Influence of Mixing Coal Composite Iron Ore Hot Briquettes on Blast Furnace Simulated Reaction Behavior in a Packed Mixed Bed

Hiroyuki MIZOGUCHI,1) Hironori SUZUKI1) and Shoji HAYASHI2)

1) Graduate Student, Graduate School of Materials Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466-8555 Japan.
2) Graduate School of Materials Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466-8555 Japan.

(Received on January 18, 2011; accepted on April 27, 2011)

For iron making processes which need decreasing CO₂ exhaust, coal composite iron ore hot briquette (CCB) is promising. This agglomerate contains coal with iron ore by utilizing the thermal plasticity of coal, where, carbonaceous material and iron ore are closely adjoined at the micro level, and which enables reactions to proceed from lower temperatures and finish earlier.

In this study, we assumed mixed charging of CCB in ore bed aiming at improvements of permeability and gas utilization and performed high temperature reaction tests under load simulating blast furnace conditions using mixed samples consisted of iron ore mini pellet and briquette.

As a result, gasification and reduction in mixed bed were accelerated around 910°C to 1000°C. This reaction acceleration was presumed to derive from mutual acceleration between gasification in briquette and indirect reduction in pellet. However, if the residual carbon in briquette is consumed completely by gasification, reduction is possibly delayed through the deterioration of permeability by sintering of pellet and briquette.

It was also found that increase of reduction gas flow rate prevented the residual carbon in briquette from being consumed and accelerated reduction by sustaining the role of briquette as a spacer. And it was found that lowering thermal reserve zone temperature aggravated reducibility of pellet and delayed reduction of mixed bed. Moreover, it was found that shrinkage behavior of the bed had strong relation to amount of residual carbon in briquette and reduction behavior of pellet.

KEY WORDS: iron making; carbon composite iron ore hot briquette; mixed charging; blast furnace simulated condition.

1. Introduction

For every ironmaking processes, which need drastic improvements to reduce CO₂ emission, coal composite iron ore hot briquette (CCB), having high reducibility, is under development in Japanese steel companies. This agglomerate contains carbonaceous material and iron ore fines adjoined closely at the micro level unlike conventional burden such as sinter and coke. Therefore, mutual acceleration between gasification and reduction reactions, namely coupling reaction, is enhanced to begin and finalize reduction in lower temperature ranges, leading strong self reducibility in this agglomerate. Besides, compared with usual agglomerates such as cold bond pellet which needs cement as a binder, CCB has several merits such as binder less, no curing, high strength in high temperatures, and low slag ratio. Based on these reasons, it is expected to use CCB in blast furnace.

It is thought to be best usage for CCB to be mixed in ore layer as well as small size coke in blast furnace. In some studies on mixed charging of small size coke, enhancement of reduction by improvements of permeability and gas utilization was confirmed. Also, in a study on mixed charging of CCB, it was found that starting temperature of reaction was lowered by mixing small amounts of CCB and appropriate mixing rate for packed ore bed existed. However, these researches still have insufficiency on how reactions proceeded in mixed bed.

Based on above backgrounds, in this study we investigated reactions behavior and appropriate mixing rate on mixing charge of CCB to packed ore bed through laboratory scale examinations. In these cases, influences of total gas flow rate and thermal reserve zone temperature on the reaction behavior were examined by high temperature reaction test under conditions simulating blast furnace.

2. Experiments

2.1. Samples

In reaction test, we used mixed sample consisted of iron ore mini pellet (1.7–2.8 mm diameter, chemical composition Table 1) and CCB (expressed Briquette or B hereafter) (1.7–2.8 mm diameter). Mixing rates of briquette were given four patterns of 0, 20, 50, and 100% (mass%) and influence of mixing rate on reaction behavior was examined.
A constant height of mixed sample of 32 mm was set to remove influence on gas permeability of packed bed. Chemical compositions of mixed samples are shown in Table 2. Briquette was made by a following procedure. First, powder of iron ore (45–75 μm) and coal (–45 μm) with chemical compositions as shown in Table 3 were mixed in theoretical reaction molar ratio (C/O=1). Next, these mixed powder was hot briquetted to diameter of 15 mm and thickness of 10 mm under load of 4 ton during 2 minutes by a press machine under maximum fluidity temperature of coal (436°C). Finally, these briquettes were crushed and screened in a given particle size.

