Effect of Nut Coke-sinter Mixture on the Blast Furnace Performance

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(Received on September 29, 2010; accepted on November 4, 2010)

Among different ways to reduce the coke consumption in the blast furnace, not so much attention was paid for decreasing the coke losses through finding suitable application of small size coke called “nut coke”. In meantime modern blast furnaces use nut coke with different amount (10–140 kg/t hot metal) and different grain size (10–40 mm) in the sinter layer to reduce the coke losses. The objective of this paper is to clarify the influence of nut coke on the shaft permeability and sinter reducibility under blast furnace simulating conditions. The effect of various factors such as nut coke rate, gas flow rate, and layer thickness on the shaft permeability was estimated using cold model rig. The influence of nut coke on the isothermal and non-isothermal reduction of sinter was estimated under different gas compositions and temperatures using muffle reduction furnaces. The isothermal reduction of sinter with 30%CO–70%N₂ exhibited reduction retardation at elevated temperatures (>1 373 K). The reduction retardation increased by the presence of CO₂ gas in the reducing atmosphere while decreased by participation of H₂ gas. Mixing nut coke in the sinter bed improves the sinter reducibility and inhibits the reduction retardation phenomenon.

KEY WORDS: blast furnace; sinter; nut coke; permeability; gaseous reduction; sticking.

1. Introduction

To maintain stable blast furnace operation with low coke rate and, correspondingly, with low carbon dioxide emissions, grain size of metallurgical coke should be big enough and the size distribution should be narrow: mainly in the range of 40–80 mm. On the other hand, the use of such a fraction causes the increase in the coke costs due to the generation of big amount of under-sieve material. Prof. V. I. Loginov suggested in 1960s to charge fine under-sieve coke into the blast furnace in mixture with sinter. This idea was successfully tested.¹

Presently the majority of blast furnaces in Europe, Japan and elsewhere use nut coke although its amount is very different: from 10–20 to 70–100 kg/tHM and more.² Operation of many blast furnaces has proved the possibility of coke saving and increase of furnace productivity when using nut coke in mixture with iron burden but reasons and mechanism of this phenomenon were not very clear until the recent time.

Basically, three reasons can affect the decrease in coke rate:

- Improvement of gas permeability in “dry zone” of a blast furnace
- Improvement of reduction conditions of iron burden
- “Protection” of metallurgical coke from the solution loss reaction in the shaft due to higher reactivity of nut coke.

Hotta et al. investigated the influence of sinter and coke layers thickness and sinter–coke mixture on the gas permeability at temperatures in the range of 1 373–1 873 K.³ It was found that as the thickness of sinter and ore layers decreased the pressure drop decreased. Mixing of 90 g coke in 1 400 g sinter was able to decreased the pressure drop at 1 673 K from 380 mmH₂O to about 50 mmH₂O. The application of high ratio coke mixed charging technology in JFE Steel was accompanied by improvement of the gas permeability in cohesive zone.⁴ Calculations of gas permeability when mixing nut coke in the sinter layer showed that mixing of 10 vol% nut coke in the sinter layer resulted in a decrease in the pressure drop in the dry shaft by 5.33%.⁵ The statistical analysis of the average annual indices of some European blast furnaces showed that the introduction of 5–30% nut coke of total coke consumption gave the coefficient replacement factor close to 1.0.⁶

Nut coke segregation and radial distribution in a charging system before the entering the blast furnace was simulated using Discrete Element Method.⁷ It was reported that the circumferential balance of nut coke mass in the large bell was very important factor affected nut coke distribution. Watakabe et al.⁸ found that the application of stabilizer on the tip of charging chute is an efficient method to avoid nut coke segregation.

In several works the change in reduction processes by using coke–ore mixed charging was studied. It was found that direct reduction can be promoted in the cohesive zone and inhibited in the hearth and, hence, the heating hearth will be improved.⁹ Nut coke effect on coke consumption is dependent on the characterization of both nut coke and
metallurgical coke. Sawayama et al. studied the influence of two separate roles of coke as a reducing agent and as a bed spacer. It was found that controlling the size of mixed coke in ore layer enabled the nut coke to be mainly consumed to regenerate CO gas, while the lump coke was forming less degraded permeable bed. The results might also depend on the nut coke grain size. On the other hand, the idea of preferential consumption of nut coke by solution loss reaction was not proved by investigations at the industrial blast furnace by using coke traced with zirconium oxide.

