



A STUDY ON THE REDUCTION OF MAGNETITE ORE WITH HYDROGEN¹

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Abstract

The objective of this research was to study the total simplified estimation of hematite and magnetite ore with CO and H₂ such as reduction degree of iron ores, reduction rate and morphology analysis. The reduction degree and reduction rate data of hematite ore and magnetite ore with CO or H₂ at various temperatures (400°C to 1,000°C) were reported using a thermogravimetric analysis, respectively. The reduction degree of hematite ore with CO or H₂ increased with an increase in reaction temperature. The initial reduction rate of magnetite ore with H₂ is increased with an increase in reaction temperature for 30min. Whereas the final reduction degree of magnetite ore was shown the retardation of reduction above the reduction temperature of 800°C. Also, the reduction rate could be enhanced by the addition of H₂ to the CO-based reducing gas.

Key words: Hydrogen reduction; Hematite ore; Magnetite ore; Iron ore.

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1 INTRODUCTION

Korea government announce officially that the nation's voluntary mid-term plan for the reduction of greenhouse gas emissions outlining a 30% reduction compared to the Business As Usual (BAU) by 2020 on November 17, 2009. Therefore, Posco has examined three innovative technology routes specialized to the steelmaking process and is developing innovative technologies for reducing greenhouse gas (GHG) emissions. The first, method involves the carbon-lean steelmaking route aims at producing less CO₂ and consumption of fossil fuels, an example of which is the low-carbon Finex process. The second, the carbon capture and storage of steelmaking route isolates and locks the CO₂ produced during the steelmaking process. Posco is developing technology that uses ammonia water for CO₂ capture. The third method relies on hydrogen steelmaking route utilizes hydrogen in steelmaking.

Currently, iron ore is melted in a furnace using super-heated air from burning coal. In addition to this fuel role, coal is also used as a critical component in steel production because the carbon from burning coal captures oxygen from the molten iron ore, emitting carbon dioxide in the process. Posco is currently developing steelmaking technologies that use hydrogen as the reducing agent instead of coal, to take advantage of mass-produced, clean-burning hydrogen in the future. A short-term objective is to develop the technology to capture hydrogen in byproduct gases from steelmaking and use it for reducing iron. Over the mid-/long-term, the company is working on hydrogen reduction steelmaking technology that uses massive high-density hydrogen. Hydrogen reduction in steelmaking processes means that CO₂ is generated when iron ore is reduced with CO. However, with H₂ reduction H₂O is generated instead of CO₂, and therefore this process can be regarded as an environmentally-friendly steelmaking process. The hydrogen reduction that are based on reducibility of iron ore have certain advantages over traditional reducing gases such as higher reduction rate, very high reduction degree of iron ore, easy penetration into iron ore, and lean CO₂ emission. However, hydrogen has some inherent disadvantages such as explosiveness, endothermic reaction, and hydrogen embrittlement of steel equipments [1-3].

The objective of this research is to study the total simplified estimation of hematite ore and magnetite ore with CO and H₂ such as reduction degree of iron ore, reduction rate and morphology. The hope is to create an environmentally-friendly steelmaking process which will allow for improved reduction of iron ore when operated in hydrogen steelmaking process.

2 EXPERIMENTAL SECTION

The experiment was performed using the TG 151 thermogravimetric analyzer (Cahn Instruments, USA), which was controlled within the TG software, which was set to take a scan every 5 seconds while an experiment was running.

All iron ores used in this study were raw ores such as hematite ore (Australia) and magnetite ore (China). Before beginning the experiment, all iron ores were dried at a temperature of 110°C for 24 h. After drying, these were pulverized to a size of <125µm and were screened through a size of 63~125µm. Samples of iron ore powders were preheated (heating rate 10°C/min) under N₂ atmosphere to the desired temperature (selected from 400°C to 1000°C) and then isothermally heated under reducing temperatures. The process gases, H₂ and CO were of high purity (> 99%) for all of the experiments. The gas flow rate was 0.5 L/min. All samples initial weights



in all cases were approx. 1.5g. Chemical compositions of iron ore were using wet chemical analysis, ICP, and AA. Also, morphology was analyzed with Scanning Electron Microscopy (SEM).

The reduction degree is defined as the ratio of oxygen removed from the ore to the amount of oxygen originally present in the ore;

$$\text{Reduction [\%]} = \frac{\text{Oxygen removed}}{\text{Reducible oxygen in the ore}} \times 100$$

3 RESULTS AND DISCUSSION

3.1 Physical/Chemical Property of Hematite/Magnetite Ore

We are unaware of any previously published data on hematite and magnetite ore. The measured chemical composition, porosity and surface area data of hematite and magnetite ore were recorded in Table 1.

