Iron Ore Reduction in a Laboratory-scale Fluidized Bed Reactor —Effect of Pre-reduction on Final Reduction Degree

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Fluidized bed processes for iron ore reduction (e.g. FIOR®, FINMET®, FINEX®) operate in a continuous multi-staged countercurrent mode. To optimize iron ore reduction, different operating conditions occur in each stage. Significant influence of the first reduction stage on the final reduction degree was observed in industrial plant. The iron ore particles seem to “memorize” the precursor autoclave conditions.

To optimize iron ore reduction, as well as to develop new reduction processes, it is necessary to understand this phenomenon. Industrial plants operate on pressures up to 12 bar and temperatures up to 900°C. So a laboratory-scale pressurized fluidized bed reactor was built to perform experiments similar to industrial conditions.

Two-stage experiments with Mt. Newman hematite ore from Western Australia at variable operating conditions show significant influences of temperature and residence time of the pre-reduction stage on the final reduction degree. Microscopical analysis showed the influence of mineralogy and texture on the reduction behavior of original respectively partly reduced iron ore. Formed magnetite in the pre-reduction stage causes a degradation of final reduction degree. Additionally the amount of newly formed magnetite depends on pre-reduction temperature, composition of the reducing gas and residence time.

KEY WORDS: iron ore reduction; pressurized fluidized bed; high pressure; mineralogy; texture.

1. Introduction

To compensate the decrease of available high quality steel scrap, DRI (direct reduced iron) becomes an important feed material in electric arc furnaces. Using DRI for this application certain requirements on quality (e.g. reduction degree, metallization) are demanded.

Direct reduction processes operate in shaft furnaces, rotary kilns and fluidized beds. The reduction in fluidized bed reactors offers the advantages of no feed agglomeration, uniform temperature in the reactor and excellent heat and mass transport. Some of these fluidized bed processes produce hot briquetted iron (e.g. FINMET®, FIOR® and Circored process), whereas others produce iron carbide (Fe₃C). The second application of fluidized bed reactors in iron ore reduction is the prereduction stage in smelting reduction processes (e.g. FINEX®2,3). The reduction processes use a reducing gas produced by steam reforming of natural gas or coal gasification. Thus the reducing gas is a mixture of H₂, H₂O, CO, CO₂, CH₄ and N₂.

The industrial fluidized bed processes (FINMET®, FIOR®, FINEX®) operate in a multi-staged countercurrent mode at elevated pressures (Fig. 1). Both the gas composition and temperature are different in each stage caused by the reduction progress. Consequently thermodynamic conditions are changing in each stage.

Based on experience from industrial units, pre-reduction shows a significant influence on the final reduction degree 4).

The scope of this work is to elucidate the underlying mechanism of pre-reduction at different thermodynamic conditions with a fine iron ore in a laboratory scale pressurized fluidized bed reactor under well defined conditions similar to industrial scale fluidized bed reduction conditions.

2. Experimental

2.1. Experimental Setup

To investigate the influence of the pre-reduction stage under conditions similar to industrial-scale processes a pressurized fluidized bed reactor was developed according to similarity rules. The operating conditions of the pressurized fluidized bed reactor can be summarized as following:

• absolute pressure up to 10 bar
• temperature range from 623 to 1 173 K
• reducing gas contains H₂, H₂O, CO, CO₂, CH₄ and N₂

The concept of the “reactor in pressure vessel” as described by Habermann et al. was chosen.

The fluidized bed reactor operates in batch mode. So the
investigation of the iron ore reduction kinetics requires a differentially operating reactor. This was obtained by choosing an appropriate sample weight to get a high gas–solid-ratio.

The concept of the experimental setup is shown in Fig. 2:

The fluidized bed reactor and the electrical heating elements were set into the pressure vessel to avoid pressure difference at the hot reactor walls (up to 1 173 K).

The reducing gas was stored in gas bottles and the gas mixture was provided by mass flow controllers. For adding water vapor to the gas mixture at elevated pressure the distilled water was delivered with a HPLC-pump through a heated sinter bar. This apparatus provides a homogeneous vaporization and a constant mass flow of water was possible at high pressure. To prevent condensation of water in the gas pipe lines at high pressure, all the lines were insulated and heated.

