Evaluation of Characteristics of Coke Degradation after Reaction in Different Conditions

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In this study, post reaction strength under various conditions was measured to investigate effects of gasification with CO₂ on coke degradation in the lower shaft of blast furnace. Post reaction strength of coke samples taken at the shaft of actual blast furnace was much higher than that in NSC tests, leading to slight change in mean size. The test for coke strength after reaction with the constant weight loss of 20% was not an effective way to evaluate commercial coke with high CSR and low CRI. When coke samples were gasified at a different temperature of 1 100–1 300°C, topochemical reaction was observed at over 1 200°C by image analysis. Post reaction strength (CSR_{SBF}) in the simulated blast furnace conditions was 14.9%P higher than conventional CSRs, which is attributed to different correlation between reactivity and post reaction strength in two methods. This phenomenon seems to be caused by topochemical reaction on coke surface in blast furnaces which results into suppressing coke degradation. The post reaction strength test should be modified in accordance with the individual blast furnace operation, to simulate coke degradation due to solution loss in the shaft because solution loss in NSC tests is over-estimated.

KEY WORDS: coke; coke strength after reaction; post reaction strength; coke degradation.

1. Introduction

High productive operation of a blast furnace with high PCR (Pulverized coal injection rate) leads to thinner coke slits for the passage of reducing gas, less coke to support the burden and a longer residence time in the blast furnace, promoting coke degradation and fines generation in a blast furnace. The solution loss reaction (C + CO₂ → 2CO) is considered a key factor affecting coke degradation in blast furnaces.

The indexes, most widely renowned for the determination of post reaction strength in a blast furnace, are CRI (Coke reaction index) and CSR (Coke strength after reaction) developed from Nippon steel corporation (NSC), which is tested with 200 g of coke sample (19–21 mm) for 2 hours at 1 100°C under 100% CO₂ atmosphere. It is known that high CSR and low CRI are more desirable for the stable operation of blast furnaces. However, it has been pointed out that solution loss reaction in the NSC-tests, especially of highly reactive coke, might be overestimated, compared with that in an actual blast furnace where CO₂/CO + CO₂ of ascending gas is varied between 0 and 0.5. Moreover, Goleczka et al. and Barnaba assumed that weight loss percentages due to solution loss in actual blast furnaces were about 20–30% and 25%, respectively.

Van Der Velden et al. reported that the extent of gasification under the simulated blast furnace conditions was much lower than that from the NSC-tests and the degree of gasification had no influence on the strength because reaction mechanism in the blast furnace condition between CO₂ and coke is mainly topochemical. This means that gasification is not an overall reaction in the whole coke, but a preferential reaction on the coke surface.

Lundgren et al. charged coke sample (CRI 19.9–38.2) in baskets into the experimental blast furnace (EBF) and analyzed post reaction strength of them after quenching and dissection. No correlation was found between coke strength for coke reacted in the CSR/CRI test and in the EBF. The coke strength was considerably higher in coke from the blast furnace, regardless of the CSR value, when compared with the CSR/CRI test. The results of light optical microscopy analysis indicates that solution loss reaction seems to take place throughout the coke piece during CSR/CRI testing, while in the blast furnace the reaction tends to occur at the coke surface. Subsequently, the reaction rate in the condition of CSR/CRI test is limited by chemical reaction kinetics, whereas in the blast furnace the limiting reaction is mainly diffusion.

Yamaguchi et al. suggested that it would be more appropriate to evaluate post reaction strength of coke after reaction with constant weight loss percentage to simulate an actual blast furnace, which was based on the concept that weight loss percentage of coke gasified in a normal opera-
tion of a blast furnace could be approximately 20%. Nomura et al. applied the macro thermobalance tests to evaluating post reaction strength, where gasification reaction under the feed gas atmosphere of $\text{CO}_2/\text{CO}=1/1$ was stopped at a weight loss percentage of 20% and the reaction temperature was varied from 1000°C to 1200°C. It has been noted by Guo et al. that CSR is a useful and effective index for blast furnace operation, as long as coke with a normal reactivity is used. However, post reaction strength of coke with a special reactivity should be evaluated by a special method such as a coke reaction after the constant gasification reaction to about 25% of weight loss.