Table 1. Physical/chemical composition (weight %) of iron ores

ore	T-Fe	FeO	SiO ₂	CaO	MgO	Al ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	Combined water	Porosity	Surface Area
Hematite ore	62.65	0.14	2.21	0.15	0.064	1.56	0.081	0.018	0.024	6.21	22.57%	32.44m ² /g
Magnetite ore	68.67	28.29	4.91	0.10	0.18	0.061	0.011	0.022	0.010	0.3	-	0.867m ² /g

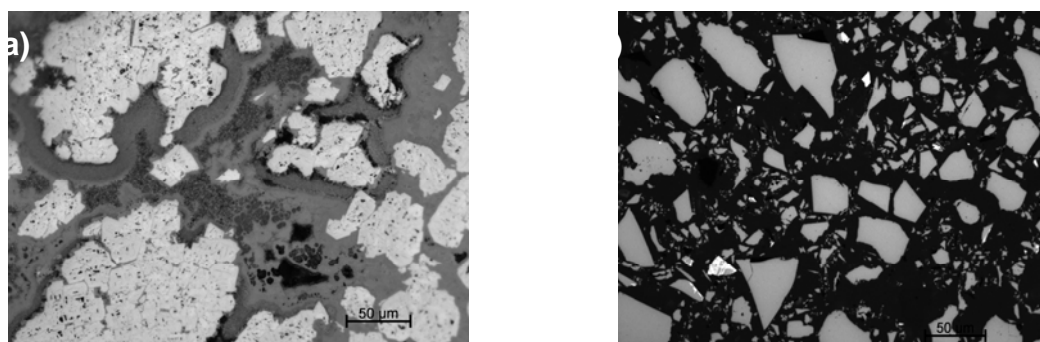


Figure 1. Photomicrograph of pore structures from iron ores. a) hematite ore and b) magnetite ore.

Chemical components were analyzed such as total Fe (T-Fe), FeO, SiO₂, CaO, MgO, Al₂O, TiO₂, Na₂O, and K₂O. T-Fe content of iron ores depends on both combined water content and gangue minerals. The combined water contents of hematite ore and magnetite ore are about 6.21% and 0.3%, respectively. T-Fe contents have about 62.65% and 68.67%. However, FeO and SiO₂ contents of magnetite ore are about 28.29%, and 4.91% higher than hematite ore (0.14% and 2.21%). The porosity and surface area of hematite ore have about 22.57% and 32.44m²/g. However, we can't measure the porosity of magnetite ore due to its dense surface. These properties were measured by mercury prosimetry on the iron samples of 63~125μm in size which were washed and dried at 110°C over 24h. And then their morphologies were determined by SEM (the results are reported in Figure.1). The hematite ore was cracked but less and narrower. These cracks were formed by dehydration of combined water contained in ore. On the other hand, magnetite ore was generally shown dense and had fewer pores than hematite ore.



3.2 Reduction Rate of Hematite/Magnetite Ore with H₂ or CO

The reduction rate of hematite ore with CO or H₂ at 400°C to 1000°C were graphically shown in Figure 2. It was found that the reduction degree of hematite ore with CO or H₂ increased with an increase in reaction temperature. As the reaction temperature was increased, the hematite ore with H₂ increased higher reduction rate than the CO for the same reaction time (30 min).

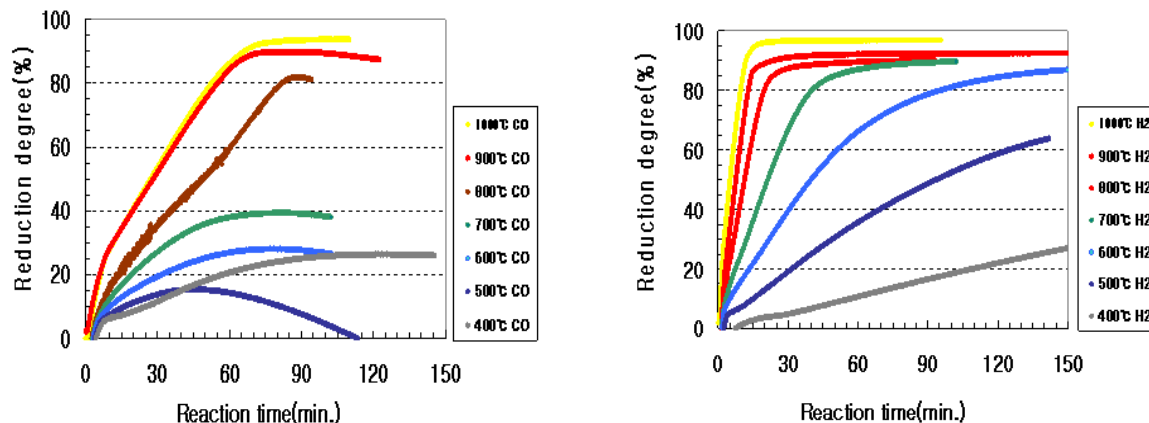


Figure 2. Reduction degree of hematite ore with CO or H₂.

