Reduction of Pellets-Nut Coke Mixture under Simulating Blast Furnace Conditions

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In recent years an intensive work has been carried out to decrease the coke losses of the blast furnace through mixing small-sized coke called “nut coke” in the iron ore burden layers. In order to clarify the influence of nut coke on the pellets reducibility, industrial iron ore pellets were reduced with and without nut coke participation under different temperatures and atmospheres. Isothermal and non-isothermal reduction tests under simulating blast furnace conditions were performed using an experimental laboratory rig. Furthermore, reflected light microscopy, scanning electron microscopy and X-ray technique were applied to characterize the microstructure and different phases developed in the origin and reduced pellets. Pellets reduced isothermally without nut coke participation exhibited reduction retardation (RR) at elevated temperature (≥1373K) whereas the presence of nut coke had a positive effect of preventing such phenomena. The non-isothermal reduction of pellets showed that, as the amount of nut coke in pellets bed increased, the reducibility of pellets increased, too. The rate controlling mechanism of pellets and pellets-nut coke mixtures was predicted from the correlation between apparent activation energy calculations and microstructure examination.

Keywords: Blast furnace, iron ore pellets, nut coke, fayalite gaseous reduction

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Introduction

The blast furnace is still the predominant process for the reduction of iron ore and will probably remain so for the next decades. Blast furnace coke constitutes a major portion of the production costs of hot metal. The coke charged to the blast furnace should be in the range of 40–80 mm depending on the furnace size. The separation of this special size results in generation of big amount of under-sieve coke size today, known as “nut coke”. In order to reduce coke losses and production costs, the majority of blast furnaces use nut coke in different amounts (10–100 kg/tHM) as a mixture in iron ore burden layers [1]. Yaroshhevskii et al. reported the statistical analysis of the average annual indices of some blast furnaces which showed that the introduction of 5–30% nut coke of total coke consumption gave the coefficient replacement factor close to 1 [2].

Many investigators studied the effect of nut coke on the blast furnace shaft permeability. Babich et al. studied the effect of nut coke on the blast furnace shaft permeability using cold models [3]. They reported that using 10 and 20 wt.% nut coke with a grain size of 5.0–15 mm in the sinter bed decreased the pressure drop by 7.0 and 8.5% respectively; these values became 9.5 and 12.0% for bigger nut coke size (20–40 mm). Hotta et al. studied the high temperature properties of sinter and sinter-coke mixture. It has been found that mixing of 6.4 wt.% coke in the sinter bed decreased the pressure drop from 380 to about 50 mmH₂O at 1400 °C [4]. Sawayama et al. studied the influence of two separate roles of coke as a reducing agent and as a bed spacer, and found that controlling the size of mixed coke in the ore layer enabled the nut coke to be mainly consumed to regenerate CO gas, while the lump coke formed a less degraded permeable bed [5].

The influence of nut coke on the reducibility of iron ore sinter under different conditions of temperatures and reducing atmosphere was studied [6, 7]. It has been found that the mixing of nut coke in the sinter bed improves the reduction behaviour by increasing the reducing efficiency of CO gas and prevents the sticking of the sinter pieces at temperatures above1373 K. Other studies were carried out on the effect of coke-sinter mixture on both, gas permeability and sinter reducibility. Watakabe et al. found that the reducibility of iron ore and gas permeability in the cohesive zone were improved by coke mixing [8]. They reported that the ore-coke segregation behaviour during charging can be avoided by using stabilizers in order to achieve a uniform mixed coke distribution across the furnace shaft. Zhaoxiang et al. studied the sinter reducibility and gas flow in the softening and melting zone under simulated blast furnace conditions [9]. They found that the mixing of ore-coke charge not only improves the gas permeability in the cohesive zone but also promotes the reducibility of Fe, Si, Mn, Ti and V oxides.