Three main gas lines are completed:
- pressure vessel gas line
- preheating gas line
- reducing gas line

The iron ore was submitted in the reactor under low N₂-flow. Both the reactor and the pressure vessel were pressurized with N₂ (preheating and pressure vessel gas line). The pressure in the pressure vessel was regulated to minimize the pressure difference between the fluidized bed reactor and the pressure vessel. After reaching the required pressure, the reactor was heated up. At constant temperature the

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N₂-flow was increased to get a bubbling fluidized bed. Meanwhile the gas was mixed in the reducing gas line. The gas mixture was by-passing and burned in the chimney until demand temperature and pressure in the fluidized bed reactor as well as the reducing gas concentrations were reached. The gas concentrations were checked by using fourier transform infrared (FTIR) spectroscopy and after reaching constant conditions the preheating gas (N₂) was changed to reducing gas.

After the demanded residence time the reducing gas was changed back to N₂, the pressure decreased to atmospheric condition and simultaneously the iron ore was cooled down with pure nitrogen to prevent reoxidation. The reduced iron ore samples were removed and analyzed by titrimetric method (iron chlorid method) for total Fetot, Fe⁰ and Fe²⁺.7)

To obtain knowledge about structural changes, polished sections of raw iron ore particles as well as of reduced iron ore particles were investigated in reflected light on a Leitz MM6 largefield metallographic microscope.

2.2. Reduction Tests

To investigate the influence of pre-reduction on final reduction degree two-stage experiments were carried out. In the first stage pre-reduction conditions similar to the industrial process were simulated, in the second stage the iron ore was reduced at final reduction conditions.

The reduction tests were carried out with Mt. Newman hematite ore from Western Australia (Table 1) at different temperatures and residence times. Standard operating conditions were defined from which temperatures and residence times of the pre-reduction stage were varied. Afterwards the samples were reduced under final reduction conditions in the final reduction stage (Table 2). The concentrations of H₂O, CO, CO₂ and CH₄ as well as the run of temperature, mass flow and pressure were recorded.

2.3. Determination of the Degree of Reduction

The progress of reduction can be described by the molar ratio of oxygen to iron as given in Eq. (2).

\[ X = \frac{\text{mol O}}{\text{mol Fe}} \quad \text{(1)} \]

The reduction degree is calculated by the following term

\[ R = \left( 1 - \frac{X}{1.5} \right) \times 100 \% \quad \text{(2)} \]

\[ X \] is calculated with Fetot, Fe⁰, Fe²⁺ and Fe³⁺ (by difference) determined by the iron-chlorid method.7)

\[ X = \frac{1}{2} \frac{2 \cdot \text{Fe}^{2+} + 3 \cdot \text{Fe}^{3+}}{\text{Fetot}} \quad \text{(3)} \]

2.4. Morphological Investigation

Polished sections of raw iron ore as well as of the reduced material were investigated in reflected light on a Leitz MM6 largefield metallographic microscope with an attached Nikon A101CP digital camera. Its 2/3"-CCD color image sensor features a resolution of 1300×1300 pixels.

In contrast to magnetite, hematite is optically anisotropic. Some images were taken with polarized light and partly crossed polarizers. So intergrown hematite crystals cut in different crystallographic planes could be distinguished by their brightness.

3. Results and Discussion

Standard conditions of pre-reduction and final reduction were defined as shown in Table 2.

Starting from standard conditions, temperature and residence time of the pre-reduction stage were varied. Final reduction conditions were the same for all experiments.

3.1. Variation of Temperature in Pre-reduction Stage

The curve trace of the final reduction degree shown in Fig. 3 results from variation of temperature in the pre-reduction stage.

