Reaction Behaviors of Various Agglomerates in Reducing the Temperature of the Thermal Reserve Zone of the Blast Furnace

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As an innovative measure to mitigating CO₂ emissions during ironmaking, the enhancement of carbon reactivity in blast furnaces is promising. It can reduce the temperature of the thermal reserve zone (TRZ), which is among the limiting factors to reaction efficiency in blast furnaces, thereby enabling operation under a low reducing agent rate (RAR). Therefore, reaction behaviors of two types of agglomerates with high carbon reactivity, composite agglomerates (CAs), and Ferro-coke, were evaluated using a softening-melting tester and via large-scale thermogravimetry. Process estimation of the blast furnace using them was also performed using a counter-current reaction simulator. CAs exhibited low-temperature gasification, efficiently promoting reduction by mixing with sintered ores. The carbon-consumption ratios of CAs and Ferro-coke were higher than that of coke. The reactive coke agglomerate, which is reinforced CAs with high carbon content toward reducing the RAR, exhibited the highest carbon reactivity, because of the coupling phenomena between the gas reduction of iron oxide and gasification of carbon. The addition of metallic iron to the CA increased the consumption of carbon and reduction of sintered ores, because of the catalytic effect. A combined use of the CA and Ferro-coke in the blast furnace successfully reduced the temperature of the TRZ by 150°C, offering the potential to decrease RAR by 35 kg/t-HM. Estimation of the distance between carbon and iron oxide or metallic iron in these agglomerates revealed that reducing the temperature of the TRZ by them was closely associated with shortening the distance.

KEY WORDS: ironmaking; blast furnace; agglomeration; composite; Ferro-coke; carbon reactivity; gasification; reduction; reducing agent rate (RAR); catalyst.

1. Introduction

CO₂ must be reduced for mitigating global warming. The product emissions from Japan account for 3.5% of the global CO₂ emissions, 14% of which are from the steel industry.¹⁾ Half of these are generated by ironmaking, as it uses coal as a resource. Using high-reactivity raw materials is one of the promising measures for decreasing the reducing agent rate (RAR) of blast furnaces to reduce CO₂ emissions in ironmaking. In this decade, many types of high-reactivity raw materials have been proposed to control the reduction equilibrium state (the W point in RIST diagram), which is one of the limiting factors for reaction efficiency in blast furnaces.

One of the measures controlling the reduction equilibrium of blast furnaces is reducing the temperature of the thermal reserve zone (TRZ) by increasing the carbon reactivity. Both the enhancement of chemical reactivity and reduction in the

size of carbonaceous materials are methods to increase the carbon reactivity. Accordingly, two types of agglomerates were investigated in this study, as depicted in Fig. 1.

The first type is the agglomerate comprising fine carbonaceous materials and fine iron oxides, hereafter referred to as the composite agglomerate (CA). It has high carbon reactivity and high reducibility because of the coupling phenomena between the gas reduction of iron oxides (Eq. (1)) and gasification of carbon (Eq. (2)).²⁾

Although the high reactivity of CA was known,³⁾ we previously observed an excellent potential of reinforced CAs with high carbon content toward reducing the RAR,⁴⁾ and accordingly, we commercialized the aforementioned CAs as reactive coke agglomerate (RCA).⁵⁾

The second type of agglomerate is Ferro-coke, which has a structure with homogeneously distributed fine metallic

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iron in a coke matrix. It also has high carbon reactivity^{6,7)} because of the redox cycle between the direct reduction of iron oxide (Eq. (3)) and oxidation of iron (Eq. (4)).⁸⁾

In addition to the advantage of having the high carbon reactivity similar to that of CA, Ferro-coke might further decrease RAR because of M.Fe charging to blast furnace. The reduction of the RAR was successfully confirmed in the plant tests using the Ferro-coke-based agglomerate called carbon iron composite (CIC).⁹⁾

However, investigations on the reaction behavior, particularly on the carbon reactivity of these agglomerates, are lacking. The information comparing their reaction behaviors is still limited.

Therefore, in this study, we investigated the reaction behaviors of CA and Ferro-coke, as well as their potential toward decreasing RAR through reducing the temperature of TRZ, by using a softening-melting tester and performing large-scale thermogravimetric analysis. We also estimated the process of the blast furnace by charging these agglomerates using a counter-current reaction simulator.

Fig. 1. Innovative agglomerates for breaking through the operational limit due to the reduction equilibrium of blast furnace. (Online version in color.)

2. Experimental Methods

2.1. Preparation of Various Agglomerates

Four kinds of CA and two kinds of Ferro-coke were used in this study. **Tables 1** and **2** show the chemical compositions and properties of these agglomerates.