This survey indicates that the mixing of nut coke with iron ore sinter can improve blast furnace operations and save coke but there are no studies on the reduction behaviour of pellets-coke mixtures and the reduction kinetics and mechanism which control the overall process. Consequently, the present study aims at the investigation of the influence of nut coke on the reduction behaviour of iron ore pellets under simulating blast furnace conditions. The reduction was carried out isothermally at temperatures in the range of 1173–1523 K and non-isothermally in the
temperature range of 673–1523 K using different gas mixtures. The structure and morphological changes of reduced pellets were intensively studied and correlated with the reduction kinetics and mechanisms. The temperature range and gas composition were selected to simulate the reaction in the lumpy and cohesive zone of the blast furnace.

Experimental Techniques

The reduction of industrial acidic pellets and pellets-nut coke mixtures was carried out using a laboratory system as shown in Figure 1. The system is based on a muffle furnace with inlet and outlet tubes.

For the isothermal reduction which took place in steps of 1173–1523 K, a stainless steel reactor \((d_i = 45 \text{ mm}, l_i = 150 \text{ mm})\) was used which hermetically closed after inserting the sample in a stainless steel boat \((d_i = 30 \text{ mm}, l_i = 100 \text{ mm})\) as shown in Figure 2a. The weights of the iron ore pellets and nut coke used in isothermal reduction were 45 and 15 g, respectively (pellets/nut coke mass ratio = 3:1). The average size of pellets was 10–12 mm while that of nut coke was 12–14 mm. The gas composition which was applied in the reduction process consisted of 30% CO - 70% N2. After heating up the furnace to the ambient temperature and checking the gas connections, the stainless steel reactor containing sample was inserted into the muffle furnace under flow of nitrogen atmosphere. When the furnace temperature became stable, the CO–N2 gas mixture was adjusted and the holding time was 2 hours.

The non-isothermal reduction was conducted using a bigger steel reactor \((d_i = 100 \text{ mm}, l_i = 170 \text{ mm})\) and steel boat \((d_i = 90 \text{ mm}, l_i = 160 \text{ mm})\) as shown in Figure 2b. The size of the reactor is selected in order to give the chance for different types of packing of materials in the form of layers, mixtures, or both as given in Figure 3.

The weights of pellets and coke were 600 and 200 g, respectively. Two different sizes of coke were used: nut coke 12–14 mm used as a mixture and larger size coke 35–40 mm used as layers. The heating rate and gas composition were selected by simulating the actual conditions in the blast furnace as given in Table 1.

The pellets and coke which were used for both, isothermal and non-isothermal reduction were dried at 393K for 24 hours to ensure the complete removal of moisture. The composition of the outlet gases were measured at 1 s interval time and recorded by an on-line gas analyser (X-STREAM\textsuperscript{®} Emerson). The gas flow was precisely controlled by mass flow controllers (Rotameter\textsuperscript{®} E and L models) with a total gas flow rate of 8.0 NL min\(^{-1}\).

The reduction degrees of the pellets and the pellet-nut coke mixture were calculated by the oxygen and carbon balance based on CO and CO2 flow rates obtained from the gas analyser. The reduction degree was calculated according
to Eq. (1) [9, 10].

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

with \( A = 0.714 \nu^\prime N_2^0 \left[ (CO/N_2 - CO^o/N_2^o) + 2(CO_2/N_2 - CO_2^o/N_2^o) \right] \)
and \( B = 0.427 \left( \% Fe - 0.111 \left( \% FeO \right) \right) W \)
where;

\( CO^o, CO_2^o, N_2^o \): volume percentage of CO, CO_2, and N_2 in inlet gas
\( CO, CO_2, N_2 \): volume percentage of CO, CO_2, and N_2 in outlet gas
\( \nu^\prime \): total gas flow rate of inlet gas (8.0 NL min^{-1})
\( \% Fe, \% FeO \): mass concentration of Fe and FeO in iron ore pellets
\( W \): weight of pellets (45 g)
\( \Delta t \): reduction time (s)

On the other hand, total oxygen weight loss from pellets and also total carbon solution loss (TCS) from coke were calculated by measuring the weights before and after the reduction processes. The total reduction degree was determined depending on the calculation of reducible oxygen represented in iron oxides of pellets.

