Reduction Behavior of Hematite to Magnetite under Fluidized Bed Conditions

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Reduction kinetic tests of Mt. Newman hematite ore from Western Australia were carried out in a laboratory-scale fluidized bed reactor at temperatures from 623 to 873 K and an absolute pressure of 10 bar. The reducing gas mixture was thermodynamically in equilibrium with magnetite and consisted of a mixture of H2, H2O, CO, CO2 and CH4. The effect of temperature and residence time was studied. The original ore and its mineralogical and petrographical changes with increasing reduction time were analyzed. A reflected light microscope technique with CCD-camera was used to determine the progress and the mechanism of reduction. According to the mineralogy and texture the ore could be classified in four types (coarse hematite, microplaty hematite, limonite and martite) with different reduction characteristics. Limonite and martite showed better reducibility than coarse and fine hematite.

At all ore types the growth of dense magnetite rims was observed. The thickness of these layers was found to be in linear proportion to reduction time. After analyzing the single steps of the reduction process the phase interface reaction turned out to be rate controlling between 673 and 773 K. Its activation energy is 91 kJ/mol.

KEY WORDS: iron ore reduction; fluidized bed; hematite; magnetite; elevated pressure; rate controlling step.

1. Introduction

The capacity of DRI (direct reduced iron) producing plants is increasing continuously to satisfy the upcoming demand on scrap substitutes as feed material in electric arc furnaces. In 1985 the annually produced DRI exceeded 10 million tons, in 1992 20 million tons and in 1999 38 million tons.1,2) One branch of processes reduces fine iron ore directly with steam-reformed natural gas in fluidized bed reactors (e.g. the Circored®, the FIOR®- and the FINMET®- process).3) Installed capacities are 5.2 million tons per year (in 2000). The reduction in fluidized bed reactors offers the advantages of uniform temperature in the reactor, excellent heat and mass transport and the direct feed with cheap fine iron ore without agglomeration.

In the 1960’s investigations on the fluidized bed reduction of iron ore fines by pure H2 or H2/N2-mixtures were started.4–12) One branch of processes reduces fine iron ore directly with steam-reformed natural gas in fluidized bed reactors (e.g. the Circored®, the FIOR®- and the FINMET®- process).3) Installed capacities are 5.2 million tons per year (in 2000). The reduction in fluidized bed reactors offers the advantages of uniform temperature in the reactor, excellent heat and mass transport and the direct feed with cheap fine iron ore without agglomeration.

In the 1960’s investigations on the fluidized bed reduction of iron ore fines by pure H2 or H2/N2-mixture were started.4–12) The reduction processes use reducing gas produced by steam reforming of natural gas consisting of H2, H2O, CO, CO2, N2 and CH4. Thus a strong interest in kinetics of reduction by a reducing gas containing CO2, CO and CH4 exists. Some authors tested the kinetics of reduction by mixtures of H2, CO and CO2 and H2O.13–17) others the carburization of iron ore fines by adding CH4 to the reducing gas.18,19) Industrial scale fluidized bed reduction units operate at elevated pressure, but only a few kinetic studies for the reduction of iron ore in fluidized beds were done at such conditions.20–23)

Moreover it was shown that the first reduction step from hematite to magnetite had significant influence on the achievable final metallization degree.24) In order to provide better understanding of the fine iron ore reduction, experiments with Mt. Newman hematite ore from Western Australia were conducted in a laboratory-scale fluidized bed reactor in batchwise operation. A mixture of CO, CO2, H2O, H2, N2 and CH4 was used as reducing gas which was thermodynamically in equilibrium with magnetite. The experiments were carried out under elevated pressure (10 bar absolute). So the first reduction step could be investigated similar to industrial conditions. Residence time and reaction temperature were varied. By the means of microscopical analysis the growth of dense magnetite shells could be observed, and their thickness was measured in order to determine the rate controlling step and its kinetics.

