coke oven at Nippon Steel Chemical's Kimitsu Works and sinter that was produced by a sintering machine of the Works were used. The reducing conditions were as follows: reducing agent ratio (RAR) 495.8 kg/t [pulverized coal ratio (PCR) 160 kg/t], bosh gas 1,328 Nm^3/t-p, CO 37.5%, H$_2$ 8.0%, N$_2$ 54.5%. As shown in **Fig. 8**, it was confirmed that the temperature of the thermal reserve zone decreased and the reduction degree of sinter increased when the Ca-rich coke was used. On the basis of this result, it was decided to carry out the usage test of the Ca-rich, high-reactivity coke in an actual blast furnace.

4.3 Results of usage test of Ca-rich, high-reactivity coke in No. 2 BF at Hokkai Iron & Coke Muroran Works

As mentioned earlier, a high-reactivity coke was manufactured by the addition of Ca-rich coal in a coke oven at Hokkai Iron & Coke Muroran Works, and a usage test was conducted of the coke using the No. 2 blast furnace at the Works for a period from June to September 2002. During the test period, the productivity of pig iron was 1.89 to 2.08 (ton/d.m^3) and the PCR was 146 to 154 (kg-coal/t-pig iron). The original coke strength was maintained and no change in permeability in the blast furnace due to the use of a high-reactivity coke was observed at all. Since the chemical compositions of the sinter were significantly changed during the test period, they were stratified by the Al$_2$O$_3$ and FeO levels to compare the effect of Ca-rich coal addition on the reducing agent ratio (RAR) during the pe-
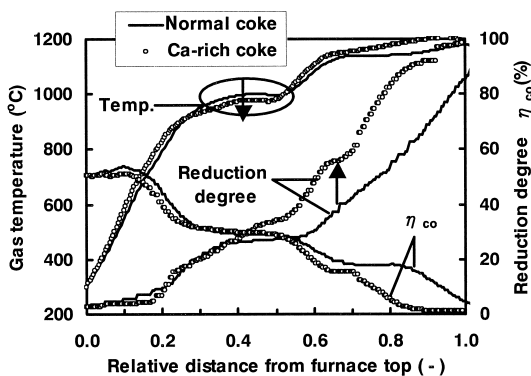

Fig. 8 Effect of Ca-rich coke on the temperature and sinter reduction behavior in the adiabatic blast furnace simulator
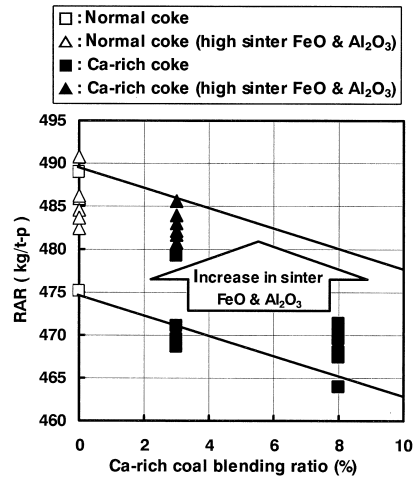

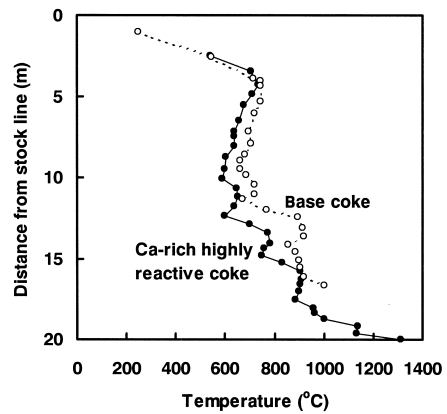**Fig. 9 Effect of Ca-rich coal blending ratio on RAR**

Fig. 10 Temperature distribution in the blast furnace during highly reactive coke operation

riod for which the chemical compositions of the sinter were similar. As a result, as shown in **Fig. 9**, it was confirmed that the higher the Ca-rich coal blending ratio, the lower the RAR, and that the use of Ca-rich, high-reactivity coke obtained by 8% addition of Ca-rich coal reduces the RAR by 10 kg/t-p. In addition, as a result of measurement by probes of the temperature distribution in the direction of blast furnace height during operation, it was confirmed that when the Ca-rich, high-reactivity coke was used, the temperature of the thermal reserve zone was lower than when ordinary coke was used (**Fig. 10**).

5. Conclusion

With the aim of decreasing the reducing agent ratio in blast furnace operation, the technology for manufacturing a high-strength, high-reactivity lump coke was studied by the addition of a suitable catalyst. As a result, the following facts were found.

(1) Coke obtained by carbonizing coal to which a Ca compound was added shows a high carbon gasification rate even in the low temperature region.

(2) It was confirmed that by properly adjusting the rate of Ca-rich coal addition and the composition of blended coal, it was possible to manufacture a high-reactivity coke comparable in strength to ordinary coke in an actual coke oven.

(3) It was confirmed by an off-line test that the use of Ca-rich coke lowered the temperature of the blast furnace thermal reserve zone. In addition, as a result of the prolonged and continuous use of the Ca-rich coke in the No. 2 blast furnace at Hokkai Iron & Coke Muroran Works, it was confirmed that the use of Ca-rich, high-reactivity coke obtained by 8% addition of Ca-rich coal lowered the reducing agent ratio by 10 kg/t-p.

As has been described so far, the catalyst-doped, highly reactive coke is considered very promising for improving the blast furnace reaction efficiency. In the future, studies will be conducted to effective new catalysts, other than Ca rich coal, and to effective new methods of catalyst addition in order to enable application of the technology on an industrial basis.

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