7th International Symposium on High-Temperature Metallurgical Processing

Edited by: Jiann-Yang Hwang, Tao Jiang, P. Chris Pistorius, Gerardo R.F. Alvear F., Onuralp Yücel, Liyuan Cai, Baojun Zhao, Dean Gregurek, and Varadarajan Seshadri TMS (The Minerals, Metals & Materials Society), 2016

FLASH REDUCTION OF MAGNETITE AND HEMATITE CONCENTRATES WITH HYDROGEN IN A LAB-SCALE REACTOR FOR A NOVEL IRONMAKING PROCESS

Yousef Mohassab, Mohamed Elzohiery, and Hong Yong Sohn

Department of Metallurgical Engineering, University of Utah, Salt Lake City, Utah 84112, USA

Keywords: Flash Reduction, Magnetite Concentrate, Hematite Concentrate, Hydrogen Reduction, Ironmaking

Abstract

As part of the development of a novel flash ironmaking process at the University of Utah, a labscale flash reactor was used to produce iron directly from iron oxide concentrate. This work tested the feasibility of the novel flash ironmaking process using the partial combustion of hydrogen as fuel and reductant. In this flash reactor, the energy required to reduce concentrate particles was obtained from the internal combustion of hydrogen and oxygen with complementary energy from electrical resistance heating to compensate for the heat loss. After the reaction shaft was electrically pre-heated, hydrogen and oxygen streams produced a non-premixed flame inside the reaction shaft. Various conditions such as flame configuration, flame power, positions of concentrate feeding ports, excess hydrogen amount and residence time were tested. More than 90% reduction of magnetite or hematite was achieved at temperatures as low as 1175 °C with \leq 100% excess hydrogen in <10 s of residence time.

Introduction

Recent developments in the ironmaking industry are mainly dedicated to reducing energy consumption and hazardous emissions. A novel flash ironmaking process is under development at the University of Utah^[1-13] where hydrogen, natural gas, or coal gas is used as the reductant and fuel in a gas-solid flash reactor. In this process, iron is produced directly from iron oxides concentrate particles without the need of pelletization, sintering or coke reducing energy consumption and CO₂ emissions significantly. As part of the continuing effort to develop this process, a flash reactor was built and utilized to produce iron from iron oxides using the partial combustion of hydrogen as fuel and reductant. This was the first flash reactor used for the experimental realization of the flash ironmaking process where fuel/reductant is partially combusted in an oxy-fuel flame.

The factors affecting the extent of the reduction of iron oxide are mainly the nominal particle residence time and the reductant excess driving force. Also tested in this work, two different flame configurations two concentrate feeding ports. This work is important in understanding the process as well as developing pilot and industrial reactors.

Experimental Work

Two types of iron oxide concentrates were used in this work: magnetite and hematite ore. Both concentrate particles used were of irregular shapes or mean particle sizes of $\leq 40 \,\mu$ m. Magnetite

concentrate was from the Mesabi Range of the U.S. The hematite concentrate came from the Yuanjiacun Range, Shanxi Province, China.

Figure 1 shows the apparatus used in this work. The apparatus consisted of a vertical electrically heated furnace housing the reactor tube, an electric power control system, gas delivery lines, and pneumatic powder feeding system. The reactor tube was made of stainless steel 316 with 8.7" ID and 84" long. The furnace was electrically heated by six SiC heating elements grouped into two series and controlled by two SCR controllers with a maximum temperature of 1200 °C. Temperature was monitored inside the reactor tube at various locations and outside around the reactor body. Temperature and power were monitored and controlled with the aid of computer. The powder feeding system consisted of a syringe pump, vibrator, carrier gas line, powder container, and powder delivery line. The system was heated up under nitrogen flow until the temperature reached 1150 °C measured at depth 30" along the vertical axis of the reactor tube, nitrogen was switched to hydrogen with the predetermined flow rate then oxygen was introduced to the system to start the flame. Nitrogen was flowed through the powder feeder lines to carry the powder into the reactor. The flame ignition was indicated by an increase in the temperature measured by thermocouple placed near the burner nozzle. The system then was heated by both the flame and the electric power until the temperature at 30" is 1200 °C. The electric power was controlled to maintain the 30" measured temperature within 1205 \pm 5 °C. Temperature profiles were measured for the reactor in order to define the reaction zone. The profiles were measured along the center of the reactor tube and close to the inner walls of the tube. All the profiles were measured while feeding powder under typical experimental conditions spanning wide range of flame power with and different flame configurations. The reaction zone was defined where the temperature is 1175 ± 25 °C and it was of 27"length. The radial variation in the temperature was negligible.