2. Physical and Chemical Processes

The iron ore grains are fluidized in the reactor. According to various observations and theories a bubbling fluidized bed can be divided into an emulsion and a bubble phase.25) The gas of the emulsion phase directly reaches the gas boundary layer surrounding each grain, the gas of the
bubble phase partially passes over to the emulsion phase before reaching the gas boundary layer of the grains. The reducing gas components (H\textsubscript{2} and CO) diffuse through the pores of the grain, step 4: phase interface reaction at the crystal surface and diffusion of iron ions through dense magnetite layers.

$3\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$ .................(1)

$3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$ ..................(2)

The actual heterogeneous reaction is illustrated in Fig. 2. During the tests dense magnetite layers grew concentrically around the hematite core. The reduction gas is not able to permeate through the magnetite layer, thus the oxygen atoms are removed from the external surface of the magnetite lattice:

$\text{H}_2 + \text{O}^2- \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ .................(3)

$\text{CO} + \text{O}^2- \rightarrow \text{CO}_2 + 2\text{e}^-$ ...................(4)

Two electrons remain in the lattice and reduce Fe\textsuperscript{3+} to Fe\textsuperscript{2+} (Reaction (5)). Due to a gradient of iron activity (Fig. 2: a\textsubscript{1} higher than a\textsubscript{2}) iron cations and electrons diffuse through the magnetite layer to the hematite core where they form additional magnetite:

$4\text{Fe}_2\text{O}_3 + \text{Fe}^{2+} + 2\text{e}^- \rightarrow 3\text{Fe}_3\text{O}_4$ .................(5)

The actual reaction step is the reduction of Fe\textsuperscript{3+} to Fe\textsuperscript{2+} with one electron:

$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ ..............................(6)

The gradient of oxygen activity in the magnetite layer is located in reverse direction. Oxygen would diffuse from the internal border of the magnetite to the external border, but the mobility of the oxygen anions in magnetite and wuestite is negligible in comparison with the iron cations.\textsuperscript{26}

The gaseous reaction products (CO\textsubscript{2} and H\textsubscript{2}O) migrate the way back to the emulsion phase (Fig. 1 – step 5, 6 and 7) where they can be removed from the fluidized bed by the gas flow. The physical and chemical processes are summarized by Bogdandy and Engell.\textsuperscript{27}

3. Experimental

The reduction tests were carried out in a laboratory-scale fluidized bed reactor in batch-wise operation. To ensure homogenous conditions the reactor is operated as differential reactor, i.e. gas concentration and temperature can be considered as constant within the reactor volume. Therefore high excess of reducing gas is required. The internal reactor diameter is 40.3 mm, the superficial velocity is 0.23 m/s. Detailed information on the experimental setup is given in an earlier work.\textsuperscript{13} An overview of the operating conditions is given in Table 1.

The sample was heated up within 30 min under constant purge of nitrogen. At the defined temperature and pressure the nitrogen flow was switched to the pre-mixed flow of reduction gas. The concentration of CO\textsubscript{2}, CO, H\textsubscript{2}O and CH\textsubscript{4} were measured in the flue gas of the fluidized bed reactor every 10 seconds via FT-IR spec-
troscopy in combination with a long-path length, low-volume heated gas cell. At the end of the reduction test the fluidizing gas was switched back to pure nitrogen and the reactor was cooled down to ambient temperatures. All tests were carried out with 80 g of Mt. Newman hematite ore from Western Australia. Chemical analysis and physical properties of the ore are listed in Table 2 and Table 3. The following grain size fractions were used in the tests: 50 wt% 125–250 μm and 50 wt% 250–500 μm.

4. Microscopical Analysis

4.1. Methodology

Polished sections of raw 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 1300×1030 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 (e.g. Fig. 3).

Some definitions are discussed by means of Fig. 3. A grain is a particle of ore which is not connected mechanically to other pieces of ore. Only in rare cases it is homoge-


tous. In contrast to that a crystal is a homogenous part of a grain. The term ore type refers to a cluster of crystals of the same type.

4.2. Ore Feed

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

1. Coarse sized hematite (50–200 μm crystal size)—Fig. 4.
2. Fine and medium sized hematite=micropaty hematite (<50 μm crystal size)—Fig. 5.
3. Martite (2–20 μm crystal size)—Fig. 6.
4. Limonite (<2 μm crystal size)—Fig. 7.

