Review on the Oxidation Behaviors and Kinetics of Magnetite in Particle Scale

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1. Introduction

In the past few decades, the ironmaking industry has consumed most of the high-grade hematite ore, which was used as the main iron carrier in the blast furnace process. As a result, good quality hematite ores are about to run out. The available ores are becoming much more expensive and the quality is decreasing. The global production of magnetite iron ore in 2015 is 583 million tons, which accounts for 28% of the total iron ore production. It is time to come up with an idea to use lower-cost iron ores with sufficient reserves for ironmaking.

The natural magnetite is widely present in various rock minerals. Because isomorphous substitution occurs in the structure of such magnetite iron ores, a beneficiation process is required to decrease the gangue and increase the total iron content. Usually, the magnetite iron ore is ground to a small particle size to release magnetite from its rock matrix, followed by magnetic separation. These kinds of magnetite iron ore fines cannot be used directly within the blast furnace or in common direct reduction facilities. The current practice of ironmaking from magnetite concentrates usually involves a pelletization process before charging it into the ironmaking facility. Reduction of iron ore fines is an economically reasonable process. For a net-zero greenhouse gas emission, one possible route for future crude steel production is using a hydrogen-gas-based fluidized bed to produce hydrogen direct reduced iron (HDRI), followed by an electric arc furnace. The fluidized bed provides an opportunity to directly use the magnetite in particle scale.

Reduction by H₂ is an endothermal reaction. Before charging the iron ore into the reduction unit, a preheating system could help to ensure a sufficient energy supply. Generally, the preheating process occurs in oxidizing atmosphere. As a result, the magnetite particles become oxidized. The oxidation of magnetite is an exothermic reaction, generating considerable heat, which in turn helps to reduce the primary energy. Rarely literature quantitatively evaluated the exothermic effect of the oxidation of magnetite iron ore. The fundamental structural evolution and crystal transformation of magnetite during oxidation is essential and necessary information, which helps to understand the oxidation process and effect of oxidation on the subsequent reduction behavior. The aim of this article is to provide a brief review and overall appraisal of the published works that related to the oxidation of magnetite in particle scale. Furthermore, the influence of oxidation of magnetite on its subsequent reduction behavior is discussed.

2. Stages of the Oxidation Process

Natural magnetite, which is purified by magnetic separation, still contains small amounts of impurities. The oxidation of magnetite at least contains two stages. Colombo et al. investigated the first stage of oxidation of magnetite. The results confirm that in the first oxidation stage, an intermediate phase exists, which consists of a solid solution of γ-Fe₂O₃ in Fe₃O₄. The impurities could stabilize the γ-Fe₂O₃ phase. However, the final oxidation product depends largely on oxidation temperature. Chen et al. illustrated the main structural and chemical difference between γ-Fe₂O₃ and Fe₃O₄. The difference is the existence of vacancies in γ-Fe₂O₃, which reduces the symmetry of γ-Fe₂O₃ (primitive Bravais lattice) with respect to Fe₃O₄ (face-centered Bravais lattice). Fe³⁺ in Fe₃O₄ is completely replaced by Fe⁵⁺ (Fe⁵⁺ → Fe⁵⁺ + e⁻), so the positions that were occupied by 1/3Fe²⁺ in octahedron...
become the vacancies. \( \gamma\)-Fe\(_2\)O\(_3\) shows a ferromagnetic behavior, whereas \( \alpha\)-Fe\(_2\)O\(_3\) shows an antiferromagnetic behavior.

The oxidation mechanism of magnetite is assumed as the following. The oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) causes diffusion of iron ions from inside the crystals of Fe\(_3\)O\(_4\) toward the surface. The solid solution of \( \gamma\)-Fe\(_2\)O\(_3\) in Fe\(_3\)O\(_4\) is formed at the beginning of the oxidation. As the oxidation proceeds, the formation of \( \alpha\)-Fe\(_2\)O\(_3\) and the solid solution appears at the surface of the magnetite particle. Later, through a reaction catalyzed by the presence of \( \alpha\)-Fe\(_2\)O\(_3\), the solid solution is transformed into \( \alpha\)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\). The secondary Fe\(_3\)O\(_4\) will be oxidized directly to \( \alpha\)-Fe\(_2\)O\(_3\) at high temperatures. Therefore, the oxidation stages of magnetite particles can be interpreted, as shown in Figure 1.