2.2. High Temperature Reaction Test under Load

Schematic experimental apparatus for high temperature reaction test under load is shown in Fig. 1. The apparatus has external heating and a sample in a graphite crucible (internal diameter 18 mm) is heated in an isothermal zone under load of 1 kg via Al2O3 tube. The graphite crucible is coated with Al2O3 water slurry to prevent the crucible from reactions with a sample and reduction gas. N2–CO–CO2 reducing gas content and heating pattern until 1 200°C are shown in Fig. 2, where two conditions in thermal reserve zone temperatures 1 000°C and 900°C were simulated referring to the practical blast furnace. Vertical shrinkage of a mixed packed bed was measured by a displacement meter. Total outlet gas flow rate was measured by a quantity flow meter. The contents of outlet gas were measured with a CO–CO2 infrared gas analyzer and a gas chromatography. After partial reaction tests, the graphite crucible was taken out from the apparatus, and rapidly cooled in N2 gas stream. Then, measurement of weight loss of the sample, determination of carbon and sulfur contents in the sample, obser-

---

Table 1. Chemical composition of iron ore mini pellet (mass%).

<table>
<thead>
<tr>
<th>Chemical composition of pellet</th>
<th>T.Fe</th>
<th>FeO</th>
<th>CaO</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>MgO</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>66.23</td>
<td>0.07</td>
<td>1.57</td>
<td>1.56</td>
<td>0.75</td>
<td>0.85</td>
<td>0.007</td>
<td>0.047</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of mixed sample (mass%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>T.Fe</th>
<th>T.O</th>
<th>C</th>
<th>Gangue</th>
<th>CaO</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>MgO</th>
<th>H,N,S,O</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%B</td>
<td>66.23</td>
<td>28.46</td>
<td>0.00</td>
<td>1.57</td>
<td>1.56</td>
<td>0.75</td>
<td>0.85</td>
<td>0.01</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>20%B</td>
<td>63.79</td>
<td>27.41</td>
<td>3.10</td>
<td>1.27</td>
<td>1.54</td>
<td>0.66</td>
<td>0.68</td>
<td>0.71</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>50%B</td>
<td>60.12</td>
<td>25.84</td>
<td>7.75</td>
<td>0.81</td>
<td>1.50</td>
<td>0.52</td>
<td>0.43</td>
<td>1.76</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>100%B</td>
<td>54.01</td>
<td>23.21</td>
<td>15.51</td>
<td>0.05</td>
<td>1.46</td>
<td>0.29</td>
<td>0.00</td>
<td>3.52</td>
<td>1.95</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Chemical composition and characteristic of ore and coal.

<table>
<thead>
<tr>
<th>Chemical composition of iron ore (Samarco)*</th>
<th>T.Fe</th>
<th>FeO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>CaO</th>
<th>S</th>
<th>P</th>
<th>C.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>66.7</td>
<td>0.68</td>
<td>0.35</td>
<td>1.76</td>
<td>0.06</td>
<td>0.005</td>
<td>0.051</td>
<td>2.35*</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical composition of coal (Mt. Owen)*</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>74.7</td>
<td>5.34</td>
<td>1.84</td>
<td>0.52</td>
<td>9.25</td>
<td>8.35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Characteristic of coal (Mt. Owen)</th>
<th>VM (mass%)</th>
<th>TMF (°C)</th>
<th>MF (ddpm)</th>
<th>RO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>38.6</td>
<td>436</td>
<td>236</td>
<td>0.66</td>
</tr>
</tbody>
</table>

VM: Volatile matter. TMF: Temperature of maximum fluidity. MF: Maximum fluidity. RO: Mean maximum reflectance.
vation of microstructures with an optical microscope and so on were conducted.

In order to investigate reaction behavior of a mixed packed bed with several conditions, three patterns of the reaction test shown in Table 4 were conducted. Setting Test I as basis, influence of increasing total gas flow rate was examined with Test II and influence of lowering thermal reserve zone temperature (hereafter TRZT) was examined with Test III.