Combination of ore types:

(a) Intergrowth of limonite, martite and micropaty hematite.
(b) Intergrowth of limonite and martite—Fig. 7.

Magnetite is quantitatively negligible (Table 2).

4.3. Ore after Reduction Tests

The reduction progress is very sensitive to temperature.
variation. At 623 K very few grains contain traces of magnetite. Only limonite and sometimes martite show signs of reduction. At 673 K and higher temperatures dense magnetite layers are generated during the reduction (Fig. 8). They surround single crystals as well as groups of crystals without interstitial pores which are packed very close together and thus do not permit the transport of reducing gas between them. Sometimes pores can be observed where only a part of their surface is reduced to magnetite (Fig. 9). These pores are closed and, therefore not accessible for the reducing gas. Moreover this observation proves that the reducing gas is not permeating the dense magnetite layer, otherwise the whole pore surface would show signs of reduction. Therefore oxygen removal has to take place at the external surface of the magnetite layer.

The magnetite layers grow from the external surface of a crystal or crystal group inwards and have a sharp border to the remaining hematite core. In the majority of cases the magnetite thickness at crystals situated in the center of a grain, and crystals at the external grain surface is the same (Fig. 10). Therefore gas diffusion within pores of a grain is not limiting the reduction process.

The reducibility of a grain strongly depends on the contained ore types. Ores containing fine crystals like limonite and martite are reduced faster than coarse and medium sized hematite (Fig. 11). After 20 min reduction time limonite is totally reduced at 723 K, martite and microplaty hematite at 773 K. In contrast to microplaty hematite, martite shows higher reduction rate at lower temperatures. Coarse hematite crystals still show some unreduced cores at 773 K. The observations are summarized in Table 4.

In order to quantify the reduction progress the thickness of the magnetite layers was measured. As it can be seen in the sections, the thickness is varying due to the natural geometry of the crystals. The measurements were taken from crystals situated at the surface of a grain to exclude any influence of pore diffusion within the grain. Moreover the thinnest layer thickness of one crystal was used. Parts of
the layer which appear thicker in the section can be generated by higher diffusion portions perpendicular to the section plane.

5. Results and Discussion

5.1. Magnetite Layer Thickness

The measured values are summarized in Table 5. The layer thickness at 773 K is plotted versus reduction time in Fig. 12. A clear positive linear correlation was observed. At 623 K no magnetite layers were found, at 823 and 873 K the hematite crystals were reduced completely.

5.2. Limiting Step

As discussed in Sec. 4.3 gas diffusion in the pore system is not the rate controlling step of the process. If diffusion of iron ions (Fe²⁺) through the magnetite layer would limit the reduction, the layer thickness would have been proportional to the square root of reduction time. To achieve this dependence the bulk diffusion through plane layers can be considered. This is a good approximation for grains with thin magnetite layers in relation to their diameter. The change of volume during the reduction is 1.5%, and thus is negligible for the kinetics. After Reaction (4) the specific diffusion flow of iron ions causes magnetite growth.

Fig. 10. Polished section of a partly reduced grain. Reaction conditions: Variation 3 (T=723 K; t=20 min). The magnetite layer thickness is not varying with its position inside the grain. Thus the pore diffusion is not limiting the process. Grey=magnetite, light grey=hematite, dark grey=resin, black=void.

Fig. 11. Polished section of a partly reduced grain. Reaction conditions: Variation 2 (T=673 K; t=20 min). Original limonite structure (Lim) is completely reduced to magnetite. Other ore types show magnetite layers of about 3 μm in thickness. Grey=magnetite, white=hematite, dark grey=resin, black=void.