The carbon composite agglomerate (CCA) is a CA with 1.2 C/O (bearing carbon to reducible oxygen in molar ratio). Industrial hematite powder (66 wt%), 19 wt% of plant coke-dust (83.5 wt% of F.C, 53 μm of d_{50} and 250 μm of top size) and 15 wt% of high-early-strength Portland cement (HPC, JIS R5210) were mixed, and then formed by an extruder.³⁾ Subsequently, the mixture was cured to obtain the CCA. Furthermore, RCA had a high C/O (1.6) and was a commercialized CA made using dust. We also synthesized artificial coke pellet (ACP) in a laboratory for comparing their reactivity with that of RCA. Plant coke-dust (85 wt%) and HPC (15 wt%) were mixed, pelletized, and subsequently cured to obtain ACP. In addition, the carbon composite briquette (CCB) that contained M.Fe was prepared to analyze the influence of the M.Fe catalyst on the carbon reactivity of CA (Table 2). Fine iron ores, plant coke-dust, electrolytic iron powder (98% purity), and HPC were used as raw materials, and their particle sizes (d_{50}) were 50, 53, 50, and 13 μm , respectively. The raw materials were mixed, formed into briquettes, and subsequently cured. The resulting briquettes (4 cm^3 in volume) were immersed in a KOH solution for a predetermined time to obtain CCB.

We made a normal Ferro-coke without pre-forming and a formed Ferro-coke. The manufacturing method was the same as that used in previous report.⁶⁾ Pulverized coal and

Table 2. Chemical compositions and properties of CCB.

	T.Fe	M.Fe	FeO	T.C	CW	Moisture	Crushing strength	Porosity
	wt%	wt%	wt%	wt%	wt%	%	kg/Piece	%
CCB1	49.77	0.73	0.40	12.22	1.94	3.0	89.9	27.2
CCB2	42.50	0.41	0.26	20.85	1.67	3.3	80.5	25.6
CCB3	35.44	0.28	0.17	29.30	1.63	3.2	59.2	30.1
CCB4	51.50	6.61	0.17	13.02	1.91	2.7	99.8	24.8
CCB5	44.14	6.93	0.22	21.52	1.62	3.1	71.4	24.3
CCB6	35.96	6.19	0.29	30.79	1.55	2.5	35.8	26.1

Table 1. Chemical compositions and properties of agglomerates, sintered ore, and coke used in this study (tr: trace, n.a.: not analyzed, *: after consideration of oxidation during ash measurement).

	T.Fe	M.Fe	FeO	Ash	CaO	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O+K ₂ O	VM	T.C	F.C	True density	Porosity
	wt%	wt%	wt%	wt%dry	wt%	wt%	wt%	wt%	wt%	wt%dry	wt%	wt%dry	g/cm ³	%
CCA	42.25	tr	0.33	—	9.83	4.06	1.36	0.43	n.a.	—	16.63	—	3.32	39.9
RCA	35.11	0.23	2.47	—	10.96	6.35	2.61	0.68	0.15	—	17.97	—	3.14	24.9
ACP	1.78	tr	n.a.	—	11.72	8.32	2.79	0.67	0.25	—	71.00	—	1.98	38.3
Sintered ore	58.71	tr	7.18	—	9.25	4.92	1.62	0.72	n.a.	—	tr	—	4.66	22.5
FC3	8.46	6.17	1.21	20.84	0.11	6.04	3.35	0.08	0.15	0.00	—	79.16*	1.96	46.4
FC6	27.03	19.74	4.30	40.09	0.23	5.32	2.47	0.09	0.13	0.00	—	59.91*	2.31	45.3
Coke	tr	tr	tr	11.27	—	—	—	—	—	0.94	—	87.79	1.98	44.6

the iron ores of 10 wt% were mixed and carbonized in a test coke oven to obtain FC3. Pulverized coal and the iron ores of 30 wt% were mixed and formed into briquettes, and subsequently carbonized to obtain FC6.

Plant-sintered ores (10–15 mm in size) were mixed with the agglomerates. A plant coke (10.0–12.7 mm in size) was used as a reference.