3. Results and Discussion

3.1. Gasification and Reduction Behavior of a Mixed Packed Bed

3.1.1. Discussion with Results from Sample Analysis

Weight loss and carbon content obtained from Test I and both gasification and reduction degrees calculated according to our previously research are shown with reaction time in Figs. 3–6. In addition, predicted values of weight loss and carbon content for 20%B and 50%B samples calculated from test values of 0%B and 100%B samples by using Eqs. (1) and (2) and both predicted gasification and reduction degrees calculated by the way of our previous research are also plotted in Figs. 3–6, as dotted lines.

\[
W_{B%} = W_{0%B} \times (100 - B\%) / 100 + W_{100%B} \times B\% / 100 \quad (1)
\]

\[
C_{B%} = C_{0%B} \times (100 - B\%) / 100 + C_{100%B} \times B\% / 100 \quad (2)
\]

Weight loss (Fig. 3) tended to rapidly increase beyond 80 min with reaction time as the mixing rate increased. Especially, weight loss of 100%B sample (only briquette) gradually reached the theoretical weight loss which is calculated from the reduced oxygen and gasified carbon amounts. This implies strong self reducibility of briquette. On the other hand, regarding carbon content (Fig. 4), 100%B sample finally indicates carbon content of 6 mass%, which mostly means existence of the residual carbon.

Gasification of the carbonaceous material in briquette is prevented by CO in reducing gas. Therefore, it is supposed that high CO gas content contributed to generation of residual carbon. On the other hand, in the cases of 20%B and 50%B, carbon content finally indicates almost zero and residual carbon is consumed in spite of mixing briquette. In addition, gasification degree (Fig. 5) reached almost 100%. These results imply acceleration of gasification by mixing pellet and briquette. As gasification reaction, reactions (3) and (4) are considered. But in this study, as H2O gas did not include in reduction gas, it is probably that reaction (4), carbon solution loss reaction, was mainly enhanced.

\[
C(s) + H_2O(g) = CO(g) + H_2(g) \quad (3)
\]

\[
C(s) + CO_2(g) = 2CO(g) \quad (4)
\]

Then, regarding the reduction degree (Fig. 6), it was confirmed that the measured values were higher than the pre-
dicted values in 20%B and 50%B samples near 140 min (1,000°C), and this implies acceleration of reduction. As liquid phase did not exist at 140 min, such reduction acceleration was supposed to be due to reduction by gas, namely indirect reduction reaction (5).

\[ \text{Fe}_n\text{O}_\alpha + \text{CO} / \text{H}_2(g) = \text{Fe}_n\text{O}_\alpha(s) + \text{CO}_2 / \text{H}_2\text{O}(g) \quad \text{.... (5)} \]

Reactions (3), (4) and (5) have a relation to accelerate their reactions each other via CO, CO$_2$, H$_2$ and H$_2$O gases, and these acceleration relationship are thought to be due to reactions between pellet and briquette particles rather than coupling reactions inside a briquette. This idea arises because briquette can achieve complete reduction even in a mixed packed bed and the iron oxide which contributed to reduction acceleration was thought to exist mainly in pellet rather than in briquette.

By the way, the reason why reduction degree in Fig. 6 exceeds 100% at 180 min would be due to slight gasification of graphite crucible.

Figure 7 shows microstructures in cross section of pellet and briquette in a mixed packed bed observed under optical microscope after Test 1 at 110 min (1,000°C). In the pellet in the left position of Fig. 7(a), most part of the microstructure consists of FeO as seen in Fig. 7(b). In contrast, in the briquette in the right position of Fig. 7(a), white metallic iron appears a lot as seen in Fig. 7(c). Therefore, rapid progress of reduction in the briquette is implied.

Figure 8 shows sites adjoining between pellet and briquette. In pellet, the area where white metallic iron appears a lot can be seen in the neighborhood of the briquette. This implies that CO gas regenerated in briquette diffused into pellet, and accelerated reduction of oxide iron in pellet.

Above results and discussions on gasification and reduction behaviors can be summarized as followings. First, in early stage, gasification and reduction reactions proceed personally in briquette and finish in earlier period. Second, CO$_2$ derived from indirect reduction in pellet diffuses into briquette and gasification of carbonaceous material in briquette is induced. And through the regeneration of CO with this, reduction of pellet in the neighborhood of briquette is accelerated. By repetition of these reactions, gasification and reduction reactions are accelerated.

Considering above discussion and the fact that reaction of briquette is hardly influenced by total gas flow rate (section 3.2.1), we can presume reduction behavior of pellet in 20%B and 50%B samples.

If reduced oxygen amount of a mixed bed is set as $W_O$, $W_O$ can be calculated by Eq. (6). Here, $W$ expresses weight loss of a mixed bed. $W_C$ and $W_{CHNSO}$ express amounts of gasified carbon and other volatile matters with gasification of carbonaceous material. $W_C$ and $W_{CHNSO}$ can be calculated by the way of previous report. Reduced oxygen amount of a mixed bed $W_O$ equals to summation of reduced oxygen amount of pellet $W_{O\text{pellet}}$ and that of briquette $W_{O\text{briquette}}$, so that Eq. (7) is established.