In Hyundai-steel’s Dangjin steel complex, three blast furnaces with the inner volume of 5 250 m$^3$ have been operating at the high production rate of about 2.3 t m$^{-3}$−1. Therefore, relatively high strength coke of more than 67% of CSR and 87.5% of DI150/15 has been demanded for the stable blast furnace operation. To keep CSR higher than the target, unlike cold mechanical strength (DI150/15), the use of premium low volatile coking coals in large quantity is essential, resulting in the rise in the coal blending cost. In this study, post reaction strength tests under various conditions were performed to ascertain whether such a high CSR is needed to suppress coke degradation in a blast furnace.

Solution loss associated with direct reduction between cokes and molten FeO in cohesive zone can be regarded as the surface reaction, thereby causing less fine generation than that between cokes and CO$_2$ related to indirect reduction. Moreover, solution loss in direct reduction was reported to be independent of coke reactivity by Sunahara et al. We, therefore, focused on the investigation of fine generation of cokes due to gasification between coke and CO$_2$ in the lower shaft over cohesive zone in which gas permeability can be inhibited by accumulation of coke fines.

In order to investigate the effect of solution loss reaction on coke degradation in the lower shaft zone of blast furnace, commercial coke samples were tested in different reaction conditions: (1) constant gasification degree of 20% under feed gas composition of shaft zone, (2) different temperature under feed gas composition of shaft zone, (3) simulated blast furnace conditions based on shaft probe measurement by van der Velden et al. and Sunahara et al. This was compared with NSC’s test results and post reaction strength of coke samples taken from the lower shaft zone of an actual blast furnace. In addition, characteristics of coke deterioration due to gasification was examined by the microscopic analysis.

2. Experimental Methods

2.1. Coke Sampling
Coke samples used for post reaction strength tests were taken at the belt conveyor prior to charging into #1 blast furnace. Under the normal coke oven operation, CSR and DI150/15 varied from 65 to 69% and from 88% to 89%, respectively. During repairing the cooling device on the steel shell of #1 blast furnace, coke samples inside the blast furnace were taken at the B2 and B3 levels which are assumed to correspond to the lower shaft zone. Coke samples at tuyere level were obtained by a core drilling machine.

2.2. Post Reaction Strength Tests
The CRI and CSR tests are conducted according to JIS K2151. The CSR$_{10}$, which is the strength after solution loss reaction in the actual blast furnace, is determined by measuring $I^{(10\%)}_{600}$, percentage of coke mass retained on a sieve with 10 mm apertures to the mass of the reacted coke sample after 600 revolutions in the I-type drum tester. In the thermobalance tests, a reaction tube hanging on a balance is placed in a heated oven of which reaction temperature and gas composition can be automatically adjusted by a programmable control. The CSR$_{WL,20\%}$, the post reaction strength ($I^{(10\%)}_{600}$) after reaction with the constant weight loss of 20% (CSR$_{WL,20\%}$) under a gas composition of $\text{CO}_2/\text{CO}=1/1$, is measured in the same way proposed by Nomura et al. The simulated blast furnace reaction condition in Fig. 1 is based on the test condition which was set up from shaft probe measurement in actual blast furnaces by van der Velden et al. and Sunahara et al.

2.3. Microscopic Analysis
Coke pieces were mounted in the resin and their surfaces were polished prior to analysis. The coke samples reacted under different conditions were analyzed microscopically to investigate characteristics of gasification. Porosity distribution in coke was measured using the image analysis software (Clemex Vision PE, Clemex Technologies Inc., Canada), in order to check the reaction degree at different positions from core to rim of coke. As shown in Fig. 2, only pore part in the coke piece was projected on the image which was divided into 5 layers with the same width from the core to the rim. Porosity was calculated by image analysis and average value of 2 or 3 coke pieces in each case was used in this case.