2.2. Softening-melting Test

Generally, CA is mixed in ore layers in the blast furnace. Therefore, the reduction behaviors of the mixed ore layers with sintered ores and CCA were evaluated using a softening-melting tester.¹⁰⁾ The particle sizes of the sintered ores and CCA were 10–15 mm. The test conditions were the same as those in the previous report.¹⁰⁾ The samples were charged to form a 70 mm-high layer between the 20 mm-high coke layers in the graphite crucible. The samples were then heated to 800°C in the presence of N₂ and, subsequently, heated in the presence of a reducing gas mixture with the composition of CO (29.4%)-H₂(3.6%)-N₂(67.0%) with the superficial velocity of 10 cm/s. During the heating, the samples were subjected to a 98-kPa load. Both the rate of carbon consumption (RCC) and carbon consumption ratio (CCR) were evaluated using Eqs. (5) and (6). In addition, reduction degree was similarly evaluated using Eq. (7).

$$RCC(g/min) = ((CO_o + CO_{2o}) - (CO_i + CO_{2i})) / 0.0224 \cdot 12 \quad (5)$$

$$CCR(\%) = \frac{\int_0^t RCC dt}{C_{before}} \cdot 100 \quad (6)$$

$$O(g/min) = ((CO_o + 2 \cdot CO_{2o}) - (CO_i + 2 \cdot CO_{2i})) / 0.0224 \cdot 16 \quad (7)$$

where CO_o denotes the exhaust CO rate (Nm³/min), CO_{2o} the exhaust CO₂ rate (Nm³/min), CO_i the inlet CO rate (Nm³/min), CO_{2i} the inlet CO₂ rate (Nm³/min), C_{before} the carbon amount before reaction (g), and O the oxygen-reduction rate (g/min).

The reduction degrees at 800°C, 1 000°C and 1 200°C, carbon consumption until 1 200°C, T₅₀ (the temperature at which shrinkage reached 50%), T_s (the temperature at which pressure drop reached 2.0 kPa), dP_{MAX} (maximum pressure drop), and S-value (the time integral of pressure drop) were evaluated as a function of the CCA ratio in the mixed layers.

2.3. Reactivity Test

The carbon reactivities of the agglomerates were evaluated in two measurement conditions, CRT1 and CRT2, by performing a large-scale thermogravimetric analysis.⁷⁾ To that end, 200 g of the agglomerates with sizes of 10.0–12.7 mm was used. In CRT1, samples were heated until 1 200°C at the heating rate of 10°C/min, and 0.02 Nm³/min of CO-CO₂-50%N₂ gas was flowed at a constant CO₂/(CO+CO₂) ratio during the tests. In each test, the CO₂/(CO+CO₂) ratio was varied from 0.05 to 0.5. The RCC during the tests was evaluated using Eq. (5). The CCR of the agglomerates was evaluated using Eq. (8) on the basis of

the chemical analysis of the agglomerates before and after the tests. Only the CCR of coke without iron was evaluated using Eq. (6) on the basis of the exhaust-gas analysis.

$$CCR(\%) = \left(1 - \frac{(T.C / T.Fe)_{after}}{(T.C / T.Fe)_{before}} \right) \cdot 100 \quad (8)$$

The starting temperature of carbon consumption was defined as the temperature at which RCC exceeded 0.04 gC/min.

In CRT2, the carbon reactivities of the agglomerates under the gas condition demonstrating plant blast furnaces were evaluated. 0.02 Nm³/min of CO-CO₂-N₂ gas was flowed, and the concentrations of CO and CO₂ were varied with temperature until 1 200°C (Fig. 2). In these tests, exhaust-gas analysis should be avoided for ensuring precise evaluation, as both the heating rate and composition of the inlet gas changed with time during the test. Therefore, the carbon consumption was evaluated via factor analyzing of the weight loss after the test. While analyzing ACP and RCA, the weight loss until 500°C was considered because of the dehydration of cement-hydrate and combined water. In the evaluation of CCB, homogeneously mixed layers with 350 g of sintered ores and 150 g of CCB were evaluated.

2.4. Process Estimation

A previously conducted investigation⁷⁾ reported the reduction in the temperature of TRZ and the increase in shaft efficiency of the blast furnace upon using Ferro-coke by a counter-current reaction simulator, called BIS¹¹⁾ in the non-alkali-recirculation condition. In this study, we estimated the process of the blast furnace by using CA or Ferro-coke, and CA+Ferro-coke in the alkali-recirculation condition. CCA and FC6 were mixed in the ore layers, and FC3 and FC6 were mixed in the coke layers. The particle sizes of CCA and Ferro-coke were 8–11 mm and 9–13 mm, respectively. The charged amounts of the sintered ores and coke were changed to attain the constant values of T.Fe and T.C in every charge. The replacement ratio of carbon (charged carbon of the agglomerates to the total carbon) was changed in the range of 30–100%. The composition

Fig. 2. Experimental conditions of the CRT2 test simulating blast furnace.