In this work three above mentioned reasons of the nut coke effect on the blast furnace performance has been consequently studied.

2. Materials and Experimental Techniques

The influence of nut coke on the blast furnace shaft permeability has been simulated using cold model rig as shown in Fig. 1. The model was designed as a set of plexiglas segments that can be added or removed and thus the model can be easily adapted for various simulation conditions. Air was blown via six tuyeres and streams through the packaged bed. The air flow was measured and controlled by a flow meter. Pressure drop in the packaged bed was measured by a U-tube manometer. Distance from the tuyere level to the lower measuring point and the bottom of the stack was chosen to maintain vertical parallel streaming through the packaged bed. The sinter size was in the range of 8–12 mm (80 mass%) and below 8 mm (20 mass%). The nut coke size was 15–20 mm while that of lump coke was 35 and 45 mm.

The effect of layer thickness, gas velocity or flow rate, and nut coke rate on the pressure drop in different packed beds was examined. Two test series were conducted at the ratio of layer thickness of coke and burden (sinter and sinter–nut coke mixture) 1:1 (50 and 100 mm of each layer) which corresponds roughly to coke-only operation. For the third test series the ratio of coke and burden layer thickness was set at 1:2 (50 and 100 mm respectively) which corresponds to the modern blast furnace operation with PCI while the packed bed height was kept at 500 mm in all tests.

The influence of nut coke on the sinter reducibility was studied under isothermal and non-isothermal conditions. The isothermal reduction process took place in steps between 1173 K and 1523 K using different gas mixtures. The reduction system consisted of a muffle furnace with inlet and outlet tubes as given in Fig. 2. The isothermal reduction carried out in stainless steel reactor (diameter=45 mm, length=150 mm) as shown in Fig. 3(a). The weights of sinter and nut coke were kept constant in all isothermal tests, 45 and 15 g; respectively (sinter/nut coke mass ratio=3:1) while the average size of both, sinter and coke were 5.0–7.0 mm.

The non-isothermal reduction was conducted in Nabertherm muffle furnace using a bigger steel reactor (diameter=100 mm, length=170 mm) as shown in Fig 3(b). The size of the reactor was selected to give the chance for different types of packing modes in the form of layers, mixtures, or both. The weights of sinter and coke were 600 g and 200 g respectively while the materials size and the packing mode are given in Fig. 4. The heating rate and gas composition were selected by simulating the actual conditions in the blast furnace as given in Table 1.
The gas flow was precisely controlled by mass flow controllers (Rotameter E and L models). An on-line gas analyser (BINOS 100) was installed to analyse off-gases at 1 s interval time. The reduction degree of sinter and sinter–nut coke mixture were calculated by the oxygen and carbon balance based on CO and CO$_2$ flow rates obtained from gas analyser. The reduction degree was calculated on applying Eq. (1).\(^9\)

\[
R(\%) = \left( \frac{A \cdot \Delta t}{B} \right)
\]

with \(A = 0.714 \nu^0 N_2^0 (CO/N_2 - CO^0/N_2^0) + 2(CO_2/N_2 - CO^0/N_2^0)\)

and \(B = [0.427(\% Fe) - 0.111(\% FeO)] W\)

where

- \(CO^0, CO_2^0, N_2^0\) : Volume percentage of CO, CO$_2$, and N$_2$ in inlet gas (vol%)
- \(CO, CO_2, N_2\) : Volume percentage of CO, CO$_2$, and N$_2$ in outlet gas (vol%)
- \(\nu^0\) : Total gas flow rate of inlet gas (8.0 L/min)
- \(% Fe, % FeO\) : Mass concentration of Fe and FeO in sinter or pellets (wt%)
- \(W\) : Weight of sinter or pellets (45 g)
- \(\Delta t\) : Reduction time (s)

On the other hand total oxygen weight loss from iron burden materials and also total carbon solution loss from coke were calculated by measuring the weight loss after the reduction processes. The iron ore sinter was examined by reflected light microscope (RLM-Leica Aristomet) and scanning electron microscope-backscattered electron image (SEM-EDX/BSE, ZEISS DSM 962). The phases were identified by X-ray diffraction technique (XRD, PW 1730 with Ni filtered Cu K\(\alpha\) radiation). High pressure mercury pore size analyser (Micromeritics Pore Sizer, 9320) was used for measuring total porosity of sinter and nut coke.