3. Results and Discussion

3.1. Post Reaction Strength in the Actual Blast Furnace
When the cooling devices of #1 blast furnace of Hyundai-steel company was under repair, coke samples inside the actual blast furnace were taken from near steel shell of B3 and B2 levels (refer to 2.1). The vertical distances from the tuyere and the top to each sampling position are summarized in Table 1. B3 and B2 level inside blast furnace are assumed to be in the temperature range from 1 100°C.
to 1 200°C, which was identified by the measurement of crystallite height (Lc) of coke samples (18–20 Å). Post reaction strength after reaction in the actual blast furnace (CSRBF) was evaluated by measuring $I_{600}^{10}$ of coke samples gasified in the shaft (B3–B2 level) of #1 blast furnace. Figure 3 shows the variation in $I_{600}^{10}$ and mean size (MS) of coke at different levels in the blast furnace, indicating that as the charged coke descends from the top of the blast furnace, $I_{600}^{10}$ decreases due to solution loss reaction in the blast furnace. $I_{600}^{10}$ of the charged coke without reaction were 87.7%. $I_{600}^{10}$ at B3 level showed a slight decrease from 87.7% to 86.2%, but $I_{600}^{10}$ at B2 level was sharply dropped to 80.2%. When descending from B2 level to tuyere level, there was no significant change in $I_{600}^{10}$. This means that the charged coke can be deteriorated by solution loss reaction in the shaft of the blast furnace. Though post reaction strength of coke was remarkably dropped in the shaft, decrease in mean size between B3 and B2 level was just 1.1 mm. It is very similar to the results of dissection of Nagoya #1 blast furnace that lump coke, which begins to degrade due to selective solution loss and to decrease its strength at 1 000°C, did not change its mean size up to 1 400°C but begins to reduce it sharply above 1 400°C. Cheng reported that solution loss reaction of coke in the shaft takes place on the surface and core part remains unreacted. Therefore, coke degradation occurs mainly on the surface, called “peeling-off”, and change in coke size due to solution loss in the shaft can be estimated to be just about 1.3 to 2.5 mm.

Microscopic examination is a useful tool to gain insight into the progress of the reaction from the surface to the core of a coke piece. The microscopic examination was performed with different coke samples which were gasified.
under the condition of NSC-tests and actual blast furnace. As shown in Fig. 4, there was a clear difference in the reaction site of coke with CO₂. Solution loss reaction appears to occur both in the rim and core part of coke piece in the NSC test, but mainly in the rim of coke piece in the actual blast furnace. This can be caused by the difference in reaction temperature and gas composition. Topochemical reaction in the blast furnace can explain peeling-off of coke due to solution loss reaction, leading to the slight decrease in mean size of coke especially in the shaft zone of blast furnace. However, further study on the effect of reaction temperature and gas composition on the deterioration of lump coke is required to elucidate these phenomena in detail.

3.2. Strength after Reaction with Constant Weight Loss

According to the method proposed by Nomura et al., tests for CSR WL = 20%, strength after reaction with constant weight loss of 20%, were carried out to see if it can be substituted for the conventional CSR. The coke samples, taken from #1 coke plant of Hyundai-steel company, were gasified until reaching to 20% of weight loss at 1 100°C under the feed gas atmosphere of N₂:CO:CO₂ = 6:2:2. Figure 5 shows that cokes with CSR of 62–68% are measured to be CSR WL = 20% of 66–70%. This can be reasonable, given that CRI values, weight loss percentage in the NSC-tests, of coke samples used in this study were more than 20%, ranging from 23% to 28%. When CSR is more than 66% and CRI is less than 25%, there is no significant change in CSR WL = 20%. However, CSR WL = 20% decreases drastically with decreasing CSR of less than 65% and increasing CRI of more than 25%. In Fig. 5(C), CSR WL = 20% increases with increasing I60010 of coke before reaction. This concurs with the opinion suggested by Shimoyama that only cold mechanical strength may be enough for the practical coke strength management because there is a tendency that coke with high strength after reaction with a constant weight loss percentage generally has high cold mechnacal strength.

