Influence of H₂–H₂O Content on the Reduction of Acid Iron Ore Pellets in a CO–CO₂–N₂ Reducing Atmosphere

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Using hydrogen as a reducing agent for iron production has been the focus of several studies due to its environmental potential. The aim of this work is to study the influence of H₂–H₂O content in the gas phase on the reduction of acid iron ore pellets under simulated blast furnace conditions. Temperature and gas compositions for the experiments were determined with multi-point vertical probes in an industrial blast furnace. The results of the reduction tests show that higher temperatures and H₂ content increase the rate and extent of reduction. For all the gas and temperature combinations, morphological, mineralogical, and microstructure changes were observed using different characterization techniques. Microscopy images reveal that H₂–H₂O, in the gas phase, has a positive influence on reduction, with metallic iron forming at the pellet’s periphery and core at lower temperatures compared to CO–CO₂–N₂ reducing gas. Porosity and surface area changes were determined using a gas pycnometer and the BET method. The results indicate that increasing the reduction temperatures and H₂ content results in greater porosity and a larger surface area. Moreover, carbon deposition did not take place, even at lower temperatures. A rate minimum was detected for pellets reduced at 800°C, probably due to metallic iron formation, hindering the diffusion of reducing gases through the product iron layer.

KEY WORDS: ironmaking; iron ore pellet; reduction; blast furnace; hydrogen.

1. Introduction

The steel industry contributes to approximately 4–7% of man-made greenhouse gases.¹ According to a statistical report published by the World Steel Association, blast furnace-converter route contributed to more than 70% of its environmental potential. The aim of this work is to study the influence of H₂–H₂O content in the gas phase on the reduction of acid iron ore pellets under simulated blast furnace conditions. Temperature and gas compositions for the experiments were determined with multi-point vertical probes in an industrial blast furnace. The results of the reduction tests show that higher temperatures and H₂ content increase the rate and extent of reduction. For all the gas and temperature combinations, morphological, mineralogical, and microstructure changes were observed using different characterization techniques. Microscopy images reveal that H₂–H₂O, in the gas phase, has a positive influence on reduction, with metallic iron forming at the pellet’s periphery and core at lower temperatures compared to CO–CO₂–N₂ reducing gas. Porosity and surface area changes were determined using a gas pycnometer and the BET method. The results indicate that increasing the reduction temperatures and H₂ content results in greater porosity and a larger surface area. Moreover, carbon deposition did not take place, even at lower temperatures. A rate minimum was detected for pellets reduced at 800°C, probably due to metallic iron formation, hindering the diffusion of reducing gases through the product iron layer.

KEY WORDS: ironmaking; iron ore pellet; reduction; blast furnace; hydrogen.

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thermodynamic computations carried out by Qie et al., the \( \text{H}_2 \) content should not exceed 20% of the reduction gas to maintain the exothermic nature of reduction. Researchers have come to different conclusions regarding adequate \( \text{H}_2 \) content in the reducing gas phase. Some suggest that when the \( \text{H}_2 \) content is above 15%, hydrogen’s influence on the reduction rate is insignificant, and when the \( \text{H}_2 \) content is below 5%, its influence is minimal. Others suggest that the first 5% of \( \text{H}_2 \) added to the reducing gas significantly increases the reduction rate. The latter opinion is supported by our previous work, in which hydrogen was used in a reducing atmosphere of \( \text{CO}–\text{CO}_2–\text{H}_2–\text{H}_2\text{O}–\text{N}_2 \).

The earlier studies are contradictory when reporting the behavior of iron oxide reduction with \( \text{H}_2 \) at temperatures of 700–800°C as some sources report decreased rates of reduction in the presence of \( \text{H}_2–\text{H}_2\text{O} \). However, the rate-controlling mechanism is, reportedly, temperature-dependent as the increased temperature is found to promote solid-state diffusion. Similar observations are reported frequently in the literature. Some studies indicate that the reasoning behind such behavior is due to changes in product layer porosity, which increases along with temperature and, subsequently, enhances gas diffusivity. It is suggested that pore-diffusion control is the main driver of hydrogen reduction of hematite particles that are larger than 7 mm in size, accounting for 60–99% of the degree of reduction. However, other researchers report an increase in overall reduction rate with increased temperatures. One possible reason for such contradictions is the varying particle sizes of iron oxides being tested as the rate-controlling mechanism is highly dependent on particle size.

Some sources in the literature suggest that water vapor plays a role in blocking active sites on wüstite surface, which, consequently, decreases the reduction rate. A similar conclusion was reached by other researchers, who suggest that a water vapor content as low as 5% is enough to stop the reduction process. Others report increased reduction rates in the presence of water vapor. In our previous work, increasing the \( \text{H}_2\text{O} \) content of reducing gas was accompanied by an increase in the extent of reduction at temperatures up to 850°C but not at temperatures above 900°C. This observation was attributed to a water-gas shift reaction, which promotes the formation of \( \text{H}_2 \) below 850°C according to Eq. (1). However, above 850°C, the reaction proceeds in the reverse direction.