Here, from the results of 100%B sample in later Fig. 14, it was found that the reduction behavior of briquette was hardly influenced by gas flow conditions probably due to strong self reducibility. Therefore, reduction behavior of briquette in 20%B and 50%B samples can be supposed to be identical with that in 100%B sample, so that Eq. (8) is established. Therefore, $W_{O\text{pellet}}$ can be calculated by Eq. (7) and reduction degree of pellet in a mixed bed $Dr_{\text{pellet}}$ can be calculated from Eq. (9).

\[ \text{W} = \text{W}_0 + \text{W}_C + \text{W}_{CHNSO} \quad \text{................. (6)} \]
\[ \text{W}_0 = \text{W}_{\text{O\text{pellet}}} + \text{W}_{\text{O\text{briquette}}} \quad \text{................. (7)} \]
\[ \text{W}_{\text{O\text{briquette}}} = \text{W}_{0\text{100%B}} \times B\% / 100 \quad \text{................. (8)} \]
\[ \text{Dr}_{\text{pellet}} = \text{W}_{\text{O\text{pellet}}} / \text{W}_0 \times 100 \quad \text{................. (9)} \]

\[ \begin{array}{l}
B\% : \text{briquette mixed rate} \\
\text{%O}_0 : \text{initial reducible oxygen content}
\end{array} \]
Change of reduction degree of pellet in a mixed bed calculated by above procedure is shown in Fig. 9. Pellets in 20%B and 50%B samples indicate maximum reduction acceleration compared with 0%B sample at 140 min. The reason why 50%B indicates bigger acceleration is likely because 50%B has much contact site between pellet and briquette, and reduction acceleration by CO from briquette occurs more frequently.

In addition, finally a little reduction delay occurred in 20%B. This would be due to formation of low melting point slag which is formed from unreduced FeO and gangue in pellet in the upper of a packed bed where gas flow is sluggish. Unreduced FeO is thought to arise from deterioration of reducibility of pellet with decrease of gas permeability in a packed bed sample caused by disappearance of carbon in briquette. Therefore, no reduction delay occurs in 50%B sample because it has relatively more residual carbon in briquette and lower pellet ratio.

Also, it is said that solid reduction under 1 200°C depends on amounts of fine pores under 15 μm. So, it is predicted that low melting point slag blocked in the fine pores to cause further deterioration of reducibility. These deterioration phenomena are thought to lead final significant delay of reduction in 20%B sample. (Low melting point slag will be volatile matters from briquette. By the way, C2H4 and C2H6 were not almost detected.

3.1.2. Discussion with Results from Outlet Gas Analysis
Gasification and reduction behavior are discussed with results from outlet gas analysis. First, changes of contents of H2 and carbon hydrides (CH4, C2H4, C3H6) obtained from gas chromatography in Test I are shown in Fig. 10. H2 and CH4 indicate extreme values from 600°C to 700°C in samples containing briquette. As these detected H2 and CH4 increase with mixing ratio of briquette, they are thought to be volatile matters from briquette. By the way, C2H4 and C3H6 were not almost detected.

It is supposed that H2 from volatile matters influences reduction reaction. But in this study, as no reduction acceleration before 110 min was seen in Fig. 6, reduction acceleration by H2 from volatile matters is thought to have been negligible small. In addition, gas yield of CH4 was only up to 0.41vol%, and influence to gasification of mixed sample would be small compared with CO and CO2. So, it can be said that degree of reduction acceleration for 20%B and 50%B samples is almost determined by gas generation of CO and CO2.

Figures 11 and 12 show reaction time dependence of total outlet gas flow rate and mole number differences of outlet CO and CO2 gases from basis by outlet gas analysis for Test I respectively. Test results for a packed bed of aluminum ball (3 mm φ) was used as basis. Mole number differences of outlet gas are calculated by substituting gas contents, total flow rate and temperature into the equation of state and subtracting mole number of basis from that in 20%B, 50%B. Besides, predicted values of mole number difference are shown in Fig. 12 which are calculated by distributing values of 0%B and 100%B according to weight of pellet and briquette in 20%B, 50%B.

From result of total gas flow rate, we can confirm that increase of gas flow rate begins around 100 min (approximately 910°C), indicates extreme value around 110 min (1000°C), and diminishes over 125 min. This is probably derived from gas volume increase by gasification reactions (3) and (4), and the higher the briquette mixing rate is, the more the outlet gas flow rate is evidently obtained.