The method for CSR WL = 20% was basically invented to evaluate highly reactive coke such as catalyst-added coke. It seems to be not a very effective way to evaluate post reaction strength of normal commercial cokes for large blast furnaces. However, futher study is need to be conducted at a constant gasification degree derived from with operational conditions of antucal blast furnaces, such as coke rate, productivity, PCR, etc., in hyundai-steel company.

3.3. The Effect of Reaction Temperature and Feed Gas Composition

Solution loss reaction of coke, associated with indirect reaction in blast furnaces, occurs mainly from 1 000°C to 1 300°C. At low temperature with low reaction rate, the reaction gas diffuses into the inner parts of the coke, but the solution loss reaction is primarily with the surface of the coke at high temperature with high reaction rate. Therefore, the characteristics of post reaction strength was investigated using coke samples with different level of CSR after reaction at different temperature from 1 100°C to 1 300°C. CRI and CSR value of sample A were 27% and 64% and those of sample B were 25% and 67%, respectively. 80 g of coke sample is placed on the reaction tube where gasification reaction occurs for 2 h at the desired temperature (1 100–1 300°C) under the feed gas atmosphere of N₂:CO:CO₂ = 6:2:2 (1.5 L min⁻¹). Post reaction strength was evaluated by measuring I60010 of coke samples after reaction. Figure 6 shows weight loss percentages and post reaction strengths of sample A and B at different reaction temperature. Weight loss percentages are linearily increasing with increasing reaction temperature and are lower than CRI in the NSC-tests. This was attributed to the retarded reaction rate which might be caused by the decrease in partial pressure of CO₂ in feed gas. Post reaction strength shows the similar pattern, but the degree of decrease in post reaction strength is dwindled as the reaction temperature increases from 1 200°C to 1 300°C, regardless of CSR levels of coke samples. This can be explained by peeling-off due to topochemical reaction on the coke surface. Though the solution loss reaction occurs vigorously at high temperature over 1 200°C, it might be restricted mainly on the coke surface, preventing from the overall deterioration in the whole coke piece.

In order to check the reaction degree over radius of coke piece at different reaction temperatures, the change in

![Fig. 4. Microscopic images of cokes before and after reaction in different conditions.](image-url)
porosity distributions from the rim to the core after reaction were measured by microscopic and image analysis (refer to 2.3). Figure 7 shows the reaction degree at 5 different layers of the coke piece of sample A from the rim to the core. The porosities of coke samples before reaction were between 50% and 60% and there was nearly no change in porosity of the core in all cases after reaction under the feed gas atmosphere of N₂:CO:CO₂ = 6:2:2. Thus, reaction degree was derived from the increasing ratio of the porosity in each layer in comparison with that in the core, assuming that the core (layer 1) is unreacted. At reaction temperature of 1100°C, solution loss reaction appears to occur overall in the whole coke piece, proceeding to the direction of the core from the rim through the penetration of CO₂ into coke.
piece due to the moderate reaction rate. On the contrary, as the reaction temperature increases over 1200 to 1300°C, it seems that reaction takes place primarily near the surface at reaction, thereby restricted somewhat in layer 1–3.

It is ascertained that topochemical reaction on the surface at high temperature over 1200°C leads to different correlation between reactivity and post reaction strength in comparison with that in the NSC’s test at 1100°C.

3.4. Post Reaction Strength in Simulated Blast Furnace Conditions

In order to investigate post reaction strength in the simulated blast furnace conditions, temperature and gas composition with time courses were programmed as shown in Fig. 1. Overall reaction time was about 240 min, corresponding to descending time of coke in the shaft of actual blast furnaces. CO2/(CO + CO2) of feed gas with inert N2 was varied from 0.25 to 0 as temperature increases.