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad \text{........................(1)}
\]

A mixture of \( \text{CO} \) and \( \text{H}_2 \) reducing gases is, supposedly, a more powerful reducing agent. The presence of \( \text{CO}_2 \) gas results in the deposition of carbon on the wüstite/iron layer. The deposited carbon then reacts, producing a mixture of \( \text{CO}–\text{CO}_2 \) gas, which drives the gas’ pressure higher, eventually bursting the formed layer. With the shell busted open, the more superior reducing agent, \( \text{H}_2 \), is allowed access to the iron oxide’s inner, unreduced layers.

In this study, a series of isothermal laboratory experiments were conducted to investigate the roles \( \text{H}_2 \) and \( \text{H}_2\text{O} \) play in reduction under simulated blast furnace conditions. Commercial acid iron ore pellets within a narrow size range were used to obtain representative results. Carbon deposition, morphology, microstructure, and phase changes were observed in this study.

2. Experimental

2.1. Blast Furnace Simulator and Acid Pellets

The conditions for the reduction experiments were designed based on a multi-point vertical probing (MPVP) campaign performed on an operating BF, Dillingen BF-4. Probes were placed at six points horizontally at the top of the blast furnace (BF) and allowed to descend into the BF until damaged. Simultaneously, a gas analysis was performed, including the \( \text{CO}, \text{CO}_2, \text{and H}_2 \) content. A detailed description of multi-point vertical probing technology can be found elsewhere. The mean value of all working thermocouples was used in the experimental design. Because no \( \text{H}_2\text{O} \) measurements were available, the \( \text{H}_2\text{O} \) content was computed using thermodynamic software, HSC Chemistry version 8.1, so that the partial equilibrium pressure of oxygen for the \( \text{CO}_2 \) and water vapor formation reactions were equal in \( \text{CO}–\text{CO}_2–\text{N}_2 \) gas and in \( \text{CO}–\text{CO}_2–\text{H}_2–\text{H}_2\text{O}–\text{N}_2 \) gas. Hence, the reduction potential of hydrogen and \( \text{CO} \) were equal during the reduction process. The remainder of the gas was assumed to be nitrogen.

Gas utilization was calculated for \( \text{CO} \) and \( \text{H}_2 \) using Eqs. (2) and (3):

\[
\eta_{\text{CO}} = \frac{\text{CO}_2}{\text{CO} + \text{CO}_2} \times 100 \quad \text{........................(2)}
\]

\[
\eta_{\text{H}_2} = \frac{\text{H}_2\text{O}}{\text{H}_2 + \text{H}_2\text{O}} \times 100 \quad \text{........................(3)}
\]

where \( \eta_{\text{CO}} \) and \( \eta_{\text{H}_2} \) are numerical indices for gas utilization. The reducing conditions are illustrated in \( \text{Fe}–\text{O}–\text{C} \) and \( \text{Fe}–\text{O}–\text{H} \) phase stability diagrams (also called Bauer-Glaessner diagrams) in Figs. 1(a) and 1(b), respectively. Additionally, a Boudouard reaction line is drawn to the \( \text{Fe}–\text{O}–\text{C} \) diagram. The Bauer-Glaessner diagrams and Boudouard reaction line have been drawn from the collected data using HSC Chemistry software version 8.1. The Bauer-Glaessner diagrams show the iron’s most stable phase in each experimental setup. The most stable phase will be reached if the duration of the experiment is sufficient. Table 1 shows the reducing gas compositions and the corresponding oxygen partial pressure \( (\rho_0) \) used in each reduction experiment.

The pellets’ chemical composition was analyzed by an accredited laboratory and is shown in Table 2. The total iron content \( (\text{TFe}) \) and the oxidation stage of the iron were accredited laboratory and is shown in Table 2. The total iron content \( (\text{TFe}) \) and the oxidation stage of the iron were
experimental run, 30 pellets weighing a total of 100 ± 0.1 grams were used. Special care was given to choose round-shaped and crack-free pellets.

In this study, a modified Blast Furnace Simulator (BFS) setup presented in our previous work\textsuperscript{17} was used. The BFS is a tube furnace with an inner diameter of 95 mm. It utilizes a pre-determined program with varying gas compositions and temperatures through the test run, which allows performing both isothermal and dynamic tests. Several gases are available in the BFS, including N\(_2\), CO, CO\(_2\) and H\(_2\), which were used in this study. The new setup shown in Fig. 2 utilizes a pumping system used to introduce H\(_2\)O into the furnace as part of the reducing atmosphere. The tests can be conducted with BFS at temperatures up to 1 100°C. The weight of the sample, along with the basket, is continuously measured with the scale and is recorded in the computer system.