### 3. Oxidation Behaviors

The oxidation of magnetite, which is an exothermic reaction, can be simply expressed by Equation (1).\[^{[16]}\] The heat generated from the oxidation of 1 mol Fe\(_3\)O\(_4\) is roughly equivalent to that of 0.29 mol carbon combusted into CO\(_2\).\[^{[17]}\] In addition to the exothermic effect, the oxidation behavior is also accompanied by crystal transformation and structural evolution.

\[
\text{Fe}_3\text{O}_4 + \frac{1}{4} \text{O}_2 \rightarrow \frac{3}{2} \text{Fe}_2\text{O}_3 + \frac{1}{2} \Delta H^{\circ}_{298} = -114.6 \text{ kJ mol}^{-1}
\]

#### 3.1. Exothermic Effect

One possible technique for the description of the exothermic behavior is differential thermal analysis (DTA). The sample is heated side by side with a thermally inert material in a suitable sample holder, recording the occurring temperature difference \( \Delta T \) between the two materials while heating.\[^{[21]}\] When the temperature reaches a certain characteristic value for the sample, physical changes or chemical reactions will occur, accompanied by heat absorption or heat release. By recording the temperature difference \( \Delta T \) and time, the thermal effect can be identified.

DTA tests have been widely used to study the oxidation of magnetite.\[^{[22,23]}\] The latest quantitative study on the exothermic effect of the oxidation of natural magnetite was conducted by Yur’ev et al.\[^{[24]}\] The natural magnetite, which contained 99.2 wt.% Fe\(_3\)O\(_4\), 0.12 wt.% SiO\(_2\), 0.12 wt.% TiO\(_2\), 0.30 wt.% Al\(_2\)O\(_3\), 0.12 wt.% MgO, and few other oxide gangues, was heated under air flow. As shown in Figure 2, the two peaks represent two reaction stages. The first exothermic effect is assumed as a surface oxidation of magnetite forming an \( \alpha\)-Fe\(_2\)O\(_3\) layer. After the complete surface oxidation of the magnetite grains, the oxidation process slows down significantly due to the low diffusion coefficients of oxygen atoms and iron ions through the product layer. This corresponds to the horizontal line between the two peaks in Figure 2. After surface oxidation, the formation of microcracks and lattice defects is accelerated with increasing temperature. In addition, the diffusion coefficients increase with the temperature and therefore speed up the oxidation process, which corresponds to the second exothermic effect in Figure 2. Schmidt et al.\[^{[23]}\] pointed out that the peak shapes can be linked to the magnetite particle size. With increasing particle size, the height of the first peak decreases but leads to an increase in the second peak.

**Figure 1.** Stages of magnetite during nonisothermal oxidation.

**Figure 2.** Temperature variation on sample heating: 1) differential heating curve of natural magnetite; 2) baseline with \( \Delta T = 0 \); 3) temperature variation of the material; and 4) differential heating curve for calcium carbonate. Adapted with permission.\[^{[24]}\] Copyright 2016, CC BY 4.0.
As discussed by Yur’ev et al., the quantitative calculation of the thermal effect of magnetite oxidation can be conducted in reference to the analytical-grade calcium carbonate sample, as shown in Figure 2. The Curie point of magnetite is at around 573 °C (846.15 K). On reaching the Curie point, accounting for the sharp change in magnetic state and the internal magnetic energy of the material, heat is absorbed or liberated. Consequently, the Curie point appears on the differential heating curves as a slight reversible endothermal peak shown in the red circle part of Figure 2. Based on Equation (2), the heat liberated in the oxidation of 1 kg of magnetite is about 491 kJ kg⁻¹ (113.9 kJ mol⁻¹), which is close to the ideal value of 114.6 kJ mol⁻¹ shown in Equation (1).

\[ Q(\text{Fe}_3\text{O}_4) = Q(\text{CaCO}_3)S(\text{Fe}_3\text{O}_4)/S(\text{CaCO}_3) \]  \hspace{1cm} (2)

where \(Q(\text{CaCO}_3)\) is the heat required for the decomposition of 1 kg CaCO₃; \(S(\text{Fe}_3\text{O}_4)\) is the total area of the figure for the differential heating curve associated with magnetite oxidation; and \(S(\text{CaCO}_3)\) is the area of the figure for the differential heating curve associated with CaCO₃ decomposition.