3. Results and Discussion

3.1. Nut Coke and Shaft Permeability

The influence of nut coke rate on the pressure drop of sinter is given in Figs. 5 and 6. Generally, it can be seen that the pressure drop decreased with rising nut coke rate in the sinter–nut coke mixture. This effect became more remarkable at higher flow rate and Reynolds number (Reynolds number under the blast furnace conditions 600\(<\)Re\(\approx\)800). Decrease of coke layer thickness caused by low coke rate led to increasing of the pressure drop as shown in Fig. 6. The effect of nut coke on the pressure drop under the influence of different flow rate and layer thickness is given in Fig. 7. It can be seen that the influence of nut coke rate and nut coke layer thickness became apparent as the flow rate increased (from 28 to 49 m$^3$/h).

The pressure drop in the blast furnace lumpy zone was affected by gas velocity and blast volume; increasing of the blast volume per unit of time raises the furnace productivity as given in Eq. (2).

\[
\frac{\Delta P_1}{\Delta P_2} = \frac{\rho_1^2}{\rho_2^2} = \frac{Q_1^2}{Q_2^2} = \rho_1/\rho_2 \quad \text{.........(2)}
\]
where:

\[ \Delta P : \text{Pressure drop (N/m}^2\text{)} \]
\[ \omega : \text{Gas velocity (m/s)} \]
\[ Q : \text{Blast volume (m}^3/\text{min)} \]
\[ \rho : \text{Productivity} \]

The experimental relation between the pressure drop and the square of gas velocity at different layer thickness is confirmed Eq. (2) as given in Figs. 8 and 9. It can be seen a linear dependence of pressure drop on the square of gas velocity for constant packaged bed voidage, height, equivalent diameter and gas density. The linear character of this dependence allowed for estimation of nut coke effect on pressure drop for the blast furnace conditions despite lower gas velocity in the lab tests. Calculation of the line inclination based on the test results for coke/sinter layer thickness ratio 1:2 (operating conditions with low coke rate of 310–320 kg/tHM and high PC rate) showed that for blast furnace with average shaft gas velocity of 2.53 m/s (blast velocity 250 m/s, average shaft diameter 10 m) the pressure drop decreased by 20.5 and 31.5% when using 10 and 20 wt% of nut coke in the sinter mixture respectively.

Based on Eq. (2), the reserve for increase of blast volume and, consequently, of productivity makes up:

\[ Q_2 = \sqrt{\frac{\Delta P_2}{\Delta P_1}} \cdot Q_1 = \sqrt{0.795} \cdot Q_1 = 0.89 \cdot Q_1 \]
or 11.0% at 10 wt% of nut coke in sinter layer,

\[ Q_2 = \sqrt{0.6823} \cdot Q_1 = 0.826 \cdot Q_1 \]
or 17.4% at 20 wt% of nut coke in sinter layer.

Assuming that solid materials occupy about 70% of the furnace working height (it corresponds to above mentioned operating conditions and centre coke charging), blast furnace productivity can be increased by 7.7–12.2% for 10 and 20 wt% nut coke in sinter layer or by 1.5–2.5% for 10 and 20 wt% nut coke to bell coke rate respectively.

### 3.2. Nut Coke and Sinter Reducibility

#### 3.2.1. Isothermal Reduction

The chemical analyses of the applied sinter and nut coke are given in Table 2 and 3 respectively. X-Ray analysis of sinter exhibited that the sinter was composed of three main phases: hematite, calcium silicate, and calcium ferrites as given in Fig. 10. Typical reduction curves of sinter and sinter–nut coke mixture isothermally reduced by 30%CO–70%N₂ at different temperatures (1 173–1 523 K) and total carbon solution loss of sinter–coke mixture are given in Fig. 11. The reduction degree of sinter reduced without nut coke participation increased with rising temperature in the range of 1 173–1 373 K. With further increase in the temperature the reduction degree decreased which is known as reduction retardation (RR). On the other hand the reduction of sinter–nut coke mixture showed a continuous increasing in the reduction degree between 1 173 K and 1 523 K. The reduction degree sharply increased in the range of 1173–1523 K.