Origin pellets, nut coke and reduced pellets were examined by reflected light microscopy (RLM- Leica Aristomet) and scanning electron microscope-backscattered electron image analysis (SEM-EDX, ZEISS DSM 962). The formed phases were identified by X-ray diffraction technique (XRD, PW 1730 with Ni filtered Cu Kα radiation). A high pressure mercury pore size analyser (Micromeritics Pore Sizer, 9320) was used for measuring total porosity, pore area, and mean pore diameter.

Results and Discussion

Characterization of raw materials. The chemical analysis of industrial iron ore pellets is given in Table 2. The basicity (wt.% CaO/wt.% SiO_2) of pellets is equal to 0.2, which indicates the acidic properties of the applied pellets. X-ray analysis of the applied pellets exhibits that the pellets are composed of two main phases: Fe_2O_3 and SiO_2, as shown in Figure 4. The microstructure of the pellet samples was examined in order to determine the most common structure that characterises the investigated pellets. Figure 5 shows the typical microstructure of pellets examined by SEM-EDX. Figure 5a illustrates that the microstructure consists of Fe_2O_3, SiO_2 and pores with different diameter distributed across the matrix structure. Figure 5b gives more focus on the microstructure which illustrates the presence of Ca_2SiO_4 as very small patches between hematite grains.

The chemical analysis of the nut coke is given in Table 3. The coke microstructure was examined by RLM and SEM as shown in Fig. 6. It is clear that the microstructure of the applied metallurgical coke is highly porous with uniformly distributed pores across the matrix structure. The comparison between the pore size distribution of pellets and coke is given in Figure 7. The porosity of pellets was 30% with a main pore diameter of 1–6 μm while the total porosity of coke was 43% with the main pore diameter between 10–140 μm.
Isothermal reduction of pellets. Typical reduction curves of the pellets and pellets-coke mixture isothermally reduced by 30% CO-70% N2 at different temperatures (1173–1523 K) are given in Figure 8. The reduction degree was calculated depending on the calculation of oxygen weight loss after reduction to the reducible oxygen of iron oxides in pellets. The reduction degree of pellets reduced without nut coke participation increases with rising temperature in the range of 1173–1323 K. With further increase of temperature (1373–1523 K) the reduction degree decreases, which is known as reduction retardation (RR). On the other hand, the reduction of the pellets-nut coke mixture shows a continuous increase in the reduction degree between 1173 K and 1523 K. The total carbon solution loss (TCS) increases slowly at temperature below 1273 K followed by a sharp increase at temperatures above 1273 K.

Rate of reduction. The reduction curves of the pellets and the pellets-nut coke mixture isothermally reduced at 1173–1523 K are given in Figures 9 and 10. For a single reduction curve the rate of reduction is highest at the initial stages and decreases with time at all temperatures of both pellets and pellet-nut coke mixture. For pellets reduced without nut coke participation (Fig. 9), a sharp decrease in the reduction rate takes place at temperatures above 1323 K as the time proceeds. The comparison between the reduction extent of pellets and pellet-nut coke mixture at different temperatures is given in Figure 11. It can be noticed that there is no remarkable difference in the reduction degree between pellets and pellet-nut coke mixture at 1173 K. At temperatures above 1273 K the difference between the reduction curves increases, which indicates the positive effect of nut coke on pellet reducibility.

In order to clarify the positive effect of nut coke on pellets reducibility, the reduction rate \( \frac{dr}{dt} \) at the initial stages (15% reduction degree) and at advanced stages (45% reduction degree) of reduction was calculated and plotted against the corresponding temperature, respectively. It can be observed that, at the initial stages (15%) the reduction rate increases gradually with temperature for both pellets and pellet-nut coke mixture, as shown in Figure 12a. As the reduction proceeds (45%), the reduction rate is still continuously increasing with temperature for pellets-coke mixture while it decreases with temperature above 1373 K for pellets reduced without nut coke participation, as shown in Figure 12b.