Table 4. Reduction progress of each ore type after 20 min reduction time. Reduction conditions according to Table 1.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Limonite</th>
<th>Martite</th>
<th>Microporpy Hematite</th>
<th>Coarse Hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>xx</td>
<td>x</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>873</td>
<td>xxx</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>723</td>
<td>xxx</td>
<td>xx</td>
<td>xx</td>
<td>xx</td>
</tr>
<tr>
<td>773</td>
<td>xxx</td>
<td>xxx</td>
<td>xxx</td>
<td>xx</td>
</tr>
<tr>
<td>823</td>
<td>xxx</td>
<td>xxx</td>
<td>xxx</td>
<td>xxx</td>
</tr>
<tr>
<td>873</td>
<td>xxx</td>
<td>xxx</td>
<td>xxx</td>
<td>xxx</td>
</tr>
</tbody>
</table>

Symbols:
- No signs of reduction observable.
- x Some grains are partly reduced, some without signs of reduction.
- xx Some grains are totally reduced, some partly.
- xxx All grains are totally reduced.

*Apart from magnetite, wuestite and few very small iron seed crystals (less than 0.5μm in size) can be observed.

Table 5. Measured magnetite layer thickness in μm. Var=variation/MAX=Maximum of the measured values/MIN=Minimum of the measured values/AV=average value/SD=absolute standard deviation/SD-rel=relative standard deviation related to the average value. The number of measurements was between 18 and 53 for each variation.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Var.</th>
<th>MAX</th>
<th>MIN</th>
<th>AV</th>
<th>SD</th>
<th>SD-rel</th>
</tr>
</thead>
<tbody>
<tr>
<td>673K - 20 min</td>
<td>2</td>
<td>3.7</td>
<td>1.7</td>
<td>2.5</td>
<td>0.5</td>
<td>21%</td>
</tr>
<tr>
<td>723K - 20 min</td>
<td>3</td>
<td>8.0</td>
<td>3.0</td>
<td>5.0</td>
<td>1.3</td>
<td>25%</td>
</tr>
<tr>
<td>773K - 20 min</td>
<td>4</td>
<td>27.7</td>
<td>14.9</td>
<td>20.8</td>
<td>3.6</td>
<td>17%</td>
</tr>
<tr>
<td>723K - 10 min</td>
<td>7</td>
<td>6.0</td>
<td>2.3</td>
<td>3.7</td>
<td>0.9</td>
<td>25%</td>
</tr>
<tr>
<td>723K - 60 min</td>
<td>8</td>
<td>21.5</td>
<td>11.5</td>
<td>16.8</td>
<td>3.2</td>
<td>19%</td>
</tr>
</tbody>
</table>

Fig. 12. Average magnetite layer thickness after reduction at 723 K and 10 bar. Reduction conditions according to variation 7, 3 and 8 (10, 20 and 60 min reduction time).
According to Fick's Law the specific diffusion molar flow of iron ions is determined by:

$$j_{Fe} = \frac{1}{3} \cdot \frac{df_{M_{Mag}}}{dt}$$  \hspace{1cm} (7)

The activity difference across the magnetite layer $\Delta a_{Fe}$ is constant because the conditions at the hematite core and at the external surface of the layer are not varying in the considered case.

The change of magnetite can be described as:

$$\frac{dn_{M_{Mag}}}{dt} = \frac{\rho_{M_{Mag}}}{M_{Mag}} \cdot A \cdot dx$$  \hspace{1cm} (9)

Equations (7) to (9) lead to the dependency mentioned above:

$$x(t) = \left[ 6 \cdot D_{Fe} \cdot \frac{M_{Mag}}{\rho_{M_{Mag}}} \cdot \Delta a_{Fe} \cdot t \right]$$  \hspace{1cm} (10)

If reduction is more advanced, the process is better described by a diffusion model through spherical layers. The development of spherical layers can only be expressed implicitly:

$$r = \frac{1}{18} \left( \frac{2r^3}{R} - 3r^2 + R^2 \right) \cdot \frac{\rho_{M_{Mag}}}{D_{Fe} \cdot M_{Mag} \cdot \Delta a_{Fe}}$$  \hspace{1cm} (11)

In Fig. 13 Eqs. (10) and (11) are compared. At the beginning there is no difference in reduction progress between spheres and planes. With increasing layer thickness spherical layers grow faster because of their decreasing inner surface at the border to the hematite core. Between 0 and 0.6 relative layer thickness the reduction time is in line with a square root function. After 60 min reduction time the observed grains show relative layer thicknesses of about 0.3 to 0.5 at the most. Thus neither the layer development of spheres nor of planes with limiting bulk diffusion of iron ions through the magnetite layer correlates with the measured thicknesses.