#### Table 3. Chemical analysis of nut coke.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fixed C</th>
<th>Ash</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Volatiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>87.3</td>
<td>10.32</td>
<td>0.038</td>
<td>0.89</td>
<td>1.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

![Fig. 8. Effect of gas velocity on pressure drop for various nut coke rates at layer thickness of 100 mm.](image)

![Fig. 9. Effect of gas velocity on pressure drop for various nut coke rates at layer thickness of 50 mm.](image)

![Fig. 10. XRD phases analysis of the applied iron ore sinter.](image)

![Fig. 11. Reduction curves of sinter and sinter–nut coke mixture vs. temperatures.](image)

#### Table 2. Chemical analysis of iron ore sinter.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>FeO</th>
<th>Mn</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>P</th>
<th>S</th>
<th>CaO·SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>56.69</td>
<td>8.0</td>
<td>0.209</td>
<td>5.42</td>
<td>1.53</td>
<td>10.4</td>
<td>1.51</td>
<td>0.041</td>
<td>0.018</td>
<td>1.92</td>
</tr>
</tbody>
</table>
1,173–1,373 K and then stepwisely increased in the range of 1,423–1,523 K. The total carbon solution loss increased slowly at ≤1,273 K followed by sharp increase at temperatures >1,273 K.

The variation of the outlet gases for iron ore sinter reduced without nut coke participation at 1,373 K and 1,473 K is given in Fig. 12. It can be observed that CO₂ rate decreased with time and became more descend for the reduction at 1,473 K than that at 1,373 K which was accompanied by ascending of CO rate. The point at which the overlap took place for CO and CO₂ curves indicated the onset of reduction retardation (RR) period. Figure 13 illustrates the variation of CO and CO₂ gases during reduction of sinter and sinter–nut coke mixture at different temperatures. It can be seen that CO₂ generated during reduction of sinter–nut coke mixture was lower than that without nut coke participation and also decreased with increasing temperature. On the other hand CO rate became higher as the temperature increased and/or nut coke participated. Such behaviour of CO and CO₂ can be attributed to carbon gasification with CO₂ which is well known as Boudouard reaction as shown in Eqs. (3) and (4). A part of CO₂ which developed from the reduction process had the ability to react with nut coke at elevated temperature (≥1,373 K) that resulted in generation of CO gas which can participate in the reduction process. As the temperature increases (1,473→1,523 K), the rate of reduction increased and more CO can be developed from endothermic Boudouard reaction.

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + CO & = \text{Fe}_2\text{O}_4 + CO_2 \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \ce
which is faster than solid state diffusion mechanism.

The effect of CO₂ gas on the reduction behaviour of sinter and sinter–nut coke mixture was studied by the replacement of 10% of N₂ with 10% of CO₂ (0.8 L/min). The reduction took isothermally place for 2 h at different temperatures in the range of 1 173–1 523 K. Typical reduction curves and total carbon solution loss of sinter–coke mixture are shown in Fig. 16. There was no great difference in the reduction degree between sinter and sinter nut coke mixture at temperature below 1 373 K, after that a remarkable difference in the reduction degree obtained. The reduction behaviour of sinter reduced without nut coke participation exhibited the maximum reducibility (40%) at 1 373 K. With further increasing in the temperature, a limited decrease in the reduction degree took place. On the other hand the reduction of sinter–nut coke mixtures exhibited a sharp increase in the reduction degree at temperatures above 1 373 K and exhibited the maximum reducibility (72%) at 1 523 K. The total carbon solution loss increased slowly below 1 273 K followed by sharp increase at higher temperatures.

The negative effect of CO₂ gas on the reduction degree was attributed to the influence of CO₂ gas on the reaction equilibrium (Eq. (3)) according to Le Chatelier’s principle. The presence of CO₂ in the reducing atmosphere was decreased the power potential of CO gas to reduced the iron oxides. The positive effect of nut coke on the reduction behaviour of sinter at elevated temperature (≥1 373 K) was mainly due to the effect of Boudouard reaction (Eq. (4)). A part of participated CO₂ gas was reacted with nut coke at ≥1 273 K and generated another amount of CO gas which increased the power potential of the reducing gas.