The powder was fed to the system at a constant rate of $0.12 - 0.24 \pm 0.006$ kg/h. The particles were fed through the upper flange of the system either through the center of burner (namely burner feeding) or through two inlets on the side of the burner (namely two side feeding) as shown in Figure 2. When feeding was through the burner inlet, the feeding rate was 0.12 kg/h whereas in feeding through the two side inlets the feeding was 0.06 kg/h through each inlet with a total feeding rate of 0.12 kg/h.

Hydrogen flow rates were varied in the experiments to vary the nominal particles residence time inside the reaction zone. The amount of oxygen fed was varied to control the $\%$ excess driving force (EDF) for the reduction reaction $[9, 13]$. The flow rates of hydrogen and oxygen gases were controlled using accurate mass flow controller while the nitrogen gas flow rates were controlled using rotameters.

Reduced particles samples were collected at the end of the reactor tube where a stainless steel bowl was used for collection the powder. The samples were analyzed using ICP-OES to determine the reduction degree. The nominal residence time of the particles, excess driving force (% excess hydrogen) and the reduction degree calculations can be found elsewhere [9, 13].

The flame configuration inside the reactor was changed in some experiments by swapping the hydrogen and oxygen feeding ports in the burner nozzle. In the new flame configuration oxygen flow surrounds hydrogen feed stream. The old flame configuration had the two gas streams reversed. When the concentrate is fed through the center tube, the new configuration prevents the particles from being heated excessively and melting as shown by temperature contours in the two simulated configurations shown in Figure 3.

Figure 1. Schematic diagram for the lab-scale flash reactor used in this work.

Figure 2. Powder feeding modes: (a) burner and (b) Two side-feeding.

Figure 3. Flame configuration and temperature contours: (a) old configuration and (b) new configuration.

Results

Magnetite Concentrate

The aim of the experiments performed on the flash reactor was to investigate the conditions that yield the highest reduction degree of the magnetite concentrate particles. Various combinations of particles residence time, excess driving force, feeding ports, and flame configuration were studied for this purpose.

When feeding through the two side inlets, increasing the particles residence time and the excess driving force increased the reduction degree as shown in Figure 4.

Figure 4. Feeding through the two side-inlets using the old flame configuration. (a) Effect of EDF on reduction degree (%) (b) Effect of nominal particle residence time.

Changing the feeding port from the two side inlets to the burner inlet resulted in lowering the reduction degree significantly due to the particles melting and becoming round as a result of exposure to the high temperature in the center of the flame, as shown in Figure 5. As shown in Figure 3(a), the temperature at the center of the flame where the particles are fed in the burner feeding mode using the old flame configuration reaches 2600 K. Melting and rounding reduces the active sites on the particles as compared with side feeding where the particles retain their irregular shape and reactivity that produced higher reduction degrees.

Figure 5. SEM micrograph for samples obtained with H₂ flow rate $= 60$ L/min and O₂ flow rate $= 9.7$ L/min and feeding through (a) side (RD = 63%) and (b) burner feeding (RD = 53%).

