Reduction of iron ore pellets, sinter and lump ore under simulated blast furnace conditions

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SUMMARY
A blast furnace (BF) is the dominant process for making iron in the world. The blast furnace is charged with coke and iron burden materials including iron ore pellets, sinter and lump ore. While descending in the blast furnace the charge materials reduce. The iron bearing materials should reduce fast and remain in solid form until as high temperature as possible to ensure reaction contact with reducing gas and iron oxides. This research focuses on the reducibility of iron ore pellet, sinter and lump ore in the blast furnace shaft. The experiments were carried out isothermally with Blast Furnace Simulator (BFS) high-temperature furnace at four different temperatures (700°C, 800°C, 900°C and 1000°C) for 300 minutes. The experimental atmosphere consisted of CO, CO₂, H₂, H₂O and N₂ simulating the conditions in blast furnace shaft. It was found out that lump ore has lowest reduction rate at all test conditions. Iron ore pellets reduce fastest at lower temperature and is bypassed by sinter at higher temperatures. Furthermore, the reduction rate of sinter and iron ore pellets start to resemble each other in higher temperatures.

Key words: blast furnace, sinter, iron ore pellets, lump ore, reduction, iron making

1. Introduction
A blast furnace (BF) is the most common process for pig iron production in the world. The blast furnace is charged with coke and iron bearing materials separately which leads to layered structure. The iron bearing materials consist of iron ore pellets, lump ore and sinter. When charge material descends, the charge material reduces. In the ideal situation the iron bearing materials reduces fast and remain in solid form as high temperatures as possible.

The reduction of iron oxides occurs stepwise from hematite to magnetite, magnetite to wüstite and wüstite to metallic iron. Reduction can happen with CO and H₂ as presented here [1]:

Hematite to magnetite (around 500°C)

3Fe₂O₃ + CO(g) → 2Fe₃O₄ + CO₂(g)
3Fe₂O₃ + H₂(g) → 2Fe₃O₄ + H₂O(g)

Magnetite to wüstite (between 600-900°C)

Fe₃O₄ + CO(g) → 3FeO + CO₂(g)
Fe₃O₄ + H₂(g) → 3FeO + H₂O(g)

Wüstite to metallic iron (between 900-1100°C)

FeO + CO(g) → Fe + CO₂(g)
FeO + H₂(g) → Fe + H₂O(g)

There has been studies about low temperature reduction degradation characteristics of pellet, sinter and lump ore [2], as well as softening, shrinking and melting reduction behavior of all charge materials or just part of them [3-9].

Even though some researches considered all iron bearing materials (sinter, iron ore pellet and lump ore), the authors were not able to find research made in temperatures which simulated the upper part of the BF shaft with temperature range from 700°C to 1000°C with hydrogen and water vapor in atmosphere and for all three material types.

This research work focuses on reduction behavior of iron ore pellet, sinter and lump ore in simulated blast furnace shaft conditions where H₂ and H₂O are present in typical CO-CO₂-N₂ atmospheres.

2. Experimental section
Sinter, lump ore and iron ore pellets were used in experiments. Composition for all three materials is presented in Table 1. The total iron content (Fe₅₀) and the oxidation stage of the iron were measured with a titration method and the sulphur content with flame analysis. The contents of other components were measured with X-Ray Fluorescence (XRF).

The total mass of iron bearing materials used in one experiment was around 100 g per material (iron ore pellets, sinter and lump ore). The particle size and
sample amount differed being 30 pcs / 10-12.5 mm for pellets, 19 pcs / 12.5-16mm for sinter and 2 pcs / 25-32 mm for lump ore. These particle sizes were chosen such that they correspond to sizes which are mostly used in a blast furnace.

The experiments were made with Blast Furnace Simulator (BFS) [10] presented in Figure 1.

Gas utilization degree is determined for CO and H$_2$ gases with following equations (1).

\[
\text{etaCO} = 100 \times \frac{\text{CO}_2}{\text{CO} + \text{CO}_2}
\]

\[
\text{etaH}_2 = 100 \times \frac{\text{H}_2\text{O}}{\text{H}_2 + \text{H}_2\text{O}}
\]

where \( \text{etaCO} \) and \( \text{etaH}_2 \) are gas utilization degrees. The reducing conditions are illustrated in Bauer-Glaessner diagrams in Figure 2.

