DOE FINAL REPORT

Future Steelmaking Processes

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Industrial Partners:

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EXECUTIVE SUMMARY

There is an increasing demand for an ironmaking process with lower capital cost, energy consumption and emissions than a blast furnace. It is the hypothesis of the present work that an optimized combination of two reasonable proven technologies will greatly enhance the overall process. An example is a rotary hearth furnace (RHF) linked to a smelter (e.g., AISI, HIs melt). The objective of this research is to select promising process combinations, develop energy, materials balance and productivity models for the individual processes, conduct a limited amount of basic research on the processes and evaluate the process combinations. Three process combinations were selected with input from the industrial partners. The energy-materials and productivity models for the RHF, smelter, submerged arc furnace and CIRCOFER were developed. Since utilization of volatiles in coal is critical for energy and CO₂ emission reduction, basic research on this topic was also conducted.

The process models developed are a major product developed in this research. These models can be used for process evaluation by the industry. The process combinations of an RHF-Smelter and a simplified CIRCOFER-Smelter appear to be promising. Energy consumption is reduced and productivity increased. Work on this project is continuing using funds from other sources.

INTRODUCTION

Currently, iron for producing steel is primarily produced in the blast furnace, which is highly energy and capital intensive. Furthermore, the process uses coke that requires special coals and the cokemaking process has significant environmental

concerns. There are a few alternative commercial processes for producing iron. About 5% of iron in the world is produced by direct reduction using natural gas such as Midrex. These processes will only be niche processes where natural gas is available at reasonable prices. One process producing liquid iron has been developed which uses coal, COREX, but it represents less than 1% of the total production. COREX is capital intensive and produces excessive amounts of export energy. Recently HIs melt has proven to be feasible in extensive pilot plant trials and two commercial plants are being built.

The US and many other parts of the world requires a fossil fuel based process, low in capital and operating cost, energy efficient, and flexible with regards to capacity and raw materials. Several processes in the past 15 years were proposed and reached a reasonable level of development such as AISI Smelting (USA), DIOS (Japan), ROMELT (Russia), FASTMET (USA) and HIs melt (Australia). However, none have been successfully commercialized. As mentioned, two HIs melt commercial plants are being built. This is due in part by the fact that the individual processes could not produce iron effectively with regards to the criteria above. All have limitations with regards to energy efficiency, productivity, etc.

It is the hypothesis of the present research that a combination of two reasonable proven technologies can be used effectively to overcome the limitations of the individual processes. An example is the combination of a rotary hearth furnace using ore-coal composite pellets linked to an AISI or HIs melt smelter. The productivity limitations of the RHF is eliminated by doing the final reduction and the separation of

the gangue by feeding the product into a smelter. The smelters productivity and energy consumption are greatly improved because the ore feed is pre-reductant.

Objective

The objective of this project is to examine potential new ironmaking processes and define promising process combinations to produce iron at a lower cost and energy consumption than the blast furnace. Energy and materials balance models for the potential processes as well as fundamental research on critical aspects of the process were performed in order to evaluate the potential processes and optimize the process combination.

Research Results

The project had assistance, and advise, from its industrial partners (USS, ISG and Praxair). In particular, they helped in selecting the processes to be evaluated and the critical aspects to be researched. It was originally planned for them to aid in the research. However, due to the recent condition in the steel industry the companies did not have the resources to help conduct the research. Therefore, all of the actual research was done at Carnegie Mellon University and there was a one year no cost extension.

Task I. Examination of potential processes

With input from the industrial partners the most promising new processes were identified and their current status reviewed. An example of this evaluation was for direct smelting, which is given in Appendix A.

The individual processes selected by the team were:

Rotary Hearth Furnaces
CIRCOFER
Smelting Processes (AISI and HIsmelt)
Submerged Arc Furnaces

Task II. Selection of Process Combination

The objective of this research was to evaluate promising process combinations. Based on the strategy of overcoming the process limitation of one process by combining with another and at the same time overcoming those of the second process, three process combinations were selected.

