

# Effect of $\text{Al}_2\text{O}_3$ on the Reduction of Hematite ( $\text{Fe}_2\text{O}_3$ )

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**Abstract:** With the iron ore being mined continuously, both imported mineral iron ore and domestic ore imports are expanding, and the quality of imported iron ore is getting lower and lower. In recent years, the content of  $\text{Al}_2\text{O}_3$  in iron ore has gradually increased, especially in imported ore, and China's iron ore largely depends on imports, which brings many adverse effects on the quality of sintered ore. One of the adverse effects of  $\text{Al}_2\text{O}_3$  on sintered ore is to affect the reduction performance and reduction pulverization rate of hematite, through reading the literature, we understand the  $\text{Al}_2\text{O}_3$  on the low temperature sintering pulverization rate of hematite. Therefore, this study was carried out to calculate the thermodynamic parameter standard generation Gibbs free energy for the purpose of providing theoretical guidance to optimize the sintering process and fill in the thermodynamic data.

**Keywords:** Hematite, Reduction, Effect.

## 1. Introduction

As iron ore is mined year by year, the amount of both imported mineral iron ore and domestically produced iron ore is increasing, the quality of imported iron ore is getting lower and lower, and the content of  $\text{Al}_2\text{O}_3$  in iron ore is gradually increasing. Hematite is one of the main minerals in sintered ore, when  $\text{Al}_2\text{O}_3$  is solidly dissolved into hematite, it will change the reduction of hematite, and when reduced to magnetite, crystalline transformation occurs, accompanied by volume expansion, reducing its strength, low temperature reduction pulverization will occur, which will seriously lead to deterioration of the permeability of the blast furnace and affect the blast furnace downstream. Therefore, it is necessary to study the thermodynamic properties of Al-containing hematite to provide some theoretical guidance for optimizing the sintering process. In this study, the reduction products of hematite with different  $\text{Al}_2\text{O}_3$  contents at a certain temperature and atmosphere are experimentally clarified, the standard Gibbs free energy of aluminum-containing hematite is calculated, and the relationship between the thermodynamic stability of aluminum-containing hematite and temperature is revealed, so as to improve the sintering theory of aluminum-containing hematite and provide a theoretical basis for practical production.

## 2. Characteristics of High Alumina Iron Ore and Current Status of Utilization

### 2.1. Characteristics of high alumina iron ore and current status of utilization

With the development of ore resources, high-quality ores are becoming less and less available, while high-alumina iron ores are gradually increasing. High-alumina iron ore, as the name implies, has a high content of  $\text{Al}_2\text{O}_3$  as one of the vein components. It is well known that modern blast furnace smelting iron ore has strict requirements for  $\text{Al}_2\text{O}_3$  content, and when the  $\text{Al}_2\text{O}_3$  content in iron ore keeps increasing, the  $\text{Al}_2\text{O}_3$  content in slag also increases accordingly, which makes slag liquidity poor, desulfurization capacity decreases, coke ratio increases, and blast furnace operation difficult[1]. High-

alumina iron ore has abundant reserves in Australia, India, Indonesia, and Anhui, Guangxi, Guizhou, etc. in China. In countries with abundant iron ore resources, such as Australia and India, high alumina iron ore is mostly fine sludge after washing. Three kinds of products are produced in the washing production: lump ore with particle size larger than 10mm is directly used in blast furnace smelting; coarse grade powder ore with particle size of  $150\mu\text{m}\sim 10\text{mm}$  after crushing and grading enters into sintering plant for treatment after sorting, and the sintering plant generally uses it after matching with high-grade iron ore with low veinstone content; fine mud with particle size less than  $150\mu\text{m}$  is only about 45%~50% due to its low iron grade and high veinstone. In the case of abundant lump ore resources, these fines are discarded as tailings and not utilized[2].

Aluminum in Indian iron ore mud is present as illite, kaolinite, montmorillonite, silica, alunite and a small amount of hard hydrous alumina and alumina trihydrate, with fine particles of alumina up to  $0.03\sim 2\mu\text{m}$ [3]. Taking an iron ore mine in India as an example, the  $\text{Al}_2\text{O}_3$  content of directly mined raw ore is about 3% to 3.2%, the  $\text{Al}_2\text{O}_3$  content of primary grade powder is up to 4%, and the  $\text{Al}_2\text{O}_3$  content of fine-grained powder reaches 6% to 9%. According to incomplete statistics, for every 1 t of iron ore produced, 0.15 t of fine-grained powder ore is produced, and after years of accumulation, the reserves of such iron ore resources have exceeded 150 million tons, and a large amount of these fine-grained mud is piled up in the tailing pond, which brings great harm to the environment and ecology[4].