Assuming under adiabatic conditions, if the composition of natural magnetite and the amount of oxidation heat are available, the increasing temperature due to the oxidation heat can be calculated by Equation (3)–(4).

\[ \Delta T = Q/(m_{\text{mixture}}C_{\text{mixture}}) \]  \hspace{1cm} (3)

\[ C_{\text{mixture}} = (m_1/m_{\text{mixture}})C_1 + (m_2/m_{\text{mixture}})C_2 + \cdots + (m_n/m_{\text{mixture}})C_n \]  \hspace{1cm} (4)

where \(\Delta T\) is the increasing temperature, \(Q\) is the amount of heat, \(m_{\text{mixture}}\) is the sample mass, \(C_{\text{mixture}}\) is the specific heat capacity of the sample, and \(m_1, \ldots, m_n\) and \(C_1, \ldots, C_n\) are the mass and specific heat capacity of each component in the sample.

The specific heat capacity of each component can be referred to from the National Institute of Standards and Technology (NIST). The specific heat capacity changes with temperatures. For an easier calculation, the specific heat capacities at 926.85 °C (1200 K) are chosen. Based on earlier case, the \(C_{\text{mixture}}\) is 866.63 J (kg K)⁻¹. For 1 kg of natural magnetite, the increasing temperature \(\Delta T\) is roughly 566 °C (839.15 K).

### 3.2. Crystal Transformation

The crystal parameters of magnetite can be characterized by X-ray diffraction (XRD) measurement. The crystal consists of regularly arranged unit cells. If a monochromatic X-ray beam enters the crystal, the X-ray is to be scattered by different atoms and interferes with each other. In general, it is difficult to distinguish maghemite (\(\gamma\)-Fe₂O₃) and magnetite (\(\alpha\)-Fe₃O₄) using XRD analysis because of their similar crystal structure. The formation and identification of \(\gamma\)-Fe₂O₃ are not further discussed because they are beyond the research scope of this Review. There is no evidence to show the relations between the lattice constants and the oxidation behaviors. But it is interesting to know how the crystal transforms during oxidation.

Schmidt et al. found that the lattice constants of magnetite from different mines are likely to be slightly different. Table 1 shows the lattice constants measured from six different magnetite ores. The theoretical lattice constant of Fe₃O₄ is 8.4045 Å. There seems to be a tendency for the size of the unit cell of Fe₃O₄ to decrease with a replacement of Fe²⁺ by Mg²⁺.

During oxidation, the lattice constant also changes. Gokhale oxidized magnetite at the heating rate of 10 °C min⁻¹ from ambient temperature to target temperature and then quenched them in cooling air. The oxidation degree was not mentioned. The lattice constants after oxidation were measured after cooling and are shown in Table 2. The lattice constant decreases with temperature up to 600 °C. He states that the diversity of the lattice constant is caused by the compromise between thermal expansion and lattice modification during oxidation.

The volume and crystallite size can also be calculated using the XRD method. Each unit cell of Fe₃O₄ and Fe₂O₃ contains eight Fe₃O₄ and six Fe₂O₃ molecules, respectively, as shown in Figure 3. The detailed information on the unit cell structure can be found in the ICSD database and other literature. During oxidation, 8 Fe₃O₄ → 12 Fe₂O₃. 8 Fe₂O₃ molecules would be oxidized into 12 Fe₂O₃ molecules (two units of structure). Without considering the effects of sintering between magnetite particles, the volume should be expanded due to the crystal transformation. Based on this

Table 1. Lattice constants and chemical data.

| Magnetite ore | Lattice constant \(a_0\) [Å] | MgO [wt.%] | Al₂O₃ [wt.%] |
|--------------|-----------------------------|-----------|-------------|
| A            | 8.394 (±0.001)              | 1.48      | 0.38        |
| B            | 8.389 (±0.003)              | 1.73      | 0.45        |
| C            | 8.398 (±0.001)              | 0.67      | 0.09        |
| D            | 8.386 (±0.001)              | 1.05      | 0.07        |
| E            | 8.387 (±0.002)              | 2.55      | 0.75        |
| F            | 8.392 (±0.001)              | 0.095     | 0.46        |

Table 2. Cell dimensions of magnetite at various stages of oxidation.