Isothermal tests were made in four different temperatures (700°C, 800°C, 900°C and 1000°C). The sample was placed in the furnace which was at room temperature and nitrogen was used until the test temperature was reached. Then the gas composition was changed to simulate BFS conditions and reduction lasted 300 minutes. Cooling was also made in nitrogen atmosphere. The total gas flow rate was 15 l/min. Precise information of used atmospheres can be seen in Table 2. Used gas compositions were selected such that they simulate the blast furnace gas composition [11].

| Gas   | 700°C | 800°C | 900°C | 1000°C |
|-------|-------|-------|-------|--------|
| N$_2$ | 51.5% | 51.6% | 51.7% | 52.0%  |
| CO    | 27.0% | 29.5% | 32.0% | 42.0%  |
| CO$_2$| 17.0% | 14.5% | 12.0% | 2.0%   |
| H$_2$ | 2.8%  | 2.95% | 3.1%  | 3.7%   |
| H$_2$O| 1.7%  | 1.45% | 1.2%  | 0.3%   |
| etaCO| 38.6% | 33.0% | 27.3% | 4.5%   |
| etaH$_2$| 37.8% | 33.0% | 27.9% | 8.2%   |

Table 2. Gas compositions at experiments.

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| Table 1. Composition of iron ore pellets, sinter and lump ore. |
|-----------------|-----------------|-----------------|
|                 | Pellet          | Sinter          | Lump ore       |
| Fe(tot)         | 64.59           | 56.30           | 67.92           |
| FeO             | 0.10            | 6.80            | 4.60            |
| CaO             | 1.20            | 11.10           | 0.03            |
| SiO$_2$         | 6.00            | 5.80            | 2.00            |
| Al$_2$O$_3$     | 0.39            | 1.20            | 0.37            |
| MgO             | 0.73            | 1.60            | 0.04            |
| S               | 0.007           | 0.021           | 0.068           |
| Na$_2$O         | 0.09            | 0.06            | <0.06           |
| K$_2$O          | 0.05            | 0.04            | <0.002          |
| B2=CaO/SiO$_2$  | 0.20            | 1.91            | 0.01            |

Figure 1. A sketch of a blast furnace simulator (BFS). Layout of the BFS: (1) mass flow controllers; (2) gas inlet; (3) reduction tube; (4) sample basket; (5) thermocouple; (6) electrically heated furnace; (7) scale for TGA and (8) computer system.
Figure 2. Bauer-Glaessner diagrams for used atmospheres and temperatures using a) etaCO, b) etaH$_2$ and c) a combination of both.

Diagrams show the most stable phase of iron at each experimental temperature. The most stable phase will be reached if the experimental time is sufficient.

Furthermore, it can be seen from the Bauer-Glaessner diagrams that the gas compounds including hydrogen and carbon are not in equilibrium at 700°C.

3. Results and discussion

Reduction degree was calculated from the experimental results using equation 2. Reduction degree for sinter, lump ore and iron ore pellet is presented as

$$ R = \frac{m_1 - m_2}{m_1 (0.430w_2 - 0.111w_1)} \cdot 10^4, \quad (2) $$

where

$m_1$ is the mass of the sample before reduction,

$w_1$ is the iron (II) oxide content as a percentage by mass in the sample prior to the test obtained from chemical analysis and

$w_2$ is the total iron content as mass-% in the sample prior to the test obtained from chemical analysis.

Reduction degrees as a function of time in all temperatures (700°C, 800°C, 900°C and 1000°C) for iron ore pellet, sinter and lump ore can be seen in Figure 3. It can be seen that lump ore has the slowest reduction rate at all temperatures. Pellets were the fastest to reduce in 700°C, but already in 800°C sinter bypasses it. Sinter has the highest reduction degree in temperatures 900°C and 1000°C.
Figure 3. Reduction degree as a function of time for iron ore pellet, sinter and lump ore in 700°C, 800°C, 900°C and 1000°C.
Figure 4. Optical microscope images of samples of pellet, sinter and lump ore reduced in different temperatures.