Hydrogen is introduced into the blast furnace through the injection of hydrocarbons or the presence of moisture; therefore the effect of H₂ gas on the reduction behaviour of sinter and sinter–nut coke mixture was also studied. Ten percent of CO gas was replaced by 10% of H₂ (0.8 L/min). The reduction took isothermally place for 2 h at 1 173–1 523 K. The typical reduction curves are given in Fig. 17. The comparison between the reduction degree of sinter and sinter–nut coke mixture with and without H₂ participation (Figs. 11 and 17; respectively) indicated the positive effect of H₂ on the total reducibility of sinter. The reduction retardation in CO–H₂–N₂ gas mixture was much lower than that in CO–N₂ gas mixture. This could be attributed to the effect of gas diffusivity on the reduction rate at elevated temperature. The diffusivity of reducing gas molecule is approximately inversely proportional to the square root of its molecular weight as given in Eq. (5).\(^{14}\)

\[
D = \frac{d}{6} \left( \frac{8RT}{\pi M} \right)^{1/2}
\]  

where

- \(D\): Gas diffusivity
- \(d\): Mean diameter of pore (\(\mu m\))
- \(R\): Universal gas constant
  \((8.314 \cdot 10^{-2} \text{kJ mol}^{-1} \text{K}^{-1})\)
- \(T\): Absolute temperature (K)
- \(M\): Molecular weight of the reducing gas (\(\text{g mol}^{-1}\))

The diffusivity of H₂/H₂O gas mixture is about 3–5 times as that of CO/CO₂ for any given temperature.\(^{15}\) The diffusivity of H₂ became more effective when sinter started to soften and partially melted at elevated temperature. In this case H₂ gas had the ability to diffuse through the sinter bed and thus improved the reducibility. The higher carbon solution loss that accompanied the reduction of sinter with H₂, which reached to 36 wt% at 1 523 K compared to 25 wt% with CO, was attributed to the reaction of solid carbon not only with the in-situ formed CO₂ gas but also with the generated H₂O as given in Eq. (6). The reaction of carbon with the H₂O was developed CO and H₂ gases with lower endothermic amount of heat compared to that of Boudouard reaction (Eq. (4)).\(^{14}\)
3.2.2. Non-isothermal Reduction and Lump Coke Protection

The reduction behaviour of sinter packed in the steel reactor in 4 different modes (Fig. 4) was carried out under simulated blast furnace shaft conditions (temperature and gas composition) in order to investigate the influence of charging mode on the overall reduction process (Table 1). The non-isothermal reduction curves are given in Fig. 18.

The reduction process started at very slow rate for all types of packing materials in atmosphere of 26%CO–14%CO₂–60%N₂ at temperatures in the range of 673–1 173 K. By changing the reducing gas mixture to 30%CO–70%N₂ at 1 173–1 523 K, the reduction degrees were sharply increased in different ratios up to 1 523 K. By fixing the temperature at 1 523 K for 1 h, slow increase in the reduction degree took place for all samples. The reduction degrees of sinter and the weight loss of coke which used as a mixture or layers are given in Table 4. It can be seen that the sinter reduced without any participation of coke (case a) exhibited the smallest values of reduction degree (32.5%) and showed the earliest slow down of reduction curves (Fig. 18) as the temperature increased. The participation of large size coke (25–30 mm) as layers in the sinter bed (case b) improved the reducibility of sinter to about 41% with coke weight loss 13%. The mixing of nut coke (10–12 mm) with 50% (case c) and 100% (case d) in the sinter bed was accompanied by the increasing of the sinter reducibility to 55% and 65% respectively. The coke weight loss increased as the rate of nut coke in the sinter bed increased.

These results indicate that, the presence of CO₂ in the reducing gas atmosphere as well as the low temperatures at the beginning of reduction affected negatively the reduction rate of sinter. Replacing the CO₂ gas with CO and N₂ accompanied by the continuously increasing temperature, led to a sharp increase of reduction rate for all types of packing mode but with different ratios which was proportional to the rate of nut coke mixed in the sinter bed. The rate of carbon gasification increased with the rate of nut coke mixed in the sinter bed and consequently generated more CO gas which improved the reduction rate as can be concluded from Eqs. (3) and (4). On the other hand the gasification rate of lump coke, which used as layer, decreased by mixing nut coke in the sinter bed although the sinter reducibility increased. The higher sinter reducibility was on account of the carbon solution loss of nut coke which was closely contact with sinter pieces. This result confirmed that mixing of highly active nut coke in the sinter layers could protect the lump coke from the solution loss in the blast furnace shaft and consequently improving the combustion process in the front of tuyere zone. The lower reducibility of sinter reduced without nut coke participation at elevated temperatures (1 373–1 523 K) was attributed to the sticking between the sinter pieces as shown in Fig. 19(a). The mixing of nut coke with sinter inhibited such phenomenon by its distribution in sinter bed as can be seen in Fig. 19(b).

