May 1995

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Cyclone Reduction of Taconite— Final Report

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INEL-95/0258

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Published May 1995

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Prepared for the
Interior Department's Bureau of Mines
Under Contract No. J0134035
Through DOE Idaho Operations Office
Contract DE-AC07-94ID13223

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ABSTRACT

A cyclone reactor system for the partial reduction and melting of taconite concentrate fines has been engineered, designed and operated. A non-transferred arc plasma torch was employed as a heat source. Taconite fines, carbon monoxide, and carbon dioxide were fed axially into the reactor, while the plasma gas was introduced tangentially into the cyclone. The average reactor temperature was maintained at above 1400 °C, and reduction experiments were performed under various conditions.

The influence of the following parameters on the reduction of taconite was investigated experimentally; carbon monoxide to carbon dioxide inlet feed ratio, carbon monoxide inlet partial pressure, and average reactor temperature. The interactions of the graphite lining with carbon dioxide and taconite were also studied.

The extent of the reduction was not greatly affected by the presence of carbon dioxide in the feed gas and increasing carbon monoxide partial pressures increased the degree of metallization slightly. In contrast, the average reactor temperature exerted a pronounced influence on taconite reduction.

The reduction reactions are believed to be chemically controlled, but mass transfer limitations appear to influence these reactions at higher temperatures.

The Boudouard reaction, at the temperatures employed, was very fast; resulting in very low carbon dioxide partial pressures, and thus had insignificant influence on the final degree of metallization. Also, the reaction between the molten product and the graphite lining contributed to the high levels of oxygen removal.

An attempt was made to characterize the flow behavior of the molten product within the cyclone. The results suggest that the system may approach a plug flow reactor, with little back mixing.

Finally, a fundamental mathematical model was developed. The model describes the flow dynamics of gases and solid particles in a cyclone reactor, energy exchange, mass transfer, and the chemical kinetics associated with cyclone smelting of taconite concentrate fines. The influence of the various parameters on the reduction and melting of taconite particles was evaluated theoretically.

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CHAPTER 1

INTRODUCTION

The principle of cyclone firing entered practical boiler construction as early as the nineteen forties (1). The appeal of the cyclone configuration is that it offers the essentially flash combustion process greater efficiency through turbulence-induced increased mass transfer, heat exchange and combustion rates. Pyrometallurgical processing using cyclone reactors was first suggested in the mid-fifties, where it was put into practice in a Sardina plant to treat antimony sulfide concentrate. Due to severe wear and other difficulties, the plant is no longer in operation.

At about the same time, investigators in the USSR began using cyclone reactors to smelt copper ores and concentrates. In spite of the difficulties encountered at early stages, they pursued their research in this field, leading to the development of the well-known Oxygen-Flame-Cyclone Electrothermic (KIVCET) process (1).

Basically, KIVCET is a process for the smelting of complex sulfide concentrates with the simultaneous production

of copper, lead, zinc, and other metals such as tin and cadmium (2,3). Fine dry sulfide concentrate is introduced axially into a cyclone furnace where it is autogeneously roasted and smelted with oxygen. The concentrate particles are flash smelted in a suspended state, and the product leaving the bottom of the cyclone furnace passes into a distribution chamber where the melt and the SO_2 -content of the off-gases are separated. The melt flows into an electric-resistance furnace where settling (and volatilization of zinc, for example) takes place under reducing atmosphere. Copper, nickel, cobalt, and precious metals are extracted into the matte. Zinc and tin are either condensed to metal or may be allowed to oxidize to produce oxide powder directly.

The Flame Cyclone Reactor (FCR) (4,5) and the CONTOP (6) processes are two more technical developments in copper metallurgy where a smelting cyclone is utilized as a reaction chamber either in a horizontal (FCR) or a vertical (CONTOP) position.

In spite of the success reported in employing cyclones as reaction chambers for the processing of sulfidic ores and concentrates, little attention has been paid to its use in the pyrometallurgical treatment of iron ores. The earliest attempt was conducted by Johnson and Davidson in 1955 (7) when they investigated the feasibility of producing metallic iron from a pre-reduced iron ore in a vertical cyclone furnace. Because of technical difficulties and wear of the lining, the

research was terminated in 1964.

In iron ore reduction in the blast furnace, for instance, the reducing gas enters the furnace at the bottom of the reducing zone, and flows counter-current to the descending solid charge (8). Final conversion to metallic iron is normally achieved by solid carbon reduction in the hearth of the furnace. In the direct reduction processes, conversion to metallic iron takes place below the melting temperature of the solid charge involved. In any case, agglomeration of the ore feed (and pellets induration) is a necessity, adding to the cost of production. Severe attack on the lining of the processing unit both contaminates the final product and adds to the operating costs of production. Further, and more importantly, these processes are semi-batch, requiring high initial capital outlay. In addition, the carbon source employed (coke, coal, or methane) has to be of certain quality in many cases. For example, in a process that employs a rotary kiln, coal reactivity, volatile matter content, sulfur content, and ash content and its softening temperature are factors that must be considered and evaluated prior to its usage as a reductant. Summarizing, iron production processes suffer from one disadvantage or another, particularly the need for agglomerating and induring the ore pellets. A smelting process based on fine ore concentrates would at least avoid the high cost of agglomeration.

There is an estimated 10 billion tons reserve of oxidized

taconite assaying 30-40 percent iron located on the western Messabi Range in Minnesota (10,11,12,13). Development of an economic and applicable technology to process this reserve would ensure an adequate supply of iron for the domestic iron and steel industry and decrease significantly the growing dependence on foreign suppliers.

Cyclone smelting of fine taconite concentrate appears to be promising when the following advantages are considered. First, high through-put in a small reactor. Second, enhanced heat and mass transfer rates due to the increased mixing caused by the high turbulence within the cyclone chamber (9). Third, adiabatic conditions can be maintained locally, as a result high temperatures are achieved whereby reactions approach completion in a relatively short time. Furthermore, rapid separation of the liquid and gaseous products is accomplished within the cyclone chamber. Finally, agglomeration of the ore concentrate would not be needed, reducing the operating costs significantly. To make the process more attractive economically, co-generation of electricity by extracting the sensible and chemical energy of the effluent gas might be required. In addition and to affect the reduction reactions, the carbon monoxide to carbon dioxide ratio should be maintained at very high levels within the reactor system. Another drawback of the process might be that only partial reduction and melting of the ore would be possible, requiring subsequent bath smelting.

The use of a cyclone for melting and partial reduction of fine taconite concentrates in conjunction with bath smelting, using bath producer gas, was first suggested by Bartlett (46). The proposed process is essentially a two step process; partial reduction and melting of the solid charge in a cyclone furnace, followed by bath smelting as final reduction step. The gases coming out of the bath, being rich in carbon monoxide, are partially recycled to the cyclone reactor where reduction to liquid wustite is accomplished. Excess gas is burned in air for steam or power generation. This research project is concerned with the first step, that is the pre-reduction and melting of taconite in a cyclone reactor.

1.1 Research Objectives

The main objectives of this research were: to design, engineer, construct and operate a cyclone reactor system for the partial reduction and melting of taconite concentrates fines; to study high temperature cyclone smelting of magnetic taconite in a reducing gas mixture; to formulate a fundamental theoretical model describing the flow dynamics of gases and solids, and to develop energy exchange, mass transfer and chemical kinetics models associated with cyclone smelting of taconite fines.

The influence of the following parameters on the reduction process was investigated; inlet CO_2/CO partial pressure ratio, carbon monoxide initial partial pressure, and

the average reactor temperature. The interactions of the graphite lining with carbon dioxide and taconite were also studied.

The mathematical model developed was based on the experimental observations and results obtained. The influence of the various important parameters on the reduction and melting of the taconite fines in a smelting cyclone was evaluated.

CHAPTER 2

LITERATURE REVIEW

Interest in smelting of ores and concentrates in a cyclone-type reactor has been increasing in the last two decades, particularly after the successful development of the KIVCET process in the USSR and its adoption by several Western companies. The KIVCET technology was originally developed to treat sulfidic ores and concentrates and the subsequent production of copper matte containing 50-60% Cu. Lately, the application of the process has expanded to include, for example, the recovery of zinc, lead, and cadmium from EAF dust and hazardous waste as practiced in the FCR process.

In spite of the success in cyclone processing of sulfidic ores, little research has been reported on iron ore smelting in a cyclone reactor, apparently due to the lack of economic success of earlier attempts by Johnson and Davidson (7) where they tried to reduce wustite to metallic iron. More recent work in this field has focused on the complete reduction of hematite to metallic iron, with little success.

This chapter presents an overview of research carried out on sulfidic ores and concentrates (section 2.1), along with

the available literature on cyclone smelting of iron ores (section 2.2). Section 2.3 discusses three representative processes in which a cyclone reactor is utilized as a processing chamber. Finally, section 2.4 gives a brief summary of the different kinds of fuels used as energy source and reductants in iron production.

2.1. Sulphidic Ores and Concentrates

Research on cyclone smelting of sulphidic ores and concentrates has received a great deal of attention during the past two decades. This is due to several factors including the very high heat and mass transfer rates as a result of the intimate mixing of the reacting species. In addition, and with using commercial oxygen instead of air, the gaseous products are rich in sulfur dioxide, making it more economical to recover sulfur either as sulfuric acid or elemental sulfur, minimizing the air pollution problem and offsetting the additional cost of recovery.

Lherbier et al. (14) described the Flame Cyclone Reactor (FCR) process in detail and its application in the treatment of EAF dust and hazardous waste to separate and recover zinc, lead, and cadmium values, while producing a non-hazardous slag by-product.

Pusateri et al. (15) reported an investigation on zinc recovery from flue dust of EAF, electrolytic zinc plant neutral leach, and iron precipitation residue. A cyclone

reactor was used. High metal recoveries were observed.

Emicke (16) reported pilot plant test results on flame smelting of complex copper concentrates conducted at Norddeutsche Affinerie. The investigation aimed at minimizing the copper content in the flue dust, and at the same time, maximizing the separation of impurities to a high-grade matte during smelting. It is claimed that 65-80% Cu matte was produced at smelting rate of 10 tons/hr with very little copper carry-over into the flue dust.

Gamroth et al. (6) discussed the application of the CONTOP process in copper metallurgy and the possibility of utilizing other fuels, such as coal dust, oil, natural gas, or pyrite as combustibles. They also outlined the possibility of applying the technology for the recovery of other metals such as tin, antimony, and molybdenum, and the separation of arsenic from waste products of other processes.

Berndt and Emicke (17) described the Flame Cyclone Reactor process as it is applied for the smelting of copper based complex sulphide concentrates. The feed to the combustion shaft consists of a homogeneous mixture of concentrate and flux in oxygen-enriched air. Upon the completion of the combustion reactions, the hot gas stream laden with molten particles enters the cyclone chamber, where, upon contact with the cooled reactor walls, rapid separation of molten and gaseous products is achieved, preventing reabsorption of the previously volatilized impurities.

Torres and Melcher (18) discussed the possibility of retrofitting copper reverberatory furnaces by incorporating the CONTOP technology. Advantages and disadvantages of the two processes are presented. It is noted that CONTOP process offers a more energy efficient process and higher production rate than the traditional reverberatory furnace.

Melcher (19) described a process for smelting sulfidic ore concentrates in a vertical cyclone reactor. Oxygen is blown tangentially into the cyclone, causing the feed material to be roasted and melted while still in suspension. The melt is delivered by gravity to a furnace housing. Reducing gas is passed onto the melt to produce metal-rich phase (75% Cu) and a slag phase that is very poor in copper.

Rahn et al. (20) patented a process for the roasting of fine-grained sulfide ores in a horizontal cyclone reactor. High oxygen containing gas is blown into the reactor to form a suspension, allowing roasting to occur. The molten copper is collected from the lower portion of the cyclone, and off-gas is cooled to recover heat and entrained droplets of molten product.

Herbert et al. (21) patented a process for the treatment of solids and intermediates of ores, which form molten products at the treatment temperature. The process uses finely divided solid feed, high oxygen-containing gas, and energy carriers in a suspended state. The starting material is introduced into a vertical combustion passage, where the

components interact, resulting in a suspension containing molten particles that are introduced into a horizontal cyclone chamber. Copper concentrates and pyrite were treated in this process at a rate of 1,600-3,000 kg/hr at temperatures of 1525-1700° C. Copper-rich matte (55-80% Cu, depending on the starting material and temperature) was formed, leaving 0.8-1.1% Cu slag.

Winterhager et al. (22) patented a process for the thermal recovery of metals with the aid of a smelting cyclone. According to the invention, finely grained ores, concentrates, or metal containing intermediary products are introduced axially into a cyclone chamber, while hot air or oxygen is blown tangentially into the reactor at high velocity, such that a temperature of 1800° C is obtained. High heat transfer causes the charge to melt in a short time and flows as a thin film on the cyclone wall. The molten material flows down into a centrifuge where it is separated to form a heavy metallic phase and a lighter slag phase. The process is claimed to be applicable to melting copper metal, metallic tin, or mixed ores containing volatile components and small amounts of precious metals.

Muller et al. (1) discussed the kinetics and thermodynamics of the KIVCET cyclone smelting process for impure copper concentrates, and gave a brief description of the process. Initially, both oxygen and copper concentrates were fed tangentially into the cyclone reactor, but lately, in

order to increase the residence time of the solid charge, the concentrate is fed axially into the reactor. The feed has a particle size below 1 mm, and contains less than 2% moisture. Pure oxygen is blown at a rate of 80-120 m/sec to provide a combustion temperature of 2000° K. A matte containing 50% Cu is obtained from a charge with 25.6% Cu. The slag phase contains 0.35% Cu, while the off-gas is rich with SO₂ (80-85%).

Foard (23) patented a cyclone smelting system for both smelting and converting operations on copper-bearing materials, to produce blister copper. The process utilizes a pressurized stream of particulate copper-containing material and oxygen-enriched gas as the feed to a cyclone reactor. A gaseous fuel is burned at the upper portion of the reactor vessel to raise the temperature sufficiently to induce autogenous or partially autogenous reaction, thus allowing combined smelting and converting of the feed material to blister copper.

Reh et al. (24) described a system for the recovery of metals from copper and nickel ores or concentrates in a vertical cyclone, using 70% oxygen-enriched gas. The process was used to treat a copper concentrate (30% Cu) and a copper-nickel concentrate (5.5% Ni, 2% Cu) at a smelting temperature of 1400-1450° C. In addition, nickel metal was reported to be recovered from a nickel-iron silicate ore containing 5.5% Cu.

Blank and Ward (25) described the application of cyclone

furnace for the removal of zinc from lead blast furnace slag. Results obtained from pilot plant tests were reported to be comparable with those of a conventional batch slag fuming processes.

Blank (26) studied the recovery of zinc and zinc oxide from granulated lead blast furnace slag in a vertical cyclone reactor. High zinc recoveries and improved fuel economy were reported.

Basina et al. (27) smelted a concentrate containing 35-62% Pb, 0.2-2% Cu, 2.4-5.6% Zn, 4-22% Fe, and 12-21% S in an oil-fired cyclone furnace. Both copper and iron were retained as matte and 97.5-99.5% of lead and 83.3-89.0% of zinc were volatilized.

The fundamentals of cyclone smelting are described by Barin and co-workers (9) and by Bendt and Emicke (5). Barin estimated the heat and mass transfer coefficients, reaction rates and residence time. Bendt described the Flame Cyclone Reactor and included a comprehensive description of residence times, oxidation versus reaction times, heat and mass transfer rates versus particle size of the feed material, and the thermodynamics of the smelting process.

2.2 Iron Ores and Concentrates

Reduction of wustite to metallic iron is by far the most difficult step in iron making, requiring highly reducing conditions, elevated temperatures, and prolonged residence

time. For these reasons, and others, little attention has been given to cyclone smelting of iron oxides.

Yamuda et al. (28) patented a process for treating iron ores in a cyclone chamber. The ore is preheated, pre-reduced, and sintered in the cyclone with the hot flue gas (1200° C) from the ore smelting step.

Hanasaki et al. (29) described a process for the reduction of powdered iron ore in a series of cyclones. An ore of size +325 mesh was processed with a reducing gas at 1000° C. No sintering took place during the reduction phase.

Barker (30) used a fluidized bed to prereduce powdered iron ore (200 mesh) at 850-900° C, before final reduction to sponge iron in a cyclone chamber. Carbon monoxide and hydrogen at 1000° C were used for the final reduction step.