Microscope images, Figure 4, show that sinter has the most porous structure. This structure enables the gas flow to reach the sinter throughout. This is one explanation why in the higher temperatures sinter reduces fastest when compared to pellet and lump ore. In the lowest researched temperature (700°C)
pellet reached highest reduction degree during the whole experiment.

The lump ore is the slowest to reduce in all measured temperatures. This could be because the sample size is largest. Even when the mass of all experimented iron bearing materials is around 100 g, the number of samples for lump ore is only 2 whereas for pellets it is 30 and for sinter 19. This means that the size of a lump ore is greatest when compared with the pellet and sinter. Combining this size information with the structure information (Figure 4) it yields that lump ore has the smallest reaction surface area with which the gases can have an influence with.

One reason why sinter reduces faster in higher temperatures could be as following. When looking at the chemical composition of the pellet, sinter and lump ore, see Table 1, it can be seen that total amount of iron is over 50% in all. It was verified with FESEM that this iron comes from hematite and magnetite. This happens because the characteristics of the sintering and pelletizing processes as well as, in case of lump ore, wüstite is not present in nature. Furthermore, it can be seen that the sinter has largest proportion of magnetite. Even though magnetite has less oxygen to remove by reduction, hematite reduces easier. This is because the different crystal structure of the iron oxides. [12] The magnetite in sinter reduces slower first yielding higher reduction in pellet in lower temperatures.

The gas compositions vary as function of temperature. When looking the composition from the perspective of reactive gases, carbon monoxide and hydrogen, the reductive gases amount increase. Carbon monoxide amount rises from 27 % to 42 % and hydrogen rises from 2.8 % to 3.7 %. This change in temperature and gas composition simulates the descend of charge material inside the blast furnace. In the upper part of the furnace the temperature as well as the proportion of reducing gases are lower than in the lower part of the blast furnace. This probably is also one reason why the sinter reduces fastest in the highest temperature. When looking at the Bauer-Glaessner diagrams in Figure 2, it can be seen that the composition point shifts further from the phase border to the side of metallic iron when temperature rises.

All in all, it is interesting to see that in lower temperatures iron ore pellets are the ones to reduce fastest compared with sinter and lump ore. This order changes in higher temperatures such that sinter bypasses the iron ore pellets, while lump ore stays the last.

From the reduction point of view the optimal relation between iron ore pellets, sinter and lump ore in blast furnace is such that the amount of lump ore should be least. Thus, this already used procedure in practice can be confirmed.

As mentioned earlier in addition to reduction behavior the softening behavior of iron bearing materials is important in an industrial blast furnace. This research focused only on the reduction behavior and thus the next researched topic should be the softening behavior.

4. Conclusions

This research focused on the conditions in the dry part of the blast furnace shaft and how different temperatures combined with simulated gas compositions from blast furnace effect the reduction behavior of iron bearing materials (iron ore pellets, sinter and lump ore) prior reaching the cohesive zone. Tests were made in four different temperatures (700°C, 800°C, 900°C and 1000°C). It was seen that in lower temperatures and the gas composition tied to those, iron ore pellets are the fastest to reduce, while sinter and lump ore follow behind. In higher temperatures the sinter bypasses the iron ore pellets and lump ore stays the last in all cases. The reasons behind this reduction behavior are following: 1) the lump ore is slowest to reduce in all temperatures because it has the smallest surface area and the structure is not porous, 2) compared to iron ore pellet and lump ore, sinter has highest proportion of magnetite, which is not as easily reduced as hematite at low temperatures.

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Abbreviations

| Abbreviation | Description                      |
|--------------|----------------------------------|
| BFS          | Blast furnace simulator          |
| BF           | Blast furnace                    |
| FESEM        | Field emission scanning electron microscope |
| TGA          | Thermogravimetric analysis       |
| XRF          | X-ray fluorescence               |
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