(CO at 36.0%, H₂ at 7.0%, N₂ at 57%) and volume (1 343 Nm³/t-HM) of bosh gas were designed to demonstrate plant operation at the blast temperature of 1 178°C, blast moisture of 18.6 g/Nm³, oxygen enrichment of 2.7% in RAR of 481 kg/t-HM, and coke rate of 349 kg/t-HM. Ore/coke was 4.63. KOH (reagent grade) was added to coke to attain 1.8 wt% of K to demonstrate the recirculation of alkali within the plant (Appendix). The temperature at the minimum heating rate during the tests was defined as the temperature of TRZ.

3. Results and Discussion

3.1. Behavior of Reduction and the Softening-melting of CCA

Figure 3 shows the results of the softening-melting tests for different mixing ratios of CCA. The gasification of carbon initiated at 600°C and completed at 1 100°C in a single use of CCA. However, the gasification of coke (at the top and the bottom of the ore layer) initiated at 1 000°C in a single use of sintered ores. In addition, a rapid carbon consumption due to the smelting reduction during melting was also exhibited at 1 210°C. The reaction behavior observed upon mixing 40% of CCA to the sintered ores resembled that of CCA, rather than the middle of CCA and sintered ores. **Figure 4** summarizes the results of softening-melting tests using CCA. The reduction degrees of the mixed layer increased with increasing the mixing ratio of CCA, particularly between 800 and 1 000°C (a). The extent of the increase was larger than the extent of decrease of reducible oxygen with increasing the mixing ratio of CCA. The carbon consumption until 1 200°C before smelting reduction also increased with increasing the mixing ratio of CCA, implying the low-temperature gasification of carbon in CCA (b). Both reduction degrees and carbon consumption increased nonlinearly with increasing the mixing ratio of CCA, implying the synergistic effect due to mixing, *i.e.*,

Fig. 3. Comparison of the composition of exhaust gas (a) and RCC in softening-melting tests with a different CCA ratio in ore layers.

an enhancement in the reactivity of sintered ores or CCA. A similar synergistic effect was reported in a previously conducted investigation.¹²⁾ In addition, T₅₀ decreased with increasing CCA, mostly because of the increase in the number of voids during gasification and reduction (c). However, T_S increased and both S-value and dP_{Max} decreased with increasing CCA, mostly because of the decrease in the molten FeO near the melting temperature through an increase in the reduction degree (d). However, both S-value and dP_{Max} increased again above for 80% of the mixing ratio of CCA because of an increase in slag volume. These results were in good agreement with those in past investigations.^{3,13)}

3.2. Carbon Reactivity of the Agglomerates

3.2.1. Reactivity under iso-CO₂/(CO+CO₂) Condition (CRT1)

Figure 5 shows the results of the heating test using the agglomerates using 0.3 of CO₂/(CO+CO₂) of flow gas composition (CRT1). The carbon consumptions of Ferrocoke (FC6), RCA and ACP were higher than that of coke (b). The RCC values of RCA and ACP were low at below 950°C, whereas their starting temperatures of the reaction were low at 700°C. However, their rate of reaction became sufficiently high above 950°C. Particularly, that of RCA containing iron oxide was higher than that of ACP without iron oxide, at temperatures above 1 000°C. During the heating of RCA, CO₂ was observed to form due to reduction until 1 000°C, following which the formation of CO due to carbon gasification exceeded the CO₂ formation (c).

Robinson¹⁴⁾ observed the decomposition of Ca(OH)₂, which is a product of cement hydration, followed by the water-gas reaction of carbon at 400–600°C during the heating of CA. We also observed H₂ generation at 400–600°C during the heating of RCA and ACP; however, the gen-

Fig. 4. Reduction behavior of ore layers with CCA and sinter as a function of CCA ratio in softening-melting tests.

Fig. 5. Weight change (a), RCC (b), and compositions of exhaust gas (c) during heating tests with different agglomerates with the $\text{CO}_2/(\text{CO}+\text{CO}_2)$ ratio of the inlet gas as 0.3. (Online version in color.)

erated amount was insignificant (c). Watanabe *et al.*¹⁵⁾ observed the catalytic facilitation of carbon gasification near the gas composition in the equilibrium between Fe and FeO during the heating of CA consisting with ultra-fine iron oxide and biomass char. However, the facilitation of carbon gasification was not observed at 900°C during the heating of RCA, mostly because of the large size of iron oxide. **Figure 6** shows the relationship between the starting temperature of carbon consumption and the composition of inlet gas during the heating of the agglomerates. The starting temperatures of all the agglomerates were lower than that of coke, and decreased with increasing the $\text{CO}_2/(\text{CO}+\text{CO}_2)$ ratio. Ferro-coke had lower starting temperatures than that of coke, by 100–150°C, thereby coinciding with the result of CIC.¹⁶⁾ The starting temperature of RCA was along the line showing the Boudouard equilibrium. Kawanari *et al.*¹⁷⁾ observed carbon gasification below 700°C during heating of CA with ultra-fine iron oxide and resin. However, carbon gasification at temperatures below that of the Boudouard equilibrium was not observed during the heating of RCA and ACP, as both comprised larger-sized iron oxide and coke.