Reduction kinetics, mechanism and volume change. The values of apparent activation energy were generally calculated from an Arrhenius equation (Eq. 2) in order to determine the rate controlling mechanism at different reduction stages.

\[
K_r = K_0 e^{-E_a/RT} \quad (2a)
\]

\[
E_a = RT \ln \frac{K_0}{K_r} \quad (2b)
\]

where:

- \( K_r \): reduction rate constant (s\(^{-1}\))
- \( K_0 \): frequency factor (s\(^{-1}\))
- \( E_a \): apparent activation energy (kJ mol\(^{-1}\))
- \( R \): universal gas constant (8.314 \times 10\(^{-3}\) kJ mol\(^{-1}\) K\(^{-1}\))
- \( T \): absolute temperature (K)
Figure 9. Reduction curves of pellets vs. temperature.

Figure 10. Reduction curves of pellet-nut coke mixture vs. temperature.

Figure 11. Reduction curves of pellets and pellets-coke mixture vs. time at different temperatures: (a) 1173 K; (b) 1273 K; (c) 1373 K; (d) 1523 K.

Figure 12. Effect of temperature on the reduction rate (dr/dt) of pellets and pellets-coke mixture at: (a) 15% reduction degree; (b) 45% reduction degree.
The relationship between the logarithm of the reduction rate and the reciprocal of the absolute temperature for pellets and pellet-coke mixture were plotted at 15% and 45% reduction degree, as given in Figure 13. The computed values of apparent activation energy from the Arrhenius equation are given in Table 4. The relationship between the activation energy values and the rate controlling step is taken from Khedr [11]. These values indicated that at the initial stages (15%) the reduction is most likely controlled by a combined effect of gaseous diffusion and interfacial chemical reaction for both pellets and pellet-coke mixture. As the reduction proceeds (45%), the participation of interfacial chemical reaction in the rate controlling mechanism increases with increasing activation energy values. On the other hand, pellets reduced without nut-coke participations gives two values of apparent activation energy. This indicates that at temperatures below 1373 K the reduction is most likely controlled by interfacial chemical reaction, as that of the pellet-coke mixture, whereas at higher temperatures the reduction is controlled by solid state diffusion mechanism, as will be clarified by microstructure examination.

The microstructure of the pellets reduced at 1323 K for 30 min is given in Figure 14. Figure 14a illustrates the formation of metallic iron grains at the outer surface of pellets, and the amount of metallic iron is decreased towards the core of pellets, which indicates the participation of gaseous diffusion in the rate controlling mechanism. Figure 14b shows the microstructure of the outer layer of reduced pellets, which illustrates the formation of open matrix structure from metallic Fe and FeO. Therefore, the rate controlling mechanism at the initial stages of reduction is a combined effect of interfacial chemical reaction and gaseous diffusion. Such behaviour is also valid for the initial stages of reduction of pellet-coke mixtures at the initial stages of reduction.

In order to clarify the decrease in the reduction rate of pellets at temperatures above 1323 K which results in reduction retardation and the positive effect of nut coke on the reduction process, the microstructure examination of pellets reduced with and without nut coke participation at 1523 K for 2 hours is given in Figure 15. Figure 15a shows the formation of a dense metallic iron layer on the outer surface of pellets reduced without nut coke participation. Figure 15b gives focus on the outer layer, which indicates the presence of fayalite (Fe₂SiO₄) which results from the reaction between silica and lower iron oxides. The formation of fayalite phase which is hardly reducible compared to iron

![Figure 13. Arrhenius plots for pellets and pellet-coke mixture at: (a) 15% reduction degree; (b) 45% reduction degree.](image)

![Table 4. Apparent activation energy values for pellets and pellet-nut coke mixture.](image)

![Figure 14. Photomicrographs of pellets reduced at 1323 K for 30 min: (a) x = 50; (b) x = 200.](image)
oxides has a great influence to decrease the rate of reduction at the later stages of reduction [12]. The fayalite phase starts softening at temperatures above 1323 K and melts completely at about 1473 K. The softening and melting of fayalite phase result in a high resistance to the diffusion of reducing gas through the slag layer into the pellets. This behaviour is enforcing the reducing gas to stand at the outer surface of the pellets without further diffusion, which leads to the formation of dense metallic iron shells around the iron oxides. The shelled metallic iron exhibits an increased resistance to the gas diffusion to the inner layers. The shelled iron oxides are converted to metallic iron through oxygen transfer via solid state diffusion which is slow reduction mechanism compared to gaseous diffusion. Therefore, both the fayalite phase and shelled iron result in reduction retardation and sharp slowdown in the reduction rate at temperatures above 1323 K, as shown in Figure 8. On the other hand, the presence of nut coke in the pellets bed has the ability to prevent such behaviour and improve the pellets reducibility as indicated from the amount of metallic iron formation (Figure 15c and 15d). In this case the presence of nut coke has improved the gas diffusion in the pellets bed and result in the development of a further amount of CO gas through Boudouard reaction as given in Eqs. (3 and 4).