In Indonesia and other places, due to its location near the equator, a large amount of iron ore resources mainly hematite and limonite are formed, with high content of  $\text{Al}_2\text{O}_3$  vein minerals in the ore. This kind of high alumina iron ore resources ore particle size is very fine, weak magnetic properties, poor floatability, easy to mud during the grinding process, iron minerals are closely embedded with aluminum and silicon minerals, and the internal distribution relationship is complex; at the same time, due to the similar geochemical and crystal chemical properties of aluminum and iron, it is easy to form a homogeneous substitution, and there is a large number of  $\text{Al}^{3+}$  replacing  $\text{Fe}^{3+}$  homogeneous structure inside the ore, which leads to a low degree of monomer dissociation, and it is difficult to realize aluminum by conventional

physical sorting or magnetization roasting methods. It is difficult to separate Al and Fe by conventional physical sorting or magnetization roasting methods, so this part of the resource has not been exploited on a large scale in industry, and is a typical complex and difficult iron ore resource[5].

## 2.2. Current status of utilization of high alumina iron ore

High alumina iron ore is an important iron ore resource, and with the increasing depletion of resources, the comprehensive utilization of this kind of ore has gradually become the focus of research by scholars at home and abroad, and more progress has been made. In summary, the utilization of high alumina iron ore is mainly divided into two ways, one is directly used in blast furnace iron making or with high grade low vein content iron ore for ore blending production, and the other is to pretreat the ore for beneficiation or use other methods for processing and utilization.

A more representative study on the direct use of high alumina iron ore for blast furnace smelting is the study on the smelting of Guangdong Dabaoshan iron ore using a small blast furnace at Zhuzhou Iron and Steel Works. Dabaoshan ore is a brown iron ore with a high  $\text{Al}_2\text{O}_3$  content of about 7%, and the single use of this ore smelting, slag composition is very unsatisfactory, resulting in the deterioration of furnace conditions. In order to overcome the smelting difficulties of high Al iron ore, Zhuzhou Iron and Steel Plant smelted Dabao Mountain ore, firstly, using concentrate technology to use coke with good strength and less ash, and using calcium chloride as binder to make pellets of high Al iron ore in order to improve the permeability of the furnace charge, and the pellet ore was roasted by high temperature chlorination to improve the grade of the ore. Secondly, choose a reasonable operation system, adopt high air volume and high air temperature  $950^\circ\text{C}$  operation, adjust the charging system and strengthen the edge charging finally improve the slag making system, control the  $\text{Al}_2\text{O}_3$  content in the slag at 20%~22% by adding river pebbles. After two months of production practice, the blast furnace output and quality were stabilized at a better level, with an average utilization factor above 2t, coke ratio around 850kg, smelting intensity around 2t, and qualification rate about 90%, thus initially mapping out some experience for the smelting of high alumina iron ore[6].

In order to reduce the  $\text{Al}_2\text{O}_3$  content of sinter ore and suppress the negative impact of  $\text{Al}_2\text{O}_3$  on the sintering process, TaTa Steel uses 75% Noamundi iron ore fines mixed with fines from other iron ores, and also uses limestone and low-ash fuel with lower vein content for sintering, which has achieved more Significant results, sintered ore  $\text{Al}_2\text{O}_3$  content from 4.5% to about 2.5%, but increased the cost of auxiliary materials and fuels, higher production costs. A similar conclusion was obtained in a study on the production of allotment ore with 4.4%  $\text{Al}_2\text{O}_3$  content of fines from Goa, India, by a Japanese pipe mill[7].

## 3. Effect of $\text{Al}_2\text{O}_3$ on Hematite

### 3.1. Effect of $\text{Al}_2\text{O}_3$ on the sintering strength of hematite

It is well known that  $\text{Al}_2\text{O}_3$  is a high melting point acidic veinstone, and the  $\text{Al}_2\text{O}_3$  content in blast furnace slag is beneficial to improve the stability of slag when it is 10%-15%[8]. However, when the  $\text{Al}_2\text{O}_3$  content continues to rise,

it will have a negative impact on sintering and smelting processes, causing an increase in solid combustion consumption, a rise in slag melting point and viscosity, making it difficult to separate slag from iron and reducing the blast furnace utilization factor, so large blast furnaces generally require  $\text{Al}_2\text{O}_3 < 2\%$  in sintered ore[9].