In isothermal tests, pellets were placed in the BFS basket in a single layer because piling up the pellets inside the basket might hinder the gas flow and, subsequently, the reduction rate, which would complicate the analysis of the results. The basket was suspended inside the BFS using a wire connected to the weighted balance. The system was then heated in a nitrogen atmosphere, which was introduced to the furnace at a flow rate of 15 l/min (NTP) until the target temperature was reached. For a stationary state, temperature fluctuations of ±10°C were considered acceptable. Isothermal tests were performed at temperatures

Table 1. Gas composition during isothermal reduction.

| Temp (°C) | # | CO (Vol%) | CO\(_2\) (Vol%) | N\(_2\) (Vol%) | CO–CO\(_2\)–N\(_2\) gas | Temp (°C) | # | CO (Vol%) | CO\(_2\) (Vol%) | H\(_2\) (Vol%) | H\(_2\)O (Vol%) | N\(_2\) (Vol%) | p\(_{\text{O}_2}\) (atm) |
|----------|---|-----------|----------------|-------------|-----------------|----------|---|-----------|----------------|-------------|-------------|-------------|----------------|---------------|
| 700      | 1 | 28.02     | 20.31          | 51.67       | 6               | 26.39    | 19.13 | 3.98      | 48.66          | 3.00E-22    | 1.1E-16     | 47.37       | 47.15         | 6.31E-16     |
| 800      | 2 | 31.81     | 17.34          | 50.84       | 7               | 29.64    | 16.16 | 4.50      | 47.37          | 1.1E-16     | 47.15       | 47.56       | 6.31E-16     |
| 900      | 3 | 34.69     | 14.11          | 51.20       | 8               | 31.95    | 12.99 | 5.17      | 47.15          | 1.39E-17    | 47.56       | 47.56       | 2.14E-16     |
| 1 000    | 4 | 41.43     | 6.84           | 51.73       | 9               | 38.09    | 6.29  | 6.29      | 47.56          | 2.14E-16    | 48.15       | 48.15       | 6.31E-16     |
| 1 100    | 5 | 46.01     | 1.89           | 52.10       | 10              | 42.52    | 1.74  | 6.98      | 48.15          | 6.31E-16    | 48.15       | 48.15       | 6.31E-16     |

Fig. 1. Experimental conditions in the reduction tests, presented in Bauer-Glaessner diagrams using a) \(\eta_{\text{CO}}\) and b) \(\eta_{\text{H}_2}\).

Fig. 2. Schematic diagram of the blast furnace simulator.

Table 2. Chemical composition of the acid pellets (wt-%).

<table>
<thead>
<tr>
<th>TFe</th>
<th>FeO</th>
<th>SiO(_2)</th>
<th>CaO</th>
<th>MgO</th>
<th>Al(_2)O</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.59</td>
<td>&lt; 0.1</td>
<td>6.0</td>
<td>1.2</td>
<td>0.73</td>
<td>0.39</td>
<td>0.09</td>
<td>0.05</td>
</tr>
</tbody>
</table>
of 700–1 100°C with an interval of 100°C. The reduction program was initiated, and reducing gases were introduced into the furnace according to the isothermal programs shown in Table 1. The gas flow was maintained at 15 l/min (NTP) for 300 min during the reduction phase. After the reduction program was completed, samples were allowed to cool in nitrogen flowing at a rate of 10 l/min (NTP) to avoid re-oxidizing the samples.

Using a low gas flow rate in the current experimental setup may lead to inaccurate results due to the slow switching of the atmospheric gas from nitrogen to the pre-determined reduction gases. However, the relatively high flow rate (15 l/min through a 95 mm internal diameter furnace) used in this study helped reduce the uncertainty associated with gas switching. Moreover, a previous study by Turkdogan and Vinters showed that with a flow rate above 5 l/min of reducing gases, oxide pellet reduction became independent of the flow rate, subsequently eliminating gas-film transport as a rate-controlling step. The reduction of hematite takes place via three intermediate stages, from hematite to magnetite, magnetite to wüstite, and, finally, wüstite to metallic iron, as follows:

\[
3Fe_2O_3 + CO(\text{or H}_2) \rightarrow 2Fe_3O_4 + CO_2(\text{or H}_2O) \quad \text{(4)}
\]

\[
Fe_3O_4 + CO(\text{or H}_2) \rightarrow 3FeO + CO_2(\text{or H}_2O) \quad \text{(5)}
\]

\[
FeO + CO(\text{or H}_2) \rightarrow Fe + CO_2(\text{or H}_2O) \quad \text{(6)}
\]

At temperatures below 570°C, wüstite is not stable as can be seen in the Baur-Glaesner diagrams in Fig. 1, and reduction proceeds from hematite to magnetite, then to metallic iron. All the reduction experiments reported in this study took place at temperatures above 700°C. Therefore, wüstite is considered in the reduction’s progress. The degree of reduction is calculated based on the ISO 7215:2015 standard using the following equation:

\[
R = \frac{m_1 - m_2}{m_1 (0.430w_2 - 0.111w_1)} \times 10^4, \quad \text{(7)}
\]

where \(m_1\) is the sample’s mass before reduction, in grams, while \(m_2\) is the sample’s mass post-reduction, in grams, \(w_1\) is the mass percentage of iron (II) oxide prior to reduction, and \(w_2\) is the mass percentage of total iron in the sample prior reduction.

2.2. Microscopical and Mineralogical Study

A field emission scanning electron microscope (FESEM; Zeiss Ultra Plus, Carl Zeiss SMT AG, Germany) attached to an energy-dispersive X-ray spectroscopy (EDS) device was used to study the morphology of the outer surface of different pellets post-reduction. Pellets were cut in half so that they were easier to fix on the carbon tape. Pellets were coated with Pt, and an acceleration voltage of 5 kV was used.