Blaskowski (31) patented a process for the direct reduction of iron ore to steel or high-grade iron. The process consisted of introducing coal and oxygen (or air) tangentially into a cyclone reactor, so as to create a reducing atmosphere of the proper composition and temperature. Pulverized iron ore, fluxing materials and additional coal and oxygen are added also tangentially but at a lower elevation for intimate mixing.

Yakupov and Petrov (32) smelted an iron ore in a cyclone at 1500-1600° C, using CO/CO₂ ratio of 4:1. Liquid metal and slag were obtained with 80-90% iron recovery in the metallic phase. Dissolution of the cyclone lining was thought to be

responsible for the decrease in reduction. Coke containing 1.9% sulphur resulted in a metal containing 0.1-0.8% S, while addition of lime did not affect the sulphur content in the metal.

Chukhanov et al. (33) described the EMU-400 project for the combined power and steel producing installation. A cyclone burner is used to generate reducing gases for the reduction of iron concentrate containing 64% Fe.

Zhilin et al. (34) studied the reduction of wustite in a cyclone chamber after being dried and heated to 500° C. The reduction temperature was 1000-1100° C. With 12% CO gases, 30% reduction was achieved when ores were used, while 18% reduction was obtained for the concentrate.

Johnson and Davidson (7) reported an investigation into the application of a cyclone chamber as a final reduction step in iron ore processing. A feed containing 31.4% Fe, 13.4% O, and 55.2% gangue mixed with lime was introduced into a preheated cyclone (1500° C). Fine coal was used as a source of heat, which was burned in oxygen-enriched air. Metallic iron containing 1-2% C, 0-1.9% Si, and 1-2% S was produced. Difficulties were encountered in maintaining the proper CO/CO₂ ratio required to affect the reduction to metallic iron.

Wenzel (35) patented a process for the treatment of iron ore with various kinds of fuels, such as gaseous, liquid, and fine-grained solid fuels. Two cyclones are used, the first served as a pre-reduction chamber and the second for the final

reduction to metallic iron. Pre-reduction is carried out at 1000° C to produce a wustite phase, which is then transferred to the second cyclone for final reduction and melting at 1600° C. CO/CO₂ ratio in the exit gas of the melting chamber was maintained at 4:1.

Nogiwa (36) patented a process for the production of molten iron from powdered iron ore, carbon and limestone. The mixture was fed into a cyclone furnace, that was maintained at 1600° C, at a rate of 315 kg/hr hematite, 540 kg/hr carbon, and 93 kg/hr limestone. Molten iron was produced at a rate of a 170 kg/hr.

Ispas and Dumitrashka (37) reported an investigation into the use of a cyclone reactor to melt and reduce pulverized iron oxides with methane at 1950° C. It was claimed that the metal product could be carburized to mild steel or cast iron by regulating the combustion reaction and the flow of methane.

2.3 Cyclone Design

Several processes appear in the literature where a cyclone is utilized as a reaction chamber. The cyclone is positioned either vertically, horizontally, or inclined by 5-15° on its horizontal axis, depending on the specific application and the objective of the design.

An inclined horizontal cyclone burner is shown in Figure 2.1 (38). The unit was used to burn coal of high volatile matter and ash contents. The cyclone burner (8 ft in

Figure 2.1 A power generating pilot plant installation where an inclined horizontal cyclone is used as a burner

diameter, 11 ft long, and water cooled with three coils of 2.5 inch OD tubes) is provided with a primary air and coal inlet port at the front end, and a secondary air port section along its upper periphery. Continuous slag tapping is carried out through an opening at the bottom of the cyclone. Coal (3/8-7/8") and primary air are injected tangentially into the preheated cyclone. Total air flow rate used was 60-70 m/sec, and coal was burned at a rate of 10 tons/hr producing 150,000-180,000 lb steam per hour at 600 psi and 900° F. The inclination of the cyclone body was aimed at facilitating the continuous removal of the ash left as a molten slag phase. At the same time, by having a larger exit gas outlet at the end of the cyclone, more uniform distribution of the off-gas over the tube banks of the heat exchanger was accomplished, giving higher heat transfer rates. It was also reported that the ash content in the combustion gases was reduced considerably and that all the volatile matter was distilled and burned allowing almost complete combustion of the carbon content of the coal.

A horizontal cyclone is presented in Figure 2.2 (4). In this configuration, the vertical shaft is provided for combustion, whereas the gas/particle reactions are terminated at the outlet of the shaft. Gases and particles leaving the reaction shaft are introduced tangentially into a horizontal cyclone, and are separated. The cyclone has a cross-sectional area of 0.78 m² and a length of 0.8 m. Dried copper concentrate and sand are supplied to the burner at a rate of

Figure 2.2 FCR process representation. The horizontal cyclone is used to separate the molten and gaseous products.

10 tons per hour. Oxygen-enriched air is used for combustion. The main reactions and melting of the solid charge occur in a very short time between the burner mouth and the end of the combustion shaft. The hot gases, rich in sulfur dioxide and loaded with molten particles, enter the cyclone chamber at high speed. Upon contact with the cyclone wall (being cooled with water), the melt is rapidly separated from the gases. Slag and matte formed flow from the cyclone into a collection chamber and finally to a settler, where tapping of the two phases is carried out periodically. Seven to eight tons per hour matte containing 62-73% Cu is produced with 70% oxygen-enriched air. Residence time is reported to range from 0.05-0.2 seconds.

A schematic diagram of a vertical cyclone installation is shown in Figure 2.3 (39). The installation was utilized for the hydrothermal processing of phosphate ores in pilot plant tests conducted at MEI, USSR. The cyclone (0.4 m in diameter, 0.8 m high, a total capacity of 0.1 m³, and cooled with water) is tapered down to a diaphragm-shaped neck 18 cm in diameter. The ore is fed axially at a rate of 1000-3300 kg/hr/m³. Process gases, formed by burning kerosene in an air stream, enter the cyclone tangentially at a rate such that the exit gas velocity is 60-70 m/sec, ensuring a strong whirling of the gas stream in the cyclone chamber. The operating temperature varied with the type of ore processed and its injection rates, and ranged from 1350-1550° C. The design objective was to

Figure 2.3 A pilot plant for the hydrothermal processing of phosphate ores. Here a vertical cyclone is used as a reaction chamber

melt, defluorinate, and convert P_2O_5 to citric acid-soluble form in the cyclone reactor. The melt in the cyclone is allowed to flow out as a continuous stream through a tap hole in the gas duct that is heated by waste gases. Running down a water-sprayed iron sheet, the melt next flows into a collection bath and finally to a granulator. Gases leaving the cyclone (containing 6-10 gm/Nm³ dust) are cooled with water running inside the coil screens. A different design was used by the same authors, in which molten phosphate was removed from the cyclone as a thin jet, and collected on a water cooled tray where it became granulated. This arrangement reduced dust escape, since entrained particles are injected into the molten product. Further, it provided the necessary heat and reducing gases for further reduction of metal oxides trapped in the slag phase. This would be an added advantage for cyclone smelting of taconite concentrate, where final reduction from wustite to metallic iron would probably take place in the smelting bath just below the cyclone reactor.

2.4 Fuels Used in Iron Production

Reduction of iron ore concentrates is an endothermic process requiring large amounts of energy. In the past, nearly all oxide pellets were reduced in a blast furnace (12) using coke as energy source and reductant. Nowadays, there is a growing trend toward the implementation of direct reduction

processes, where a reductant other than coke is selected based upon its cost at a particular location and its effectiveness. Davis and co-workers (40) surveyed several direct reduction processes and grouped them under the following categories: 1) reformed natural gas processes, 2) commercial coal-based processes, 3) second generation coal-based processes, 4) coke-oven gas processes, and 5) new technology.

In the reformed natural gas processes, reducing gas rich in carbon monoxide and hydrogen is formed by reforming natural gas feed stock, primarily methane, in catalyst-filled tubes. Carbon monoxide and hydrogen are generated in the methane-steam reforming process according to the reaction:

Depending on the particular process, the reformed gas contain 88.5-95% CO + H₂. Examples of processes based on reformed natural gas include Midrex, Armco, Fior, and Purofer.

Reduction of iron ores takes place according to the following reactions:

Rotary kiln and shaft furnace processes are the only commercially available coal-based processes currently operating. The ore feed should fulfill certain requirements

regarding chemical composition, size distribution, and behavior under the reducing conditions in the rotary kiln, so that costs for further processing in the electric furnace are minimized. The coal used is selected based upon factors that include reactivity, volatile matter content, sulfur and ash content, and the ash softening temperature. In the reduction zone of the rotary kiln, iron oxide is reduced by solid carbon as represented by:

and by carbon monoxide according to reactions 2.2 and 2.3 above. Additional heat is usually supplied by combustion of pulverized coal in a burner located at the solid discharge end of the kiln.

Second generation coal-based processes utilize coal to supply 80-90% of the energy requirements, the remaining being provided by liquid and/or gaseous fuels that are cracked to carbon monoxide and hydrogen, so that reduction to metallic iron goes to completion. In addition, the fuel represents a protective atmosphere for the metallized product, preventing reoxidation.

The cost of coke-making facilities has become increasingly expensive due mainly to the pollution control equipment needed to meet environmental regulations. However, coke-making economics can be enhanced by coupling coke-making

operations with a direct reduction facility, where coke-oven off-gas can be used to reduce the iron ore. Such practice is found in the Midrex and HYL processes, where metallurgical coke is used for coke-oven underfiring and in the direct reduction process, either directly (HYL) or after being reformed to provide carbon monoxide-hydrogen gas (Midrex).

The category of new technology includes processes in which electrical energy or plasma is employed to furnish the additional heat requirements for the reduction reactions. INDREX and MIDREX EDR processes are based on the use of electricity for the melting and the reduction of the pre-reduced ore, where the reduction of wustite with coal is usually carried out at 1450-1900° C.

SKF Plasmasmelt, ELRED and EPP are examples of processes that use thermal plasma for the final reduction of wustite to metallic iron. Here, a 50% pre-reduced ore is treated with coal and flux in a low-shaft furnace. Plasma torches supply energy to the hearth. Off gases from the shaft, essentially carbon monoxide and hydrogen, pass through a fluidized bed arrangement that produces 50% pre-reduced iron ore.

The above-mentioned plasma processes operate in the transferred arc mode, with the plasma gun acting as a cathode, and the furnace hearth as the anode. In the non-transferred mode (41,42) the ore feed is injected directly into the plasma flame. The feed is thus melted forming a liquid film that flows down the reactor wall. By proper control of the

residence time of the film, the ore fines can be reduced upon treatment with reducing agent such as coal or coke.

CHAPTER 3

THERMODYNAMICS OF IRON OXIDES REDUCTION

3.1 Prevailing Chemical Reactions

There are three forms of iron oxides: hematite (Fe_2O_3), magnetite (Fe_3O_4), and wustite (Fe_{1-y}O). Production of metallic iron is believed to proceed in the following sequence, when carbon monoxide is the predominant reducing agent (43,44):

Carbon monoxide is formed by combustion of the carbon content of the fuel used. When coal (or coke) is present, carbon monoxide is generated according:

The Boudouard reaction or carbon deposition is obtained by subtracting 3.4 from 3.5:

3.2 Free Energy Change

The effect of temperature and the partial pressures of carbon monoxide and carbon dioxide on the reduction of iron oxides can be determined from the following calculations:

$$\Delta H_T = \Delta H_{298} + \int_{298}^T \Delta C_p dT \quad (3.7)$$

$$\Delta S_T = \Delta S_{298} + \int_{298}^T \Delta C_p \frac{dT}{T} \quad (3.8)$$

$$\Delta G_T = \Delta H_T - T\Delta S_T \quad (3.9)$$

where:

ΔH_T = enthalpy change of the reaction at T,

ΔH_{298} = enthalpy change of the reaction at 298° K,

ΔS_T = entropy change of reaction at T,

ΔS_{298} = entropy change of the reaction at 298° K,

ΔG_T = free energy change of the reaction at T,

ΔC_p = heat capacity, $\Delta C_p = \Sigma C_{p \text{ products}} - \Sigma C_{p \text{ reactants}}$

Upon the evaluation of the respective integral quantities on the basis of the data presented by Kubaschewski and Alcock (45), a final temperature free energy relation of the following form is obtained for the reactions 3.1 through 3.6:

$$\Delta G_T = a + bT$$

(3.10)

Table 3.1 presents the functional relationships, along with the expressions for the equilibrium constant K_p . Figure 3.1 is a plot of ΔG_T versus temperature. It clearly indicates the fact that the reduction of iron ores to metallic iron by carbon monoxide becomes increasingly more difficult as the oxide goes from higher to the lower form, at any given temperature. While reduction of hematite to magnetite can be carried out at relatively low temperatures, conversion of magnetite to wustite requires higher temperatures, and becomes only feasible above 750° K. Below approximately 1500° K, reduction of wustite to metallic iron can take place, and above this temperature the reaction is thermodynamically prohibitive (when the carbon dioxide to carbon monoxide activity ratio is unity).

These thermodynamic considerations are exemplified in the blast furnace iron production. The ascending gas temperature drops from 800-1000° C in the middle zone to 100-250° C in the upper zone, at the same time, solid temperatures rise to about 800° C. Within this temperature range it is possible then to reduce hematite and/or magnetite to wustite in the upper zone of the furnace. Aside from the lower operating temperature characteristic of this zone, the carbon monoxide content in the ascending gas need not be high to affect the reduction

Table 3.1 Free energy change and equilibrium constant for reactions 3.1 through 3.6.

Reaction	Free energy change	Equilibrium Constant K_p
1. $C + 1/2 O_2 = CO$	$-26700 + 20.95T$	$K_p = P_{CO} / (P_{O_2})^{1/2}$
2. $C + CO_2 = CO$	$40800 - 41.7T$	$K_p = P_{CO} / P_{CO_2}$
3. $3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$	$-7700 - 12.87T$	$K_p = P_{CO} / P_{CO_2}$
4. $Fe_3O_4 + CO = 3FeO + CO_2$	$7120 + 5.13T$	$K_p = P_{CO} / P_{CO_2}$
5. $FeO + CO = Fe + CO$	$-4190 + 5.13T$	$K_p = P_{CO} / P_{CO_2}$

Figure 3.1 Free Energy Change versus Temperature for Reactions listed in Table 3.1

reactions. This will be discussed further later in this chapter.

In the middle zone of the blast furnace, the temperature is relatively constant (800-1000° C) and the most indirect reductions, especially of wustite, occur in this zone. This is very consistent with the thermodynamic predictions shown in Figure 3.1. In addition, the CO/CO₂ ratio of the gas is about 2.3 and remains almost unchanged. This ratio corresponds to an equilibrium between Fe-FeO, as will be seen later. The

lower zone of the furnace is characterized by high temperature (1400-1450°) and high CO-content of the gas phase. Reduction of wustite to metallic iron takes place by the CO-rich gas in the cohesive region and by the submerged coke in the furnace hearth.

3.3 Effect of CO₂/CO Ratio

At equilibrium, the free energy change for a given reaction can be related to the equilibrium constant K_p by:

$$\Delta G_T = -RT \ln(K_p) \quad (3.11)$$

K_p can be expressed as follows for a general case such as:

$$aA + bB = rR + sS \quad (3.12)$$

$$K_p = \frac{(a_R)^r * (a_S)^s}{(a_A)^a * (a_B)^b} \quad (3.13)$$

where a_i represents the activity of the reacting species. For ideal gas, the activity of a gas is assumed to be equal to its partial pressure, P_i , or :

$$a_i = P_i = \frac{n_i}{n_T} P_T \quad (3.14)$$

where (n_i/n_T) is the mole fraction of species i , and P_T is the total pressure of the system. In addition, and for a pure solid substance, its activity is taken to be unity. With

these assumptions, the equilibrium constant for reaction 3.1 can be written as:

$$K_{p1} = \frac{P_{CO_2}}{P_{CO}} \quad (3.15)$$

If α represents the fraction of carbon monoxide reacted with the equivalent moles of iron oxide to form α moles of carbon dioxides, leaving $(1-\alpha)$ moles of CO unreacted, the partial pressures of CO and CO₂ can be expressed as follows, respectively:

$$P_{CO} = (1-\alpha) P_T \quad (3.16)$$

$$P_{CO_2} = \alpha P_T \quad (3.17)$$

Substitution of 3.16 and 3.17 into 3.15, the following expression for k_p in terms of α is obtained:

$$K_{p1} = \frac{\alpha P_T}{(1-\alpha) P_T} = \frac{\alpha}{1-\alpha} \quad (3.18)$$

Rewriting equation 3.10 in the form:

$$K_{p1} = \text{EXP}\left(\frac{-\Delta G_T}{RT}\right) \quad (3.19)$$

and substituting for K_p , one can get, after solving for α :

$$\alpha = \frac{\text{EXP}\left(\frac{-\Delta G_T}{RT}\right)}{1 + \text{EXP}\left(\frac{-\Delta G_T}{RT}\right)} \quad (3.20)$$

At a given temperature, the fractional conversion of carbon monoxide, and hence the degree of reduction from the higher to lower iron oxide, can be calculated by first determining the free energy change from equation 3.10 and then finding the fractional conversion from equation 3.20. Figure 3.2 shows such calculations, where the %CO₂ in the gas is plotted as a function of temperature. In a similar fashion one can predict the intermediate species of the wustite phase that are present at various temperatures and CO₂ partial pressures. These intermediates are also indicated in Figure 3.2, along with α -Fe, γ -Fe, and Fe₃C phases (46). Also included in the graph is the Boudouard reaction.