| \(a = b = c\) [Å] | Temperature          |
|-------------------|----------------------|
| 8.425             | Magnetite at room temperature |
| 8.402             | Oxidized till 400 °C  |
| 8.395             | Oxidized till 600 °C  |
| 8.457             | Oxidized till 800 °C  |

\[ 8 \text{Fe}_3\text{O}_4 ightarrow 12 \text{Fe}_2\text{O}_3 \]

Eight Fe₃O₄ molecules

Six Fe₂O₃ molecules

![Figure 3. Transformation from magnetite unit to hematite units.](image-url)
method, the expansion is defined to be 5.2%. It is also reported that the change of magnetite to hematite by natural metamorphism results in a volume increase of 2.5%. However, when temperature is higher than 330 °C, the volume shows contraction during oxidation due to the sintering effect. In our previous study, after oxidation of natural magnetite, the weight increases from 400 to 410 g. The apparent densities of the natural magnetite and the oxidized magnetite with oxidation degree higher than 90% are 4.96 and 5.02 g cm⁻³, respectively. Based on the weights and densities, the volume expansion is 1.27%.

The crystallite size of magnetite and hematite can be calculated using Scherrer’s equation, as shown in Equation (5). The crystallite size of Fe₂O₃ after oxidation of titanimagnetite ore is shown in Figure 4. It is reported that the smaller the size of the crystallite, the more rapid the diffusion from one crystal to another. The oxidation processes are regarded as the diffusion of oxygen and iron atoms in the lattice. The crystallite size could be a reason for the diversities of the oxidation rate for different magnetite iron ores and could result in different reduction rates in the subsequent reduction section.

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where \(D\) is crystallites size (nm); \(K\) is equal to 0.94 (Scherrer constant); \(\lambda\) is equal to 0.15406 nm (the wavelength of X-ray source); \(\beta\) is full width at half maximum (radians), and \(\theta\) is peak position (radians).

### 3.3. Structural Evolution

During the oxidation of magnetite, two different typical surface morphologies would be formed—whiskers and rough pleated structures, which are related to oxidation conditions. Song et al. found that during the oxidation of magnetite in air atmosphere, the hematite whiskers occur. During the oxidation of magnetite, the diameter of whiskers does not change much, as shown in Figure 5, indicating that the whiskers are likely to be generated in the early oxidation stages. It is explained that the whisker formation is caused by the volume increase when magnetite oxidizes to hematite. The driving force for the evolution of hematite whiskers is the compressive stress. Similar whisker structures are also found in the oxidation of fayalite and pure iron. Gaballah et al. observed the hematite whiskers in an oxidation experiment of fayalite. The particle surface is first covered by a granular layer, which then breaks before the whisker formation starts. Microprobe analysis showed that the whiskers are made of iron oxide growing on a silica substrate. Shao et al. conducted an in situ oxidation experiment of pure iron using an environmental scanning electron microscope, the growth path of the whiskers is explained, as shown in Figure 6. Above the Fe surface, there are
three oxide layers. Close to the Fe surface is a thin layer composed of small nascent oxide nuclei. Above this first layer is a relatively compact intermediate layer, which consists of agglomerated grains. Next to the intermediate layer is another layer of younger grains. The morphology of the last oxide layer depends on the inherent nature of the iron base and the reaction conditions.

However, it should be pointed out that the formation of hematite whiskers does not always occur during the oxidation of magnetite. Cho et al. observed that the magnetite particle surface becomes rough after oxidation, which is explained by the outward growth of hematite. Figure 7 shows the outgrowth of hematite, which is also the common surface morphology of

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**Figure 6.** Plausible physical model for the oxidation of Fe based on environmental scanning electron microscope observations. Reproduced with permission. Copyright 1997, John Wiley and Sons.

**Figure 7.** Scanning electron microscope image of magnetite concentrate after oxidation in air at 600 °C for 30 min. Adapted with permission. Copyright 2011, Association for Iron & Steel Technology (AIST).
oxidized magnetite particles. Hematite is generated along preferential planes, forming laths of hematite product on the surface. Wang et al.[40] conducted the oxidation of iron-sand (Ti–magnetite ore). They found from BET tests that the hysteresis loop in the adsorption–desorption isotherms shows that the pores in the preoxidized iron-sand are connected in a network, whereas for the raw iron-sand, the pores are blocked and separated from each other.