A second set of pellet specimens were mounted in epoxy and later cut, polished, and coated with Au. An Olympus BX51 light optical microscope (LOM) was used to study the structure and phases of the samples visually. A laser scanning confocal microscope (LSCM; Keyence, VK-X100K/ X200K) equipped with a motorized X-Y stage was used to obtain mosaic cross-section images of the pellets post-reduction. An image assembling application (VK-H11XJ) was used to assemble the images into a single image. However, the maximum number of images that can be assembled together is 100 images, so it was only possible to assemble part of the cross-section into one image. This procedure was repeated for each pellet to obtain mosaic pictures of the upper and lower part of the cross-section, which were later stitched together to obtain an image of the full cross-section area. The crystalline phases of the reduced pellets were determined by X-ray diffraction (XRD) using a Rigaku SmartLab 9 kW in the 2θ-range of 5–130° with a step of 0.02° at a scan speed 4.06 degree/min at 40 kV and 135 mA. The sample was acquired by grinding 3 different pellets from each reduction experiment.

2.3. Density and Porosity

It is necessary to study the morphological changes that take place in pellets during reduction and, therefore, influence reaction kinetics. The porosity of iron ore pellets has, traditionally, been determined using optical microscopy (OM) and mercury intrusion porosimetry (MIP). However, MIP was not used because an apparatus was unavailable. OM imaging was not used to determine porosity since it only quantifies porosity in two-dimensional sections, and the preparation steps may affect the results, leading to over-estimating porosity.

A gas pycnometer, AccuPyc II 1340, was used to measure the pellets’ skeletal density (\(\rho_s\)), which is defined as the mass of a substance divided by its volume, excluding open pores. The pycnometer has a 10 cm³ sample chamber and uses helium as a displacement gas. Due to the sample chamber size limitation, only three pellets were used to determine the skeletal density of pellets after each reduction experiment, as well as of the unreduced pellets. The pellets were irregular when compared to an ideal sphere. To approximately determine the pellets volume, image analysis (IA) software, ImageJ, was used to obtain the pellets’ equivalent circular area diameter (\(D_a\)) using the following equation:

\[
D_a = 2\sqrt{\frac{A}{\pi}}, \quad \text{(8)}
\]

where A is the pellets’ projected area.

Figure 3 shows the image processing procedures. The pellets’ volume was then estimated based on the pellet equivalent area diameter. Next, the envelope density (\(\rho_e\)) of the same pellets was determined using the following equation:

\[
\rho_e = \frac{m}{V}, \quad \text{(9)}
\]

where \(\rho_e\) is envelope density in g/cm³, while \(m\) is the pellet’s mass in grams, and \(V\) is the pellet’s volume in cm³, determined based on the equivalent circular area diameter.

Pellet porosity (\(\varepsilon\)) was then calculated as follows:

\[
\varepsilon = \frac{\rho_s - \rho_e}{\rho_s} \times 100, \quad \text{(10)}
\]

2.4. Surface Area and Pore Size

A surface area and porosity analyzer, Micromeritics ASAP 2020 (Micromeritics, USA), was used to obtain
information regarding the nitrogen physisorption isotherms to determine the specific surface area and pore structure (BET-BJH) of the unreduced and reduced pellets. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation, while nitrogen adsorption data were used to determine pore characteristics.

3. Results and Discussion

3.1. Sample Characterization for Isothermal Reduction Tests

3.1.1. XRD

Figures 4 and 5 show the XRD results for the unreduced and reduced pellets. At 700°C, magnetite is the dominating phase in pellets reduced in CO–CO$_2$–N$_2$, while wüstite is the dominating phase in pellets reduced in CO–CO$_2$–H$_2$–H$_2$O–N$_2$. Hematite is completely reduced to lower iron oxides at 700°C. However, at higher temperatures (e.g., 800°C and 900°C), wüstite co-exists with metallic iron when pellets are reduced in both atmospheres, confirming that reducing wüstite to metallic iron is a key step in the overall reduction process. Metallic iron presence could be confirmed for pellets reduced at 900°C in both reducing atmospheres with metallic iron peak at $2\Theta = 52.38^\circ$.

At 1 000°C, the pellets are reduced to metallic iron in a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere, while some wüstite is still detected in pellets reduced in a CO–CO$_2$–N$_2$ atmosphere. Pellets reduced in both atmospheres are reduced into metallic iron at a temperature of 1 100°C. XRD results for temperature 700°C and 1 000°C indicate that, for the same reduction temperature and duration, higher reduction degree is generally reached when pellets are reduced in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere.

Fig. 4. XRD for unreduced and reduced pellets in CO–CO$_2$–N$_2$ gas. (Online version in color.)

Fig. 5. XRD for unreduced and reduced pellets in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ gas. (Online version in color.)

3.1.2. Optical Microscope

Figure 6 shows OM images of pellets reduced at 700–900°C. In the optical microscope images, at 700°C, it appears that no metallic iron was formed in either reducing atmosphere, neither at the periphery nor at the core. At 800°C, metallic iron was formed only at the periphery of the pellets reduced in a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere, while no metallic iron appears to have formed either at the core nor the periphery for the pellet reduced in a CO–CO$_2$–N$_2$ atmosphere at the same temperature. The formed metallic iron is likely to be the reason behind the ‘rate minimum’ phenomenon at 800°C.