In the case of a limiting phase interface reaction, the amount of removed oxygen $n_{O}$ per time can be described by:

$$\frac{dn_{O_{H_{2}}}}{dt} = A \cdot k_{H_{2}}(T) \cdot (p_{H_{2}} - p_{H_{2}}^{\infty})$$  \hspace{1cm} (12)

$$\frac{dn_{O_{CO}}}{dt} = A \cdot k_{CO}(T) \cdot (p_{CO} - p_{CO}^{\infty})$$  \hspace{1cm} (13)

It was shown\textsuperscript{13} that low concentrations of CO (up to 10%) in $H_{2}$ did not affect the rate of reduction. The reason for this is the relatively slow reaction properties of CO in comparison with $H_{2}$. So the simplified equations are as following:

$$\frac{dn_{O}}{dt} = A \cdot k_{ph}(T) \cdot \left( p_{ph}(T) - p_{H_{2}}^{\infty} \right)$$  \hspace{1cm} (14)

With the stoichiometric correlations of Reaction (1) at supposed plane geometry the magnetite layer thickness is:

$$x(t) = 2 \cdot \frac{K_{ph}}{M_{Mag}} \cdot \frac{\rho_{M_{Mag}}}{\rho_{ph}} \cdot t$$  \hspace{1cm} (15)

With spherical geometry:

$$x(t) = R - \sqrt{R^2 - 6 \cdot \frac{K_{ph}}{M_{Mag}} \cdot \frac{\rho_{M_{Mag}}}{\rho_{ph}} \cdot t}$$  \hspace{1cm} (16)

In Fig. 14 these two equations are compared. Up to a relative magnetite layer thickness of 0.25 a straight proportionality correlation between reduction time and layer thickness can be observed in both cases. At higher thicknesses the spherical layer is growing superproportionally fast.

In order to be able to exclude limitation by the diffusion
through the gas boundary layer of the grain, the mass transfer of H₂O from the grain surface to the bulk flow was calculated. H₂O is considered, because the diffusion coefficient of H₂O in the gas mixture is 4 times smaller than the one of H₂. After La Nauze and Jung 28) the Sherwood number describing the mass transfer in a bubbling fluidized bed is defined:

\[ \text{Sh} = 2 \cdot \varepsilon_b + 0.69 \left( \frac{\text{Re}_p}{\varepsilon_b} \right)^{0.5} \cdot \text{Sc}^{0.33} \] ..........................(17)

Under the predominating conditions the particle Reynolds number Reₚ is 16.9, the Schmidt number Sc is 1.1, and the averaged bed porosity εₚ is 0.7. The Sherwood number Sh results in 4.88.

\[ \text{Sh} = \frac{\beta \cdot d_p}{D_{H_2O}} \] ........................................(18)

\[ \frac{dn_{H_2O}}{dt} = \frac{A \cdot \beta \cdot \Delta N_{\text{boundary layer}}}{Sh} \] ........................................(19)

With the definition of Sh (Eq. (18)) and the assumption that at the crystal surface the whole H₂ is converted to H₂O, the possible H₂O mass transfer (Eq. (19)) amounts 528 mol/s (A=120 m²/β=0.098 m/s/ΔN=44.93 mol/m³ (=27 vol%)). To reduce the 80 g hematite ore sample to magnetite 0.167 mol H₂O has to be removed. In an assumed total reduction time of 60 min the average mass transfer is 4.64·10⁻³ mol/s. Thus the mass transfer through the gas boundary layer is not limiting the process.