On the other hand, from mole number difference of outlet CO and CO2 gases from basis, increase of CO content near 110 min can be seen in 100%B, but in 20%B and 50%B samples it is not clear. This is likely because CO generated by gasification reaction was used for indirect reduction reaction in unreduced pellet and it is supposed as if indirect reduction reaction mainly occurred.

From comparison of measured and predicted values of mole number difference of outlet CO and CO2 gases, it is confirmed that outlet CO is lower than predicted value and outlet CO2 is higher than predicted value around 110 min. This result implies mutual acceleration of gasification and indirect reduction by mixing pellet with briquette.

From above results, it can be understood that acceleration of reduction reaction occurs largely around 910°C to 1000°C. By the way, though we can generally calculate changes of gasification and reduction degrees from outlet gas analysis, they were not obtained likely due to deposition of tar in lower temperatures and so on.

3.2. Influence of Several Conditions on Reaction Behavior of a Mixed Bed
3.2.1. Influence of Gas Flow Rate
As influence of gas flow rate, comparison of gasification and reduction degrees for Test I and Test II are shown in Figs. 13 and 14. Predicted values were calculated by substituting predicted values of weight loss and carbon content.
into the equations shown in our previous report. From Fig. 13, suppression and stagnation of gasification with increase of gas flow rate can be seen in 20%B and 50%B samples. This is likely because CO₂ rich atmosphere in a mixed bed with reduction of pellets was diluted by a reducing gas flowing inside the packed bed, leading to decrement of CO₂ gas content as driving force for gasification.

On the other hand, from reduction behavior of 20%B and 50%B samples in Fig. 14, it can be seen that reduction for Test II finished earlier than that for Test I. Considering reduction acceleration by increasing gas flow rate in 0%B and no influence of increasing gas flow rate on reaction behavior of 100%B, reduction acceleration with increase of gas flow rate for 20%B and 50%B samples would be caused by reduction acceleration of pellet.

Moreover, even during gas flow rate increasing, measured reduction degrees indicate higher values than predicted reduction degrees in 20%B and 50%B samples, showing reduction acceleration. This is probably because briquette as a spacer prevented deterioration of permeability caused by sintering of each pellet and shrinkage of a packed bed.

In Test I, sintering of each pellet and shrinkage of briquette itself proceeded due to consumption of residual carbon in briquette. But in Test II, because consumption of residual carbon was prevented by increase of gas flow rate, the role of briquette as a spacer is thought to have been sustained.
3.2.2. Influence of Thermal Reserve Zone Temperature

As influence of TRZT, comparison of gasification and reduction degrees in Test I and Test III are shown in Figs. 15 and 16. Predicted values were calculated by substituting predicted values of weight loss and carbon content into the equations shown in our previous report.6)

Both gasification and reduction reactions are seen to become slower by decreasing TRZT. However, comparing with predicted values for 20%B and 50%B samples, gasification degrees indicate higher values than predicted values even when TRZT decreases, and carbon contents finally indicate almost zero and residual carbon is consumed. The reason why acceleration of gasification occurred even when TRZT decreased is probably because metallic iron arising in briquette acted as a catalyst for gasification of carbonaceous material on the condition that CO2 arising from pellet reduction increased CO2 content around the briquette, and reaction conditions were favorable for gasification even when TRZT decreased.

Also, from change of reduction degree in Fig. 16, acceleration of reduction was found in 50%B, but in 20%B, acceleration was not found and reduction finally delayed a little. From observation of microstructure in an optical microscope, low melting point slag was found analogous to Test I, this reduction delay is thought to be due to decrease of open pores in an early stage.

From above discussion, it is supposed that not only gasification and reduction characteristics of briquette but also reduction behaviors of iron ore or sinter charged with briquette would influence reduction behavior of a mixed packed bed when TRZT decreases.

3.3. Shrinkage Degree and Softening Melting Behavior

Changes of shrinkage degree in a mixed bed for Tests I, II, and III are shown in Fig. 17. Comparing Test II with Test I, it is found that rapid shrinkage from nearly 150 min for 20%B and 50%B samples is suppressed by increase of gas flow rate. This shrinkage suppression probably derives from prevention of carbon consumption by the coupling reaction and prevention of generation of low melting point slag in pellet by acceleration of reduction.