The hematite phase does not appear in Figure 3.2; this is because, even at room temperature, carbon monoxide in the presence of hematite is extremely unstable, as predicted thermodynamically. This means that hematite can be completely converted to magnetite at low temperatures and with negligible amounts of carbon monoxide in the gas. In contrast, reduction of magnetite to wustite becomes more and more difficult with decreasing CO content, at a given temperature. And it does not begin until a 10% CO gas is present at temperatures above 1500° C. With higher CO Partial pressures, conversion to

Figure 3.2 Equilibria between iron, wustite, magnetite, and carbon monoxide, carbon dioxide and carbon at $P(\text{CO}) + P(\text{CO}_2) = 1.0 \text{ ATM}$.

wustite becomes thermodynamically possible at lower temperatures. As to wustite, it is obvious from the figure that this phase is very stable over a wide range of temperatures and CO partial pressures, and that reduction to metallic iron does not occur above 1000° C unless the CO content of the gas is 80% and higher.

In view of these thermodynamic considerations, reduction of magnetite to wustite in a cyclone reactor appears to be feasible, given that a suitable operating temperature and adequate carbon monoxide partial pressure can be maintained, and that the residence time of the feed materials is long enough so as to effect the reduction reactions. Axial injection of taconite concentrate into the cyclone will prolong the average residence time, while introducing the coal and oxygen (or air) just ahead of the plasma flame before injection tangentially into the cyclone chamber will result in intense combustion of the coal, yielding a gas of high temperature and rich in carbon monoxide. Such a gas will possess a high reducing potential to effect the conversion of taconite to wustite. As the reacting mixture flows downward, both temperature and CO-partial pressure are expected to drop, resulting in a decreasing reduction potential of the gas. Since conversion of wustite to metallic iron requires high carbon monoxide pressures, it is believed that wustite would be the final product emerging from the cyclone reactor. One of the objectives of this research is to convert taconite to a

liquid wustite phase of an average composition of $\text{Fe}_{.90}\text{O}$ at temperatures above 1500°C . At this degree of conversion, the gas composition should be about 40% CO , as indicated by Figure 3.2.

CHAPTER 4

KINETICS OF IRON ORE REDUCTION

Reduction of iron oxides by carbon monoxide is a very complicated process involving many physical and chemical variables (47). Further, the reduction process is so varied and complex that there is very little agreement amongst investigators regarding the rate controlling mechanism that determines the kinetics of the process. The entire field has been covered thoroughly by Bogdandy and Engell (48) and reviewed by Tokuda et al. (49) and Ross (50).

The reduction sequence of hematite can be represented by the following reactions (44,47):

Accordingly, starting with a dense sphere of hematite an initial reaction with carbon monoxide will produce a shell or layer of metallic iron in contact with a layer of wustite, beyond which there will be a layer of magnetite surrounding the core of hematite, as depicted in Figure 4.1. Such a layered structure is typical of topochemical reactions where

the reacting interface between solid reactants and solid products moves parallel to the original solid surface.

4.1 Reduction Mechanism

The mechanism of the reduction process is believed to be one or all of the following:

1) Solid state diffusion (51) of iron ions, released from the removal of oxygen from the wustite lattice, towards the core due to concentration gradient. The migrating iron ions reduce magnetite to wustite and hematite to magnetite without loss of oxygen, resulting in the layered structure of Figure 4.1. Chemically, the reduction takes place according to:

This mechanism, therefore, assumes diffusion of gaseous reactant through the iron layer and transfer of oxygen from the solid phase to the gas phase at the wustite-iron interface only. Structural changes that take place according to this mechanism result in iron vacancies in the wustite layer and lattice distortion when magnetite is formed, giving rise to a large vacancy concentration and hence a porous structure.

2) Diffusion of gaseous reactant inward through the porous layers of iron (52), wustite, and magnetite and the simultaneous reduction of all oxides at all interfaces.

3) Adsorption of gaseous reactant on iron surface, and oxygen ion diffusion through the iron layer to react at the

surface (53). This mechanism is likely to occur when a dense impervious layer of iron is formed. In such a case, the reduction will be very slow and occurs as indicated by reactions 4.4 and 4.5.

4.2 Rate Laws in Reduction (47-50, 54)

Reduction of iron oxides occurs in a series of sequential steps, where the slowest step(s) will eventually determine the rate of the overall reaction. The possible steps are;

- 1) Gaseous diffusion from the bulk gas to the particle surface through a boundary gas film.
- 2) Molecular diffusion of the gaseous reactant through the product layer to the reaction interface.
- 3) Adsorption of the reactant at the interface.
- 4) Reaction between adsorbed reactant and oxygen of the lattice at the interface.
- 5) Desorption of the gaseous products from the interface.
- 6) Mass transfer of iron and oxygen ions and transformation in the solid phase (formation and growth of reaction products: magnetite, wustite, and iron).
- 7) Molecular diffusion of gaseous products through the product layer to the particle surface.
- 8) Transport of gaseous products from the particle surface through the boundary gas film to the bulk gas phase.

Figure 4.1 Schematic representation of the model of gaseous reduction of a spherical taconite particle. Possible concentration gradients of the reducing gas across the iron layer are also shown.

In view of these possibilities, the rate limiting cases are (Figure 4.1):

Case I: chemical control (steps 3, 4, 5, and 6, curve 1).

Case II: fluid film diffusion control (steps 1 and 8, curve 2).

Case III: pore diffusion control (steps 2, 6 and 7, curve 3).

These three cases will be discussed in combinations assuming a reversible chemical reaction at the interface for a solid

particle of unchanging size. The following mathematical treatment considers the reduction process to proceed in three steps (reactions 4.1, 4.2, 4.3), such that a hematite particle is first converted to magnetite, which is then reduced to wustite. Finally, the wustite particle is transformed to metallic iron. This proposed sequence is adopted to simplify the mathematical derivations only.

4.2.1 Reduction of Hematite to Magnetite:

Assuming the reduction of hematite is first order with respect to carbon monoxide (47, 55), then the rate of disappearance of carbon monoxide is given by:

$$\frac{-dN_{\text{CO}}}{dt} = 4\pi r_c^2 K_{s1} (C_s - C_{e1}) \quad (4.7)$$

where k_{s1} is the first order rate constant for the surface chemical reaction, r_c is the radius of the reacting interface, C_s and C_{e1} are the surface and equilibrium concentrations of carbon monoxide, respectively, and N_{CO} is the number of moles of carbon monoxide.

The rate of disappearance of hematite is related to that of carbon monoxide by:

$$\frac{dN_{\text{Fe}_2\text{O}_3}}{dt} = 3 \frac{dN_{\text{CO}}}{dt} \quad (4.8)$$

where $N_{\text{Fe}_2\text{O}_3}$ is the number of moles of hematite. Writing the number of moles of hematite in terms of the shrinking radius r_c :

$$\frac{-dN_{\text{Fe}_2\text{O}_3}}{dt} = -\frac{d\left(\frac{4\pi\rho_1 r_c^3}{3}\right)}{dt} \quad (4.9)$$

The molar flux (J) of the diffusing carbon monoxide can be found from the following, assuming fluid film resistance is negligible:

$$(4\pi r^2 J)|_r - (4\pi r^2 J)|_{r+dr} = 0$$

at steady state, or:

$$\frac{\partial(r^2 J)}{\partial r} = 0 = \frac{\partial}{\partial r} \left(r^2 \left(-D_e \frac{\partial C}{\partial r} \right) \right) \quad (4.10)$$

Equation 4.10 is solved with the boundary conditions:

$$C(r=R) = C_B, C(r=r_c) = C_S$$

where C_B is the carbon monoxide concentration in the bulk of the gas. The following is then obtained:

$$C = -(C_B - C_S) \frac{Rr_c}{r(R-r_c)} + (C_B - C_S) \frac{Rr_c}{R(R-r_c)} \quad (4.11)$$

Then the molar flux J is given by:

$$J = -D_e \frac{dC}{dr} = -D_e (C_B - C_S) \frac{Rr_c}{r^2 (R - r_c)} \quad (4.12)$$

At the reaction interface, total molar flux of carbon monoxide is related to its rate of disappearance, such that at steady state the following equality holds:

$$4\pi r_c^2 (J)|_{r=r_c} = k_{s_1} 4\pi r_c^2 (C_S - C_e)$$

or:

$$D_e (C_B - C_S) \frac{Rr_c}{r_c (R - r_c)} = k_{s_1} (C_S - C_e) \quad (4.13)$$

Solving for the surface concentration C_s :

$$C_s = \frac{k_{s_1} C_{e_1} + \frac{D_e R C_B}{r_c (R - r_c)}}{k_{s_1}} + \frac{D_e R}{r_c (R - r_c)} \quad (4.14)$$

From equations 4.7, 4.8, 4.9, and 4.14 the following expression is obtained:

$$\frac{-dr_c}{dt} = \frac{3(C_B - C_{e_1}) \frac{1}{\rho_1}}{\frac{1}{k_{s_1}} + \frac{(R - r_c)}{D_e R} r_c} \quad (4.15)$$

In the above expressions R is the initial particle radius, and D_e is the effective diffusivity of carbon monoxide in the

magnetite layer.

4.2.2 Reduction of Magnetite to Wustite:

Assuming that pore diffusion is fast relative to the rates of the chemical reaction and the diffusion through the film boundary, then the molar flux of carbon monoxide arriving at the reacting interface is given by:

$$J = k_g (C_B - C_S) \quad (4.17)$$

Here k_g is the mass transfer coefficient of carbon monoxide. Also, if the chemical reaction is first order with respect to carbon monoxide, similar expressions to those given by equations 4.6 through 4.8 can be obtained, namely:

$$-\frac{dN_{\text{CO}}}{dt} = 4\pi r_c^2 k_{s_2} (C_S - C_{e_2}) \quad (4.18)$$

$$\frac{dN_{\text{Fe}_3\text{O}_4}}{dt} = \frac{dN_{\text{CO}}}{dt} \quad (4.19)$$

$$\frac{dN_{\text{Fe}_3\text{O}_4}}{dt} = 4\pi r_c^2 \rho_2 \frac{dr_c}{dt} \quad (4.20)$$

where k_{s_2} is the first order rate constant for reaction 4.16, C_{e_2} is the equilibrium concentration of carbon monoxide at the

interface, and ρ_2 is the molar density of magnetite.

At the reaction interface:

$$4\pi r_c^2 k_{s_2} (C_S - C_{e_2}) = 4\pi R^2 k_g (C_B - C_S)$$

or:

$$C_S = \frac{R^2 k_g C_B + r_c^2 k_{s_2} C_{e_2}}{R^2 k_g + r_c^2 k_{s_2}} \quad (4.21)$$

Combining equations 4.18 through 4.21 one gets:

$$-\frac{dr_c}{dt} = \frac{(C_B - C_{e_2}) \frac{1}{\rho_2}}{\frac{1}{k_{s_2}} + \frac{r_c^2}{R^2 k_g}} \quad (4.22)$$

4.2.3 Reduction of Wustite to Iron:

Following the preceding analysis, similar expressions can be derived for the conversion of wustite to metallic iron. For instance, expression 4.22 will be modified by the stoichiometric coefficient, and will have the form:

$$-\frac{dr_c}{dt} = \frac{(C_B - C_{e_3}) \frac{1}{\rho_3}}{\frac{1}{k_{s_3}} + \frac{r_c^2}{R^2 k_g}} \quad (4.24)$$

where C_{e_3} is the equilibrium concentration of carbon monoxide for reaction 4.23, ρ_3 is the wustite molar density, and k_{s_3} is

the first order rate constant for the reaction.

4.3 Mechanism of Iron Oxide reduction

It is widely believed that mass transfer limitations do not exist in iron ore reduction when the linear gas velocity far exceeds the critical one where the influence of the boundary gas film almost disappears (47, 48, 57). In this case, depending on the structure of the product layer formed, the overall reaction rate will be either controlled chemically or by gaseous transport through the product layer, or by both.

If the product layer is very porous, permitting unrestricted access of the reactant molecules to the reaction interface, then the partial pressure of the reductant on the particle surface and at the interface will be the same at any moment. Therefore, gaseous transport will not be limiting, and depending on the activation energy, the reaction rate will increase with temperature and with the partial pressure of the reductant (58). This implies that the chemical reaction itself is rate controlling, and that the adsorption of carbon monoxide or desorption of carbon dioxide may have the greatest effect on the reduction rate.

But, the gas diffusion through the pores of the product layer becomes more and more restricted as the reaction proceeds by the reduced cross-sectional area available for mass transport. In addition, the porosity of the product layer does not remain constant but changes with time. As a

result, and as the reaction proceeds, a point will be reached where the resistance of the product layer becomes significant enough to influence the reaction rate. At this point the overall rate will be controlled by both pore diffusion and the chemical reaction (57). This would be valid for relatively large particles. For fine particles, the diffusion paths are naturally shorter giving rise to higher pore diffusion rates. If that is the case, the diffusion paths may constitute insignificant resistance to the reaction rate, and the overall reaction would be chemically controlled.

However, there are cases where a dense metallic layer is formed surrounding the oxides core (58, 59). Here, the overall rate will be limited by oxygen diffusion in metallic iron. When this happens, the thickness of the iron product layer will depend on the oxygen removed per unit area, and will be proportional to the square root of the reaction time.

On the other hand, reduction of the higher oxides to the lower ones can also occur by iron ions diffusion (through vacancy mechanism) in the solid oxide according to reactions 4.4 and 4.5. Usually, this takes place in a situation where the composition of the reducing gas is adjusted so that the higher oxides are reduced to the lower ones only, without forming a metallic iron layer. Reduction by solid state diffusion has been confirmed by many researchers (60-62).

4.4 Rate and Mechanism of Carbon Oxidation

Reaction of fuel carbon with oxygen and carbon dioxide are of great importance in iron ore reduction. The reactions are:

subtracting 4.25 from 4.26

Reactions 4.25 and 4.26 are approximately first order with respect to the gaseous products at temperatures above 1000-1050° C (47).

The combustion reaction is believed to be diffusion controlled. Meanwhile, reaction 4.26 can be controlled by any mechanism depending on the temperature (63-67). At temperatures below 1000-1050° C, the rate is greatly affected by temperature and the reaction is chemically limited. At very high temperatures (>1450° C) the reaction rate becomes dependent only upon gaseous transport through the boundary layer. At intermediate temperatures, pore diffusion may become rate controlling.

4.5 Mixed Kinetics

The time-conversion expressions derived previously assume that a single resistance was negligible throughout the reaction of the particle. However, as pointed out in the last two sections, the relative importance of each resistance will

vary as conversion proceeds. For instance, for a constant size particle, the gas film resistance remains unchanged, whereas the resistance to chemical reaction increases as the surface of the un-reacted core decreases. At the same time, the ash layer resistance is non-existence at the start, but becomes progressively more and more important as the product layer builds up. Therefore, it may not be reasonably accurate to consider that one mechanism controls throughout the reaction.

In cases where the three mechanisms are significant, it can be shown that the rate expression for the conversion of a single particle of unchanging size is given by:

$$-\frac{dr_c}{dt} = \frac{b(C_B - C_e) \frac{1}{\rho_s}}{\frac{r_c^2}{R^2 k_g} + \frac{R - r_c}{R D_e} r_c + \frac{1}{k_g}} \quad (4.28)$$

where b is the stoichiometric coefficient, and ρ_s is the molar density of solid particles.