A. RHF and Smelter: The problem with the RHF is low productivity when attempting high degrees of reduction and the product has large amounts of gangue and ash. Therefore, in the proposed process, the degree of reduction is limited to 70%, increasing productivity by 50-75% and carrying out final reduction, melting and phase separations in a coal based smelter. The problem of the high energy generation and post combustion required in the smelter when using un-reduced or even 33% reduced ore is overcome by using the product from the RHF (70% reduced) and limiting post combustion to 30%. The CO-H₂ rich off gas from the smelter is then used as a fuel in the RHF in place of natural as (Figure 1).

- B. CIRCOFER-Smelter:** In the CIRCOFER process, coal and ore are fed into two fluid beds. The first is a circulating fluid bed (CFB) where the coal is charred and the ore 50% metallized, the second a bubbling bed (BFB) where final reduction using the char is achieved. Productivity is limited because of high retention times required in the BFB. In the proposed process combination only the CFB is used to produce char and a 50% metallized product which is fed into a smelter. In a smelting, using char, 80% post combustion is possible and final reduction is very rapid (Figure 2).
- C. RHF-Submerged Arc Furnace (SAF):** In this case, reduction in the RHF is about 90% and the SAF is used primarily for melting and phase separation (Figure 3). This case was primarily chosen to compare to cases A and B since it is nearly commercialized.

Task III. Energy and Materials Balances and Productivity Models

In order to technically evaluate, economically evaluate and optimize the selected process combinations, energy and materials balance computer models are required. This was a major effort and accomplishment of this research. The models must be comprehensive to account for variations in the input material, final product, and operating variables. The library of energy and materials balances developed is a valuable asset to any company or organization evaluating new processes.

Energy and materials balances and kinetic or productivity models were developed for the RHF (Appendix A), the SAF (Appendix C) and the smelting process (Appendix D). Work is currently underway for CIRCOFER.

Task IV. Role of Volatiles in processes

The industry partners and academic researchers concluded that for a fossil fuel process to be energy efficient, the volatiles in the coal must be used effectively. In particular, in the RHF and smelting processes. Therefore a program was designed to determine how volatiles can be used effectively.

In an RHF, reduction by carbon begins at about (900°-1000°C) while reduction begins at 600°C and volatiles are released below 600°C. In multi-layers, pellets or a bed of coal-ore is used, the top maybe over 700°C while the lower level is releasing its volatiles. So the H₂ and CO in the volatiles can reduce iron oxide the top level of ore (Figure 4).

The research consists of basic measurements on the reduction of ore by H₂ at low temperatures and the building and operation of a special radiant heating furnace to simulate the RHF process. The rate of reduction of ore by hydrogen is complex but is significant, below 500°C. More importantly as shown in Figure (5) the rate of reduction of ore-carbon composite in H₂ is significantly faster than in an inert gas which demonstrates how volatiles can be used for reduction. Details are given in Appendix E.

A special experimental devise was built to test the hypothesis. Pellets, or a pile of ore-coal mixture, is heated by radiant heat transfer as in an RHF. The top layer will be 200-600°C higher than the lower. The top level will then be reduced by the volatiles

in the lower level. The equipment and experiments are given in Appendix F. Work on this Task is continuing using other funds.

Task V. Process Combination Optimization

It is the hypothesis of the present research that a strategic combination of two processes will overcome the disadvantages of the individual processes. For the process combination to be economical and consume the lowest possible energy, the combustion must be optimized. This is different than optimizing the individual processes. In optimization, the criteria must be stated. In the present work the processes are initially being optimized with regards to energy, then productivity and finally cost.

An example of the optimization is given for the RHF-Smelter. The specific operating condition for the RHF is for 70% reduction and for the smelter 30% post combustion. The energy and materials balance for the system is given in Table (1). The energy required is greatly reduced requiring a total of 370 kg of coal. For the RHF using coal the productivity of the RHF for 70% reduction is 40% higher than for normal operation (95% reduction). Furthermore, the productivity of the smelter increases by 50% compared to ore preheating but with no prereduction. The energy requirement is reduced by over 60% and the total energy is less than a blast furnace. Even though the process combination requires more capital for the RHF than the ore preheater the increase in productivity reduces the cost per annual tonne. Of course, the RHF and smelter must be sized to match each other's productivity.