Figure 7 shows the CCR and reduction degree of the agglomerates after reaction until 1 200°C in CRT1. The CCRs of all the agglomerates were higher than that of coke and increased with increasing the $\text{CO}_2/(\text{CO}+\text{CO}_2)$ ratio (a). Although the reduction degrees of Ferro-coke and RCA were lowered in conditions with higher $\text{CO}_2/(\text{CO}+\text{CO}_2)$ ratio, they remained above 90%, thereby showing the prevention of re-oxidation even in the stable-FeO condition (b).

These results showed that the carbon-consumption behaviors of the agglomerates varied significantly with the gas conditions, thereby implying the importance of designing their arrangement both along the radial and vertical direc-

Fig. 6. Relationship between the starting temperature of carbon consumption and inlet-gas composition.

Fig. 7. Changes in CCR (a) and reduction degree (b) of the agglomerates after reaction until 1 200°C with respect to inlet-gas composition.

tions in ore layers.

3.2.2. Reactivity under Plant Condition (CRT2)

Figure 8 shows the results of the heating test using the agglomerates under the gas composition demonstrating plant (CRT2). Similar to the results shown in Fig. 5, the carbon consumptions of Ferro-coke (FC6), RCA and ACP were higher than that of coke (b). In addition, the formation of CO_2 was also observed until 900°C during the heating of RCA (c).

Table 3 presents the result of the weight-loss analysis of the agglomerates after heating until 1 200°C in CRT2. The carbon consumption of Ferro-coke was higher than that of coke, thereby coinciding with the results of past investiga-

Fig. 8. Weight change (a), RCC (b), and exhaust-gas compositions (c) during heating tests with different agglomerates with respect to the gas composition of blast furnace. (Online version in color.)

Table 3. Results of the weight-loss analysis of the agglomerates after heating until 1 200°C in CRT2.

		Coke	FC3	FC6	ACP	RCA
Carbon content before reaction	wt%	87.0	79.2	59.9	71.0	18.0
Weight loss	wt%	0.5	5.8	12.3	15.8	33.3
Oxygen	wt%	0.0	0.8	2.7	0.0	14.6
Water	wt%	0.0	0.0	0.0	3.8	2.1
Carbon	wt%	0.5	4.9	9.7	12.0	16.6
Carbon consumption ratio	%	0.5	6.2	16.1	16.9	92.6

tions.¹⁸⁾ In addition, ACP presented higher carbon consumption, mostly because of the smaller size of carbon¹⁹⁾ and catalytic effect of Ca²⁰⁾ from cement. Furthermore, RCA had higher carbon reactivity. Because RCA and ACP had similar alkali contents (Table 1), the high carbon reactivity of RCA was mainly attributed to the coupling phenomena²⁾ due to the close arrangement of carbon and iron oxide.

3.2.3. Influence of M.Fe in CAs

The starting temperature of the carbon consumption of RCA increased with increasing the $\text{CO}_2/(\text{CO}+\text{CO}_2)$ ratio from 0.3 to 0.4, thereby implying that the reduction mechanism of the temperature was related with the formation of metallic iron during the heating (Fig. 6). A similar consideration was made in a past investigation.²¹⁾ Therefore, the reaction behavior of CCB with M.Fe under plant condition (CRT2) was investigated to clarify the influence of M.Fe on the reaction of CA. **Figure 9** shows the results achieved by evaluating the reactivity of CCB. Although the CCR of CCB

Fig. 9. Influence of the M.Fe addition to CCB on CCR (a) and reduction degree after heating ore layers with sinter (70 wt%) and CCB (30 wt%).

decreased with increasing the T.C content in CCB, the M.Fe addition enhanced it. The reduction degree of the ore layers were the highest at 30 wt% of T.C with M.Fe addition. From these results, it is concluded that the catalytic effect of M.Fe on coke reactivity could be effective not only in Ferro-coke but also in CA.