For pellets reduced at 800°C in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere, no XRD peaks confirm the presence of metallic iron as shown in Fig. 4. However, in the microscopic images presented in Fig. 6(b), metallic iron can be detected at the periphery. The reason why metallic iron was not detected through XRD is probably that metallic iron content is very low (< 3%).

At 900°C, metallic iron formed at the periphery of both pellets. However, it is obvious that more metallic iron
formed at the periphery of the pellet reduced in a CO–CO₂–H₂–H₂O–N₂ atmosphere. Moreover, metallic iron also formed at the core of the pellet reduced in a CO–CO₂–H₂–H₂O–N₂ atmosphere but not at the core of the pellet reduced in a CO–CO₂–N₂ atmosphere. This provides evidence that H₂ is superior in terms of its ability to diffuse through the pellet surface and into the core when compared to CO, which can be explained by the small molecular size of H₂.5,21

Figure 7 shows OM images of pellets reduced at 1 000°C and 1 100°C. At 1 000°C, metallic iron formed at the periphery and core of pellets reduced in both atmospheres. The distribution of metallic iron at the periphery appears to be similar for both pellets, indicating that iron oxides were reduced the most, near the pellets’ surface. However, the core of the pellet reduced in a CO–CO₂–H₂–H₂O–N₂ atmosphere appears to have also been reduced to a higher extent compared to the core of pellet reduced in CO–CO₂–N₂ atmosphere.

At 1 100°C, highest reduction appears to be achieved for both pellets at the periphery and core with similar distribution. The slag formed is fayalite, which has small amounts of dissolved MgO and CaO. Iron oxide reduction by CO and H₂ would be most effective near the outer surface of the pellets. These observations suggest that the gases’ reduction potential decreased as the gas penetrated into the inner body of the pellet. Similar observations are reported in the literature.22

3.1.3. Porosity and Surface Area

Figures 9 and 10 show the pellets’ porosity changes and BET surface area changes, respectively after each reduction test. It appears that porosity always increases with a temperature increase. The porosity of pellets reduced in CO–CO₂–H₂–H₂O–N₂ gas is generally higher than that reduced in CO–CO₂–N₂. The BET surface area is as low as 0.057 m²/g for unreduced pellets. Pellets reduced at 700°C had the highest surface area for both reducing atmospheres. As the reduction temperature increased, the specific surface area decreased, except at test temperature of 1 000°C, where the specific surface area of pellets increased compared to pellets reduced at 900°C. The surface area dropped again to a minimum value at 1 100°C. This behavior was consistent for both reducing atmospheres, which suggests it is temperature-dependent. Moreover, the pellets reduced in a CO–CO₂–H₂–H₂O–N₂ atmosphere exhibited higher surface areas than pellets reduced in CO–CO₂–N₂.
The change in BET surface area at 1000°C can be explained by morphological changes observed through SEM. When reduction temperature is increased to 1000°C, semi fibrous metallic iron starts to form a net like structure, resulting in an increase in the surface area. Figure 8 shows the surface of pellet reduced at 1000°C in CO–CO₂–N₂ atmosphere (a) and CO–CO₂–H₂–H₂O–N₂ (b) with the same magnification (1000X).

The increase in porosity accompanied by a decrease in the specific surface area indicates that larger but fewer pores formed as the temperature increased. This is likely to be due to sintering as dense iron was formed, which contains isolated, large pores. The effect of sintering was more pronounced in pellets reduced at 1000°C in a CO–CO₂–H₂–H₂O–N₂ atmosphere. These observations are in agreement with the literature. Ore reducibility is highly dependent on porosity. As porosity increases, the reducing gases can more readily access the core of iron oxides. At temperatures above 1075°C, the literature reports a decrease in the reduction rate due to several factors, including pore closure and plastic deformation of the outer iron shell. Such a decrease was not observed in this study since, at 1100°C, the reduction rate and porosity continued to increase.

3.1.4. Laser Microscope Images

Figures 11 and 12 show the full cross-section areas of the reduced pellets with the metallic iron phase segmented into a green color for better visibility.

Complementary to the optical microscope images, the cross-section area images verify the sequence of reduction in iron ore pellets in the two reducing atmospheres. It is obvious that the metallic iron began to form only at the periphery of the pellets, near the outer surface, at temperatures of 900°C and 800°C when reduced in a CO–CO₂–N₂ and CO–CO₂–H₂–H₂O–N₂ atmosphere, respectively. A reduction degree of more than 95% was achieved at 1100°C and 1000°C in CO–CO₂–N₂ and CO–CO₂–H₂–H₂O–N₂ atmosphere, respectively. In an image of a reduced pellet at 1100°C in a CO–CO₂–H₂–H₂O–N₂ atmosphere, it appears that the pellet was partially broken during the polishing procedure. This confirms that porosity determination via image analysis would likely result in overestimating porosity.

Fig. 8. Surface morphology of pellets reduced in at 1000°C in CO–CO₂–N₂ atmosphere (a) and CO–CO₂–H₂–H₂O–N₂ (b) with 1000X magnification.

Fig. 9. Changes in the pellets’ porosity post-reduction. (Online version in color.)