The complete optimization including the economics is extremely complex. It also depends on the unit cost which vary with time and location. Using the results from this

research, it is possible to compute and optimize the economics for the RHF-Smelter and RHF-SAF processes for specific conditions. Work is continuing on the CIRCOFER-Smelter process.

Accomplishments and Future Work

The research project was very ambitious and accomplished most of its goals. It screened the new ironmaking processes and selected three process combinations for detailed analysis. Energy and materials balances and productivity models were developed for most of the individual units. It as demonstrated that the combination process of an RHF and Smelter could reduce energy and significantly increase productivity. Complete optimization is extremely complex and is site and input cost sensitive. However, the present results are capable of performing such an analysis. Research on this project is continuing using other funds. In particular, work on an energy and materials balance on a simple CIRCOFER (50% reduction) which will be used for optimization of the CIRCOFER-Smelter combination.

Table 1. Estimated consumption of materials in the combination process per ton of hot metal produced with 70% metallized DRI and 30% post combustion in the smelter.

RHF			Output
Ore (kg) 1422	Coal (k/g) 250	Smelter gas (Nm ³) 158	70% metallized pellets, 5% gangue (k/g) 1148

SMEILTER			Output
RHF pellets (k/g)	Coal 30% Volatiles (k/g)	Oxygen (Nm ³) 45	Hot metal with 4.5% carbon (kg)

1148	120		1000
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Figure 1. RHF-Smelter schematic

Figure 2. 1st stage Circofer-Smelter schematic

Figure 3. RHF-SAF schematic

Figure 4. Schematic of a multiple layer RHF

Figure 5. The reduction of iron oxide and graphite composite powders at 900°C.

Appendix A

Direct Smelting Processes

Introduction

Direct smelting processes are also referred to as bath smelting processes. The process uses iron ore which may be prereduced or preheated, coal and oxygen or air for combustion. The processes have been under development for about 15 years and reached the pilot plant scale in many cases.

Current Status

There are four processes which have reached a reasonable degree of development: HIs melt, DIOS, AISI and ROMELT. The status and operating characteristics of these four processes are given in Table 1.

The Cyclone Converter Furnace (CCF) is a prereduction furnace which can be placed on top of the smelters. It swirls the off gas from the smelter and preheats and prereduces a fine ore feed to a mixture of molten FeO and Fe_3O_4 . The Ausmelt process is similar to DIOS and AISI but combusts a portion of the coal in the slag. Ausmelt is currently only operating a small furnace (1.5-2.0 t/hr) but has produced nearly 1000 t as of February 2002.

Of the processes developed, only HIs melt has definite plans for a commercial/demonstration plant. They have a number of undisclosed partners and are building a merchant pig iron plant in Kwinana Western Australia. The

plant will have an ore preheater and is designed to produce 92 t/hr using 525-575 kg of coal per tonne. ROMELT has tentative plans for a 300,000 tpy plant in India.

Process Compatibility

Since it is the present concept to couple two processes the product from the first process must be compatible with the feed requirements of the next process.

DIOS and AISI can use a CCF, a rotary hearth furnace (RHF) or CIRCOFER as the first stage. Hismelt must inject the ore so the use of an RHF is not possible but it can use a CIRCOFER. It would be difficult for ROMELT to use a CCF but could use an RHF or CIRCOFER.

Energy and Materials Balances

CMU is developing a generic energy and materials balance computer program, which will be applicable for any of the smelting processes. It can also use the feed material from any prereduction process, i.e., RHF, CIRCOFER, etc.

Productivity Model

CMU is considering production limiting processes such as reduction, foaming and energy generation. Based on the results of this, a productivity model which can estimate the production rate for various inputs and operating conditions will be developed.

Energy Consumption and Environmental Concerns

It is claimed that these processes consume 5% less energy than the coke oven and blast furnace. However, these figures are vague and depend on how energy credits are taken. These figures will be confirmed as part of the current project. The processes eliminate the coke plant and associated environmental concerns. CO₂ generation is slightly lower than blast furnace.

Table 1.