Under the same hydrogen flow rate, the flame power increases with oxygen flow rate. As mentioned earlier the particle nominal residence time is mainly controlled by the gas flow rates in this experiment. This means the power of the flame (directly linked to the flame temperature) increases with the decrease in residence time under the same excess driving force and temperature. For example, at 1175 ºC and EDF of 0.5, flow rates of hydrogen 60 L/min and 9.7 L/min of oxygen (nominal particle residence time of \sim 1.9 s), respectively, generated higher flame power than that the hydrogen flow rates of 20 L/min and 2.9 L/min of oxygen (nominal particle residence time of \sim 4.6 s). In the former case, the high flame power results in increasing the particles temperature in the reaction zone and subsequently increased the reduction degree of the particles $(RD = 60\%$, although shorter residence time, 1.9 s) as compared with latter case with the lower flame power $(RD = 30\%$, although longer residence time, 4.6 s) as shown in Figure 6.

Changing the flame configuration by swapping the hydrogen and oxygen inlets ports resulted in changing the temperature profile at the top of the reactor. When feeding through the two side inlets, the particles experience higher temperature compared to the old flame configuration specially for higher flame power experiments where the H₂ flow rate is (40-60 l/min) and EDF = 0.5 as shown in Figure 7.

In burner feeding with the new flame configuration, the temperature in the center of the flame was lower (see Figure 3(b)) than in the old flame configuration (see Figure 3(a)). Thus, particle melting was not evident; rather the particles retained their irregular shape even when passing through the flame. Figure 7 shows the change in the reduction degree $\binom{9}{0}$ with the residence time while Figure 8 shows the change in the particles shape with the flame configuration under otherwise the same conditions.

A reduction degree > 90% with % excess hydrogen driving force of less than 100 at temperature as low as $1175 \degree$ C and a feeding rate of ~ 0.2 kg/h in a few seconds of residence time was achieved.

Figure 6. Reduction degree (%) vs. nominal particle residence time at different EDF when feeding through the burner inlet.

Figure 7. Reduction degree $(\%)$ vs. nominal particles residence time with EDF = 0.5 and different flame configurations for (a) side and (b) burner feeding.

Figure 8. SEM micrographs of the powders from the collection plate from experiment with EDF $= 0.5$, particle residence time $= 1.9$ s, and feeding through the burner using (a) old (RD = 59%) and (b) new flame configurations $(RD = 75\%)$.

Hematite Concentrate

Hematite concentrate was used in the flash reactor and experiments were performed with varying the EDF, residence time, feeding ports and flame configuration. Under certain conditions hematite reduction degree was found to be the same or higher than that of magnetite at the same conditions as shown in Figure 9. More experiments are being conducted to compare hematite flash reduction with hematite and magnetite concentrate particles. Hematite reduction degree $> 90\%$ with % excess hydrogen driving force of less than 100 at temperature as low as 1175 °C and a feeding rate of \sim 0.2 kg/h in a few seconds of residence time was achieved.

Conclusions

Hematite and magnetite concentrate particles were reduced in a gas-solid flash reactor heated by hydrogen/oxygen flame and electric power. Hydrogen gas was utilized as a reductant and fuel. Different conditions were tested such as the particle residence time, excess hydrogen driving force, feeding ports, and flame configuration. Hematite and magnetite reduction degree > 90% were

Figure 9. Comparison between magnetite and hematite showing the effect of nominal particle residence time on the reduction degree when $EDF = 0.5$ for (a) burner feeding with old flame configuration, (b) side feeding with old flame configuration, and (c) burner feeding with new flame configuration.

achieved at a temperature as low as 1175 \degree C with % excess hydrogen driving force of less than 100 % and a feeding rate of \sim 0.2 kg/h in a few seconds of residence time. Melting was found to decrease the reduction degree.

Acknowledgments

The authors thank Deqiu Fan, Brian Willhard, Andrew Laroche, Udo Fischer, Omar Kergaye, Osama Kergaye, Tuvshinbat Ganbat, and Jacqueline De Oliveira Cota for the help with the experimental runs and analytical work using ICP and. The authors acknowledge the financial support from the U.S. Department of Energy under Award Number DEEE0005751 with cost share by the American Iron and Steel Institute (AISI) and the University of Utah.