The surface hematite layer of the particle does not grow uniformly. The hematite in the product layer could grow inward to the magnetite core and generates a needle-like structure, as shown in Figure 8. It is postulated that the hematite needles are formed by solid-state diffusion of ions into the magnetite matrix.[41]

4. Thermodynamics of Magnetite Oxidation

Spreitzer et al.[42] calculated the thermodynamically stable phases in the binary Fe–O system, as shown in Figure 9. Hematite phase is the oxide with the highest oxygen content, followed by magnetite. The ideal stoichiometries of hematite and magnetite are Fe$_2$O$_3$ and Fe$_3$O$_4$, respectively. Theoretically, magnetite is in equilibrium with hematite at low temperature. There are two small magnetite-phase stable areas at high temperatures. A closer look into the equilibrium of Fe$_3$O$_4$ and Fe$_2$O$_3$ under different temperatures and O$_2$ partial pressures is shown in Figure 10. The diagram shows the stable area of a single Fe$_3$O$_4$ phase under different temperatures and O$_2$ partial pressures. From a thermodynamic point of view, magnetite can be completely oxidized to hematite even at normal ambient conditions. However, because of the complexity of the oxidation process and the restriction of kinetic conditions, a complete oxidation of magnetite is generally impossible. In the following sections, the oxidation kinetic analysis is examined.

5. Rate-Limiting Mechanisms

The International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommended the kinetics-analyzing methods and guidance for reliable evaluation of kinetic parameters.[43,44] It must be pointed out that the oxidation process is not only influenced by the oxidation conditions but also the facilities and even the sample containers. Figure 11 shows three typical thermogravimetric analysis (TGA) apparatuses. The differences are the direction of gas flow and the sample containers. It is difficult to decide which kind of apparatus is the best option. When a crucible is used as the container, the gas flow can only penetrate the sample from top to bottom, because the gas flow cannot pass through the crucible. The interruption of the gas flow caused by the crucible and the thickness of the sample layer may influence the kinetic analysis. In the case of the basket, the gas flow is able to pass through the sample from the bottom to top with minor disturbances. In the oxidation TGA test of magnetite in particle scale, the most important thing is to prevent the experimental errors that are caused by mass transfer or mixing issues.
From a thermodynamic point of view, the oxidation of magnetite to hematite is a spontaneous reaction. The chemical reaction is rarely the rate-limiting step. It is well established that, for oxidation of the pellet, the oxidation kinetics follows mixture rate-limiting steps: gaseous mass transfer of molecular oxygen through macroscopic pores into the pellet and solid-state diffusion within the oxidized particles. However, in particle scale, the gaseous mass transfer between particles is usually neglected. It is almost impossible for oxygen molecules to diffuse into the particle due to the dense structure of both magnetite and hematite layer. The rate-limiting step for oxidation of magnetite in particle scale is considered as solid-state diffusion. The solid-state diffusion can be described by parabolic law. In this case, the nature of solid-state diffusion is ion (Fe$^{2+}$, Fe$^{3+}$, or O$^{2-}$) diffusion through the hematite layer. When the chemical reaction at the interface occurs much faster than the diffusion, the interface should move uniformly inward to the center of the particle. However, the magnetite particles usually are not spherical. The hematite shows being preferentially oxidized in a certain orientation, where the ion diffusion is faster than other orientations, resulting in the inward growth of hematite needles. The irregular shape of the particles and the inward-growth hematite may have an impact on kinetic analysis. Monsen believes that the O$^{2-}$ has limited mobility in magnetite and hematite, which is only possible to diffuse along the hematite—magnetite boundaries to a small extent. In pellet oxidation, the effect of inward-growth hematite is usually ignored because it contributes to a limited oxidation degree. Therefore, the oxidation process of magnetite in pellet and particle scale is shown in Figure 12.

Monsen found that under a polarized light microscope, hematite that oxidized from the magnetite particle was found to be formed by several subgrain structures. The higher the oxidation temperature, the bigger each hematite subgrain. Figure 13 shows the schematic of hematite subgrains in an oxidized magnetite particle. It is possible to describe the growth of subgrain structures by nucleation and growth mechanism. The model is known as the JMA model that is developed by Johnson, Mehl, and Avrami. The nucleation and growth mechanism do not contradict with the parabolic law. The nature of these two mechanisms both involves ion diffusions. In the following sections, these two kinetic mechanisms are discussed.