The microstructure examinations of sinter surface non-isothermally reduced in absence and in presence of nut coke in the sinter bed is given in Figs. 20(a)–20(d). In absence of nut coke a dense matrix structure of reduced sinter was formed (Fig. 20(a)) in addition to large growth of metallic iron grains (Fig. 20(c)). Such structure represented a resistance for the gas diffusion and lowering the reduction rate. The surface structure of sinter reduced in presence of nut coke (Figs. 20(b) and 20(c)) was relatively porous which was suitable for the gaseous diffusion into the core of sinter pieces and thus improved the sinter reducibility.

The rate controlling mechanism can be expressed schematically in Figs. 21(a) and 21(b). The formation of dense metallic iron shell around the iron oxides prevented the reducing gas from further diffusion; therefore the gaseous diffusion was not possible and the only mechanism for further reduction was atomic diffusion of oxygen through the iron layer (Fig. 21(a)). Such mechanism is very slow because the oxygen solubility of oxygen in solid iron is only a few parts per million, and hence the driving force

![Fig. 18. Non-isothermal reduction curves of sinter packed with different modes.](image)

![Fig. 19. Sinter bed non-isothermally reduced at 673–1 523 K, (a) without nut coke participation, (b) with nut coke in sinter bed.](image)

<table>
<thead>
<tr>
<th>Case</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction, %</td>
<td>32.52</td>
<td>40.65</td>
<td>54.55</td>
<td>65.38</td>
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<tr>
<td>Coke wt. loss, %</td>
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<td>C_{lay} = 12.76</td>
<td>C_{lay} = 20.68</td>
<td>C_{lay} = 23.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C_{lay} = 9.35</td>
<td>C_{lay} = 15.01</td>
<td></td>
</tr>
</tbody>
</table>

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for diffusion is very low.\textsuperscript{16)} Figure 21(b) represents the reduction mechanism of sinter–nut coke mixture. Mixing of nut coke in sinter bed prevented the formation of dense metallic iron shell and resulted in the formation of relatively porous outer shell. In this case the reduction was controlled by a combined effect of gaseous diffusion and interfacial chemical reaction and can be described as follow:

(i) Diffusion of CO gas through the outer metallic iron layer

(ii) Reduction of lower iron oxides with CO gas

(iii) Gasification of coke carbon through the \textit{in-situ} formed CO\textsubscript{2} gas

(iv) Participation of the generated CO gas in the reduction process

It can be concluded that mixing of nut coke in the iron ore sinter layers is not only required to decrease the coke losses and reduce the hot metal production costs but also to improve the shaft permeability and sinter reducibility. The positive effect of nut coke should be most significant in the critical cohesive zone when the materials soften and partially melt. Under such difficult situation nut coke has the ability to improve the permeability, iron burden reducibility and decreasing CO\textsubscript{2} emission through its close contact with the iron burden materials as can be schematically represented in Fig. 22.

4. Conclusion

In this study, the influence of nut coke on the shaft permeability and sinter reducibility under blast furnace simulating conditions were investigated. The main finding can be summarized as follows:

(1) The pressure drop in shaft decreased as nut coke rate increased and nut coke effect became remarkable with increasing the gas flow rate. The experimental results confirmed the theoretical relation between the pressure drop in shaft and the gas velocity. As the pressure drop decreases by nut coke application the blast volume increases and consequently the furnace productivity increases.

(2) The isothermal reduction of sinter with 30\%CO–70\%N\textsubscript{2} in absence of nut coke was exhibited reduction retardation at elevated temperatures (1 373–1 523 K). This phenomenon was attributed to the formation of liquid slag which blocked the pores in the sinter pieces and inhibited the further diffusion of reducing gas. Mixing nut coke in the sinter bed has improved the sinter reducibility through improving the gas permeability.

(3) The reduction of sinter in presence of 10\% CO\textsubscript{2} in the reducing atmospheres was decreased the reduction de-
gree compared to that with 30%CO–70%N₂. The presence of nut coke improved the sinter reducibility through the increasing of the power potential of reducing gas. The replacement of 10% CO with 10% H₂ increased the reduction degree of sinter especially at elevated temperatures due to the effect of the higher diffusivity of H₂ compared to that of CO gas.

(4) The non-isothermal reduction of sinter indicated that the sinter reducibility increased as the nut coke ratio increased while the lump coke solution loss decreased.

Acknowledgements

The authors wish to express thanks to M. Sc. N. Marinakis for conducting the cold model experiments and to the Egyptian Ministry of Higher Education and Scientific Research for funding the scholarship of the corresponding author.

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