$$\text{Fe}_x\text{O}_y + \text{CO} = \text{Fe}_x\text{O}_{y-1} + \text{CO}_2$$  \hspace{1cm} (3)

$$\text{C} + \text{CO}_2 = 2\text{CO} \Delta H = +172.467 \text{ kJ/mol}$$  \hspace{1cm} (4)

A part of CO$_2$ gas which is generated from the reduction of iron oxide is reacting with nut coke at temperatures above 1273 K to give CO gas, which increases the reduction potential of CO gas and decreases the concentration of CO$_2$ gas in the reducing atmosphere as shown in Figure 16. Another benefit of nut coke can be clarified from the examination of the surface microstructure of pellets reduced at 1523 K without and with nut coke participation using SEM-EDX. Figure 17a shows pellets reduced without nut coke participation, the presence of fayalite phase is obvious as holes or bubbles on the surface structure of pellets, which is mainly due to the melting of fayalite phase at higher temperatures than 1373 K. The formed fayalite phase is difficult to reduce with CO gas while the presence of nut coke has the ability to reduce this fayalite phase through the direct contact with carbon to give metallic iron and SiO$_2$, as shown in Figure 17b. The direct reduction of fayalite with carbon can be obtained at temperatures around 1323 K [13].

The volume relative change (ΔV%, concerning the initial volume) accompanying the reduction of iron ore pellets at different temperatures was calculated using Eq. (5) [14].

$$\Delta V\% = [(r_f/r_i)^3 - 1] \times 100$$  \hspace{1cm} (5)

Figure 15. Microstructure of pellets reduced for 120 min at 1523 K: (a) and (b) without nut coke; (c) and (d) with nut coke.

Figure 16. Variation of CO and CO$_2$ gases during reduction of pellets and pellet-nut coke mixture at 1523 K.
where \( r_i \) is the initial radius (mm), and \( r_f \) is the final radius (mm).

The external shape and the values of volume change (\( \Delta V\% \)) accompanying the reduction process are given in Figure 18: The reduction process shows a normal swelling of pellets at temperatures below 1373 K, after which the shrinkage of pellets volume takes place. The surface microstructure of pellets reduced at 1173 K was examined by SEM-EDX as given in Figure 19: Metallic iron whiskers are formed, which is mainly responsible for the swelling of pellets. It is well known that the formation of metallic iron whiskers is always associated with abnormal or catastrophic swelling, however in this case, the formation of fayalite has the positive effect of preventing the catastrophic swelling. The formation of the fayalite phase during reduction has the ability to increase the pellets strength and limits the growth.

Figure 17. SEM photomicrographs of the surface structure of pellets reduced for 120 min at 1523 K: (a) without nut coke; (b) with nut coke.

Figure 18. Volume change accompanied the reduction of pellets at different temperatures.

Figure 19. SEM photomicrographs of pellets reduced at 1173 K; (a) \( x = 500 \); (b) \( x = 2000 \).

Figure 20. SEM photomicrographs of pellets reduced at 1473 K; (a) \( x = 500 \); (b) \( x = 2000 \).
of metallic iron whiskers, and thus prevents the catastrophic swelling [12]. On the other hand, the examination of the surface microstructure of pellets reduced at 1473 K and accompanied by shrinkage of pellets volume evidences in Figure 20: The formation of dense metallic iron grains in the form of sticking balls, which coalesce with each other as a result of sintering effect at high temperature, leads to the shrinkage of the overall volume of pellets.