Figure 3 shows the reduction rate and reduction degree of magnetite ore as function of time with CO or H₂. Reduction rate and reduction degree of magnetite ore show the highest at the 1000°C point in the reducing gas, CO. Also, it was found that the reduction rate and reduction degree of magnetite ore with CO increased with an increase in the reaction temperature. Whereas the reduction rate and reduction degree of magnetite ore with H₂ show the highest at the 700°C point. The initial reduction rate of magnetite ore with H₂ was increased with an increase in reaction temperature for 30min. Whereas, the final reduction degree of magnetite ore was shown the retardation of reduction above the reduction temperature of 800°C. It is not reasonable to postulate that the retardation of reduction rate with H₂ in magnetite ore show in the range of temperatures (from 800°C to 1000°C) studied. The reduction reaction of magnetite ore under H₂ is complex and has not yet been accurately investigated. Therefore, this study lays the foundation for future work on thermodynamics properties, kinetics, reduction mechanism (interfacial chemical reaction and gaseous mass transport) of magnetite ore with H₂.

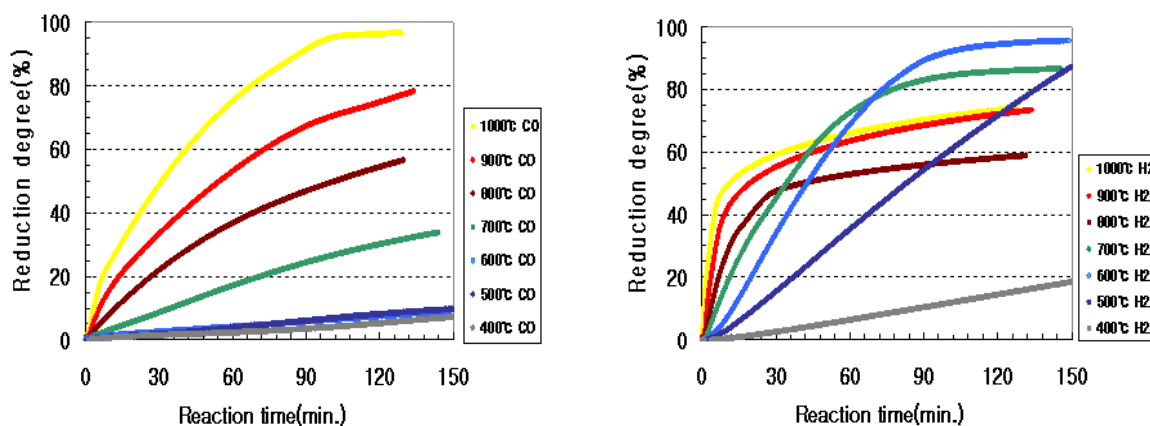


Figure 3. Reduction degree of magnetite ore with H₂ or CO.



3.3 Reduction Rate of Magnetite Ore with H₂-CO Mixtures

The reduction equilibrium rate of hematite and magnetite ore usually shift by the change of the mixing ratio of the introducing H₂ and CO, because the equilibrium of H₂ reduction differs with that of CO reduction at arbitrary temperature [3]. The variations of the outgoing gas composition with time at 700°C were shown in the reduction of magnetite ore by H₂-CO mixtures in Figure 4. It had been found that H₂ has better reduction degree for magnetite ore under the same temperature studied. The reduction rate of magnetite ore profile shifted toward lower the left, when the H₂ contents were increased. Similar trend was also reported for the reduction reaction of iron ore with CO-H₂ gas mixture by Ono-Nakazato, Yonezawa e Usui [3] and Usui et al. [4].

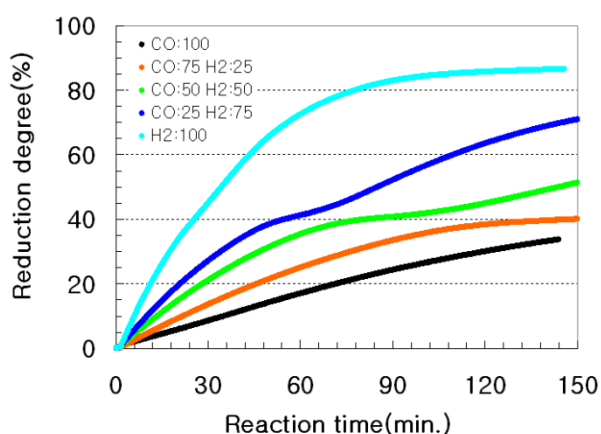


Figure 4. The reduction degree of magnetite ore under CO-H₂ mixture at 700°C.

4 CONCLUSIONS

We have investigated the reduction capacity of CO, H₂, CO-H₂ mixtures with at least two different iron ore materials.

The conclusion which could be drawn from this study of hydrogen reduction of iron ore are these: First, the reduction rate and reduction degree of hematite ore with H₂ demonstrated higher than CO under the same temperature conditions. Second, the initial rate of reduction rate of magnetite ore with H₂ was shifted earlier in 30min at the range from 800°C to 1000°C but the reduction degree of magnetite ore with H₂ is rapidly decreased when the reduction reaction is produced. Third, the reduction rate and reduction degree of H₂ seemed superior compared to the CO tested.

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