Disclaimer: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors

expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

References

- 1. M.Y. Mohassab-Ahmed and H. Y. Sohn, *Method and Device for Digestion of Materials in a Microwave Oven*, 2012, US Patent App. 61/651.
- 2. M.Y. Mohassab-Ahmed, H. Y. Sohn, "Effect of Water Vapor Content in H₂-H₂O-CO- $CO₂$ Mixtures on the Equilibrium Distribution of Manganese between CaO–MgO_{sat}–SiO₂– Al2O3–FeO–P2O5 Slag and Molten Iron." *Steel Res. Int.*, 85 (2014), 875-884.
- 3. M.Y. Mohassab Ahmed, "*Phase Equilibria between Iron and Slag in CO/CO2/H2/H2O Atmospheres Relevant to a Novel Flash Ironmaking Technology*" (PhD Dissertation, The University of Utah, 2013).
- 4. M.Y. Mohassab-Ahmed, H. Y. Sohn, "Effect of Water Vapor Content in H₂-H₂O-CO-CO₂ Mixtures on the Activity of Iron Oxide in Slags Relevant to a Novel Flash Ironmaking Technology." *Ironmaking Steelmaking*, 41(2014), 665 - 675.
- 5. Y. Mohassab and H. Sohn, "Effect of Water Vapour on Distribution of Phosphorus between Liquid Iron and MgO Saturated Slag Relevant to Flash Ironmaking Technology." *Ironmaking Steelmaking*, 41 (2014), 575-582.
- 6. Y. Mohassab and H.Y. Sohn, "Effect of Water Vapor on Sulfur Distribution between Liquid Fe and MgO Saturated Slag Relevant to a Flash Ironmaking Technology." *Steel Res. Int.*, 86 (2014), 753–759.
- 7. Y. Mohassab and H.Y. Sohn, "Analysis of Slag Chemistry by FTIR RAS and Raman Spectroscopy: Effect of Water Vapor Content in H₂-H₂O-CO-CO₂ Mixtures Relevant to a Novel Green Ironmaking Technology." *Steel Res. Int.*, 86 (2014), 740-752.
- 8. M.Y. Mohassab-Ahmed, H.Y. Sohn, and L. Zhu, "Effect of Water Vapour Content in H2- H2O-CO-CO2 Mixtures on MgO Solubility in Slag under Conditions of Novel Flash Ironmaking Technology." *Ironmaking Steelmaking*, 41 (2014), 575-582.
- 9. F. Chen, Y. Mohassab, T. Jiang, and H.Y. Sohn, "Hydrogen Reduction Kinetics of Hematite Concentrate Particles Relevant to a Novel Flash Ironmaking Process." *Metall. Mater. Trans. B*, 46 (2015), 1133-1145.
- 10. F. Chen, Y. Mohassab, S. Zhang, and H.Y. Sohn, "Kinetics of the Reduction of Hematite Concentrate Particles by Carbon Monoxide Relevant to a Novel Flash Ironmaking Process." *Metall. Mater. Trans. B*, 46 (2015), 1716-1728.
- 11. H. Pinegar, M. Moats, and H. Sohn, "Flowsheet Development, Process Simulation and Economic Feasibility Analysis for Novel Suspension Ironmaking Technology Based on Natural Gas: Part 2 – Flowsheet and Simulation for Ironmaking Combined with Steam Methane Reforming." *Ironmaking Steelmaking*, 40 (2012), 44-49.
- 12. H. Pinegar, M. Moats, and H. Sohn, "Flowsheet Development, Process Simulation and Economic Feasibility Analysis for Novel Suspension Ironmaking Technology Based on Natural Gas: Part 1 Flowsheet and Simulation for Ironmaking with Reformerless Natural Gas." *Ironmaking Steelmaking*, 39 (2012), 398-408.
- 13. M.E. Choi and H.Y. Sohn, "Development of Green Suspension Ironmaking Technology Based on Hydrogen Reduction of Iron Oxide Concentrate: Rate Measurements." *Ironmaking Steelmaking*, 37 (2010), 81-88.