4.6 Particle Size and Residence Time

Distributions

When the solid feed consists of a mixture of different particles, the size distribution can be represented by a continuous distribution function. Several empirical

expressions are available in the literature, and the most widely used is of the form:

$$Y = \left(\frac{R}{R_m} \right)^b \quad (4.29)$$

where Y is the cumulative probability density function, b is a constant, R is particle size, and R_m is the radius of the largest particle in the feed. The probability of a particle of size R is found by taking the derivative of equation 4.29:

$$y = Y' = \frac{b}{R_m} \left(\frac{R}{R_m} \right)^{b-1} \quad (4.30)$$

Equation 4.30 can be incorporated into the conversion models presented previously, so that the mean conversion of solids is obtained. This is done as follows:

$$1 - \bar{X} = \int_R^{R_m} [1 - X(R_i)] y dR = \int_R^{R_m} [1 - X(R_i)] \frac{b}{R_m} \left(\frac{R}{R_m} \right)^{b-1} dR \quad (4.31)$$

where $[1 - X(R_i)]$ is obtained from equations 4.15, 4.22, or 4.24, depending on the rate controlling mechanism(s). This expression applies for plug flow type reactors only.

In case that the length of stay is not the same for all particles in the reactor, an exit time distribution function ($E(t)$) is included in the time-conversion equation to arrive at the mean solid conversion in the reactor. For a mixed flow reactor, $E(t)$ takes the form:

$$E(t) = \frac{1}{\bar{t}} \exp\left(-\frac{t}{\bar{t}}\right) \quad (4.32)$$

Here, $\bar{t}$ represents the average residence time of the particles. Thus, for the case of a chemical reaction controlling, the mean conversion X can be determined from

$$1 - \bar{X} = \int_0^{\tau_c} (1 - X)^3 \frac{\exp\left(-\frac{t}{\bar{t}}\right)}{\bar{t}} dt \quad (4.33)$$

or:

$$1 - \bar{X} = \int_0^{\tau_c} \left(1 - \frac{t}{\tau_c}\right)^3 \frac{\exp\left(-\frac{t}{\bar{t}}\right)}{\bar{t}} dt \quad (4.34)$$

Equations 4.30 and 4.32 can be incorporated in the time conversion models to account for the effect of particles size distribution and residence time distribution on the final conversion in a mixed flow reactor. Both Y and $E(t)$ are found experimentally.

In spite of their use and applications as a process reactor chambers, no definite characterization of the flow type in cyclones has been reported. Although Szekely and Carr (68) suggested that the flow pattern of solids was of plug flow type. In their investigation, a slug of similarly sized iron particles was sandwiched into a bronze inlet stream. Upon observations made on the outlet stream, collected in a glass tube, it was found that the plug of iron particles maintained its identity with definite boundaries at each end.

CHAPTER 5

TRANSPORT PHENOMENA IN CYCLONE REACTORS

5.1 Heat Transfer

Although a great deal of work has been done on flow patterns of both gas and solids (79-97), there is little information available on heat and mass transfer in a cyclone chamber (68). The pertinent heat transfer modes in cyclone processing of a gas-solid feed are: heat transfer by convection and radiation to/from the cyclone walls, heat convection and radiation from the gas to the solid particles, or vice versa, and heat conduction through the cyclone walls to the surroundings.

5.1.1 Heat Convection:

Heat convection to the walls has been studied by Haspra and co-workers (69) and by Szekely and Carr (68). Haspra et al. found that heat transfer rates through the cyclone walls were much higher than those obtained in pipes. A plot of their data in the form of $\log (h/k)$ versus $\log (Re)$ showed a linear relation with a slope of 0.8. Here, h is the heat transfer coefficient, k thermal conductivity of the gas, and Re is the Reynold's number. Szekely and Carr measured heat transfer rates into a cyclone wall in the presence of solids

(glass spheres) and compared them with those obtained in the absence of solids. Their results were correlated using the formula:

$$N_u = 0.42 R_e^{0.8} \quad (5.1)$$

when solids were absent. When solids were fed into the cyclone, a sharp drop in the outlet gas temperature (T_i) was observed. The drop in the outlet temperature was more pronounced when finer dense particles were used. Beyond a certain solid flow rate, further increase in solid loading depressed T_i only by a small amount. They explained the last observation by assuming that at a critical solid feed rate, the walls become completely covered with solid particles, forming an effective barrier to the passage of heat to the gas phase.

5.1.2 Heat Transfer to Solid Particles:

Several correlations appear in the literature that predict the heat transfer coefficient to particles suspended in a flowing fluid stream. Ranz and Marshal (70) correlated their results on the rate of evaporation from a stationary droplet by:

$$N_u = 2 + 0.6 R_e^{0.5} P_r^{0.33} \quad (5.2)$$

Fiszdon (71) and Lee and co-workers (72) suggested similar expressions. Vardelle et al. (73) used the following

expression to correlate the heat transfer coefficient to spherical particles:

$$N_u = 2 + 0.514 R_e^{0.5} \quad (5.3)$$

Under plasma conditions, particle heating is characterized by the presence of steep temperature gradients in the boundary layer. In this case a correction factor is necessary for the correlation equation, where the properties of the fluid are evaluated at the arithmetic mean temperature. Lewis and Gauvin (74) suggested using a kinematic viscosity ratio (ν_f/ν) for the correction factor in their equation:

$$N_{u_f} = 2 + 0.515 R_{e_f}^{0.5} \left(\frac{\nu_f}{\nu} \right)^{0.15} \quad (5.4)$$

Subscript f refers to properties corresponding to the film temperature.

Sayegh and Gauvin (75) proposed the following equation:

$$N_{u_w} = 2 f_o + 0.475 P_r^m (Re_{0.19})^{0.522} \quad (5.5)$$

where $Re_{0.19}$ is the Reynold's number corresponding to $T_{0.19}$ defined as:

$$T_{0.19} = T_w + 0.19 (T - T_w) \quad (5.6)$$

The Prandtl's number in equation 5.5 has a value of 0.672 and its exponent m is found from:

$$m=0.78 (Re_{0.19})^{-0.145} \quad (5.7)$$

The correction factor f_o is a function of the gas temperature (T) and the surface temperature (T_w) of the particle and is given by:

$$2f_o = 2 + \frac{[1 - (\frac{T_w}{T})^{1+X}]}{[(1+X)(1 - \frac{T_w}{T})(\frac{T_w}{T})^X]} \quad (5.8)$$

where $x = 0.8$ for argon plasma.

Szekely and Carr (68) proposed the following correlation for heat transfer coefficient to a spherical glass particle being heated in a cyclone reactor:

$$h = \frac{170d}{\tau} [1 - \text{EXP}(-\frac{476\tau}{d^2})] \quad (5.9)$$

where d is the particle diameter, and τ is residence time. To allow for particles of different properties, the following relation can be employed:

$$h_2 = h_1 \frac{k_2 C_{p_2}}{k_1 C_{p_1} \tau_1} \quad (5.10)$$

Here, subscript 1 and 2 refer to properties of glass and the new particle, respectively, C_p and k are the heat capacity and thermal conductivity of the solid particles.

5.1.3 Heat Losses Through the Wall:

Total heat conducted through the walls of the cyclone can be calculated using the relationship:

$$Q = 2\pi KL \frac{T_i - T_o}{\ln(R_o/R_i)} \quad (5.11)$$

Where K is the thermal conductivity of the wall, L is the cyclone length, T_i and T_o are the inside and outside wall temperatures, and R_o and R_i are the outside and inside cyclone radius, respectively. The driving force ($T_i - T_o$) might not be constant throughout the length of the cyclone, in this case equation 5.11 can be written in a differential form as follows:

$$\frac{\partial Q}{\partial Z} = 2\pi K \frac{(T_i - T_o)}{\ln(R_o/R_i)} \quad (5.12)$$

If the temperature profile of the wall is known, equation 5.12 can be integrated to yield the total heat losses by conduction. In addition, appreciable amounts of energy are lost through the cyclone lid, which can be estimated from the an appropriate heat transfer correlation.

5.2 Mass Transfer

In cases where molecular diffusion of a gaseous species to a reacting solid interface is rate limiting, cyclone processing should offer a better contacting scheme due to the

enhanced heat and mass transfer rates characteristic of cyclone reactors. The work of Kosecky (76), for instance, has shown that mass transfer coefficients in cyclone columns were 10-15 times higher than those measured in packed bed columns. The author measured and correlated the mass transfer coefficient of carbon dioxide and ammonia in air stream. Tap water was used for the sorption of the gas under consideration. The data were correlated using the formula:

$$K_{mg} = 0.62 V^{0.8} W \quad (5.13)$$

for $W \leq 1.4$ m/sec, and

$$K_{mg} = 0.42 V^{0.75} W^{3.2} \quad (5.14)$$

for $W > 1.4$ m/sec, for the gas phase, and

$$K_{ml} = 2.45 V^{1.64} \quad (5.15)$$

for the liquid phase. Here, K_{mg} and K_{ml} are the mass transfer coefficient in the gas and liquid phases, respectively, W is the average axial gas velocity, and V is the liquid velocity at the outlet of the tangential inlet.

In the absence of experimental data, and for the purpose of estimating the mass transfer coefficient in a given system, the analogy between heat and mass transfer is usually employed

(77). For instance, an expression for mass transfer coefficient to a spherical particle is normally written in a form similar to that for of equation 5.2 by substituting Sherwood number (Sh) and Schmidt number (Sc) for their counterparts Nusselt number (Nu) and Prandtl number (Pr):

$$Sh=2+0.6Re^{0.5}Sc^{1/3} \quad (5.16)$$

Equation 5.16 has been suggested to be valid only for constant composition and small mass transfer rates.

The diffusion coefficient $D_{A,B}$ appearing in the Schmidt number is estimated from the expression (at pressures upto 10 atmospheres):

$$D_{AB} = \frac{0.0018583 T^{1.5}}{P(\sigma_{AB})^2 \Omega_{D_{AB}}} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad (5.17)$$

Where $\sigma_{A,B} = 1/2 (\sigma_A + \sigma_B)$ is the collision diameter, $\Omega_{A,B}$ is the collision integral for A-B gas mixture, M_A and M_B are the molecular weights of A and B, respectively, T is the absolute temperature, and P is the pressure of the system.

In cases where the resistance of the fluid boundary layer to mass transfer is negligible compared to pore diffusion and/or the chemical reaction, the mass flux (J) of the reacting gas is controlled by the concentration gradient and the effective diffusivity according to:

$$J = D_e (C_B - C_S) \quad (5.18)$$

The effective diffusion coefficient is found from (78):

$$D_e = D_{AB} \frac{\varepsilon}{Z} \quad (5.19)$$

where ε is the porosity of the solid particle and Z is the tortuosity. This expression is valid as long as the pores are large relative to the mean free path of the gas molecules. If the gas density is low or the pore size is small, Knudsen diffusion becomes important. When this happens, Knudsen diffusion coefficient is found from:

$$D_k = 9700 r \sqrt{\frac{T}{M}} \quad (5.20)$$

where r is the pore radius, T is the absolute temperature and M is the molecular weight of the diffusing species. Thus, the effective diffusivity becomes:

$$D_e = D_K \frac{W}{T} = 9700 r \left(\frac{W}{T} \right) \sqrt{\frac{T}{M}} \quad (5.21)$$

CHAPTER 6

CYCLONE DESIGN CONSIDERATIONS

Cyclone smelting of taconite concentrate is a promising concept, since it provides much higher heat exchange and mass transfer rates due to the intense mixing of the reacting constituents; thus increasing the rate of the reactions taking place and probably driving them to near completion. A proper design, therefore, should take into account these physio-chemical phenomena encountered in iron ore processing.

In general, a chemical reaction can be limited by either a chemical step, physical step, or both. Physical constraints consist of energy exchange and mass transfer between the reacting species and their environment. Mass transfer limitations are of two types: molecular diffusion of a fluid species involved in a chemical reaction through the fluid boundary, and/or its transport through the pores of the solid particles into/from the reacting interface. Limitations due to mass transfer may be minimized by thorough mixing, operating at higher temperatures, and/or reducing the solid particle size and its size distribution.

Energy exchange between a reacting solid and its surroundings is very important in many situations. For

example, in iron ore processing, huge amounts of energy are required to drive the reduction reactions. The energy required is usually supplied by burning a fuel, such that the combustion products act as reducing agents. Unless enough energy is transferred to the ore, the reaction rates are very slow, and the reduction process is limited by the rate of energy transfer to the ore.

The following sections describe in some detail estimations of the time required for complete conversion of a hematite particle for different controlling mechanisms discussed above. The purpose here is to come up with a cyclone size within which a hematite feed would be effectively converted to wustite in liquid state, at a given operating temperature and CO/CO₂ ratio.

6.1 Diffusion Through the Boundary Layer

Assuming that the reaction rate is controlled by carbon monoxide diffusion through the fluid film, its mass transfer rate to a spherical hematite particle can be estimated from:

$$Sh = \frac{K_m d}{D_{CO, CO_2}} = 2 + 0.6 Re^{0.5} Sc^{1/3} \quad (6.1)$$

When the particle travels with the same velocity as that of the gas phase, a limiting value of Sherwood number (Sh) is reached. This value (Sh = 2) would be obtained in a situation in which carbon monoxide in a stagnant gas phase is diffusing

into the surface of a solid particle. This value of Sherwood number would predict the maximum time a hematite particle must stay in the reactor before it is completely transformed to wustite. Thus,

$$\frac{K_m d}{D_{CO, CO_2}} = 2 \quad (6.2)$$

or

$$K_m = \frac{2D_{CO, CO_2}}{d_p} = \frac{D_{CO, CO_2}}{R_p} \quad (6.3)$$

The diffusivity of carbon monoxide can be calculated from:

$$D_{CO, CO_2} = \frac{1.8583 (10)^{-3} T^{1.5}}{\sigma_{CO, CO_2}^2 \Omega_n} \sqrt{\frac{1}{M_{CO}} + \frac{1}{M_{CO_2}}} \quad (6.4)$$

and at 1773° K, D_{CO, CO_2} is found to be 3.018 cm²/sec.

The time for complete reaction is given by :

$$\tau_f = \frac{\rho_s R_p}{3bK_m(P_{CO} - P_{CO_2})/RT} \quad (6.5)$$

Upon substituting for K_m from equation 6.3:

$$\tau_f = \frac{\rho_s R_p^2}{3bD_{CO, CO_2}(P_{CO} - P_{CO_2})/RT} \quad (6.6)$$

Figure 6.1 shows τ_f as a function of particle size at $P_{CO}/P_{CO_2} =$

3.0 ($P_{CO} + P_{CO_2} = 0.33$ atm) and a temperature of 1773° K. The figure indicates that the time for complete reduction increases rapidly with particle size. And that, when the boundary layer is rate controlling, a $320\text{ }\mu\text{m}$ particle would be converted to wustite only if it stayed approximately 0.55 seconds in the reactor. Stated differently, for a reaction time of 0.55 seconds, particles with diameter less than $320\text{ }\mu\text{m}$ will be completely transformed to wustite, while those larger than $320\text{ }\mu\text{m}$ are expected to be only partially reduced.

Figure 6.2 represents τ_f as a function of P_{CO}/P_{CO_2} for a $160\text{ }\mu\text{m}$ particle. With P_{CO}/P_{CO_2} ratio approaching 6, the time for complete reaction reaches a limiting value of approximately 0.10 seconds, as indicated in the figure. At lower partial pressure ratios the time for complete reduction becomes larger and larger. At an average residence time of 1.4 seconds and a P_{CO}/P_{CO_2} ratio of 3 a particle of $160\text{ }\mu\text{m}$ will be completely reduced to wustite in less than 1.4 seconds. In practice, P_{CO}/P_{CO_2} ratio will decrease as the reaction proceeds, so that the minimum P_{CO}/P_{CO_2} ratio of 3 would correspond to an average value within the reactor.

6.2 Pore Diffusion Control

Molecular transport of carbon monoxide through the product layer(s) might become limiting in the event that the torturous paths are long, a dense metallic product forms on the unreacted core, or both. In such case, the effective

diffusivity of carbon monoxide is given by:

$$D_e = \frac{D_{CO, CO_2} \varepsilon}{Z} \quad (6.7)$$

where ε is the porosity and Z is the average torturous path length. A knowledge of the pore structure of all product layers that might form when hematite is reduced is necessary in order to properly calculate D_e . In fact, one would expect the effective diffusivity to change with time as the product layers grow with the progress of the reaction.