Supposing that at the beginning of the reduction the mass transfer of H₂O is about 3 times higher than the average mass transfer of H₂O, the overall mass balance of H₂O in the fluidized bed was calculated. For this the mass transfer coefficient Kₑ of the 3-phase-model of Kunii and Levenspiel 25) was used. It amounts to 3.656·10⁻³ m/s. The concentration of H₂O in the bubble phase results in 19.76 vol%, in the emulsion phase 19.97 vol%. The mass transfer from the emulsion to the bubble phase is 3.19·10⁻⁵ mol/s, which is 22.9% of the generated H₂O. It is calculated according to Eq. (20).

\[ \frac{dn_{H_2O}}{dt} = Kₑ (c_{H_2O,\text{em}} - c_{H_2O,\text{bl}}) \cdot V_b \] ........................................(20)

The remaining 77.1% are removed by the gas flow through the emulsion phase. The rise in H₂O concentration is very low in both phases (bubble phase: +0.16 vol%, emulsion phase: +0.37 vol%), thus the fluidized bed would be able to transfer a higher amount of reduction product. It is not limiting the process under the supposed conditions.

After this examination it is concluded that the rate controlling step is the phase interface reaction. The development of the magnetite layer thickness corresponds best with the phase interface reaction limitation. Moreover it is consistent with the fact that the chemical reaction usually limits at lower temperatures. Backhaus-Ricoult and Dieckmann 35) also observed that phase interphase reaction can be the rate controlling step under these conditions.

To assure this position the activating energy of the reduction was calculated. A plane reaction surface with limiting phase interface reaction and an Arrhenius dependency of the kinetic constant kₑ (Eq. (21)) was assumed. The reduction by CO was neglected.

\[ kₑ(T) = kₑ(0) \cdot \exp \left( - \frac{E_A}{R \cdot T} \right) \] ..........................(21)

Using Eq. (14) and Eq. (15) kₑ can be written as:

\[ kₑ(T) = \frac{x(1200, T) \cdot \rho_{\text{mag}}}{2 \cdot (\rho_{H_2} - \rho_{H_2}^*) \cdot M_{\text{mag}} \cdot 1200} \] ..........................(22)

In equilibrium with magnetite nearly all H₂ is converted to H₂O. With ρₘₐ₉=0 Pa, ρₜₚ=4.6·10¹⁵ Pa, Mₚₚ=0.23155 kg/mol, ρₖₑₚₚ=5150 kg/m³ and the measured values of the magnetite layer thickness (Table 5) Fig. 15 can be drawn.

The kinetic constant kₑ of the phase interface reaction results in:

\[ kₑ(T) = 4.871 \cdot 10^{-4} \frac{\text{mol}}{\text{m}² \cdot \text{Pa} \cdot \text{s}} \cdot \exp \left( - \frac{9.77}{R \cdot T} \right) \] ..........................(23)

In the literature only the reduction of hematite or magnetite directly to iron is described. 29–31) There the measured activation energy varies between 49018 and 61870 J/mol, the constant kₑₕₑ between 128 and 641 mol/(m²·Pa·s). These values cannot be compared directly with the results in this paper because in those cases the considered reaction phase was the interface between iron and wuestite.

In order to apply the determined kₑₕₑ the molar flow of generated H₂O was calculated at 723 K and 10 bar (Δpₜₚ=4.6 bar). The 80 g hematite ore probe was assumed to consist of dense spheres with 25 μm diameter (0.0558 m³/g external surface). 25 μm is the estimated mean diameter of the hematite crystals in Mt. Newman ore. kₑₕₑ was calculated to 27.7·10⁻³ mol H₂O/s, which is about six times higher than the average molar flow of H₂O (within 60 min total reduction time). This can be explained with the fast reaction of the assumed crystals. They would be entirely reduced within 12.5 min (according to Eq. (16)). Crystals with a bigger diameter in relation to the magnetite layer thickness...
will react according to Eq. (15). After 20 min a layer of 6.7 μm thickness is calculated. That agrees with the averaged measured value of 5.0 μm for variation 3 (723 K, 10 bar, 20 min).

6. Conclusions

Samples of 80 g Mt. Newman hematite ore from Western Australia were reduced to magnetite. The tests were carried out in a fluidized bed reactor at temperatures between 623 and 873 K at an absolute pressure of 10 bar. The grain fraction used was 125 to 500 μm. The analysis of the reduction tests lead to the following conclusions:

(1) Dense magnetite layers are formed during the reduction.

(2) Ore crystals in the center of grains and at the external border show the same reduction degree, thus gas diffusion within pores (with a diameter>0.3 μm) of a grain is not limiting the reduction process.