3.3. Process Estimation of Blast Furnace Using the Agglomerates

3.3.1. Process Estimation

Table 4 presents the results of the BIS test, along with the RAR estimated using a mathematical model.²²⁾ Notably, 30% replacement of carbon by the CCA reduced the temperature of TRZ by 150°C, thereby decreasing the RAR by 29 kg/t-HM even in the alkali-recirculation condition. The decrease corresponded to 0.3 kg/t-HM per 1 kg/t-HM of carbon from CA, and was fairly smaller than those in the past investigations performed using smaller replacement ratios; *i.e.* 0.6,²³⁾ 0.4,¹³⁾ 0.5²⁴⁾ and 0.4.⁴⁾ The result implied that the RAR-decreasing efficiency by CA depended on the amount of CA used. The estimated RAR of the blast furnace using FC6 in full replacement was similar to that using CCA caused by the effect of M.Fe charging, whereas the temperature of the TRZ was limited to 915°C. The combination of CA and Ferro-coke was examined to further reduce RAR. Mixing CCA in the ore layer by 30% replacement and simultaneously mixing FC6 in the coke layer by 35% replacement decreased the temperature of the TRZ to 842°C, thereby resulting in 466 kg/t-HM of the estimated RAR. A check test was performed by decreasing the RAR by 35 kg/t-HM, corresponding to the increase of charging Fe/C from 3.06 to 3.33 and the reduction of the bosh gas volume from 1 343 to 1 174 kg/t-HM. The heating and reduction behaviors of ores in the low-RAR condition were similar to those in the high-RAR condition (**Fig. 10**), thereby confirming the validity of the estimation. However, the decrease in the top gas temperature upon using a signifi-

Table 4. Results of the BIS tests using the agglomerates.

Agglomerates			Base		FC3		FC6		CCA		CCA+FC6	
Replacement ratio of carbon			%	—	50		100		30		65	
Arrangement of charging materials	Ore layer	kg/t-HM	Sinter	1 616	Sinter	1 616	Sinter	1 127	Sinter	1 040	Sinter	1 040
			—		—		FC6	153	CCA	611	CCA	611
	Coke layer	kg/t-HM	Coke	349	Coke	175	Coke	0	Coke	244	Coke	122
			—		FC3	196	FC6	359	—		FC6	179
Temperature of thermal reserve zone			°C	987	898		915		835		842	
CO ₂ /(CO + CO ₂)·100	Raw data	%	50.9		51.8		47.9		55.9		55.2	
	Hematite base	%	51.9		53.7		58.4		53.4		56.2	
H ₂ O/(H ₂ +H ₂ O)·100	Raw data	%	40.5		39.7		30.1		23.4		23.1	
Shaft efficiency	Raw data	%	95.2		93.9		89.1		94.0		93.5	
	Hematite base	%	95.4		95.4		103.7		94.2		98.5	
Estimated RAR		kg/t-HM	507		489		479		478		466	
Estimated temperature of top gas			°C	209	172		194		142		148

Fig. 10. Changes in temperature and gas composition during the BIS test with CCA and Formed Ferro-coke (FC6). (Online version in color.)

Fig. 11. Relationship between CCR and the reduction degree of CCA in the BIS test. The numerical values represent temperatures.

cant quantity of these agglomerates (Table 4) would be one of the factors limiting their use, in addition to their physical properties related to the permeability of the blast furnace.

3.3.2. Reaction Behavior of the Agglomerates during the BIS Test

Figure 11 shows the relationship between CCR and the reduction degree of CCA during the BIS test, together with the molar ratios of consumed carbon to reduced oxygen. Because CCA was completely reduced at low temperature (1 035°C), the carbon consumption was assumed to occur only because of gasification until the end of reduction, by referring to past investigations that reported a slight carburization of the formed iron, *i.e.*, 2.0 wt% at 1 300°C²⁵⁾ and 0.1 wt% at 1 100°C.²⁶⁾ The insignificant values of carbon consumption until achieving 30% of reduction degree showed that CCA was reduced only by CO in the surrounding bulk gas. For above 30% of reduction degree, both carbon consumption and reduction proceeded simultaneously to attain 1.0 C/O. This finding proved the self-reduction with coupling phenomena within CCA, and was in agreement with the assumption by Ueda *et al.*¹⁹⁾ They assumed gas reduction at the initial stage and the self-reduction at the

later stage, during the reaction of CA in a reaction model.