In any event, and for a conservative estimate only, it will be assumed that the effective diffusivity of carbon monoxide is 20% of its molecular diffusivity in the carbon dioxide phase. That is, $D_e = 0.2 D_{CO, CO_2}$, D_e would be 0.622 cm²/sec.

With this value for D_e , the time for complete conversion (τ_D) when pore diffusion is limiting is found from:

$$\tau_D = \frac{\rho_s R_p^2}{6bD_e(P_{CO} - P_{CO_2})/RT} \quad (6.8)$$

τ_D is plotted versus particle size in Figure 6.1 at $P_{CO}/P_{CO_2} = 3$. As the figure shows, τ_D increases with particle size, going from 0.2 seconds for $d_p = 120 \mu\text{m}$ to about 1.4 seconds for $d_p = 320 \mu\text{m}$. For an average residence time of 1.4 seconds, it is expected that particles with diameter less than 320 μm would be completely converted to wustite, while those greater than 320 μm would be partially reacted only.

Figure 6.1 Time for complete reaction vs particle size

Figure 6.2 Time for complete reaction vs CO/CO_2 ratio for 160 μm particle

Figure 6.2 is a plot of τ_0 as a function of P_{CO}/P_{CO2} for a 160 μm particle. The figure indicates that τ_0 is not affected significantly beyond a partial pressure ratio of 6. At lower ratios, τ_0 is extremely sensitive to P_{CO}/P_{CO2} ratios. Notice that Figure 6.1 and 6.2 were constructed at $P_{CO} + P_{CO2} = 0.33$ atm.

6.3 Heat Transfer Limitations

In processing Taconite in a cyclone reactor, it is very important to raise the temperature of the particles to the highest possible value in the shortest period of time, so that the reaction rate is as fast as possible. In addition, melting the product(s) within the cyclone chamber would ensure effective utilization of the input energy for the whole process.

To calculate the time required to heat up and then melt a solid particle, it is necessary to calculate the average heat transfer coefficient to a spherical particle entrained in a gas stream at a given temperature. The simplest correlation available takes the form:

$$N_u = \frac{hd}{K_g} = 2 + 0.6Re^{0.5}Pr^{1/3} \quad (6.9)$$

Equation 6.9 predicts a limiting value of 2 for Nusselt number. This value corresponds to heat transfer to a solid particle from a stagnant fluid phase. This situation is equivalent to the case where the relative velocity of the

particle is essentially zero. The limiting Nusselt number gives a minimum value for the heat transfer coefficient, that is:

$$h = 2 \frac{k_g}{d} = \frac{K_g}{R_p} \quad (6.10)$$

Knowing the particle size, its physical properties as well as the properties of the gas phase, it is possible to estimate the time required to raise the temperature of a spherical particle to any given value.

Biot number is a measure of the rate of energy arriving at the particle surface to that dissipated through it by conduction. Mathematically:

$$Bi = \frac{h}{K_s/R_p} \quad (6.11)$$

where h is the average heat transfer coefficient, k_s and R_p are the thermal conductivity and radius of the particle.

Depending on the value of Biot number, the internal resistance of the particle can be neglected. In general, for $Bi < 0.1$ the rate of heat conduction through the solid particle is considered to be very fast in comparison to heat convection to the surface. For the situation considered here:

$$\frac{hR_p}{K_s} < 0.1 \quad (6.12)$$

From 6.10 and 6.11, it can be shown that the internal

resistance is negligibly small as long as :

$$K_g < 0.1 K_s \quad (6.13)$$

For wustite, $K_s = 0.032$ cal/cm.sec. $^{\circ}$ K, and that of air is 2×10^{-4} cal/cm.sec. $^{\circ}$ K (at 1800 $^{\circ}$ K). Thus, it can be assumed that the inequality in equation 6.13 holds. Then the time required to reach a given temperature can be calculated from:

$$\frac{T - T_f}{T_i - T_f} = \text{EXP}\left(-\frac{hA}{\rho C_p V} t\right) \quad (6.14)$$

where T is the desired solid temperature, T_i its initial temperature, T_f is the fluid temperature, ρ , A , V , and C_p are the particles density, surface area, volume, and heat capacity, respectively. Substituting equation 6.10 into 6.14, and noting that $A/V = 3/R_p$ for a sphere, the following relation is obtained:

$$\tau_h = -\frac{\rho C_p R_p^2}{3 K_g} \text{Ln}\left[\frac{T - T_f}{T_i - T_f}\right] \quad (6.15)$$

Once the melting point is reached, the time required to melt the particle can be obtained by relating the total amount of energy required (Q) to melt a given sized particle to the rate of heat arriving at its surface:

$$Q = \frac{4}{3} \pi R_p^3 \rho \Delta H_m \quad (6.16)$$

Rate of energy transfer to the surface is given by:

$$q = \frac{4}{3} \pi r_p^2 h (T_f - T_m) \quad (6.17)$$

The time required to completely melt the particle (τ_m) is the ratio Q/q , that is:

$$\tau_m = \frac{\rho R_p \Delta H_m}{3h(T_f - T_m)} \quad (6.19)$$

Substituting for h from equation 7.10:

$$\tau_m = \frac{\rho R_p^2 \Delta H_m}{3K_g(T_f - T_m)} \quad (6.19)$$

Equations 6.15 and 6.19 are shown graphically in Figures 6.3 and 6.4. Figure 6.3 represents τ_h and τ_m as a function of particle size (assumed to be wustite) at a gas temperature of 1700° C and initial solid temperature of 25° C. As the figure indicates, the melting time and the heating time are sensitive to the particle size (D_p), particularly beyond $D_p = 150 \mu\text{m}$. Nevertheless, the figure shows that for a residence time of 1.4 seconds, all particles of diameter less than 300 μm will be melted before exiting the reactor, as long as the gas temperature is 1750° C or higher.

Figure 6.4 shows τ_h and τ_m as a function of gas temperature for a 160 μm particle. At higher gas temperatures

Figure 6.3 Heating and melting times vs particle size.

Figure 6.4 Heating and melting time vs gas temperature for 160 μm particle.

($T_f > 1700^\circ \text{C}$) both τ_h and τ_m are less sensitive to the gas temperature. At lower T_f , the time for melting increases rapidly as T_f decreases. Again, for residence time of 1.2 seconds all particles of size $150 \mu\text{m}$ will be melted as long as the gas temperature is 1500°C or higher.

Figures 6.3 and 6.4 neglected the energy radiation to the particle surface, which led to a conservative estimates of the heating and melting times.

6.4 Falling Film Reactor

There are situations in which the ore feed is injected directly into the plasma flame (41,42). The feed is thus melted forming a liquid film that flows down the reactor wall. By proper control of the residence time of the film, the ore fines can be reduced upon treatment with a reducing agent such as coal or coke.

The residence time of the molten film can be predicted by performing momentum balance calculations, and solving the resulting differential equations with the appropriate boundary conditions. The equation obtained is:

$$\frac{\partial(r\tau_{rz})}{\partial r} = r\rho g \quad (6.20)$$

Equation 6.2 is solved with the boundary conditions:

$$\frac{\partial(\tau_{rz})}{\partial r} = 0 \quad (6.21)$$

at $r = RI$, and:

$$V_z = 0, \quad (6.22)$$

at $r = R$

where r is the radial distance, τ_{rz} is the shear force, ρ is the liquid density, V_z it's velocity, R is the reactor radius, and $(R - RI)$ is the film thickness. Upon solving equation 6.20, the following expression is obtained for the film velocity distribution:

$$V_z = -\frac{\rho g}{4\mu} (r^2 - R^2) - \frac{\rho g}{2\mu} \ln\left(\frac{R}{r}\right) \quad (6.23)$$

where μ is the viscosity of the liquid film.

The film maximum velocity occurs at $r = RI$ and is given by:

$$V_{z,max} = \frac{\rho g}{4\mu} (R^2 - RI^2) + \frac{\rho g RI^2}{2\mu} \ln\left(\frac{RI}{R}\right) \quad (6.24)$$

$V_{z,max}$ is presented graphically in figure 6.5 as a function of the film thickness, as well as the wustite flow rate. As shown, the film velocity increases rapidly with the film thickness (i.e, wustite flow rate). At a flow rate of 9 Kg/Hr, the velocity is 0.85 cm/sec. At this velocity, the estimated residence time is 72 seconds for a reactor length of 24 inches.

In the previous calculations, the reactor radius was taken to be 4.5" (11.43 cm). Also, it was assumed that all taconite was melted and reduced to wustite, and that all liquid was carried to the wall to form the film.

6.5 Other Design Factors

Other factors considered in designing the cyclone reactor include heat losses through the walls, plasma gas flow rate, total energy requirements, and materials and energy balance calculations.

Several of these factors are interrelated, off course. For example, the plasma output energy is a function of the gas flow rate, as well as the nature of the gas itself. From previous experience, a flow rate of 6-7 SCFM of a gas mixture of argon and helium was required to attain an output energy of 33-37 Kw. Based on a residence time of 2 seconds for the gas phase, the reactor volume needed is 1.2 cubic feet (assuming an average temperature of 1800° K). For a reactor diameter of 11", the height would be 21.8". Based on these estimates, the final cyclone size selected is 11" ID, 24" long for the cylindrical part, and 6" long for the conical part, as will be described in a later chapter.

Figure 6.5 Liquid film velocity and its flow rate vs film thickness

CHAPTER 7

EXPERIMENTAL SYSTEM

AND PROCEDURES

As stated in Chapter 1, the primary objectives of this research are to investigate the reducibility of fine taconite concentrates at high temperatures, using a plasma heat source in a cyclone reactor, and to study the chemical kinetics associated with the reduction and melting of the iron ore in a carbon monoxide-carbon dioxide atmosphere.

7.1 Experimental Equipment

The experimental system used in this study is shown in Figure 7.1. A photograph of the system is shown in Figure 7.2. The central part of the system is the cyclone reactor. It is fabricated out of a steel shell 14" ID, 16" OD, 24" long, with a 1/4" cooling jacket. The cyclone consists essentially of three sections: the upper section is 12" long with two tangential inlets that are 6" in diameter and 180° apart. They are centered at approximately 5" down from the top of the upper section. One inlet is used as the burner port and the other one as the plasma torch port. A sampling

Figure 7.1 Schematic representation of the experimental system

Figure 7.2 Photograph of the experimental system

port and a thermocouple inlet are located at the center of this section and are 180° apart. The section is closed at the top with a circular steel lid that has a 1" inlet port to allow axial injection of the taconite feed. The steel cover and the tangential ports have 1/4" cooling jackets.

The middle section is also 12" long with a sampling port and a thermocouple inlet that are 180° apart and are located at the center. The conical section is 6" high with an exit diameter of 6". It allows gaseous sampling and temperature measurement through two ports that are located just above the tubular discharge. All three sections are water-cooled through separate cooling lines, and all water flow rates and temperatures are monitored and measured. The cyclone is assembled gas-tight through bolts after applying a layer of high temperature sealant around the periphery of each section.

Graphite (grade 6222-P from Graphite Products) is used as a lining and it has the same general construction as that of the steel shell. Initially, based on an argon-helium mixture as the plasma gas, the cylindrical lining was 11" ID, 12" OD, with 1" graphite felt as an insulator. After it was found that nitrogen could be used in place of helium as the second plasma gas component, another lining was inserted inside the original one (see section 7.2). This new lining is 9" ID, 10" OD, allowing 1/2" of additional graphite felt insulation to be added. The conical section is also lined with graphite and is insulated with graphite felt. This exit lining has a diameter

of 3" and extends 2" inside the collection chamber. The two tangential inlets of the upper section of the cyclone are lined with 3" ID, 4" OD graphite sleeves and are insulated with graphite felt.

The cyclone reactor sets on top of a rectangular collection chamber that is 12" high, 12" wide, and 24" long. All six faces of the chamber are water-cooled (1/4" cooling jacket) through separate lines. Also, a cooling coil (made out of 1/2" copper tubing) is installed at the discharge end of the chamber to remove as much heat as possible from the gases leaving the chamber. A ceramic crucible sets inside the chamber where the molten product is collected. The crucible is 6" high and 4" in diameter. Gases leaving the chamber enter a cylindrical filter so that the entrained particles are trapped and collected. The filter is made of a tubular steel shell (8" ID, 12" long) with a filter bag inside. The bag is made of a 0.5 micron size Nomex cloth and has a 12 sided-star shaped folded periphery in order to maximize the surface area of the filter. The filter is water-cooled using a cooling coil to ensure a temperature of less than 150° C. A pressure gauge is installed at the filter inlet to monitor the incoming gas pressure.

Gases leaving the filter pass through a burner in order to convert the carbon monoxide present to carbon dioxide, thus minimizing the hazardous potential of the gases. The burner is designed in such a way as to ensure complete combustion of

the outgoing gases. A pilot flame is maintained in the burner using propane and air. The combustion gases are then vented to a stack.

A non-transferred arc plasma torch (model PT50C612 acquired from Plasma Energy Corporation) is used to provide the energy that is required. It has two tubular hollow electrodes. The front electrode is the cathode while the rear electrode is connected to the positive terminal and serves as the anode. Both electrodes are made of a copper alloy and are extensively water-cooled. The plasma torch water flow rate is in the range of 17-18 gallons per minute. A "macor" gap insulator is used to electrically separate both electrodes. The plasma gas is injected through a vortex generator which is placed after the gap insulator and between the electrodes. A mixture of argon and nitrogen is used as the plasma gas. Flow rates of both gases are measured and recorded separately. The torch is attached to a 96 KW power supply (made by Halmar).

The plasma torch is attached to the inlet port through a flat 1/4" thick steel plate that is bolted to the end of the plasma inlet. A Teflon disk and plastic bolts provide electrical insulation. The plate is protected with a graphite lining and graphite felt insulation. The torch is inserted through the center of the plate into the arm to a distance of 5" from the plate, allowing about 6" distance between the front electrode and the inner graphite lining. With this arrangement, energy losses through the plasma port are kept to

a minimum, and, at the same time, interactions between the reactants and plasma gas are avoided. A stainless steel pipe union is used to avoid any gas leakage from the insertion area and to allow easy detachment of the torch. The burner attachment to it's port is similar to that of the torch. The burner port is plugged with a graphite rod after the conclusion of the preheating period. The graphite rod is mounted on a steel plate which in turn is bolted to the burner inlet.

Reactants are fed axially into the cyclone through a 3/8" copper pipe that is connected to a graphite tube through a pipe union. A Metco powder feeder (model 3MP) is used to feed the taconite powder. The feeder has a hopper for powder storage. From the hopper, taconite goes to an adjustable speed rotating wheel. The feeder has a vibrating system to prevent the material from clogging. The carrier gas (usually, carbon dioxide and argon mixture) is introduced into the section housing the rotating wheel, from there it carries the powder to the cyclone through the copper tubing. Carbon monoxide is introduced into a tee at the end of the copper tube carrying the taconite feed. Flow rates of the three gases are measured and recorded separately.

The system includes multiple ports along the cyclone reactor to take samples of the gases and solid species (if any) at different intervals and to measure the temperature. Three sampling lines are mounted at the geometric center of

each section. Each line has a 1/4" graphite tube (1/8" ID) inserted into the reactor, a micron filter, and a shut-off valve. The micron filters are used to separate any condensed species that are entrained in the gas phase. The graphite tube can be inserted to any depth along the radial position, but most of the gas samples are taken from half the radial distance of the inner lining. The top two lines are connected to a Varian Gas Chromatograph (model 3300) that has an air actuated sampling valve to take samples at a certain time from the reactor. Gaseous samples are taken, by suction, using a vacuum pump that is placed at the end of the sampling lines. The third line is attached to an IR gas analyzer (Siemens, model Ultramat-22P) and is used to monitor and record the carbon monoxide and carbon dioxide composition at the discharge end of the reactor.

Temperatures are measured and recorded at three locations along the cyclone using type "C" thermocouples. Thermocouples one and three (TC-1 and TC-3) indicate the graphite lining temperature at the top and conical sections, respectively, while thermocouple two (TC-2) measures the geometric center temperature of the second cylindrical section. All sections of the cyclone and the collection chamber have separate cooling lines. All water lines have flow meters on them and type "K" thermocouples.

The information from the experimental system is interfaced with a data acquisition system. The system

consists of an IBM personal computer (model 30) and Metrabyte analog and digital boards. The conversion boards are connected to the thermocouples, flow sensors, pressure transducers, and meters on the power supply. Data from each experimental test are recorded and stored separately.