Non-isothermal reduction behaviour of pellets. The reduction behaviour of pellets packed in the steel reactor in 4 different modes (Figure 3a-d) under simulating blast furnace conditions as given in Table 1 was studied. The non-isothermal reduction curves are given in Figure 21. It can be seen that the reduction process started at a very slow rate for all modes of packing, which is mainly attributed to the effect of the lower temperature and the presence of CO₂ in the reducing atmosphere. When replacing CO₂ by CO gas at 1173 K and continuously increasing the temperature, the reduction curves started to increase sharply. The reduction degrees of pellets and the weight loss of coke applied as a mixture or layers are given in Table 5: The pellets reduced without any participation of coke (case a) gave the smallest values of reduction degree (26%) and showed the earliest slowdown of reduction curves (Figure 21) with increasing temperature. The participation of large coke size (35–40 mm) as layers in the pellets bed (case b) improved the reducibility of pellets to about 32% with the coke weight loss of 10.96%. The mixing of nut coke (12-14 mm) with 50% (case c) and 100% (case d) in the pellets bed was correlated with an increase in pellets reducibility to 46 and 55%, respectively. It can be seen that the coke weight loss increased as the amount of nut coke in the pellets bed increased. This indicates that the mixing of nut coke in the pellets bed improved the rate of coke gasification (Eq. 4) and CO generation by closer contact between pellets and coke while the degradation of lump coke, which was used as layers, was less. This is in good agreement with the results obtained in practice by the application of nut coke in a blast furnace [5].

The worse reducibility of pellets reduced without nut coke participation can be mainly attributed to the sticking phenomenon which occurs between pellets due to the softening and melting of fayalite phase at temperatures above 1323 K, as shown in Figure 22. The sticking phenomenon results in reduction retardation through the negative effect on the gas diffusion in the pellets bed and the formation of a metallic iron shell on the outer surface of pellets, as displayed in Figure 23. The mixing of nut coke in the pellets bed has the ability to prevent the sticking between the iron ore pellets, as shown in Figure 24. The distribution

Table 5. Reduction percent and coke weight loss obtained for non-isothermal reduction pellets.

<table>
<thead>
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<th>Case</th>
<th>a</th>
<th>b</th>
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<td>R, %</td>
<td>26</td>
<td>32</td>
<td>46</td>
<td>55</td>
</tr>
<tr>
<td>Coke wt. loss, %</td>
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<td>10.96</td>
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Figure 22. Sticking of pellets reduced without nut coke participation.

Figure 23. Area of contact between pellets reduced without nut coke participation.
of nut coke between pellets has the ability to reduce fayalite phase through the direct contact with coke carbon in addition to increasing of the reduction potential of CO gas by Boudouard reaction (Eq. 4). In real blast furnace operations, it has been found that the best reducibility and smooze operation can be achieved by mixing 50–60% coke in the burden layers [9]. The kinetic study of non-isothermal reduction and its correlation to the isothermal reduction is being investigated.

Conclusions

In this study, the isothermal and non-isothermal reduction of pellets and pellet-coke mixture were investigated under simulating blast furnace conditions. The main findings can be summarised as follows:

1. The isothermal reduction of pellets without nut coke participation was accompanied by reduction retardation at temperatures higher than 1323 K, which was attributed to the softening and melting of fayalite phase hindering gas-ore contact.

2. The mixing of nut coke in the pellets bed improved the reduction degree of pellets by increasing the efficiency of CO gas by Boudouard reaction and direct reduction of fayalite phase.

3. The apparent activation energy values and microstructure examination of reduced pellets showed that the reduction process was controlled by a mix of gaseous diffusion and interfacial chemical reaction mechanism at the initial stage. For pellets reduced without nut coke participation above 1323 K the reduction process was controlled by a solid state diffusion mechanism at the final stage due to the formation of a dense metallic iron shell around the outer surface of pellets.

4. The reduction of pellets was accompanied by normal swelling (5–22%) at temperatures below 1373 K, which was attributed to the formation of metallic iron whisker which is inhibited by the formation of fayalite phase during reduction.

5. The non-isothermal reduction of pellets illustrated that, as the amount of nut coke in the pellets bed increased, the reducibility increased, which was attributed to the inhibition of sticking between the reduced pellets and the promotion of gaseous diffusion in the pellets bed.

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