5.1. Parabolic Law

Cho and Pistorius investigated the oxidation kinetics of magnetite concentrates using parabolic law. The parabolic law refers to solid-state diffusion. Taking particle size into consideration, then, oxidation process is shown in Equation (6). The particle size was obtained by wet screening.

$$t = \frac{d^2}{24k_p} \times \left[3 - 2\alpha - 3(1-\alpha)^{\frac{3}{2}}\right]$$

where $t$ is the oxidation time, $d$ is the diameter of magnetite particle, $k_p$ is the parabolic rate constant, and $\alpha$ is the oxidation degree. To quantitatively estimate the parabolic rate constant, magnetite concentrate particles with a narrow size range between 53 μm and 63 μm were oxidized at 500, 600, and 800 °C under 80 pct N$_2$–20 pct O$_2$ gas mixture for 24 h. If the oxidation progress follows the parabolic law, a straight line would be obtained based on Equation (6). Monsen analyzed the oxidation of magnetite concentrate particles with size range between 74 and 100 μm in air flow at the temperature range of 400–800 °C using the same model. The oxidation process follows the parabolic law in these two works. The parabolic rate constant was estimated from the changes in hematite thickness. In another word, the measured parabolic rate constant indicates the macroscopic movement of the reaction front. Cho found that the parabolic rate constants in his work were similar to those calculated by Monsen and the oxidation rate is independent of oxygen contents (20 pct and higher). Pistorius found that only in extremely low partial pressure of oxygen can the parabolic rate
constant change with the oxygen content. The relationships between parabolic rate constants and partial pressure and temperature are shown in Figure 14. The parabolic rate constant is supposed to be stable in the same temperature. The average parabolic rate constant calculated by Cho and Pistorius is as follows.

\[
k_p = 220 \exp\left(-\frac{65100}{RT}\right) \mu m^2 \text{min}^{-1}
\]  

(7)

Himmel et al.\cite{53} measured the self-diffusion coefficient \((D)\) for iron in magnetite and hematite. For an easier comparison between \(k_p\) and \(D\), they are transferred into the same unit with \(\mu m^2/\text{min}\) and shown in Table 3 and 4. Table 3 indicates that the diffusion rate of iron in magnetite is several orders higher than that in hematite. The parabolic rate constants shown in Table 4 are similar to the self-diffusion coefficients for iron in magnetite. Therefore, the solid-state diffusion mechanism is plausible. The movement of the reaction front is probably the diffusion of iron in magnetite.

Kumar et al.\cite{54} conducted an isothermal oxidation of magnetite concentrate particles by TGA in the temperature range of 500–800 °C. The concentrate is wet sieved into a narrow size
range from 38 to 53 μm with average particle diameter of 45.5 μm. The oxidizing gas flow rate was set as 200 ml min⁻¹ to ensure the gas diffusion to be negligible. The result shows that the later stage of oxidation follows the solid-state diffusion mechanism. As discussed earlier, the parabolic rate constant should only depend on temperature. As shown in Figure 15, the slopes of the fitted lines indicate the values of the parabolic rate constants. The slopes in Figure 15a increase with temperature, whereas those in Figure 15b are almost constant. The resulting data support the mechanism of parabolic law.

5.2. Nucleation and Growth

The oxidation process can be also regarded as the nucleation and growth of hematite grains. The growth of hematite grain is realized by the solid-state diffusion of iron ions. The JMA model is a typical approach to describe such a reaction, which is designed by the solid-state diffusion of iron ions. The JMA model is a growth of hematite grains. The growth of hematite grain is real-

\[
\alpha = 1 - e^{-\alpha t}
\]  

where \(\alpha\) is the oxidation degree, which is achieved after a reaction time \(t\); \(\alpha\) represents the Avrami constant, which depends on the nucleation frequency or the linear rate of grain growth; and \(n\) is the kinetic exponent that provides insight into the type of nucleation and growth mechanism. Sharp and Hancock \([55]\) summarized the relationship between the value of \(n\) and the reaction mechanism. Generally, if \(n\) is smaller than 1, the reaction is controlled by solid-state diffusion; if \(n\) is close to 1, the reaction is likely to be controlled by first-order reaction; if \(n\) is close to 2, the reaction is controlled by nucleation.