7.2 Experimental Procedure

Fine taconite concentrates and carbon monoxide-carbon dioxide gas mixtures are the primary reactants in this research. The taconite powder contains different sizes as shown in Figure 7.3, and as can be seen, it consists mainly of 5-45 micron particles. The chemical composition of the concentrate is reported in Table 7.1, which shows that the ore is mainly magnetite (67.70% Fe_3O_4 , 25.81% Fe_2O_3) with approximately 7% impurities. The taconite was obtained from LTV Steel Mining Company.

Technical grade carbon monoxide is used as a reductant. Carbon dioxide is fed to the powder feeder and acts as a carrier gas (after being mixed with argon). The reactants are injected axially at the top of the cyclone just above the point of plasma gas injection. Flow rates of carbon monoxide, carbon dioxide, and taconite are adjusted such that a theoretical CO/CO_2 ratio is maintained at the cyclone discharge. The argon flow rate is adjusted so as to maintain a fixed flow rate of the carrier gas. The gas flow rates are measured and recorded using mass flow meters. Delivery

Figure 7.3 Size Distribution of the Taconite Concentrates.

Table 7.1 Chemical Composition of Taconite Concentrates as provided by LTV Steel.

Component	Percentage
Iron	67.04
Silica	4.50
Phosphorous	0.20
Wustite	21.01
Magnetite*	67.70
Hematite*	25.81

* Calculated.

pressures of these gases are fixed at 50 PSI. The taconite concentrate is dried in an oven for eight to ten hours at about 110-120° C to remove any moisture present so as to prevent any clogging of the powder feeder, and to maintain a more uniform flow of the concentrate into the reactor. The taconite feed rate is fixed at 40 grams per minute for most of the experiments.

The plasma torch is operated using an argon-nitrogen mixture as the plasma gas. Nitrogen is used in order to increase the power of the torch with a minimum plasma gas flow rate. Since nitrogen has a higher ionization potential than argon, the voltage across the electrodes is increased and, consequently, higher power is achieved. The delivery pressures of argon and nitrogen are kept at 130 PSI, but due to many flow restrictions in the gas lines, the actual delivery pressure drops to 60-70 PSI, as monitored and recorded, at the gas pressure gauge provided with the power supply. The flow rate of argon ranges from 2.2-2.5 SCFM and that of nitrogen is 0.8-1.0 SCFM. The operating parameters of the plasma system are essentially fixed for most of the experimental work and are given in Table 7.2. These parameters provide a good arc attachment to the face of the cathode, and hence, a smooth arc for a uniform erosion of the cathode and stable operating conditions.

The voltage and current settings (i.e. the power input to the reactor) are chosen so that the graphite lining

Table 7.2 Operating Parameters of The Plasma System.

Voltage, V	230-250
Current, A	190-195
Power, KW	44-49
Argon Flow Rate, SCFM	2.2-2.5
Nitrogen Flow Rate, SCFM	0.8-1.0
Argon Pressure, psi	125-130
Nitrogen Pressure, psi	125-130
Plasma Gas Delivery Pressure,psi	65-70

temperature at the cyclone discharge is maintained at approximately 1400° C ensuring that any wustite formed is in a liquid form within the reactor (provided the taconite feed has sufficient time to react and melt). At this point, the wall temperature of the top section is 1550° C and above, while that of the middle section has a temperature of about 1650° C.

The plasma torch is initially operated with argon alone for 10-12 minutes. During this period the current and voltage readings are 180-185 amperes and 100-120 volts, respectively. Nitrogen is then introduced as a second plasma gas component, resulting in a voltage increase to 220-250 volts. While the system is being heated up to the desired temperature, argon (as part of the carrier gas) is continuously fed into the cyclone in order to maintain a positive pressure at the top of the reactor. As the temperature at the cyclone discharge wall reaches 1350° C, the carrier gas flow rate is increased to the desired value (usually 0.6 SCFM). The carbon dioxide flow rate is controlled so that the CO/CO₂ partial pressure ratio is fixed at the cyclone exit, as theoretically calculated. After the cyclone temperature has stabilized, the carbon monoxide and taconite are fed into the reactor. While the flow rate of taconite remained unchanged at 40 grams per minute for most experiments, the carbon monoxide flow rate is varied in the experiments in order to determine the effect of the CO/taconite molar ratio on the reduction of the concentrate.

Taconite is fed for about 20 minutes in most experiments. After taconite injection has begun, the cyclone temperature drops by 25-30° C before it reaches a new steady state temperature. As this time is reached, gas samples are withdrawn and analyzed using the gas chromatograph. Meanwhile, the IR gas analyzer is monitored continuously and carbon dioxide and carbon monoxide analysis are recorded for the gas exiting the cyclone. During taconite feeding, the pressure gauge at the filter inlet is checked every few minutes to detect any pressure increase within the system.

When the taconite and reacting gas feeding is stopped, the plasma torch is kept operating for 10 minutes to prevent solidification of molten material inside the reactor and to give the melt additional time to flow out of the reactor into the crucible. After the plasma torch is shut off, the argon flow continues into the cyclone to prevent re-oxidation of the product formed by any infiltrating air during the cyclone cooling. Once the cyclone temperature drops to 250-300° C, the argon flow is terminated, and the system is allowed to cool down to near room temperature. The door of the collection chamber is then opened and the crucible is removed to collect the product. The filter is also disassembled from the system and fines trapped in the filter cloth are collected. Typically, less than 8% of the product collected is in the filter, about 50% is in the crucible, and the rest is always found to have been solidified at the inside wall of

the discharge end of cyclone.

The gases leaving the cyclone reactor are extensively cooled in the collection chamber to about 280-300° C at the chamber exit. Expansion of the flowing gas results in some cooling. As the gases enter the filter they are further cooled by expansion and water cooling through the cooling coil to about 100-120° C, well below the maximum operating temperature of the filter cloth of 150° C. The cooling water flow rates to all sections of the cyclone are controlled so as to extract the minimum amount of energy without exceeding exit water temperatures of 90° C. In contrast, the collection chamber's water flow rates are kept as high as possible to ensure a filter temperature below 150° C. The plasma torch cooling water flow rate is kept at 17-18 GPM, which results in an inlet water temperature of 45-50° C, well below the design specification of 80° C. Water flow rates in all lines are adjusted at the beginning of each experiment and recorded, as well as their individual exit temperatures.

7.3 Iron Analysis

Products collected from the crucible, cyclone discharge, and the filter bag are chemically analyzed for total iron. The procedure used consists of precisely weighing 0.1 gram

sample and dissolving it in hot hydrochloric acid. The solution is then treated with few drops of SnCl_2 solution until the yellow color disappears completely. Distilled water is added to bring the volume to 150 ml, and the solution is allowed to cool down before adding 5 ml of HgCl_2 saturated solution. After an oxidizing period of 5 minutes, 25 ml of a buffer solution (15% H_3PO_4 +15% H_2SO_4) are added followed by 5 drops of sodium methylphenolamine indicator. Finally, titration is carried out with Standardized $\text{K}_2\text{Cr}_2\text{O}_7$ solution and the iron analysis of the sample is determined.

7.4 Silica Analysis

Determination of silica in the product formed is conducted as follows: 0.2 gram samples are measured accurately and dissolved in hydrofluoric acid at 50-60° C using nickel crucibles. After the sample is completely dissolved, 20 ml of 1:1 HCl solution are added followed by dissolving 2 grams of KCl. After waiting 15 minutes or more, the solution is filtered slowly, washing the filter paper and the crucible 3-5 time with 5% KCl solution. The filter paper is then transferred to a plastic container where 15 ml of 80% alcohol solution saturated with KCl are added, followed by 1 ml of phenolphthalein indicator. The solution PH is adjusted with dilute NaOH (1 gram/liter) followed by addition of 100 ml of boiling water. Titration is performed using 0.1 N NaOH and

the silica analysis is found.

CHAPTER 8

EXPERIMENTAL DATA AND ANALYSIS

8.1 Preliminary Experimental Work

Three different sets of preliminary experiments were carried out and served as guides for the subsequent work. The scope and nature of these experiments were: pre-heating with propane, plasma pre-heating, and finally the initial taconite experiments. The objectives of each set of experiments are presented in the following sub-sections.

8.1.1 Pre-Heating with Propane

During the design stages of this research project, a preliminary energy and materials balance calculations revealed that a large amount of input energy was required to maintain an average cyclone temperature of 1500° C, or higher. One obvious conclusion that emerged was that the plasma torch was required to be operated for extended periods of time for the reactor to reach a steady state temperature of 1500° C. Concern over the rapid erosion of the torch electrodes led to the idea of attaching a natural gas burner to the system so that it could be used to pre-heat the cyclone to 1000-1200° C prior to operating the plasma system. For this purpose, a

Braun natural gas burner was acquired, as well as a high capacity blower. The burner was attached to one tangential inlet of the reactor through a steel plate that screwed onto the end of the burner and bolted onto the burner inlet port. Propane was delivered into the burner at a measured rate and air was delivered at a rate such that a hot light blue flame was established. The burner was then inserted through the port and tightly bolted to the steel plate. The temperature inside the reactor was measured and recorded at the three locations mentioned previously, as well as the water flow rates and their respective exit temperatures for the cyclone, collection chamber, and the plasma torch. Several tests were conducted and the data collected and analyzed.

Several observations were made from this set of experiments. First, due to the intensive cooling of the collection chamber, water vapor condensed on the walls of the chamber, as well as inside the filter, resulting in rusted walls. To prevent further erosion of the chamber and the filter, they were coated with high temperature paint. The water condensate could have caused another problem by interacting with the product once taconite feeding has started. Such interaction would distort the results and made the analysis and conclusions less reliable. Second, and more importantly, the maximum temperature attained was 780°C (Figure 8.1), which is well below the intended range of $1000\text{--}1200^{\circ}\text{C}$. Due to the last observation in particular, propane

Figure 8.1 Temperature VS Time for Propane Pre-Heating (EXPB3).

preheating was terminated and abandoned for the present work.

In spite of the discouraging results of these tests, they reflected some positive points. Figure 8.1 shows the temperature at three positions as measured over time. It is obvious that these three temperatures are different by less than 50° C, which suggests that the cyclone configuration could approach an isothermal reactor. Whether or not this temperature proximity would hold at higher operating temperature was still to be seen. Another positive aspect of these tests was that they provided information concerning the relative amounts of energy losses through the cyclone sections and through the collection chamber. Figure 8.2 shows the percentage of energy losses through the cyclone sections for various tests. It is clear that a relatively high percentage of the energy losses was through the burner inlet, cover, and the top cylindrical section. These observations led to three modifications. First, the water flow rates to the cyclone sections were reduced drastically by employing a new set of flow meters. Second, the reactor was modified to provide more insulation at the cover of the cyclone. And thirdly, the plasma torch attachment was redesigned so that the torch was inserted to a distance of 4.5" deep into its port, thus reducing the energy losses there.

8.1.2 Plasma Pre-heating

The objective of this set of experiments was to determine

Figure 8.2 Energy Losses Through Cyclone Sections for EXPB 3 and EXPB 4 (Propane Preheating). Percent of Total Energy Losses Through the System.

the operating parameters of the plasma system necessary to reach and maintain a steady temperature of 1400°C at the cyclone discharge. The parameters included the current, voltage, argon and helium flow rates, and the gas delivery pressure. One concern was the stability of the plasma arc so that uniform erosion of the front electrode was achieved. A few tests were conducted with argon and helium as the plasma gas. The output energy was 30 KW or less, giving a steady temperature of about 1000°C . Then, nitrogen was used instead of helium as the second plasma gas component, and tests were conducted to ensure plasma arc stability and to determine the parameters required to attain an output energy of 45 KW and higher. These tests were carried out without attaching the torch to the cyclone. Upon establishing the stability criteria of the plasma arc, heating tests were performed at an output energy of 45-50 KW. This range was proven to be sufficient to reach a cyclone exit temperature of 1450°C (Figure 8.3). The operating parameters determined were reported in Table 7.2. The rest of the experimental work was conducted using these parameters.

One important observation that was particularly significant was that the total plasma gas flow rate required was 3.0-3.2 SCFM. The reactor design was based on a flow rate of 6.5-7.0 SCFM. Since the actual flow rate was about 50% less than the design, it was concluded that decreasing the cyclone inside diameter from 11" to 9" would not affect the

Figure 8.3 Temperature VS Time for Experiment 6 (Plasma Preheating). C-1 Top wall Temp., C-2 Geometric center temperature of second cylindrical and conical sections, Respectively.

Figure 8.4 Comparison of Energy Losses Through Cyclone Sections for Experiment 7 and 10. Percent of Total Energy Losses Through the System.

residence time and would reduce the energy losses through the cyclone walls. For this reason, a 9" ID and 10" OD graphite lining was inserted inside the original one and 1/2" more insulation was added. The effect of these changes on the energy losses through the reactor is shown in Figure 8.4, where a comparison is made between losses before the changes (Experiment 7) and those after the changes (Experiment 10).

8.1.3 Initial Taconite Experiments

The primary objective of this research project is to reduce taconite to liquid wustite at smelting temperatures of 1500° C. To determine the feasibility of this objective, several tests were performed. Excess amounts of carbon monoxide were injected to the reactor (3-5 times the stoichiometric amount). Taconite feeding time ranged from 10-20 minutes. At the end of each experiment, the product was collected from the crucible, the filter bag, and from the cyclone discharge. Samples were drawn from each product and analyzed chemically to determine the total iron present. Table 8.1 shows the range of the experimental conditions for these tests. The results of these experiments are reported in Table 8.2. A material balance was performed based on the following assumptions. First, all silica present in the feed material appeared in the product as SiO_2 . Second, carbon analysis is insignificant. And finally, iron is present as metallic iron and as wustite (FeO) only (preliminary X-ray

diffraction indicated that the cyclone product consisted of three phases; metallic iron, wustite, and a wustite-silica-calcium oxide phase). The calculations are summarized in Figures 8.5 through 8.8. Figures 8.5 through 8.7 show the percentage of iron, wustite and silica in the product collected in the crucible, cyclone discharge, and the filter bag, respectively. Figure 8.8 shows the percentage of oxygen removal from the feed. These preliminary results clearly indicate that the taconite concentrate was reduced to iron and wustite, including the portion of the material trapped in the filter bag. The degree of reduction always exceeds that calculated for reduction to wustite and oxygen removal was 1-3 times higher (29-32 % oxygen removal if reduction to wustite only). Apparently, the high degree of reduction achieved resulted from several factors including the high CO/CO₂ ratios due to the interactions between carbon dioxide and the graphite lining at the high smelting temperatures, and the reaction between the iron oxides and solid carbon. In addition, the liquid film that formed on the lining walls had extended periods of time to react with both carbon monoxide and the lining.

Based on these finding, the experimental work was continued with no further modifications and design changes. The experimental program followed is summarized in Table 8.3.

Table 8.1 Experimental conditions for experiments 8 through 16.

EXP #	FLOW RATES			WALL TEMP. (°C)		CO ₂ /CO RATIO	
	CO SCFM	CO ₂ SCFM	TACONITE g/min	TOP	EXIT	INLET	EXIT
8*	0.6	0.00	15	1485	1320	0.00	n/a
9	0.7	0.00	15	1550	1410	0.00	n/a
10	0.7	0.29	15	1510	1330	0.41	n/a
11	0.5	0.23	15	1500	1320	0.46	n/a
12	0.7	0.14	19	1505	1345	0.20	n/a
13	0.7	0.16	40	1445	1305	0.23	n/a
14	0.6	0.17	19	1460	1350	0.28	0.078
15	0.4	0.08	22	1425	1230	0.2	0.003
16	0.6	0.16	38	1180	1050	0.27	0.001

* Lining ID = 11". n/a values were not measured.

Table 8.2 Total Iron Analysis as Determined Chemically.

EXPERIMENT #	CRUCIBLE	CYCLONE	FILTER BAG
8	84.44	95.07	76.85
9	90.39	92.15	85.24
10	90.53	92.48	82.67
11	89.88	92.51	78.50
12	83.20	92.26	82.08
13	89.46	92.23	83.50
14	90.81	89.94	N/A
15	90.05	89.45	78.49
16	91.33	87.82	77.13

N/A: not measured.

Figure 8.5 Percentage of Iron, Wustite, and Silica in the Material Collected from the Crucible.

Figure 8.6 Percentage of Iron, Wustite, and Silica for the Material Collected in the Cyclone.

Figure 8.7 Percentage of Iron, Wustite And Silica for Material Collected in the Filter Bag.

Figure 8.8 Percentage of Oxygen Removal From the Taconite Feed.