The mechanical strength of sintered ore directly affects the amount of powder fed into the blast furnace, which in turn affects the internal permeability of the blast furnace during smelting and thus the blast furnace output. The mechanical strength of sintered ore is closely related to both the raw material conditions and the sintering process, and the content of  $\text{Al}_2\text{O}_3$  in the raw material has a great influence on the strength of sintered ore[10]. The influence of  $\text{Al}_2\text{O}_3$  on the quality of sintered ore depends to a large extent on the form of its presence in iron ore. Data show that, according to the results of X-ray micro-area analysis,  $\text{Al}_2\text{O}_3$  hematite, calcium ferrate and silicate slag phases in sintered ore[11]. A certain amount of  $m(\text{Al}_2\text{O}_3)/m(\text{SiO}_2)=0.1\sim 0.35$  in sintered ore is beneficial to the formation of quaternary system of acicular calcium ferrate, which can improve the strength of sintered ore; however, the content of  $\text{Al}_2\text{O}_3$  above a certain value increases the viscosity of the primary fused phase during sintering, which in turn forms many irregular, interconnected pores in sintered ore, glassy mass is easily formed[12].

### 3.2. Effect of $\text{Al}_2\text{O}_3$ on low-temperature reduction pulverization of hematite

The sintered ore will break and pulverize during the reduction in the low temperature zone in the upper part of the blast furnace, which reduces the porosity of the material column and deteriorates the permeability. Production practice shows that for every 5% increase in low-temperature reduction pulverization rate, blast furnace output decreases by 1.5%, and the gas utilization rate decreases so that the ironmaking coke ratio increases[13].

The most fundamental reason for low-temperature reduction pulverization of sintered ore is that the regenerated  $\text{Fe}_2\text{O}_3$  in sintered ore is reduced from  $\alpha\text{-Fe}_2\text{O}_3$  to  $\gamma\text{-Fe}_2\text{O}_3$  at low temperatures of  $450^\circ\text{C}\sim 550^\circ\text{C}$ ).  $\alpha\text{-Fe}_2\text{O}_3$  is a tripartite crystal system hexagonal lattice and  $\gamma\text{-Fe}_2\text{O}_3$  is an equiaxed crystal system cubic lattice, and under the action of reducing gas, the change of the lattice causes distortion of its structure, resulting in a great internal stress, leading to severe fragmentation under mechanical action[14].

In addition to the factors affecting the low temperature reduction pulverization rate, which are related to the ore type, alkalinity of the sintered ore, reduction temperature and reducing gas composition, the influence of the chemical composition of the sintered ore is also prominent.  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ , and  $\text{TiO}_2$  in sinter ore all have a certain influence on the low-temperature reduction pulverization rate of sinter ore[15].  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{FeO}$  all contribute to the improvement of reduction pulverization performance, while the increase in the content of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  deteriorates the low-temperature reduction pulverization performance of sinter ore. Many studies at home and abroad have concluded that  $\text{Al}_2\text{O}_3$  has a serious influence on the low-temperature reduction pulverization of sinter ore pulverization has a serious effect [16].

$\text{Al}_2\text{O}_3$  exacerbates low-temperature reduction pulverization mainly because  $\text{Al}_2\text{O}_3$  contributes to the concentration of reduction stress and crack expansion in

Fe<sub>2</sub>O<sub>3</sub>, which results not only in the widening of the rupture but also in the creation of new gas channels and the acceleration of the reduction process of Fe<sub>2</sub>O<sub>3</sub>, which increases the volume expansion stress sharply, thus increasing the reduction pulverization rate[17]. On the other hand, electron probe analysis confirmed that with increasing Al<sub>2</sub>O<sub>3</sub> content, Al<sub>2</sub>O<sub>3</sub> is not uniformly distributed in different minerals, but concentrated in hematite. According to the fracture mechanics, fracture toughness is a parameter that measures the ease of crack diffusion in the material. Among the mineral phases the hematite phase has the lowest hardness and the lowest fracture toughness, and it decreases with increasing Al<sub>2</sub>O<sub>3</sub> content[18]. Therefore, when the reduction expansion of α-Fe<sub>2</sub>O<sub>3</sub> produces cracks, it tends to diffuse and extend in the hematite phase with high Al<sub>2</sub>O<sub>3</sub> content, which increases the RDI of sintered ore[19].