Process	Feed Materials	Operating Characteristics	Current Status
Developer			
HIsmelt HIsmelt Ltd. Rio Tinto	Fine Ore Coal Air plus O ₂	Injection of coal and ore into the melt in a water cooled vertical vessel. Ore can be preheated or prereduced. Air with O ₂ is used for combustion using a large diameter lance at low velocities	Successfully ran an 8 t/h pilot plant for over 30 days. Process stability was excellent. Achieved post combustion greater than 60%. They are building a commercial/demonstration plant which is designed for 92 t/h, 700,000 tpy, using 525-575 kg of coal per tonne
DIOS Japanese Iron and Steel Federation Currently NKK	Fine ore Coal Oxygen	Coal and ore are gravity feed into a vertical reactor. Ore is prereduced to about FeO in two fluid beds. An oxygen lance is used for combustion. Extensive water cooling is used.	Ran a 15-20 t/hr pilot plant with 35-45% post combustion at NKK Keihin Works and produced over 2000 t of iron. Developed flow sheets with a RHF prereducer. No current activity for commercialization
AISI AISI and US DOE	Pellets or Waste Oxides Coal Oxygen	Pellets are prereduced to FeO in a shaft furnace or waste oxides are added directly, both by gravity feed. An oxygen lance with two sets of nozzles are used for combustion. Recycle and some coal injected into slag. Uses water cooling in upper vessel.	Completed pilot plant trials at 4 to 5 t/hr. Achieved 35-45% post combustion. Developed flow sheets and pre-engineering studies for a 400,000 tpy plant. No current activity
ROMELT Currently	Fine Ore Coal	A large horizontal reactor with two sets of	Produced over 0.5 million tonnes in Russia.

Hatch Engineering	Oxygen Air	tuyeres, one oxygen, other air. Direct gravity feed, no prereduction. Uses extensive water cooling.	Considering a 3000,000 tpy plant in India.
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Appendix B

RHF Model

Introduction

The Rotary Hearth Furnaces can be used for final reduction but suffers from low productivity with high degrees of metallization. RHF's are currently used in at least six ironmaking technologies: INMETCO, Redsmelt, Iron Dynamics, FASTMET, Sidcomet, and ITmk3. Among these six technologies, only ITmk3 uses the RHF as a stand-alone unit for the production of gangue free metal. In all other processes, the RHF reduces to about 80% and is combined with a secondary smelting facility for gangue removal. The DRI produced is usually taken to an electric arc furnace for final reduction and gangue removal. In the traditional design of RHF technologies such as in the INMETCO and FASTMET, coal and iron oxides are first mixed into green pellets and charged in the RHF as layers of 2 to 3.

Model Development

The productivity of a Rotary Hearth Furnace is usually expressed in terms of the amount of DRI produced per unit times per unit area of hearth or simply kgDRI/m²hr. The metallization degree of the DRI produced is controlled adjusting the speed of rotation of the moving hearth. Usually, pellets span angles

close to 270 degrees in 10 to 20 minutes to achieve 90% of average metallization. In this work, a model was constructed aiming at the estimation of changes in RHF productivity according to the types of carbon employed, sizes and number of layers of the pellets used, as well as with RHF operational temperatures. The productivity model considers three main reaction zones assigned to the pre-heating, pre-reduction, and final reduction of the pellets. In the model, the transition of the first to the second zone was taken as the limit where the pellets attain a minimum temperature of 600°C marking the end of pre-heating. During the evaluation of different operational scenarios, the transition between the second and third zones was taken as the first formation of iron corresponding to the end of pre-reduction of the pellets to wustite and, finally, the third zone ends when the pellet bed achieves the desired average metallization degree. Typical temperatures for the gas in each of the three zones were taken as 1100, 1280, and 1280°C respectively.

The transfer of heat from the RHF to the surface of the pellets in the reduction bed was considered due to radiation alone. A view factor of 1 was assumed for the transfer of heat to pellets at the top layer. The model solves transport equations using two main sets of parameters to define reaction rates and heat transfer inside the pellets and computes the overall rates of reduction based on the external conditions of heat transfer to the surface of the pellet. The division of the RHF in three zones can allow the consideration of the interplay of mass transfer from the RHF gas to the pellets and reduction reactions taking place

inside the pellets. The model developed is not expected to predict the exact production rates due to the lack of certainty regarding the parameters defining the external conditions of heat transfer. However, the model should predict the relative productivity rates for different operating conditions such as the carbon type and degree of reduction required.