8.2 Effect of Various Parameters on the Reduction of Taconite

The experimental program that was conducted is presented in Table 8.3. As indicated previously, the objective is to evaluate the effect of various factors on the reduction and melting of the taconite concentrates. The factors studied were: $P(\text{CO}_2)/P(\text{CO})$ inlet ratio, initial partial pressure of carbon monoxide, average cyclone temperature, carbon dioxide interaction with the lining, and finally, solid carbon reduction of taconite.

8.2.1 General Observations

As explained previously, the material collected in the crucible, filter bag, and the cyclone discharge was removed, weighed, and saved for later analysis. The typical product distribution was 3.5-10.0% in the filter bag, 10-27% in the crucible, and the rest in the reactor, mostly at the wall of the cyclone discharge. The filter product consisted of very fine powder that was apparently swept away with the gas phase and trapped in the filter bag. The crucible material was composed of three portions; fine powder that settled out upon expansion and rapid cooling of the gas as it entered the collection chamber, a portion that had a plate-like structure with loosely-held frozen particles, and the last portion consisted of condensed, spherically-shaped solid mass. The cyclone product had a plate-like structure in the form of

Table 8.3 Table of experimental runs

Parameter	Range
1. CO ₂ CO inlet flow rate	0.100-0.25
2. CO flow rate, SCFM	0.313-0.833
3. Temperature at discharge end of the cyclone	987-1175
4. CO ₂ interactions with the lining Temperature at exit wall	890-1085
5. Taconite reaction with the lining Temperature at the exit wall	875-1160
6. Nickel oxide experiments	See 5 above
7. CO ₂ feeding pattern	Axial vs side feeding

an ingot. The plates were relatively tightly bonded.

Upon dismantling the reactor lid at the conclusion of each experiment, it was always observed that the lower portion of the graphite lining was coated with a very thin film. In addition, there were numerous spherically-shaped particles that were frozen at the walls. The size of these spheres appeared to be random and ranged from less than 0.1 cm to more than 1 cm in diameter. Complete removal of these spheres was not possible, since they were fused with the graphite lining and their removal could have resulted in breaking the lining. It is believed that some of these spheres melted and passed out of the reactor and were collected in the crucible while the reactor temperature was increasing and stabilizing at the desired point. Once taconite feeding was started, fine particles entrained in the gas phase dropped out and collected on top of these spheres, as well as the re-solidified plate-like material. This observation was confirmed later by heating up the cyclone and maintaining it at 1400° C (at the exit) for about 20 minutes without introducing any of the reactants. The crucible was removed and shiny spheres were found to have collected there. Chemical analysis of this material was always consistent and showed more than 95% iron.

8.2.2 Carbon dioxide/Carbon Monoxide Feed Ratio

In this set of experiments, the taconite feed rate was fixed at about 40 gm/min, the carbon monoxide flow rate was

0.6 SCFM, and the input energy was 39-41 Kw. The measured wall temperatures were; TC-1 = 1281-1321 °C, TC-2 = 1175-1280°C, TC-3 = 1183-1234°C. From energy balance calculations the geometric center temperature was estimated to be; 1657-1705°C for the top section, 1390-1495°C for the bottom section, and 1386-1416°C for the conical section. The carbon dioxide flow rate was varied between 0.06 to 0.148 SCFM to give an inlet CO_2/CO ratio of 0.100-0.247. The experimental conditions are reported in more detail in Table 8.4.

Two to three samples were drawn from each product fraction and analyzed chemically for total iron. In some cases, samples weighing 0.5-0.7 gm were also analyzed, particularly from the material collected in the crucible and the cyclone discharge, and the weighted average for all samples was calculated. Figure 8.9 shows the iron analysis as a function of the inlet $P(\text{CO}_2)/P(\text{CO})$ ratio. Figure 8.10 presents the percentage of oxygen removal from the feed material, based on the materials balance calculations and the assumptions made earlier. These figures clearly indicate that the inlet CO_2/CO partial pressure ratio has no significant effect on the degree of reduction, within the experimental range studied and when considering one product fraction at a time. On the average, the cyclone product analyzed 89.82% iron, compared with 86.67% for the crucible material and 82.54% for the filter samples.

Table 8.4 Experimental conditions for Experiments 17 to 20.
Effect of CO₂/CO feed ratio.

EXP #	FLOWRATE (SCFM)		TACONITE Gm/min	WALL TEMP. (°C)			CO ₂ /CO	
	CO	CO ₂		TOP	MID.	EXIT	IN	OUT
17	0.6	0.15	37.80	1292	1150	1207	.247	.034
18	0.6	0.10	38.96	1285	1173	1193	.165	.038
19	0.6	0.07	11.36	1321	1173	1165	.123	.004
19R	0.6	0.07	39.98	1288	1178	1148	.123	.000
20	0.6	0.06	39.48	1303	1174	1191	.100	.015

Figure 8.9 Total Iron Analysis as a Function of inlet $P(\text{CO}_2)/P(\text{CO})$.

Figure 8.10 Oxygen removal versus inlet $P(\text{CO}_2)/P(\text{CO})$

The filter bag samples show lower iron analysis, partly because the fines collected there seemed to have been suspended in the gas phase and flew out of the reactor before having spent enough time to be reduced further. The three flow zones in smelting cyclone described by Taylor and co-workers (100) and by Hou (101) might have contributed to the lower degree of conversion (hence less oxygen removal) of this portion of the product. Towards the cyclone center, there is a low pressure zone where the gas and suspended particles short-circuit and flow out of the reactor with no significant tangential velocity. When that happens, particles flowing in this zone travel at essentially the same speed as that of the gas phase. The result would be a much shorter reaction time and the lowest conversion. The reduction reactions in this zone are between the carbon monoxide present in the gas phase and the suspended solid particles (gas-solid reactions).

In contrast, the cyclone product exhibits the highest iron analysis (or oxygen removal). This could have resulted from several factors. First, the carbon monoxide to carbon dioxide ratio was consistently very high within the cyclone, ensuring that the reduction of iron oxides could go to completion, provided the reaction time is sufficiently long. The high $P(\text{CO})/P(\text{CO}_2)$ ratio was due to the reaction between the carbon dioxide and the graphite lining at the elevated smelting temperatures employed. Second, this fraction formed as a molten film covering the lower portion of the lining.

The liquid film would then react with the solid carbon according to:

as well as with carbon monoxide in the gas phase:

Carbon dioxide can react with the carbon to regenerate carbon monoxide through the gasification reaction:

The net results of these reactions would be higher oxygen removal and lower CO_2/CO ratios. See also section 8.2.8.

The liquid film that formed on the walls resulted from that portion of the feed that was immediately thrown onto the walls either as solid particles, molten droplets, or both. Once the film has developed it flows downward by gravitational forces, and due to its high viscosity it travels at very low speed, in comparison with the gas, giving it extended periods of time to react with the carbon monoxide and the lining. At the cyclone discharge walls, the temperature drops below the melting point of the melt, leading to its solidification. Once solidified, the frozen material continues to react with the carbon monoxide as the gas flows past it. The overall effect of these factors would be the higher degree of metal-lization observed.

Of course, some of the melt would flow into the crucible and collect there before it's solidification at the discharge walls. In addition, molten droplets entrained in the gas

phase, particularly in the high flow zone (100) may discharge into the crucible before being carried to the lining walls. These droplets would have less reaction time than the molten film. Also, in the high flow zone, the main reactions are between these molten droplets and the carbon monoxide, as shown in reaction 8.2. When taking these factors together, one would expect lower reduction and less oxygen removal for the crucible material, as compared with the cyclone product.

8.2.3 Carbon Monoxide Feed Rate

The experimental conditions for this set of experiments are summarized in Table 8.5. No carbon dioxide was fed to the reactor. The taconite flow rate was fixed at approximately 40 grams/min, and the input energy was in the range of 39-40 KW, resulting in wall temperatures very similar to those of the previous set. The center temperature was estimated to be 1671-1712° C for the top section, 1493-1510° C for the middle section and 1397-1428° for the conical section. The carbon monoxide flow rate was varied between 0.313 to 0.833 SCFM, giving an inlet CO partial pressure of 0.11-0.19 atm, $P_{co,i}$, (assuming the system's total pressure is 1.0 atmosphere. This assumption is based on the observation that no pressure increase was detectable with the pressure gauge installed at the discharge end of the collection chamber).

Iron analysis is shown graphically in Figure 8.11 as a function of $P_{co,i}$. The percentage of oxygen removal is

Table 8.5 Experimental Conditions For Experiments
21 Through 24. Effect of CO flowrate.

EXP #	FLOWRATE (SCFM)		TACONITE Gm/min	WALL TEMP. (°C)	
	CO	CO ₂		MIDDLE	EXIT
21	0.833	0	40.61	1175	1189
22	0.686	0	39.20	1183	1192
23	0.532	0	38.71	1171	1178
24	0.313	0	39.7	1163	1171

Figure 8.11 Total Iron Analysis versus inlet P(CO)

Figure 8.12 Oxygen Removal versus Inlet P(CO)

presented in Figure 8.12. Clearly, these results suggest that the degree of metallization is not significantly affected by the initial partial pressure of carbon monoxide. Also, there appears to be no difference between the crucible and the cyclone materials, given the absolute experimental error of 3% in the procedure employed in determining the total iron in a given sample. The filter samples exhibit lower degree of reduction for the reasons stated in section 8.2.2.

It should be noted that there was some difficulty in sampling both the crucible and the cyclone products. As mentioned previously, these materials consisted of frozen mass that collected as plates, spheres, and/or both. Several attempts were made to crush and grind this material without any appreciable success. In each case, the portion high in iron came out as thin plates, while the rest of the material was somewhat crushed. To make the analysis more reliable, additional samples of larger size were taken (0.2-1.0 gm) and the iron composition was determined. The results reported are the weighted average of all samples. As can be seen, the variability in iron analysis does not appear to improve greatly with larger sample size.

The inconsistency in iron analysis is believed to be due to the formation of a wustite-silica-calcium oxide phase that separated out of the molten product. As reported in Table 7.1, the taconite feed contains 4.50% silica, and atomic absorption analysis indicated a calcium composition of 0.10%

and a magnesium analysis of 0.19%. The solubility of wustite in $\text{SiO}_2\text{-CaO}$ system will be discussed later in this chapter; but the product formed is not a homogeneous phase, and the inability to grind it to smaller size made it difficult to obtain a representative sample. This was also the case for total silica analysis, to be discussed later.

Comparing Figure 8.11 with Figure 8.9 one could conclude that the extent of reduction was not affected greatly by the presence of carbon dioxide, except for the filter bag material. This could be an indication of a fast chemical reaction between carbon dioxide and the graphite lining to produce carbon monoxide, resulting in the partial pressure of carbon dioxide to reach small value such that it had no significant effect on the reduction reactions. The free energy change of reaction 8.3 is given by:

$$\Delta G^0 = 40,800 - 41.7T (\text{Cal/mole}) \quad (8.4)$$

At an average cyclone temperature of 1500°C , the equilibrium constant of reaction 8.3 is about 12150, indicating that nearly all the carbon dioxide will be reduced to carbon monoxide, given excess carbon is present and the reaction time is sufficiently long. The fact that carbon dioxide analysis was always small in these two sets of experiments suggests that the average residence time was long enough for reaction 8.3 to approach completion. This will be discussed further

later in this chapter.

8.2.4 Temperature Effect

To evaluate the influence of temperature on the reduction of taconite, several experiments were conducted in which the input energy to the system was varied between 34-41 Kw, depending on the temperature desired. Since the plasma torch output energy is dependent upon the gas flowrate, the average residence time of the gas phase was not constant but varied with the input energy (i.e. with the plasma gas flowrate and the reactor average temperature). The exit wall temperature was varied from 1000 °C to 1190 °C. From energy balance calculations, along with the wall temperatures of the top and bottom cylindrical sections, the average reactor temperature was between 1400-1610 °C. In these experiments, the carbon monoxide flowrate was fixed at 0.62 SCFM, taconite feed rate was 40 grams/minute, and no carbon dioxide was injected to the cyclone. Table 8.6 summarizes the experimental conditions of this set of experiments.

Figure 8.13 presents the percentage of iron in the product collected in the cyclone, crucible, and the filter bag as a function of the wall temperature at the cyclone discharge. The percentage of oxygen removal from the

Table 8.6 Experimental conditions for experiments 25 through 29. Effect of temperature.

EXP #	FLOWRATE (SCFM)		TACONITE gm/min	WALL TEMP. (°C)		
	CO	CO ₂		TOP	MID.	EXIT
25	0.635	0	39.21	N/M	1175	1189
26	0.625	0	32.70	1105	987	1000
27	0.620	0	43.30	1124	1100	1105
28	0.632	0	41.3	1165	1147	1162
29	0.623	0	42.23	1128	1103	1010

Figure 8.13 Iron analysis vs exit wall temperature

Figure 8.14 Oxygen removal vs exit wall temperature

taconite feed is shown in Figure 8.14. As can be deduced from these figures, at temperatures above 1100 °C, the degree of metallization does not change greatly with temperature, and below 1100 °C the extent of reduction decreases rapidly as the temperature is lowered, except for the filter bag samples. The oxygen removal from the filter fines appears to remain constant up to a wall temperature of 1150 °C, then it drops thereafter. One reason for this behavior is the significant difference in the residence time for these experiments. In addition, while the flowrate of carbon monoxide was fixed at 0.62 SCFM, its inlet partial pressure actually decreased with increasing temperature due to the higher plasma gas flowrate (higher energy input requirements).

An Arrhenius plot representing the data can be constructed when the following assumptions are made. First, the average reaction time of the fines trapped in the filter bag is equal to that of the gas phase. Second, the reactions proceed at constant temperature that can be approximated by the arithmetic average of the three temperatures estimated at the geometric center of each section. Third, the iron analysis of these fines corresponds to the steady state conversion of the taconite. Fourth, the reduction reactions cease at the cyclone discharge, that is, once these fines exit the cyclone no further significant reaction with carbon monoxide takes place within the collection chamber (the chamber is extensively cooled such that the gas temperature

drops to below 300 °C at the chamber's exit).

With these assumptions in mind, the reaction time can be determined from the total gas flowrate, cyclone volume, and average temperature within the reactor. But, the total gas flowrate is not constant due to the fact that the carbon monoxide flowrate changes with the progress of the reduction reactions and with the Boudouard reaction. For simplicity only, it is further assumed that the carbon monoxide flowrate is equal to $(Q_i + Q_o)/2$, where Q_i and Q_o refers to the inlet and outlet carbon monoxide flowrates, respectively.

Figure 8.15 shows the rate of oxygen removal at steady state versus reciprocal temperature. The data fit a straight line up to a temperature of 1775 °K, below which the rate of oxygen removal appears to increase at a faster rate with temperature. The slope of the line joining the first three data points is -5241, giving an activation energy of 10.42 Kcal/mole (43.56 KJ/Mole). The slope of the line at the other portion of the figure is -8896, resulting in an activation energy of 17.68 Kcal/mole (73.90 KJ/Mole). Similar findings were reported by several investigators (102,103). The low activation energy of the reduction reactions could be attributed to a shift in the controlling mechanism governing the reduction reactions. At high degree of metallization, reduction of iron oxides is believed to be the controlling step, but the carbon gasification reaction is more important in limiting the overall reaction rate at lower degree of

Figure 8.15 $\ln\{\text{Rate of oxygen removal (moles O per sec.)}\}$ vs reciprocal temperature ($^{\circ}\text{K}$)

reduction (102). It has been reported that at about 20% reduction, the Boudouard reaction is rate controlling with an activation energy of approximately 86 Kcal/mole, and at 80% reduction, the activation energy drops to 13-18 Kcal/mole (102). In any case, the activation energy reported in this research suggests that the chemical step is rate limiting up to 1500 $^{\circ}\text{C}$, and at higher temperatures mass transfer may influence the reduction reactions.

The indication that the chemical step is rate controlling at these elevated temperatures is believed to be due to the extremely high turbulence in the reactor, such that the fluid film boundary layer becomes insignificantly small, and thus contributes very little to the overall resistance to the reduction reactions.

8.2.5 Carbon dioxide interactions with the lining

During the previous sets of experiments, it was found that the carbon dioxide composition in the exit gas was always small. This was attributed to the fast kinetics of the Boudouard reaction. In order to determine the extent to which carbon dioxide reacts with the graphite lining, several experiments were conducted at three different temperatures as shown in Table 8.7. The carbon dioxide flowrate was fixed at 0.40 SCFM. No taconite or carbon monoxide were introduced into the reactor. The plasma torch input energy was varied between 35-40 Kw, resulting in an average cyclone temperature between 1290-1502 °C. The gas exiting the cyclone was continuously analyzed for carbon monoxide and carbon dioxide using the IR gas analyzer. These experiments were terminated when the IR reading indicated constant gas composition. Figure 8.16 shows the amounts of carbon monoxide and carbon dioxide (moles/min) in the exit gas as a function of time.