While maintaining RDI, sinter ore needs to be sufficiently reducible to promote indirect reduction in the blast furnace and reduce coke consumption. The reducibility of sinter ore is mainly determined by the chemistry, pore structure and mineralogy of sinter ore, which are often interrelated and determined by the feedstock and operating conditions. Because of the complexity of the effect of alumina on these factors, studies of the effect of alumina on the reducibility of sinter ores have shown mixed results. Mineralogically, decreasing the alumina content of sintered ores increases hematite and promotes the SFCA bonded phase, resulting in sintered ores with improved reducibility. In addition, during reduction, alumina reduces the liquid phase line of the melt and increases its viscosity. The mechanism of RDI deterioration with increasing alumina content is not fully understood. Some Japanese researchers have suggested that secondary hematite, also known as skeletal rhodochrosite hematite, is the main reason for the poor resistance of sintered ores to reductive degradation. This is based on the frequent observation of cracks around the narrow neck of this hematite. However, low to moderate levels of alumina have been reported to reduce the amount of secondary hematite and increase the SFCA in the sinter structure, both of which should favor RDI. On the other hand, some researchers have also suggested that the cracking that accompanies the volume change of the crystalline hematite to magnetite phase transition is the main cause of the reductive degradation of sintered ores[20].

### 3.3. Effect of Al<sub>2</sub>O<sub>3</sub> on the reduction of hematite

Chen, Xu-Ling[21] et al. analyzed the essential characteristics of the pulverization of sintered ore by combining the structural micromechanical properties of each mineral phase on the basis of the evolution of different mineral phases during the low temperature reduction process. It was shown that the main structural changes in the low-temperature reduction stage were the transformation of hematite from coarse grains to continuous crystalline, irregular agglomerates, platelets, and finally to granular magnetite; the fracture toughness of hematite with different morphologies decreased by 12%-19% on average after reduction; skeletal hematite decreased by more than 20%, and its ability to withstand internal stress and impede crack expansion became poor, which resulted in pulverization.

Chen Jiang et al[22] studied the mechanism of gaseous reduction of hematite particles to magnetite in a CO-CO<sub>2</sub>

atmosphere in the temperature range of 500°C to 1100°C. The pore size distribution in reduced magnetite was measured by mercury porosimetry and partially reduced grains were examined by optical microscopy. It was shown that the hematite grains were reduced to magnetite at temperatures below 800°C. The average pore size of the magnetite formed at 600°C is 0.03 μm. Estimates of the CO diffusion rate through pores of this size indicate that the reaction rate at 600°C is controlled by steps near the hematite-magnetite interface. At temperatures above 800°C, the reaction mechanism changes due to the preferential growth of magnetite in each hematite grain in a single direction. The reduction rate decreases with increasing temperature, no micropores are present in magnetite formed at 1000°C and above, and the rate of reaction obtained is controlled by the rate of formation of new nuclei and their subsequent growth rate.

Monazam[23] et al. performed several experiments by using a mixture of N<sub>2</sub> and CO atmosphere and selected different ratios of CO of 5%, 10% and 20%, respectively, in the temperature range of 750°C to 900°C and performed thermogravimetric analysis (TGA) of the reduction behavior of hematite. The data analysis showed that the reduction could be described by a single constant-rate step and was controlled by the chemical reaction on the particle surface, and no carbon deposition was found when operating in the temperature range (750°C to 900°C), while two reduction steps (Fe<sub>2</sub>O<sub>3</sub>→Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>→FeO) were found to proceed simultaneously.

## 4. Summary

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## References

- [1] BISWAS B K. Principles of blast furnace ironmaking[M]. Principles of blast furnace ironmaking, 1981.
- [2] UMADEVI T N, DEODAR A V, MAHAPATRA P C, et al. Influence of Alumina on Iron Ore Sinter Properties and Productivity in the Conventional and Selective Granulation Sintering Process[J]. Steel Research International, 2010,80(9):686-692.
- [3] SAMIEE A, MERATIAN C, PRAKASH S, et al. Influence of alumina percentage on hot deformation of aluminium-alumina matrix composite[J]. International Journal Cast Metals Research, 2015,56(12):247-253.
- [4] Allen C , Day G . Does China's demand boom curb Australian iron ore mining depletion? [J]. Australian Journal of Agricultural and Resource Economics, 2014,58(7):145-149.
- [5] KURNIAWAN A D, ABE K Y, NOMURA T M, et al. Integrated Pyrolysis-Tar Decomposition over Low-Grade Iron Ore for Ironmaking Applications: Effects of Coal-Biomass Fuel Blending[J]. Energy & Fuels, 2017,32(1):396-405.
- [6] JIANG D J, HE M G, GAN Q, et al. Influence of Superhigh Basicity on Sinter Properties and Sintering Parameters[J]. Iron & Steel, 2009,44(2):98-104.
- [7] UMADEVI T, PRAKASH S, BANDOPADHYAY U K, et al. Influence of Alumina on Iron Ore Sinter Quality and Productivity[J]. World Iron & Steel, 2010,10(24):12-18.
- [8] KAPELYUSHIN Y B, XING X, ZHANG J D, et al. Effect of Alumina on the Gaseous Reduction of Magnetite in CO/CO<sub>2</sub>