Kumar et al.\([54]\) assumed that the oxidation process of magnetite occurred in series and analyzed the same data from Figure 15 by JMA model. Because only few data points can be obtained in the initial stage by the weighing system, further analysis from his work was only focused on the later stage of the oxidation process. Figure 16 shows results analyzed by the JMA model. The measured value of \(n\) is expressed as follows.

\[
\eta = 1.76 \times 10^{-4}T + 0.1255\ln(p_{O_2}) - 2.03 \times 10^{-4}T\ln(p_{O_2})
\]  

The values of \(n\) obtained in the experimental conditions are all smaller than 1 and show more sensitivity to temperature than partial pressure of oxygen, which is consistent with solid-state diffusion mechanism.

Monazam et al.\([41]\) used this model to examine the oxidation of magnetite particles, which are generated from reduced hematite. The difference is that he assumed a parallel process of two reactions occurring during oxidation. Pursuant to the JMA model, a parallel process of two reactions is defined by the Equations (11)–(12).

\[
\alpha_1 = w_1(1 - e^{-n_1\alpha t}) + w_2(1 - e^{-n_2\alpha t})
\]  

or

\[
(\ln(-\ln(1 - \alpha)) = n\ln(t) + \ln(\alpha)
\]  

\(w_1 + w_2 = 1\)

Table 4. The parabolic rate constants.

| Temperature [°C] | \(k_p\) [μm² min⁻¹] | Average \(k_p\) [μm² min⁻¹] |
|------------------|---------------------|-----------------------------|
| 400              | 2.5 × 10⁻¹          | 220 exp\((-50100/T)\)       |
| 500              | 1.9 × 10⁻²          |                             |
| 600              | 8.0 × 10⁻²          |                             |
| 800              | 3.2 × 10⁻¹          |                             |

Figure 15. Isothermal oxidation evaluated by the solid-state diffusion: a) different oxidation temperatures and b) different partial pressures of oxygen. Adapted with permission.\([54]\) Copyright 2018, CC BY 4.0.
The model hypothesizes that isothermal conversion of particles proceeds by nucleation and growth in parallel. Each process is manifested by the value of the weight factors $w_1$ and $w_2$. The parallel processes $P_1$ and $P_2$ corresponding to nucleation and diffusion are shown in Figure 17. It should be noted that the particle size he used is between 100 and 300 μm, which is quite a wider size fraction compared with other works. The wide size range may cause the fitting result to be less reliable.

In the initial stage of oxidation, $P_1$ dominates the two processes, which indicates that $P_1$ is the rate-limiting step. Regarding the reaction time, $P_2$ dominated the whole oxidation. $P_2$, which can be related to diffusion, has little influence on the initial part of the oxidation process. In other words, the nucleation of hematite dominates initially, whereas the solid-state diffusion dominates the later stage of oxidation. There is no evidence to confirm that the multistep kinetics of the oxidation reaction is in parallel or in series.

5.3. Discussion on the Kinetic Models

The two models based on the parabolic law and the nucleation and growth mechanisms can be occupied to describe the oxidation process of magnetite. The nature of these two mechanisms both involves ion diffusions. The solid-state diffusion is derived based on parabolic law, which can be simply described by Equation (13). The reaction rate is supposed to decrease with the thickness of the product layer. Equation (13) can be integrated in Equation (14), which is known as the parabolic law.

$$\frac{dl}{dt} = k_1 l$$  \hspace{1cm} (13)

$$l^2 = k_p t$$  \hspace{1cm} (14)

where $l$ is the thickness of the product layer and $k_p$ is the parabolic rate constant. Ginstling and Brounshtein[57] provided a solid-state diffusion model in the reaction taking place in

![Figure 16](image1.jpg) Isothermal oxidation evaluated by the nucleation and growth: a) different oxidation temperatures and b) different partial pressures of oxygen. Adapted with permission.[54] Copyright 2018, CC BY 4.0.