Also, comparing Test III with Test I, all samples indicate rapid shrinkage beyond 140 min (955°C), particularly 50%B sample indicates drastic shrinkage. This rapid shrinkage probably derives from large generation of slag containing FeO by reduction delay and progress of carbon consumption reaction beyond this temperature range.

From above results, it is supposed that shrinkage behavior has a close relation to amounts of residual carbon in briquette and reduction behavior of pellet.

Next, from further analysis of low melting point slag, microstructure and EDS results for slag observed in the central upper of pellet after reaction test (Test I, 20%B, 1200°C) are shown in Fig. 18 and Table 5(a) respectively.

From EDS result, it was found that slag contained Fe, Ca, Si, and Al and the low melting point slag provided FeO–CaO–SiO2–Al2O3 mass% as shown in Table 5(b). In previous study on low melting point slag,10) it was reported that FeO–CaO–SiO2–Al2O3 quaternary slag has a tendency to have lower melting point in case of slag not containing MgO and high FeO ratio and that invariant temperature exists from 950°C to 1050°C.

In this study, FeO content indicated a little high value
Table 5. EDS analysis results of slag area in pellet after reaction (Test I, 20%B, 1200°C). (a) EDS results, (b) Conversion of results into oxide composition (mass%).

(a)  
<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Ca</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>O</th>
<th>C</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass%</td>
<td>28.5</td>
<td>16.6</td>
<td>15.0</td>
<td>3.0</td>
<td>0.08</td>
<td>33.9</td>
<td>1.8</td>
<td>0.24</td>
<td>0.89</td>
</tr>
</tbody>
</table>

(b)  
<table>
<thead>
<tr>
<th>FeO</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass%</td>
<td>37.4</td>
<td>23.6</td>
<td>33.2</td>
</tr>
</tbody>
</table>

37.4 mass%. Besides it is presumed that FeO content indicated higher value when liquid appeared at early period, so that it is probably that low melting point slag mentioned would arise. However, considering higher content of sulfur 0.24 mass% than initial value, it is also supposed that sulfur species in briquette transferred to pellet via gas phase and formed some of lower melting point slag.

Moreover, it was reported that small amounts of gaseous sulfur in reducing gas enhance shrinkage degree of pellet and sinter. So, it is possible that small amounts of gaseous sulfur might influence softening melting behavior of sample.

4. Conclusion

We performed high temperature reaction tests under load assuming briquette mixed charge to ore layer in a blast furnace and obtained the following findings regarding influence of gas flow rate and TRZT on reaction behavior of the mixed packed bed.

(1) Acceleration of gasification and reduction of a mixed bed by mixing briquettes was found to occur for 20%B and 50%B samples around 910°C to 1000°C, whereas reduction of 20%B was finally delayed because of disappearance of residual carbon in briquettes and generation of melting slag containing unreduced FeO.

(2) The reduction acceleration of pellets in a mixed bed by H₂ and CH₄ derived from volatile matters in carbonaceous material was hardly observed, and acceleration of gasification and reduction in the bed was thought to be mainly affected by CO and CO₂ gases.

(3) Gasification was delayed and stagnated with increase of reducing gas flow rate for 20%B and 50%B samples. This is likely because CO₂ rich gas in a mixed bed was diluted by a reducing gas flowing inside the bed and CO₂ gas content as drive force for gasification decreased. Also, reduction delay for 20%B was prevented by acceleration of reduction of pellet by increase of gas flow rate.

Moreover, even during gas flow rate increasing, reduction was accelerated for 20%B and 50%B samples. This is probably because permeability in a packed bed was sustained due to the role of briquette as a spacer.

(4) Gasification reaction was accelerated for 20%B and 50%B samples even when TRZT decreased. This is likely because metallic iron generating in briquette acted as a catalyst for gasification of carbonaceous material on the condition that CO₂ arising from pellet reduction increased CO₂ content around the briquette, and reaction conditions were favorable for gasification, whereas reduction reaction was delayed by slag containing FeO for 20%B.

When TRZT decreases, not only gasification and reduction characteristics of briquettes but also reduction behaviors of ore or sinter charged with them would influence strongly reduction behavior of a mixed packed bed.

(5) Shrinkage behavior of the bed was supposed to have a close relation to amounts of residual carbon in briquette and reduction behavior of pellet.

REFERENCES
3) K. Miyagawa, M. Sawayama and Y. Matsui: CAMP-ISIJ, 22 (2009), 1, CD-ROM.
6) S. Hayashi, A. Inayoshi and H. Mizoguchi: CAMP-ISIJ, 22 (2009), 21, CD-ROM.