Results

The results and the prediction of the productivity of the RHF from the model described above is given in the following figures. For a typical RHF operating condition, the reported productivities of RHF operations are usually between 70 and 90 kg DRI/m².hour at 90% metallization. Figure 1 shows that beyond a certain mixture pellet diameter the productivity is highest for 2 layers. Figure 2 shows that the productivity of the wood charcoal is almost 2/3 higher than for the coal due to the higher surface area for reaction.

Figure 1. Predictions from the productivity model developed employing coal

Figure 2. Estimated change in productivity of RHF operations according to metallization degree using coal or wood charcoal as reductant.

Appendix C

Energy and Materials Balance for SAF

Introduction

The submerged arc furnace can be used for final reduction, melting, and gangue separation of materials prereduced in another reactor such as a rotary hearth furnace. The energy is supplied to a graphite electrode producing a high density arc for heat generation. The prereduction is generally in the range of 80 to 100% and the additional feed of coal or coke is used for the reduction of iron oxides only. The important variables are:

Input variables	Specifics
Ore	Metallization
	Percent gangue and its composition
	Temperature
Coal(Coke)	Composition
Energy efficiency	HTE

Model Development

For the SAF, the mass inputs and outputs for each constituent element in the total system are balanced. The energy required for the applicable reduction reactions, latent heats of phase changes and the energy to heat up each constituent has been considered. By linking appropriate variables with coherent equations of the aforementioned mass balance and heat balance equations, the model for the SAF in question has been determined.

Results

The results are exemplified by the following examples. In Case I, the feed material is 92% metallized. In Case II, the conditions are the same, but only 88% metallized. Case II is if we attempt to increase productivity of the RHF.

Table 1. Inputs for a 1 tonne Fe-4% C output.

No.	Type of Input	Amount	Units
1	Input Temperature	1173	Kelvin
2	Output Temperature	1773	Kelvin
3	% of carbon in output	4	Percent
4	amount of Fe-4%C output	1	Tonne
5	amount of electrode consumption	2.3	kg/Tonne
6	basicity of the slag	1	-
7	percentage of metallization of DRI	92/88	Percent
8	percentage of SiO ₂ in DRI	2	Percent
9	percentage of Al ₂ O ₃ in DRI	2	Percent
10	percentage of C in DRI	1	Percent
11	percentage of FeO in Slag	4	Percent
12	percentage of SiO ₂ +Al ₂ O ₃ in carbon	4	Percent
13	Heat transfer efficiency(HTE)	100	Percent

Table 2. Output values for 92% metallization.

No.	Type of Output	Amount	Units
⇒ Mass balance			
1	Fe product	960	kg
2	DRI required	1036.64	kg
3	reductant input required	45.3791	kg
4	lime input required	42.3491	kg

5	SiO ₂ in the slag	21.6404	kg
6	Al ₂ O ₃ in the slag	20.7328	kg
7	FeO in the slag	3.52909	kg
⇒ Heat balance			
1	Heat of Fe in DRI	104.379	kWh
2	Heat of FeO in DRI	14.1807	kWh
3	Heat of SiO ₂ in Slag	4.33881	kWh
4	Heat of Al ₂ O ₃ in Slag	6.09783	kWh
No.	Type of Output	Amount	Units
5	Heat of CaO in Slag	6.94687	kWh
6	Heat of input carbon	14.4869	kWh
7	Heat of the electrode	0.749242	kWh
8	Heat of carbon in the DRI	3.37693	kWh
9	Heat of reaction	53.0539	kWh
10	Required total energy	207.61	kWh

Table 3. Output values for 88% metallization.