The final reduction degree decreases with increasing pre-

\begin{table}
\centering
\caption{Chemical analysis of the Mt. Newman hematite ore in mass%}
\begin{tabular}{llllllllll}
\hline
Ore & Fe₂O₃ & FeO & CaO & MgO & SiO₂ & Al₂O₃ & TiO₂ & P & S & LOI \\
\hline
Mt. Newman & 67.9 & 96.98 & 0.09 & 0.08 & 0.05 & 1.46 & 0.7 & 0.04 & 0.04 & 0.7 \\
\hline
\end{tabular}
\end{table}

LOI: Loss on ignition. FeO refers to divalent iron present in magnetite.

\begin{table}
\centering
\caption{Operating conditions; framed: standard operating conditions.}
\begin{tabular}{llll}
\hline
 & pre-reduction stage & final reduction stage \\
\hline
p [bar] & 350 & 10° & 10° & 780° & 780° \\
T [°C] & 400 & 10° & 780° & 780° \\
τ [min] & 500 & 20° & 54° & 54° \\
H₂ [vol%] & 46° & 50° & 7.5° & 7.5° \\
H₂O [vol%] & 19° & 46° & 7.3° & 7.3° \\
CO [vol%] & 5.5° & 3.7° & 1.4° & 1.4° \\
CO₂ [vol%] & 19.6° & 6.2° & 21.3° & 21.3° \\
CH₄ [vol%] & 6.2° & 8.5° & 8.5° & 8.5° \\
N₂ [vol%] & 8.5° & 8.5° & 8.5° & 8.5° \\
\hline
\end{tabular}
\end{table}
reduction temperature up to 500°C. Then, at higher temperature final reduction degree increases up to a prereduction temperature of 650°C and decreases again with a further increase of the pre-reduction temperature.

To understand this phenomenon, the reduction conditions of the pre-reduction stage were plotted in the Baur-Glaessner-figure for a H₂/H₂O gas mixture (Fig. 4). The Baur-Glaessner-figure was calculated from thermodynamic data.8,9) For gas mixture of H₂, H₂O, CO, CO₂, CH₄ and N₂ with CO concentration less than 10 vol% 6,8) and \( P_{H₂}/P_{H₂O} > P_{CO} \) reduction with H₂ is the dominating reaction.

The boundaries of iron oxide equilibrium phases are plotted in the curve trace of the final reduction degree versus prereduction temperature and are shown in Fig. 3.

In magnetite equilibrium phase in the prereduction stage the final reduction degree decreases with increasing prereduction temperature from 350 to 500°C. Close to the wuestite equilibrium phase the final reduction degree increases and comes up to a maximum in the wuestite equilibrium phase. Prereduction in iron equilibrium phase causes a rapidly decreasing final reduction degree with increasing prereduction temperature.

To improve the understanding for the different reduction behavior depending on prereduction temperature respectively different equilibrium phases, polished sections of original ore as well as of the partly-reduced material were investigated.

### Ore Feed

The Mt. Newman iron ore grains mainly consist of Fe₂O₃ occurring in different types:

1. Coarse sized hematite (50–200 μm crystal size) (Fig. 5(a))
2. Fine and medium sized hematite = microplaty hematite (<50 μm crystal size) (Fig. 5(b))
3. Martite (2–20 μm crystal size) (Fig. 5(c))
4. Limonite (<2 μm crystal size) (Fig. 5(d))

Combination of ore types:

(a) Intergrowth of limonite, martite and microplaty hematite
(b) Intergrowth of limonite and martite

Magnetite is quantitatively negligible.

### Prereduction

Figure 6 shows reduced iron ore after pre-reduction for different temperatures.

At 350°C (Fig. 6(a)) former limonite only is reduced to magnetite, the other types of hematite remain unreacted. With increasing temperature the fraction of magnetite increases and at a temperature of 500°C nearly the entire hematite is reduced to magnetite (Fig. 6(b)). Only a few enclaves of unreduced hematite occur. The originated magnetite shows a dense texture which has a significant influence on final reduction degree. Prereduction at 650°C—conditions in wuestite equilibrium phase—generates porous wuestite (Fig. 6(c)). Reduction in iron equilibrium phase (Fig. 6(d)) causes area of wuestite and iron. Iron encloses small wuestite areas and obdurate pores. This implicates a decrease in specific surface area (Fig. 7) and in consequence of this low final reduction degree occurs.