![Figure 17](image2.jpg) Conversion curve as a function of time. Curve $P_1$ is a single Avrami equation; curve $P_2$ is a single diffusion equation. Adapted with permission.[41] Copyright 2014, American Chemical Society.
spherical particles based on parabolic law. This model is known as Ginstling–Brounshtein’s diffusion model or D4 model and gives the expression in Equation (6). Khawam et al. [58] summarized other forms of the solid-state diffusion models derived from 1D (D1), 2D (D2), and 3D (D3) diffusion. Cho et al. [51] found that the inward growth of hematite ahead of the reaction interface would have a small influence on the fitting result, but the solid-state diffusion by D4 model still describes the oxidation kinetics very well.

The advantage of JMA model is that it can be applied when the data do not fit commonly used models and it can describe the multistep kinetics in both the parallel and series way. According to the works from Kumar et al. [54] and Monazam et al. [41], the later oxidation stage of magnetite follows solid-state diffusion no matter in parallel or series way. It is difficult to determine whether the multistep kinetics occurs in parallel or series. The current approach is to fit the data using both parallel and series methods and then choose the method with the better fitting result.

As discussed earlier, the kinetic analysis of the oxidation of magnetite in particle scale generally follows the solid-state diffusion. As for how to decide the kinetic models, the current method is to choose the model that fits the experimental data better.

6. The Influence of Oxidation of Magnetite on Its Subsequent Reduction

It is well established that hematite iron ores show better reducibility than that of magnetite iron ores [59, 60]. It is of great interest to know the difference of reduction behavior between oxidized magnetite and hematite in particle scale. Edström [61] oxidized natural single crystals of magnetite (Fe3O4) and compared the reduction rate with that of hematite (Fe2O3) in CO atmosphere at 1000 °C. The results show that the reduction rate of the oxidized Fe3O4 is slightly lower than that of Fe2O3. After 120 min reduction, both Fe3O4 and oxidized Fe3O4 reach more than 90% reduction degree, whereas that of Fe2O3 only reaches around 40%. Monsen [46] has done a series of works to investigate the influence of oxidation temperatures of magnetite concentrates on its subsequent reduction in H2 atmosphere at the temperature range between 700 and 800 °C. Magnetite was almost completely oxidized at the defined temperatures (850–1250 °C). He found that the hematite oxidized from magnetite at relatively low temperatures (850–1050 °C) shows better reducibility than that oxidized at high temperatures (1150–1250 °C) because hematite that is derived at a relatively low temperature contains more and smaller subgrain structures. The boundaries of these sub grains serve as preferential reduction sites, which promote the reduction process.

7. Conclusion

This Review summarizes the oxidation behaviors and kinetics during the oxidation of magnetite in particle scale. The oxidation kinetic mechanism is introduced and summarized. Furthermore, the influence of the oxidation of magnetite on its subsequent reduction behavior is examined. Four oxidation characteristics of magnetite are summarized as follows.

1) The oxidation of magnetite proceeds through two oxidation stages. During the initial stage, the magnetite is oxidized into an intermediate phase, which is substable and further oxidized to α-Fe2O3.

2) The oxidation process of magnetite is accompanied by the exothermic phenomenon, transformation of crystal, and evolution of morphology. The heat liberated in the oxidation of 1 kg of magnetite is about 113.9 kJ mol⁻¹.

3) Without considering the interaction between magnetite particles, the change of magnetite to hematite should result in a volume increase. However, when temperature is higher than 330 °C, the volume shows contraction during oxidation due to the sintering effect.

4) During the oxidation of magnetite, two different typical surface morphologies would be formed—whiskers and rough pleated structures, which are related to oxidation conditions. Whisker structures are likely to occur at a higher oxidation temperature. One possible cause for the hematite whisker structure is the compressive stress that is generated due to the volume increase when magnetite oxidizes to hematite. However, the favorable conditions for the formation of hematite whiskers or rough pleated structures are not fully examined. Further investigations have to be conducted.

The rate-limiting step for oxidation of magnetite in particle scale is generally solid-state diffusion. Solid-state diffusion can be well described by both parabolic law and the nucleation and growth mechanisms. The parabolic rate constant increases with temperature but is the same at different oxygen partial pressures. In another word, the oxidation process depends largely on the temperature rather than oxygen partial pressure.

The preoxidation of magnetite could greatly improve its reducibility. The hematite that is derived at a relatively low oxidation temperature contains more and smaller subgrain structures. In terms of the subsequent reduction rate, lower oxidation temperature is more beneficial than higher oxidation temperature.

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Conflict of Interest

The authors declare no conflict of interest.

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