Figure 8 shows the relationship between NSC-tests and BF simulation tests. CRIs and CSRs of coke samples tested were 20.6–26.0% and 62.4–71.5%, respectively. In BF simulation tests, coke reactivities (CRISBF) were about 9.0% lower than conventional CRIs and post reaction strengths (CSRSBF) were about 14.9% higher than conventional CSRs. Averaged 66.2% of CSR corresponds to 81.1% of CSRSBF, which is very close to CSRSBF of coke taken at B3 level of actual blast furnace (Fig. 3). In such a milder oxidation atmosphere under the simulated BF conditions, it seems that solution loss reaction rate was retarded, resulting into less degradation of coke. As shown in Fig. 8(c), however, there appears to be different correlation between reactivity and post strength reaction in two methods. In NSC-tests, the increase of 1% in coke reactivity leads to the decrease of 1.6% in CSR, while in the simulated BF condition it causes the decrease of just 0.5% in CSRSBF. This infers that less degradation of coke in the simulated BF condition might be attributed to topochemical reaction as well as the milder reaction conditions, than in NSC-tests.

In actual blast furnaces, coke is contaminated by ferrous dust and recirculated alkali, catalyzing solution loss reaction.15 In addition, the catalytic effect of alkali on post reaction strength was investigated, because above results were obtained with clean cokes. Alkali content, especially K2O, in coke ash in the shaft of blast furnaces reaches up to 15–20%,1) which corresponds to approximately 1.5% of K content in the whole coke. Potassium content in coke was adjusted to around 1.5% by immersing coke samples into KCl solution. Figure 9 shows the additional decrease of about 3.4% in the post reaction strength due to alkali attachment. It is concluded that gasification degree in the shaft of actual blast furnace should be further studied in accordance with the individual blast furnace operation, including PCR and productivity as well as alkali content in coke.

Though CSRSBF shows less degradation degree than it can be expected by conventional CSR, the relationship between...
CSR and $CSR_{\text{SBF}}$ appears fairly strong as shown in Fig. 8(b). Further study can be needed to prove that $CSR_{\text{SBF}}$ is a more reliable index on gas permeability or stability of blast furnace operation than conventional CSR. We, therefore, are now studying on bench-scale experiments to simulate the reaction between iron ore and coke with different CSRs in shaft zone under varied PCR conditions using a column reactor with a movable furnace, called SIS (Shaft inner-reaction simulator), which can be compared with operational data of actual blast furnaces.

4. Conclusions

In this study, the effects of solution loss under various reaction conditions on post reaction strength of commercial coke samples were investigated in comparison with results from conventional CRI and CSR tests. The main findings can be summarized as follows:

(1) Post reaction strength of coke samples taken at the shaft of actual blast furnace was much higher than that in NSC tests, leading to slight change in mean size. It was found by microscopic analysis that the core of coke samples taken from actual blast furnace remained unreacted.

(2) The method for the determination of strength after reaction with constant weight loss of 20% was not an effective way to evaluate post reaction strength of normal commercial cokes with low CRI below 26%.

(3) When coke samples were gasified at 1 100–1 300°C under the feed gas atmosphere of $N_2:CO:CO_2=6:2:2$, topochemical reaction near coke surface occurred at the high temperature over 1 200°C, which was observed by analyzing porosity distribution over radius of coke pieces. Therefore, degree of coke granulation was relatively diminished at high temperature despite reactivity was increased.

(4) Post reaction strength ($CSR_{\text{SBF}}$) in the simulated blast furnace conditions was 14.9% higher than conventional CSRs, which is attributed to different correlation-ship between reactivity and post reaction strength in two methods.

Further study on the characteristics of gasification and granulation of coke is underway using SIS (Shaft Inner-reaction Simulator), which can simulate reactions between sinter and coke in the shaft, under conditions in accordance with PCR rate and productivity in blast furnaces of Hyundai steel company.

REFERENCES