Fig. 10. Changes in the pellets’ specific surface area post-reduction. (Online version in color.)
3.2. Reduction Rate and Curves

Figures 13–17 depict the reduction curves obtained for the reduction of acid pellets at temperatures of 700–1 100°C in CO–CO₂–N₂ and CO–CO₂–H₂–H₂O–N₂ gases. The reduction degree corresponding to theoretical complete reduction to magnetite is 11.1% for the used pellets. Similarly, reduction degree corresponding to complete reduction to wüstite is 29.7% when nonstoichiometric characteristic of wüstite is considered. Dashed lines at reduction degree of 11.1% and 29.7% corresponding to the theoretical start of magnetite reduction (11.1%) as well as lower limit of wüstite reduction (29.7%) are shown on each curve. Reduction curves are accompanied by SEM image of the pellets’ surface in both reducing atmospheres. With magnification of 15 k. Moreover, the SEM images shown in Fig. 17 include additional images at 20 k magnification to reveal micro-changes on the pellets’ surface.

Reduction curves show that the rate and extent of reduction increased as the temperature increased. Increasing the temperature is beneficial for reduction kinetics and thermodynamics as the rate of diffusion and phase boundary reactions accelerate at higher temperatures. Increasing the temperature leads to an increase in the diffusion coefficient as gas molecules’ movements become more rapid, supporting diffusion behavior. It was also shown in previous sections how porosity increases as the temperature increases.

Figure 13 indicates better reduction behavior for pellets reduced in CO–CO₂–H₂–H₂O–N₂ gas at 700°C. Reduction curves are in good agreement with XRD results shown in Figs. 4 and 5 that indicate reduction of hematite to magnetite and wüstite in a CO–CO₂–N₂ atmosphere and complete reduction of hematite to wüstite in CO–CO₂–H₂–H₂O–N₂ atmosphere.

Figure 14 shows that pellets reduced in CO–CO₂–H₂–
Fig. 14. Reduction curves for pellets reduced at 800°C (a), with corresponding surface SEM images in CO–CO$_2$–N$_2$ (b) and CO–CO$_2$–H$_2$–H$_2$O–N$_2$ (c). (Online version in color.)

Fig. 16. Reduction curves for pellets reduced at 1 000°C (a), with corresponding surface SEM images in CO–CO$_2$–N$_2$ (b) and CO–CO$_2$–H$_2$–H$_2$O–N$_2$ (c). (Online version in color.)

Fig. 15. Reduction curves for pellets reduced at 900°C (a), with corresponding surface SEM images in CO–CO$_2$–N$_2$ (b) and CO–CO$_2$–H$_2$–H$_2$O–N$_2$ (c). (Online version in color.)

Fig. 17. Reduction curves for pellets reduced at 1 100°C (a), with corresponding surface SEM images in CO–CO$_2$–N$_2$ (b) and CO–CO$_2$–H$_2$–H$_2$O–N$_2$ (c). (Online version in color.)
H$_2$O–N$_2$ gas at 800°C exhibited almost the same reduction as pellets reduced at 700°C, despite the higher temperature, as well as CO and H$_2$ content in the reducing gases present at 800°C. This finding could be attributed to the ‘rate minimum’ phenomenon, which is often reported in the literature and is associated with hydrogen reduction.\(^{10,11}\) The phenomenon is reported by many researchers in the literature; it is reported to occur as the reduction rate slows down when the temperature rises to between 600 and 900°C, and then increases at temperatures above 900°C. This phenomenon is attributed to the formation of an impermeable iron layer on the wüstite surface, which slows down gas diffusion through the formed metallic layer to reduce wüstite.

This conclusion that rate minimum takes place at 800°C is supported by microscopic images shown in Figs. 6 and 11, which confirm that metallic iron was formed at the periphery of the pellet reduced at 800°C in a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere. Also, reduction degree of pellets reduced in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere exceeded the dashed line, indicating the beginning of wüstite reduction to metallic iron. This observation is also in agreement with microscopic images in Figs. 6 and 11 which show formation of metallic iron in pellets reduced in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere. Although the slight increase in degree of reduction corresponds to the formation of metallic iron, its content was low enough to not get detected through XRD.

It can be seen from Fig. 14 that pellets reduced in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere exhibited slightly more reduction compared to pellets reduced in CO–CO$_2$–N$_2$ atmosphere. Also, reduction degree of pellets reduced in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere exceeded the dashed line, indicating the beginning of wüstite reduction to metallic iron. This observation is also in agreement with microscopic images in Figs. 6 and 11 which show formation of metallic iron in pellets reduced in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere. Although the slight increase in degree of reduction corresponds to the formation of metallic iron, its content was low enough to not get detected through XRD. The reduction degree of pellets reduced in CO–CO$_2$–N$_2$ atmosphere does not reach steady state by the end of reduction, but rather proceeds at a very low rate.