(3) Oxygen removal takes place at the external surface of the magnetite shells.

(4) The reducibility significantly depends on the mineralogy and petrography of a grain. Fine crystals can be reduced faster than coarse. Limonite has the highest reducibility, martite and microplaty hematite show a lower reducibility and coarse hematite the lowest.32)

(5) Between 673 and 773 K the magnetite layer thickness is linear proportional to the reduction time (Fig. 12).

(6) Between 673 and 773 K the mass transfer through the gas boundary layer is not limiting the process.

(7) Between 673 and 773 K the mass transfer through the fluidized bed is not limiting the process.

(8) Between 673 and 773 K the process is limited by the phase interface reaction. This could be proven by the linear growth of the magnetite layers and the exclusion of possible influencing parameters. The kinetic constant of the phase interface reaction was determined as

\[
k_{ui}(T) = 4.871 \times 10^{-4} \frac{\text{mol}}{\text{m}^2 \cdot \text{Pa} \cdot \text{s}} \exp \left( -\frac{90770}{R_0 \cdot T} \right)
\]

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Nomenclature

\[A\]: Reaction area [m²] (external surface of the magnetite layer)

\[\Delta a_i\]: Activity difference of iron ions in the magnetite layer [mol/m³]

\[a_i\]: Iron activity at the external surface of the magnetite layer [mol/m³]

\[c_{i,ai}\]: Concentration of the species i in the bubble phase [mol/m³]

\[c_{i,ei}\]: Concentration of the species i in the emulsion phase [mol/m³]

\[D_{i,HH}\]: Diffusion coefficient of iron ions through magnetite [m²/s]

\[D_{H_2O}\]: Diffusion coefficient of H₂O in the considered gas mixture = 1.0 \times 10^{-5} [m²/s] at 723 K and 10 bar.

\[d_i\]: Particle diameter [m]

\[\Delta n_{gas}/dt\]: Change of amount of substance of magnetite [mol/s]

\[\Delta n_{i}/dt\]: Oxygen removed by reduction with species i [mol/s]

\[E_i\]: Activation energy [J/mol]

\[f_{i,H}\]: Specific diffusion molar flow of iron ions [mol/m²s]

\[k_{i}\]: Kinetic constant of the phase interface reaction of species i [mol²/m² Pa s]

\[k_{0,i}\]: Frequency factor of the phase interface reaction of species i [mol²/m² Pa s]

\[K_{m,i}\]: Frequency factor of the mass transfer from the bubble to the emulsion phase [1/s]

\[K_{ph,i}\]: Generalized kinetic constant of the phase interface reaction of H₂ [mol/m³s]

\[M_{mag}\]: Molar mass of magnetite = 0.23155 [kg/mol]

\[\rho_{i} \]: Actual partial pressure of species i [Pa]

\[\rho_{i}^*\]: Partial pressure of species i in equilibrium state [Pa]

\[r\]: Internal radius of a spherical magnetite shell [m]

\[R\]: External radius of a spherical magnetite shell [m]

\[R_{G}\]: Gas constant = 8.3145 [J/mol K]

\[Re_P\]: Particle Reynolds number = u · d_P/v [-]

\[Sc\]: Schmidt number = v/D_{i,H₂O} [-]

\[Sh\]: Sherwood number [-]

\[t\]: Reduction time [s]

\[T\]: Temperature [K]

\[th\]: Thickness of a plane [m]

\[V_b\]: Volume of the bubble phase [m³]

\[vol\%\]: Percent by volume [-]

\[wt\%\]: Percent by weight [-]

\[x\]: Magnetite layer thickness [m]

\[x_i\]: Relative magnetite layer thickness = x/R or x/th [-]

\[\beta\]: Mass transfer coefficient [m/s]

\[\theta\]: Averaged porosity of the fluidized bed [-]

\[\nu\]: Kinematic gas viscosity = 1.08 \times 10^{-5} [m²/s] at 723 K and 10 bar

\[\rho_{mag}\]: Density of magnetite = 5.150 [kg/m³]

REFERENCES