No.	Type of Output	Amount	Units
⇒ Mass balance			
1	Fe product	960	kg
2	DRI required	1048.3	kg
3	Reductant input required	53.7133	kg
4	lime input required	42.9817	kg
No.	Type of Output	Amount	Units
5	SiO ₂ in the slag	22.0402	kg
6	Al ₂ O ₃ in the slag	20.9659	kg
7	FeO in the slag	3.58181	kg
⇒ Heat balance			
1	Heat of Fe in DRI	99.8446	kWh
2	Heat of FeO in DRI	21.2719	kWh
3	Heat of SiO ₂ in Slag	4.41898	kWh
4	Heat of Al ₂ O ₃ in Slag	6.1664	kWh
5	Heat of CaO in Slag	7.05064	kWh
6	Heat of input carbon	17.1476	kWh
7	Heat of the electrode	0.74924	kWh
8	Heat of carbon in the DRI	3.41491	kWh
9	Heat of reaction	80.5347	kWh

10	Required total energy	240.599	kWh
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The results indicate that when the degree of metallization decreases from 92% to 88%, the energy required increases by 33 kWh/t and carbon by 8 kg/t. In these cases, the carbon source was coke which contains only fixed carbon, SiO_2 and Al_2O_3 .

Figure 3. The productivity of the submerged arc furnace.

Figure 3 shows the productivity of a submerged arc furnace operating with an input feed of a 92% metallized DRI and a Fe-4% output product assuming 100% heat transfer efficiency. The produced iron is directly proportional to the electric energy but with increased cost of the electricity, it would be highly likely that the cost of production would limit the extent of operation of this process.

Appendix D

Smelter Model Energy and Materials Balance

A smelter is used for final reduction, melting, and gangue separation of partially reduced ore. Energy is supplied by oxidizing coal and post combustion of CO and H₂. The degree of pre-reduction can range from zero to 100%. The feed materials are ore, coal, flux and oxygen or air for combustion. The important variables include:

Input variables	Specifics
Ore	Degree of reduction
	Percent gangue and its composition
	Temperature
Coal(Coke)	Composition
Post combustion	Percent of H ₂ and CO combusted at the top gas
Energy efficiency	THE

Pre-heat temperatures: All temperatures of gases and solids used can be varied at will in order to consider the pre-heating of raw materials. Alongside, all temperatures of outputs such as off-gas and hot metal can be changed to simulate different operational conditions.

In the model, the Smelter is divided in top gas and melt. The melt receives inputs of coal, ore, flux and oxygen for primary combustion of carbon to CO. The top receives gas from the melt and extra air for post combustion of CO and H₂ to CO₂ and H₂O. The coal required is computed from the enthalpy balances of bottom and top considering that only a fraction of the energy liberated by post

combustion of the top gas is transferred to the melt. A schematic of the model is shown in Figure 4.

The solution starts with the computation of mass balances for the melt and gas. The amount of coal necessary is determined iteratively considering the enthalpy balances for top and bottom

Figure 4. Black-box model of Smelter divided into gas and melt

Figure 5. Coal requirements decrease with increasing Post-combustion ratio.

The results from the model developed are exemplified in Figure 5, where the coal, necessary to produce 1t of hot metal, is estimated at different levels of post combustion. In this example, a coal with 70% of fixed carbon is considered with a heat transfer efficiency of 80%. In this example, no preheating of ore or combustion air is considered.

Figure 6. The reduction rate of an AISI smelter as a function of slag weight.

Figure 6 shows the rate of reduction in an AISI smelter at 1550°C as a function of slag weight. Obviously other operational factors could affect the rate such as stirring intensity, but still the reduction rate is reasonably proportional to the slag weight.

Appendix E

The role of volatiles

The combined process of an RHF with a smelter or SAF incorporates coal for the reduction reactions. These coals may contain large amounts of volatiles

which can constitute up to 40% of the weight of coal with H_2 , H_2O , CO , CO_2 and CH_4 being the majority. Considering that the reaction rate of hydrogen is much faster than CO and CH_4 , some knowledge of hydrogen reduction is necessary.

Figure 7. The reduction mechanism of MNC with H_2 at $400^\circ C$

Contrary to previous works done on small particles of less than $150 \mu m$, the complete internal reduction of iron oxide where chemical kinetics is solely controlling is not observed, but a mixed control mechanism complicated by mass transfer and nucleation.