Figure 14(a) shows that structure of pellet surface reduced at 800°C in CO–CO$_2$–N$_2$ atmosphere is composed of small aggregate of varying sizes and shapes. This structure is somehow similar to pellets reduced at 700°C shown in Fig. 13. However, the aggregate size appears smaller in Fig. 14(a) compared to that in Fig. 13. On the other hand, Fig. 14(b) shows a somewhat more continuous solid structure, with the smaller constituting grains still visible. These observations are in agreement with Fig. 9 which shows that, at 800°C, pellets reduced in CO–CO$_2$–N$_2$ exhibit higher porosity compared to pellets reduced in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere. Although it was concluded that metallic iron forms at 800°C in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere based on OM and laser microscopy images, it was challenging to clearly detect metallic iron at the surface of the pellets due to its low content.

Figure 15 shows the reduction curves of pellets reduced at 900°C. The extent of reduction at 900°C was slightly greater in the CO–CO$_2$–H$_2$–H$_2$O–N$_2$ reducing atmosphere compared to that of only CO–CO$_2$–N$_2$. It also appears that reduction does not approach a steady-state at 900°C, which indicates that the extent of reduction will be greater if the reduction process is allowed to continue for a longer period of time. It can also be seen in Figs. 14, 15 that the rate and extent of reduction were not significantly higher in the reducing atmosphere containing H$_2$ and H$_2$O. A possible reason is the presence of relatively high water vapor content in the reducing gas (more than 2%), which could play a role in slowing down reduction by blocking wüstite free reaction sites.\(^{10}\)

Figure 16 shows the reduction curves of pellets reduced at 1 000°C. The enhanced reduction behavior of pellets in a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ reducing atmosphere is most pronounced at a temperature of 1 000°C, as can be seen in Fig. 16(a). The extent and rate of reduction were significantly greater compared to pellets reduced in a CO–CO$_2$–N$_2$ atmosphere, which does not approach a steady state. Enhanced reduction behavior could also be attributed to the lower H$_2$O content in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ compared to H$_2$O content at lower temperatures. A clear change in the reduction rate is obvious at the theoretical start of wüstite reduction, which may indicate a change in the reduction mechanism. It is widely reported that the reduction of wüstite to iron is the rate-controlling step in the overall reduction process,\(^{21}\) which could also explain the slowed reduction rate following the iron oxide’s reduction into wüstite.

Significant difference is observed in surface morphology between pellets reduced at 900°C and 1 000°C. Structure of formed iron appears to be more fibrous for pellets reduced in CO–CO$_2$–H$_2$–H$_2$O–N$_2$ which could be seen from SEM images in Figs. 8 and 16 which is a reason for the increased BET surface area of pellets reduced at temperature 1 000°C compared to pellets reduced at 900°C in both atmospheres as can be seen in Fig. 10.

Figure 17 shows the reduction curves of pellets reduced at 1 100°C. Figure 17 shows that pellets reduced in both atmospheres exhibited nearly complete reduction. However, the reduction rate for pellets reduced in a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere was higher. Reduction curves indicate 97.5% and 99.4% reduction degree for pellets reduced in CO–CO$_2$–N$_2$ and CO–CO$_2$–H$_2$–H$_2$O–N$_2$, respectively. The better reduction behavior of a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ reducing atmosphere is attributed to the higher diffusivity of H$_2$, as well as the greater porosity and higher surface area of pellets reduced in a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere. Porosity was confirmed via SEM images and pycnometer measurements. Moreover, the pellets’ surface area was determined using BET measurements. It is also shown, through SEM images, that pellets reduced in a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere at 1 100°C developed fissures in the iron layer, which likely allowed more reducing gases into the pellets’ core, increasing the pellet reduction rate and extent.

At 1 100°C, the product iron layer formed in pellets reduced in a CO–CO$_2$–N$_2$ atmosphere was still more porous than in a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere. The iron layer formed a net-like structure, and the layer appears to be impermeable in pellets reduced in a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ reducing atmosphere. The impermeable layer appears to develop as a result of iron grains sintering, which was not as pronounced in pellets reduced in a CO–CO$_2$–N$_2$ atmosphere. However, this impermeable layer seems to be torn at several
locations, in the form of large radial fissures across its surface. Such radial fissures were observed in previous studies at lower reduction temperatures, and their formation tended to increase with reduction potential increases.\textsuperscript{23} They may have been a result of gas pressure building up within the pellets, which eventually burst out of the impermeable iron layer, causing the obvious tear as depicted in the SEM images. Such an effect may contribute to the enhanced reducibility of a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere, with the newly formed fissures creating passages for reducing gases to reach the reaction interface at the core of the pellet, leading to faster reduction. The SEM images observed for pellets outer surface is also in agreement with BET area measurements shown in Fig. 10, indicating a decrease in the surface area. The decrease in surface area took place as a result of iron sintering in pellets reduced at 1 000°C rather than the semi fibrous structure observed for pellets reduced in 1 000°C.

3.2.1. Carbon Deposition

Figure 18 shows pellets reduced at temperatures of 700–1 100°C in both a CO–CO$_2$–N$_2$ and a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ reducing atmosphere. No noticeable swelling occurred in temperatures lower than 1 100°C in either of the considered atmospheres. Furthermore, no carbon deposition was noticed on the pellets’ surface upon visual examination.