Figure 12 shows the analysis result of the agglomerates after quenching during the BIS test, for the combination of CCA and FC6. The reduction degree of CCA was higher than that of the coexisting sintered ores (a). The higher reduction degree of coexisting sintered ores compared with that in base condition without agglomerates showed the shift in reduction equilibrium (W point) due to the reduction in the temperature of TRZ. FC6 represented a partial re-oxidation between 500 and 800°C. First, the carbon consumption of CCA initiated, followed by that of FC6 followed (b). The ash contents of coke during the test were similar to those in the base condition without agglomerates, thereby showing limited reaction of coke (c). The result showed that the coke gasification was prevented by other high-reactivity carbonaceous materials.⁶⁾

3.4. Influence of the Distance between Carbon and Iron Oxide on the Temperature of TRZ

Although all the agglomerates showed higher carbon

Fig. 12. Reduction degree (a) and CCR (b) of charged agglomerates and the ash content of coexisting conventional coke (c) in the BIS test with CCA and FC6.

reactivities than that of coke, their reactivities were different from each other. Therefore, the reasons for the difference among reactivities were discussed on the basis of the distance between carbon and iron oxide or metallic iron (hereafter denoted as only “iron oxide”). The average distance between carbon and iron oxide (L_{OC}) and the surface area of carbon were estimated for all the agglomerates. The following were the assumptions of the conventional charging condition; layer-by-layer charging ores and coke, coke diameter of 40 mm, and coke-layer thickness of 360 mm. For reference, the properties for half the aforementioned coke-layer thickness, completely mixing coke and ores, and mixing nut-coke (20 mm) were also estimated.

L_{OC} was estimated using Eqs. (9) and (10) by approximating a spherical unit. The unit contained a core of one carbon particle in the case of CA and mixing coke, and it contained a core of one particle of metallic iron in the case of Ferro-coke. The following equations show the case of CA and mixing coke.

$$L_{OC}(mm) = \frac{\int_{d_c/2}^{d_U/2} x^3 dx}{\int_{d_c/2}^{d_U/2} x^2 dx} - \frac{d_c}{2} \quad \dots\dots\dots (9)$$

$$d_U(mm) = d_c \cdot \left(1 + \frac{V_O}{V_C}\right)^{1/3} \quad \dots\dots\dots (10)$$

where d denotes the diameter (mm), V the volume (mm^3), subscript U the spherical unit, subscript O the iron ores, and

Fig. 13. Evaluation results of L_{OC} (average distance between iron oxide and carbon (a)) and surface area of coke (b) along different charging conditions.

subscript C the coke. The contents of iron oxide and carbon in CCA were converted to iron ores and coke, respectively. In addition, the bulk densities of the ores and coke were 1.6 and 0.5 mg/mm^3 , respectively. During the estimation of Ferro-coke, the true densities of M.Fe (ρ_{tM}) and FeO (ρ_{tFeO}), and the apparent density of coke (ρ_{apC} 1.1 mg/mm^3) were used. Because the metallic iron in Ferro-coke was homogeneously distributed in the coke matrix without aggregation,⁷⁾ the diameter of metallic iron (d_M) was used as 0.09 mm, by considering the shrinkage of charged iron oxide (0.12 mm in the median size) based on the increase of theoretical true density from 5.16 to 7.43 mg/mm^3 during the carbonization. The surface of the carbon in CCA (A_C) was estimated using Eq. (11). The surface of the carbon in Ferro-coke (A_{FC}), including the contact interface area between metallic iron and coke, was estimated using Eq. (12).

$$A_C(mm^2 / mg) = \frac{6}{d_C} \cdot \frac{1}{\rho_{apC}} \quad \dots\dots\dots (11)$$

$$A_{FC}(mm^2 / mg) = \frac{6}{d_{FC}} \cdot \frac{1}{\rho_{apFC}} + \frac{6}{d_M} \cdot \left(\frac{W_M}{100 \cdot \rho_{tM}} + \frac{W_{FeO}}{100 \cdot \rho_{tFeO}} \right) \quad \dots\dots\dots (12)$$

where, W denotes the weight (wt%), ρ_{ap} the apparent density (mg/mm^3), subscript FC the Ferro-coke, subscript M the Metal, subscript FeO the FeO. The measured ρ_{ap} for FC3 was 1.05 and that for FC6 was 1.22.

Figure 13 shows the estimation results of L_{OC} and surface area of carbon. Although high L_{OC} was estimated for the conventional layer-by-layer charging without agglomerations, thinning the coke layer decreased L_{OC} . Complete mix-

Fig. 14. Microstructures of CCA before and after reaction (quenched temperature: 904°C, reduction degree: 80%, CCR: 35%). C (gray): Coke, M (white): Metal.

Fig. 15. Relationship between changes in the temperature of TRZ (results of the BIS test) and L_{OC} (average distance between iron oxide and carbon).

ing further reduced L_{OC} , and nut-coke enhanced the reduction and improved the surface area of carbon. Compared with these changes, the agglomerates significantly decreased L_{OC} and increased the surface area of carbon. **Figure 14** shows the microstructures of CCA before and after the BIS test. The structure of CCA had the structure with coarse coke-dust particles embedded in fine iron oxide particles, showing several microns order of L_{OC} before reaction. The structure of CCA quenched at 904°C during the BIS test had the structure with residual carbon particles and fine metallic iron, thereby also showing several microns order of L_{OC} .