The reduction of a Western Australian Mount Newman Concentrate ore with hydrogen at low temperatures show 4 distinct regions. Region I is relatively constant to about 2.68% reduction, which is much less compared to the complete reduction to Fe_3O_4 at 11.13%. Unlike porous iron oxides where the complete

internal reduction to Fe_3O_4 and thus a linear slope of $\ln(1-F)$ vs. time can be obtained, denser iron oxides such as MNC show mass transfer affects inhibiting the reaction to Fe_3O_4 . With higher degrees of reduction, the formation of metallic Fe begins to affect the rate of reduction. Region II shows an acceleration of the reduction rate and is believed to be a combination of metallic nuclei's forming and growing with the added mechanism of reduction to Fe_3O_4 . A steady state rate is achieved in region III where from the non-linear slope of $\ln(1-F)$ vs. time implies a mixed control mechanism of possibly chemical kinetics and pore mass transfer. At, or near, the final stages of reduction, a decreased number of reaction sites results in either chemical kinetics or pore diffusion to be solely controlling.

The reduction of various iron oxides at 400°C is shown in Figure 8 where the rate is directly related to the initial density of the ore. With higher initial density, the rate decreases due to the increased effect of pore diffusion to the overall reduction mechanism.

Although the mixed control mechanism is implied indirectly, the role of mass transfer can be determined qualitatively by observations of partially reduced specimens of iron oxides. The following SEM observations show the surface reactions and the cross sectional area of partially reduced iron oxide specimens of MNC and HFIO.

Figure 8. The reduction of various iron oxides with H_2 at 400°C.

Figure 9. MNC reduced with H_2 at 773 K (a) 26.9% and (b) 50.39%

Figure 10. HFIO reduced with H_2 at 773 K (a) 26.24% and (b) 48.27%.

Figure 11. HFIO reduced with H_2 at 773 K (a) 15% and (b) 52%.

The star-like pore formation are typical for the denser oxides. The majority of the pores formed on the MNC are usually fissures and cracks with an occasional star-like pore, which also do seem to interconnect at higher reductions. The pores for denser iron oxides of HFIO are usually star-like which increase in number and size with higher reduction degrees. Figure 11(a) and 11(b) illustrates a topochemical reduction characteristic where the iron rich layer moves toward the core of the particle. This is typical of a reaction where pore diffusion through a dense iron layer is controlling.

Appendix F

Radiant Heat Transfer Experiments

The radiation, which impinges upon the surface of the pellet, is transferred via conduction to the core of the pellet. The rate at which this transfer of heat takes place controls the rate of evolution of volatiles from the pellet. A large temperature difference for a highly conductive pellet between the core and surface results in a high heat transfer rate and a large driving force for devolatilization.

Figure 12. Schematic of core to surface temperature measurement in the IR heater.

A hemispherical handpacked pellet of 18 mm is placed on the alumina brick with the IR radiation impinging on the outer surface as shown in Figure 12. The core to surface temperature is directly affected by the effective thermal conductivity of the pellet. Thus when the density of the pellet is sufficiently high, the rate at which heat is transferred is fast enough that the temperature to core difference is negligible. Thus pellets slowly sintered in the induction furnace at 450°C for 10 hrs results in fairly dense oxide pellets of hematite. XRD patterns verify the phases to be pure hematite.

The temperature profile of the core and surface of a sintered hematite pellet is shown in Figure 5. The temperature difference is initially about 15°C from core to surface and is about 10°C at steady state. Ideally, the temperature would homogenize in the sample but because of radiation from the walls of the insulator and the non-concentric heat loss to the bottom of the hemisphere it is likely that a constant temperature difference is maintained, but is negligible in the overall scheme of the qualitative analysis of the results.

Measurements of hand-packed pellets which were not sintered have shown core to surface temperature difference as high as 50°C. Also, the initial smooth surface experienced cracking which would cause a change in the surface property that govern IR heat transfer. The extent of cracking was not uniform and seems to be caused by the rapid evolution of chemisorbed water vapor. Furthermore, the texture of the surface is changed from a red color to a dark grey color which would affect the surface properties.

Figure 13. Temperature measurement of core/surface for sintered pellets.