Other researchers\textsuperscript{24} have reported that carbon deposition takes place upon the reduction of hematite pellets at temperatures lower than 900°C in a CO–H$_2$ atmosphere, where even small quantities of hydrogen promote carbon deposition, especially when the CO content is greater than 20%. Moreover, it was reported that when metallic iron is formed, it acts as a catalyst, which is necessary for extensive carbon deposition. Carbon deposition can greatly hinder or even prevent reduction.\textsuperscript{18} In this study, metallic iron formed in a CO–CO$_2$–H$_2$–H$_2$O–N$_2$ atmosphere at 800°C. However, reduction curves in Figs. 13–17 show that no weight increase occurred during the reduction process in all the testing conditions. This indicates that either no carbon deposition occurred, or the weight loss, as a result of reduction, overcame the weight gain resulting from carbon deposition. A visual examination of the pellets also did not indicate carbon deposition or accumulation on the surface.

Table 3 presents the carbon content of different pellets quantified using LECO CS-200. A ceramic crucible with iron chips was used as a combustion accelerator. The test was repeated three times for each sample measurement, and the arithmetic mean was taken. It is clear that very low carbon content was present. The highest carbon content (around 0.066%) was found in pellets reduced at 1 100°C in both reducing atmospheres.

In this study, iron began to form at low temperatures (800–900°C) when hydrogen was present in the reducing atmosphere. However, no carbon deposition took place in both reducing atmospheres. The presence of N$_2$ and CO$_2$ might have prevented the carbon from depositing.\textsuperscript{24} The deposition of carbon occurs through the following reaction:

\[ 2CO = C + CO_2 \] (11)

In this investigation, at low reducing temperatures, CO$_2$ was significantly higher than in previous investigations that reported carbon deposition taking place.\textsuperscript{18,24} With higher CO$_2$ content, there is a decrease in the temperature below which carbon forms. Therefore, carbon deposition is greatly hindered or even stopped over a wider range of temperatures.\textsuperscript{18} These observations are in agreement with Baure-Glaessner diagrams shown in Fig. 1 where experiments carried out at temperature range of 800–1 100°C are clearly above Boudouard reaction line, indicating that no carbon deposition would take place. Furthermore, experiments carried out at 700°C are located at Boudouard reaction line. However, no carbon deposition is observed for both reducing atmospheres.

4. Conclusions

In this investigation, the influence of H$_2$–H$_2$O on the reduction of acid iron ore pellets was studied isothermally at temperatures of 700–1 100°C. The influence of reducing gas containing a mixture of CO–CO$_2$–H$_2$–H$_2$O–N$_2$ was compared to reducing gas containing only CO–CO$_2$–N$_2$ with the

<table>
<thead>
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<th>Reducing atmosphere</th>
<th>Unreduced</th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
<th>1 000°C</th>
<th>1 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO–CO$_2$–N$_2$</td>
<td>0.052</td>
<td>0.040</td>
<td>0.035</td>
<td>0.016</td>
<td>0.014</td>
<td>0.066</td>
</tr>
<tr>
<td>CO–CO$_2$–H$_2$–H$_2$O–N$_2$</td>
<td>0.052</td>
<td>0.017</td>
<td>0.021</td>
<td>0.051</td>
<td>0.025</td>
<td>0.067</td>
</tr>
</tbody>
</table>

Fig. 18. Reduced pellets in CO–CO$_2$–N$_2$ (left →) and CO–CO$_2$–H$_2$–H$_2$O–N$_2$ (right →) atmospheres at 700°C (a), 800°C (b), 900°C (c), 1 000°C (d), and 1 100°C (e).
same oxygen partial pressure. The reducing gas composition at each studied temperature was determined based on data acquired from an operating BF. The results indicate that increasing the reduction temperature resulted in a higher degree of reduction in both reducing atmospheres. The temperature increase resulted in higher porosity and surface areas, contributing to increased reduction. Reducing gases containing H2 and H2O also resulted in higher porosity and surface areas in reduced pellets, leading to a better reduction performance. However, gas compositions containing more than 2% water vapor at temperatures of 800°C and 900°C did not result in a significantly better reduction performance compared to a CO–CO2–N2 reducing atmosphere, probably due to water vapor blocking wüstite’s active sites.

Microscopic images confirmed the formation of metallic iron on the pellets’ periphery in a CO–CO2–H2–H2O–N2 atmosphere, leading to a ‘rate minimum’ phenomenon as the reduction slowed down. At higher reduction temperatures, the reduced iron product seems to have had a greater tendency to sinter with H2 and H2O in the reducing atmosphere. However, the formed iron layer developed fissures on the surface of pellets reduced at 1 100°C, which created passages for the reducing gases to access the pellets’ core. No carbon deposition appears to have taken place at any reduction temperature in either of the reducing atmospheres, which implies that H2 did not promote carbon formation.

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Abbreviations

BET: Brunauer, Emmett, and Teller method
BF: Blast Furnace
BFS: Blast Furnace Simulator
EDS: Energy-dispersive X-ray spectrometer
FESEM: Field emission scanning electron microscope
IA: Image analysis
LSCM: Laser scanning confocal microscope
NPT: Normal Pressure and Temperature
MIP: Mercury intrusion porosimetry
MPVP: Multi-point vertical probing
OM: Optical microscope
SEM: Scanning Electron Microscope
TGA: Thermogravimetric analysis
XRD: X-ray diffraction
XRF: X-ray fluorescence

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