Figure 15 shows the relationship between the reduction in the temperature of TRZ in the BIS tests and L_{OC} in the cases of both mixing nut-coke and using the agglomerates in the limited replacement ratio with carbon less than 50%. The results of a past investigation without the alkali addition^{3,7)} are also shown in the figure. The condition of mixing nut-coke was the homogeneously mixing of 175 kg/t-HM of coke with 9–13 mm of size to the ore layer. As the replacement ratios of carbon were different in the tests, the reduction of temperature of TRZ at 10% replacement of carbon was evaluated. The temperature of TRZ decreased with decreasing L_{OC} . This finding agreed with the past investigation by Kasai *et al.*²⁷⁾ They also observed a larger decrease in the starting temperature of endothermic reactions by CA compared with that observed upon mixing nut-coke. The influence of alkali addition on the evaluation of various

agglomerates was insignificant, which was consistent with the results in a previously conducted investigation.⁶⁾ The dominant factor reducing the temperature of TRZ was the distance between carbon and iron oxide.

4. Conclusions

To decrease the RAR of blast furnaces, the reaction behaviors of CAs and Ferro-coke with high carbon reactivity were evaluated, and consequently, process estimation of a blast furnace was performed. The following results were obtained.

- (1) CAs exhibited low-temperature gasification, thereby facilitating reduction upon mixing with sintered ores.
- (2) The CCRs until 1 200°C of CAs and Ferro-coke were higher than that of coke. Particularly, RCA, which is reinforced CAs with high carbon content toward reducing the RAR, exhibited low starting temperature of the carbon consumption and high carbon reactivity during heating. The high carbon reactivity of RCA was primarily attributed to the coupling phenomena between gas reduction of iron oxide and gasification of carbon.
- (3) Adding metallic iron to the CA resulted in the enhancement of carbon consumption and reduction of the sintered ores due to the catalytic effect of metallic iron.
- (4) A combined use of the CA and Ferro-coke in the blast furnace reduced the temperature of TRZ by 150°C, thereby giving a potential to decrease RAR by 35 kg/t-HM.
- (5) The reduction of the temperature of TRZ due to the CA and Ferro-coke was closely associated with shortening the distance between carbon and iron oxide or metallic iron.

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Appendix Influence of Alkali Recirculation in BIS Test

In plant blast furnaces, alkali recirculation within the furnace influences both carbon reactivity and reduction of sintered ores. We consider that the aforementioned influence is essential for performing process estimation by the BIS test. The following scheme of recirculation is well known.^{A1)} K (g) and KCN (g) form from the heath slag at 1 500°C. These gases move upward with decrease in their temperature, resulting in partial condensation and oxidization to form K₂CO₃ (l) and KCN (l). With the descending of the charged materials, the temperatures of these liquids are increased and they vaporized again. Therefore, the influence of alkali in the BIS test was investigated. The condition of the BIS test was the same as that described in subsection

Fig. A1. Changes in the temperature of TRZ and gas utilization upon adding K in the BIS tests.

Table A1. Na₂O+K₂O contents (wt%) of the sum of sintered ores and coke below 1 200°C.

	BIS test		Quenched blast furnace		Probe sampling
	K 0.9 wt% addition	K 1.8 wt% addition	Hirohata ^{A2)} (1976)	Amagasaki ^{A3)} (1980)	Oita (2007)
Na ₂ O+K ₂ O	0.18	0.27	0.33	0.21	0.27

2.4. KOH (granular reagent grade, purity 85%) was charged between an ore layer and a coke layer. The amount of charge was varied to attain K content of 0 wt%, 0.9 wt%, and 1.8 wt% in the charged coke.

Fig. A1 shows the result of the BIS test. The temperature of TRZ reduced and gas utilization increased upon adding alkali. The temperature of TRZ decreased to approximately 900°C, which is a comparable value for plant measurement, between 0.9 wt% and 1.8 wt% of K addition. Table A1 shows the alkali content of the sum of sintered ores and coke until 1 200°C in the BIS test, as well as the results of samples analysis after quenching blast furnaces^{A2,A3)} and after sampling by a probe. The addition of 1.8 wt% of K in the BIS test resulted in a comparable alkali content of the changed materials, compared with those in the plant. Therefore, we decided to add 1.8 wt% of K in the BIS test, thereby demonstrating the recirculation of alkali in the plant.

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