### Final Reduction

Final reduction is carried out in iron equilibrium phase. So each iron oxide phase—hematite, magnetite, wuestite and iron—generated in the pre-reduction stage is reduced to iron.

Former hematite is transformed to iron with small grains and fine pores with less wuestite enclaves (Fig. 8(a)).

Former magnetite becomes large dense wuestite grains with iron rims. Only small areas are reduced to iron totally (Fig. 8(b)). Dense magnetite causes large dense wuestite areas in final reduction stage and therefore low final reduction degree.

Generated wuestite from pre-reduction stage becomes fine-pored iron (Fig. 8(c)). Caused by surrounding dense iron enclosed wuestite from pre-reduction at 800°C was reduced very slow and together with low specific surface area low final reduction degree occurs.

### 3.2. Variation of Residence Time

Starting from the standard operating conditions (Table 1) the residence time in the pre-reduction stage was varied.

The pre-reduction was carried out at magnetite equilibrium at 450°C (Fig. 4).

Increasing residence time in the pre-reduction stage causes a decrease in the final reduction degree (Fig. 9). This phenomenon can be explained by the magnetite formed in the pre-reduction stage. The quantity of mag-
Fig. 5. Different types of hematite: (a) coarse sized hematite, (b) microplaty hematite (MPH), (c) martite, (d) limonite (integrowth with martite).

Fig. 6. Reduced iron ore after prereduction; $\tau=20$ min: (a) 350°C: light area: hematite; dark area: magnetite; black area: pores, (b) 500°C: light area: hematite (arrows); grey area: magnetite; black area: pores, (c) 650°C: wuestite, (d) 800°C: light area: iron; dark area: wuestite; black area: pores.
netite after pre-reduction depends on the residence time. 

Figure 10 shows polished sections of the reduced iron ore after pre-reduction and the final reduction stage. There it can be seen, that dense magnetite from pre-reduction results in large dense wuestite grains with iron borders (Figs. 10(c) and 10(f)). Hematite from pre-reduction becomes iron consisting of fine-pores iron. So the final reduction degree depends on the quantity of magnetite.

4. Conclusions

Fine iron ore was reduced in a laboratory-scale pressurized fluidized bed reactor at an absolute pressure of 10 bar. Two-stage experiments were carried out to investigate the influence of pre-reduction conditions on the final reduction degree. Starting from standard operating conditions the temperature (350 to 800°C) and the residence time (10 to 60 min) of the pre-reduction stage were varied. Final reduction conditions were the same for all experiments. The final reduction degree was measured by a titrimetric method (iron chlorid method). Polished sections of original iron ore as well as of the reduced material were investigated and the following conclusions could be drawn:

1) Pre-reduction has a significant influence on the final reduction degree. The iron ore particles seem to “memorize” their pre-treating step.

2) It’s important how long and in which iron oxide phase equilibrium pre-reduction is carried out (magnetite-, wuestite-, iron equilibrium phase).
   a. Hematite is better reducible than magnetite.
   b. In pre-reduction stage generated magnetite has a negative influence on final reduction. Low final reduction degree occurs. Following from dense magnetite generated in pre-reduction stage large grains of dense wuestite with iron border occur. Magnetite-formation depends on temperature and residence time. At low
temperature (350°C, 400°C) few magnetite is generated in pre-reduction stage. At 500°C almost all hematite is transformed to magnetite. Close to wuestite equilibrium phase also wuestite is generated and has a positive influence on final reduction.

c. Compared to magnetite wuestite generated in the pre-reduction stage is better reducible. Wuestite shows a fine-pored structure which causes fine-pored iron in final reduction stage.

d. When pre-reduction is carried out in iron equilibrium phase wuestite and wuestite-enclaves enclosed by iron occur. Specific surface area of reduced iron ore in pre-reduction decreases and in combination with wuestite-enclaves final reduction degree decreases.

(3) Pre-reduction has a significant influence on reduced iron ore texture.

(4) In Pre-reduction stage generated magnetite has a dense texture which inhibits final reduction.

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