- Gas Mixtures[J]. Metallurgical & Materials Transactions B, 2015,46(3):1175-1185.
- [9] LU W K. Kinetics and Mechanisms in Direct Reduced Iron[J]. Iron & Steel, 1999,30(41):11-18.
- [10] LINDSLEY D H. Oxide Minerals: Petrologic and Magnetic Significance[M]. Oxide Minerals, 1991.
- [11] TANG J. Reduction mechanism of high-chromium vanadium-titanium magnetite pellets by H<sub>2</sub>-CO-CO<sub>2</sub> gas mixtures[J]. International Journal of Minerals Metallurgy and Materials, 2015,22(6):562-572.
- [12] NABI G V, LU W K. The Kinetics of Hematite to Magnetite Reduction in Hydrogen-Water and Hydrogen-Water-Nitrogen Mixtures[J]. Industrial & Engineering Chemistry Fundamentals, 2002, 13(4):311-316
- [13] JANOWSKI J D, WYDERKO M W, SADOWSKI A N, et al. Morphology of hematite to magnetite reduction zone[J]. Steel Research, 1995,66(4):135-139.
- [14] PAANANEN T, HEINAENEN K, HAERKKI J. Degradation of Iron Oxide Caused by Alumina during Reduction from Magnetite[J]. Transactions of the Iron & Steel Institute of Japan, 2003,43(5):597-605.
- [15] SHARMA T, GUPTA R C, PRAKASH B. Effect of Firing Condition and Ingredients on the Swelling Behaviour of Iron Ore Pellets[J]. Transactions of the Iron & Steel Institute of Japan, 1993,33(4):446-453.
- [16] KAPELYUSHIN Y, SASAKI Y, ZHANG J Q. Formation of a Network Structure in the Gaseous Reduction of Magnetite Doped with Alumina[J]. Metallurgical and Materials Transactions B, 2017,48B(2):889-899.
- [17] SHEN , SUN S, ZHU Y, et al. A Kinetic Study on the Reduction of Single Magnetite Particle with Melting Products at High Temperature Based on Visual and Surface Analytical Techniques[J]. Industrial & Engineering Chemistry Fundamentals, 2021,6(12):42-49.
- [18] SINGH R, BHATERIA R. Experimental and Modeling Process Optimization of Lead Adsorption on Magnetite Nanoparticles via Isothermal, Kinetics, and Thermodynamic Studies[J]. ACS Omega, 2020,5(19):10826-10837.
- [19] KUZIN A V, GORICHEV I G, ELISEEVA E A, et al. The Effect of Stoichiometry of Iron (II) and (III) and Magnetite Oxides on the Kinetic Regularities of their Dissolution in Orthophosphoric Acid Containing Fe (II) and Fe (III) Ions[J]. Herald of the Bauman Moscow State Technical University Series Natural Sciences, 2019(83):104-113.
- [20] WASAKI T, SATO N, KOSAKA K, et al. Direct transformation from goethite to magnetite nanoparticles by mechanochemical reduction [J]. Journal of Alloys & Compounds, 2011, 509(4):34-37.
- [21] MONSEN B E, OLSEN S E, KOLBINSEN L. Prereduction of Oxidized Magnetite[J]. Scandinavian Journal of Metallurgy, 1995,24(1):28-38.
- [22] KIM W H, LEE S, KIM S M, et al. The retardation kinetics of magnetite reduction using H<sub>2</sub> and H<sub>2</sub>-H<sub>2</sub>O mixtures[J]. International Journal of Hydrogen Energy, 2013,38(10):4194-4200.
- [23] PONOMAR V, DUDCHENKO N, BRIK A, et al. Kinetics of Hematite to Magnetite Reduction in Carbon Monoxide Atmosphere[J]. Mineralogical Journal, 2017,39(1):36-45.