Table 8.7 Experimental conditions for experiments 30 through 32. Carbon dioxide interaction with the graphite lining.

EXP #	FLOWRATE (SCFM)		TACONITE Gm/min	WALL TEMP. (°C)		
	CO	CO ₂		TOP	MID.	EXIT
30	0	0.40	0	945	883	890
31	0	0.40	0	1057	995	1010
32	0	0.40	0	1142	1080	1085

Figure 8.16 Carbon dioxide interaction with the graphite lining. Moles of CO and CO₂ exiting the cyclone vs time (min).

The data indicate that it took approximately 2 minutes to reach steady state conditions. In addition, the carbon dioxide composition in the exit gas was always less than 2% even at the lower temperature of 1290°C, and it dropped down with increasing temperatures. At An average cyclone temperature of 1500 °C almost all the carbon dioxide fed to the system was converted to carbon monoxide in less than 2.2 seconds (average gas residence time).

An Arrhenius plot is presented in Figure 8.17 (based on the assumptions made earlier). The figure shows the rate at which carbon monoxide is being generated versus reciprocal

Figure 8.17 Arrhenius plot showing the rate of CO generation (mole/sec) vs reciprocal temperature ($^{\circ}\text{K}$)

temperatures. Carbon monoxide analysis was used rather than that of carbon dioxide because of its higher analysis and thus smaller relative error in the readings. A reasonable straight line fit was obtained, the slope of which is -6743. The activation energy was calculated to be 13.40 Kcal/mole, indicating that the chemical step is rate controlling within the temperatures employed. This suggestion could be attributed to the fast diffusion rate of carbon dioxide towards the graphite surface, and the possibility that carbon dioxide could dissociate to carbon monoxide and oxygen as it

experienced the intense heat of the plasma flame. The released oxygen would then react with the graphite lining to form carbon monoxide. See section 8.2.8.

8.2.6 Taconite reaction with the lining

In a previous section it was suggested that a large proportion of the taconite feed is melted and is partially thrown onto the reactor walls by the swirling motion of the plasma gas. The melt reaching the wall forms a thin liquid film and flows downward mainly by gravitational forces. Once formed, the liquid film reacts with the graphite, as well as the carbon monoxide in the gas, resulting in the higher degree of metallization for the material collected in the cyclone. In order to confirm this suggestion and to evaluate the degree to which the film interacts with the lining, several experiments were carried out at three different temperatures. Taconite feed rate was constant at 40 gm/min, and no carbon monoxide or carbon dioxide were injected to the cyclone. The average cyclone temperature was varied between 1385 to 1620 °C. Table 8.8 presents the experimental conditions in more detail.

Iron analysis is plotted versus the wall temperature at the cyclone discharge in Figure 8.18. Figure 8.19 shows the percentage of oxygen removal. The degree of reduction increases rapidly with temperature, and at 1170 °C no significant difference can be seen between the iron analysis

Table 8.8 Experimental conditions for experiments 33
Through 35. Taconite reaction with graphite.

EXP #	FLOWRATE (SCFM)		TACONITE Gm/min	WALL TEMP. (°C)		
	CO	CO ₂		TOP	MID.	EXIT
33	0	0	41.88	1175	1154	1160
34	0	0	43.47	893	868	875
35	0	0	41.23	1025	1000	1010

Figure 8.18 Iron analysis versus exit wall temperature

Figure 8.19 Oxygen removal versus exit wall temperature

whether carbon monoxide was fed or not (see Figures 8.11 and 8.12). The steady state carbon monoxide composition in the exit gas shows about 8.7% CO by volume when the operating temperature was 1620 °C, and no carbon dioxide was detected either on the gas chromatograph or on the IR. This corresponds to 0.54 moles/min of carbon monoxide being generated by the reduction reactions, and suggests that the reaction between graphite and molten iron oxides is significant enough to influence the degree of reduction and the reaction kinetics.

Figure 8.20 is an arrhenius plot showing the steady state rate of oxygen removal for the filter fines versus reciprocal temperature. The data adequately fit a straight line. From a statistical fit the activation energy was determined to be 14.25 Kcal/mole, indicating that the reduction reactions are chemically controlled, which agrees very well with the conclusion stated earlier in section 8.2.4.

8.2.7 Nickel Oxide Experiments

The flow pattern of gases in a cyclone reactor is believed to be of plug-flow type (79-97, 107). Meanwhile, the behavior of the reacting particles depends on several factors including the gas flow rate, particle size and size distribution, and the particles feed rate in comparison to the gas flow rate. In their study, Li, et al.(108) concluded that the solid phase exhibited plug flow behavior at higher gas

Figure 8.20 Arrhenius plot showing the rate of oxygen removal (Moles O/sec) vs reciprocal temperature (⁰K)

flow rates, and showed some back mixing when the gas flow rate was decreased. In the experimental system that was employed in this research, the solid feed is mostly melted to form a liquid film covering the reactor walls, while small fraction of the fines fed leave the reactor with the flowing gas. In order to better understand the flow type of the liquid film and the fines, experiments were conducted in which 10 grams of finely divided nickel oxide were thoroughly mixed with 990 grams of taconite powder to give a 1.0% NiO-99.0% taconite

Table 8.9 Nickel Analysis and its distribution in the products collected in experiments 33-36

TOTAL NICKEL FED IN EXPERIMENT 33 = W = 5.26 GRAMS

	%Ni	WEIGHT OF PRODUCT F (GRAMS)	NICKEL IN F I (GRAMS)	I*100/W
EXP 33				
FILTER	1.150	40.00	0.4600	8.75
CYCLONE	1.050	285.00	2.9925	56.89
CRUCIBLE	0.770	98.00	<u>0.7546</u>	<u>14.35</u>
		TOTAL	<u>4.2071</u>	<u>79.98</u>
EXP 34				
FILTER	0.140	32.59	0.0455	0.86
CYCLONE	0.084	529.60	0.4449	8.46
CRUCIBLE	0.100	63.80	<u>0.0638</u>	<u>1.21</u>
		TOTAL	<u>0.5542</u>	<u>10.54</u>
EXP 35				
FILTER	0.110	20.00	0.0220	0.42
CYCLONE	0.080	389.30	0.3114	5.92
CRUCIBLE	0.090	11.10	<u>0.1000</u>	<u>0.19</u>
		TOTAL	<u>0.3434</u>	<u>6.54</u>
EXP 36				
FILTER	0.017	40.00	0.0068	0.13
CYCLONE	0.016	669.00	0.1070	2.03
CRUCIBLE	0.018	125.25	<u>0.0225</u>	<u>0.43</u>
		TOTAL	<u>0.1364</u>	<u>2.59</u>
		TOTAL	<u>5.2411</u>	<u>99.64</u>

Figure 8.21 Nickel analysis in experiments 33 through 36

mixture. The mix was fed in one experiment only, and the nickel analysis was followed in four subsequent tests. The experimental conditions were the same as reported in section 8.2.6. Nickel appearing in each product fraction was determined using a Pelkin-Elmer Atomic Absorption Spectrophotometer (model 2380), following the procedure outlined in section 8.3.2. The experimental data is shown in Table 8.9 and presented graphically in Figure 8.21.

Approximately 80% of the nickel fed appeared in the product collected in the first experiment, and 20% of nickel was un-collected. Almost all nickel fed discharged out of the reactor at the conclusion of the fourth experiment.

The filter bag fines contained some nickel in decreasing amounts after the first experiment although no nickel was fed. This could have resulted from some fines that were trapped in the filter bag when nickel was fed but not completely removed from the bag. Except for experiment 33, the crucible product always showed slightly higher nickel analysis than that of the cyclone. This might be due to the suggestion made earlier that some of the fused material inside the reactor melts and collects in the crucible while the cyclone temperature was increasing and stabilizing at the desired one.

The data presented in Figure 8.21 and Table 8.9 suggest that the behavior of the liquid film could be of plug-flow type with some back mixing. As mentioned earlier, large fraction of the solid feed is immediately thrown onto the wall

as molten droplets by the swirling motion of the gas. These droplets either reach the wall and form a molten film, or flow in spirals in the vicinity of the wall. The portion that forms a liquid film would travel downward under the influence of gravity, and, due to the wall roughness and the high viscosity of the melt, it does not exit the cyclone within one experimental run. Meanwhile, the molten droplets reach the surface of the conical section and collect there as solid material once the temperature drops below the melting point. These factors, as well as the difficulty in collecting all the product from the cyclone, led to the observed 20% hold-up of the nickel in the system.

8.2.8 Plasma Interactions with the Reactants

As described in Chapter 7, the taconite powder and the gaseous reactants were injected axially just ahead of the plasma flame. Although the plasma torch was inserted 4.5" inside its port (total length of the port is 10"), it was not possible to completely eliminate the interactions between the reactants and the plasma flame. From energy balance estimates, the plasma gas average temperature as it entered the cyclone was in the range of 3000-3500 °C. In other words, the gas possessed high thermal energy such that it was possible to melt the taconite feed almost instantly. For example, it could be shown that a 40 μm magnetite particle would be completely melted in 50-80 milliseconds if it was

Figure 8.22 Fractional decomposition of iron oxides and carbon dioxide versus temperature

exposed to such high temperatures. In addition, it is known that hematite (25.81% in the fines) decomposes to magnetite and oxygen at 1460 °C. Meanwhile, carbon dioxide dissociates to oxygen and carbon monoxide at about 2980 °C.

The available thermodynamic data for iron oxides and carbon dioxide are valid for a given temperature range only. If these data can be extrapolated beyond the recommended range, then it is possible to calculate the fractional decomposition of iron oxides and carbon dioxide at various temperatures. The procedure employed was presented in Chapter 3. The results of these calculations are shown in Figure

8.22. The figure presents the fractional decomposition of hematite, magnetite, liquid wustite, and carbon dioxide as a function of temperature. In constructing the figure, it was assumed that 5.0 moles of inert gas and one mole of the reacting oxide were initially present.

As can be seen, under the assumed conditions, hematite is completely decomposed at 1602 °K to magnetite and oxygen. Magnetite begins to dissociate at 2020 °K, and at 2300 °K it is expected that all magnetite would be transformed to wustite and oxygen. Liquid wustite does not decompose until it reaches a temperature of 3110 °K. At an average plasma gas temperature of 3500 °C (3773 °K), more than 20% of wustite would be converted to liquid iron and oxygen.

It is believed that the taconite feed is at least partially decomposed to iron, wustite, and oxygen upon its immediate contact with the plasma flame. The oxygen released combines with the graphite lining to form carbon monoxide. It is also possible that this oxygen could react with carbon monoxide to form carbon dioxide, which would then diffuse to the lining surface and reacts with the graphite to regenerate carbon monoxide.

The suggestion just stated is supported by the thermodynamic predictions presented above and, more importantly, by the experimental evidence obtained by analyzing the material that was found to have accumulated on the front electrode and its water guide. This material was

spherically shaped (0.5-1.0 mm in diameter) and a plate-like portion that was solidified on the front face of the water guide. Samples collected from several experiments were analyzed for total iron and the results are shown in Figure 8.23. Iron analysis was always higher than 80%, and oxygen removal was more than 59%. (These estimates assume that the copper present in these samples is negligible). This corresponds to approximately 34% metallic iron, 61% wustite and 5% silica and other impurities. It is believed that the high degree of metallization of this material could not have resulted from the reduction with carbon monoxide only, and that the dissociation of taconite contributed to the high degree of reduction observed.

With respect to carbon dioxide, Figure 8.22 indicates that it starts to decompose at 1800 °K, and at an average plasma temperature of 3773 °K more than 92% of carbon dioxide would dissociate to carbon monoxide and oxygen. In all the experiments presented so far, carbon dioxide was fed axially to the cyclone reactor and acted as a carrier gas for the solid fines. Several attempts were made in order to maintain a given CO/CO₂ ratio at the cyclone discharge with the feeding pattern just mentioned. The graphite lining was first coated with a thin film of zirconia cement in order to minimize the interactions between taconite and carbon dioxide with the lining. Carbon dioxide was introduced to the reactor at a rate of 34-36 SCFPH, taconite feed rate was 40 grams per

minute, and the plasma input energy was 38-40 Kw, resulting in a wall temperature of 1080 °C at the discharge end of the cyclone. The composition of carbon monoxide and carbon dioxide was continuously monitored and recorded using the IR

Figure 8.23 Iron analysis and oxygen removal for the material collected from the front electrode and it's water guide. The plasma input energy is also shown on the left scale

gas analyzer. At steady state, the CO/CO_2 exit ratio approached a value of 38 (Figure 8.24). Then, the lining was coated with zirconium diboride, and experiments were conducted at the stated conditions above. The exit CO/CO_2 ratio was still high (above 24), as shown in Figure 8.24. Finally, it was decided to feed the carbon dioxide through the sampling port located at the center of the top cylindrical section. This port is in the same vertical position as that of the plasma torch, but it is almost 180° away from the point where the plasma flame enters the cyclone. The lining was re-coated with zirconium diboride. Using the same experimental conditions above, the CO/CO_2 exit ratio was again recorded and is included in Figure 8.24. Initially and before taconite feeding was started, the CO/CO_2 exit ratio stabilized at 0.58. Then, carbon monoxide was introduced to the reactor so as to adjust the CO/CO_2 discharge ratio to 1.0. Once achieved, taconite feeding was started and the $\text{CO}-\text{CO}_2$ composition was recorded (Figure 8.24).

Comparing the results of this experiment with those of the previous one, it is clear that the CO/CO_2 exit ratio was lower when carbon dioxide was introduced through the side of the reactor. In addition, it took more than 13 minutes for the CO/CO_2 ratio to start increasing rapidly towards its steady value of 21, compared to about 8 minutes with axial injection of carbon dioxide.

Figure 8.24 Carbon monoxide to carbon dioxide exit molar ratio as measured over time for different coating materials and feeding pattern of carbon dioxide

The results of these experiments suggest that the rate at which carbon dioxide reacted changed significantly with its feeding pattern. When carbon dioxide was injected axially into the cyclone, its exit composition did not exceed 2%, but when fed through the sampling port, it was possible to obtain an 8% CO_2 in the exit gas.

Several factors could influence the CO/CO_2 discharge ratio, including the coating film thickness and its porosity, which are not easy to quantify. But, it is believed that

these two factors were not very different in the experiments reported here to influence the carbon gasification reaction to such an extent, and thus the exit CO/CO_2 , and that when carbon dioxide was fed axially it decomposed to carbon monoxide and oxygen upon its contact with the plasma flame. The oxygen released could have reacted with the zirconium diboride to form the corresponding oxides, with the exposed graphite to generate carbon monoxide, or with both. In comparison, when carbon dioxide was fed through the side of the reactor and away from the flame, it did not experience the intense thermal energy of the plasma, and consequently did not decompose appreciably, resulting in less free oxygen to react with the film or any exposed carbon. Carbon dioxide could still interact with the graphite lining as long as the porosity of the protective film permits the diffusion of gaseous species through it.

8.3 Silica and Impurity Elements

8.3.1 Silica Analysis

The composition of silica in the product was determined chemically as described in Chapter 7. Due to some difficulty in sampling the cyclone and the crucible materials in particular, it was necessary to take at least two samples from each product fraction for analysis. In spite of this, there was still some variability in the results obtained. It should

be noted that the results reported here are the weighted average of all samples taken from a given product fraction.

Figures 8.25 through 8.27 show the silica analysis (percent) in the filter fines, crucible material, and the cyclone product, respectively. For comparison, the theoretical silica composition is also included (based on the materials balance calculations and the assumptions made earlier), as well as that of the taconite concentrate. In general, the filter bag samples contain 2.5-4.0% SiO_2 (Figure 8.26), which corresponds to 45-55% of the theoretically determined values. In other words, about 50% of the silica originally present in the feed appeared to have separated out and went into the cyclone and the crucible portions of the reduced ore. This will be explained later in this section,

The silica analysis of samples drawn from the crucible (Figure 8.25) and the cyclone products (Figure 8.27) is closer to that determined from the materials balance considerations, although there is some difference. The crucible material appears to have a silica composition greater than the theoretical value in some cases, and in other samples the behavior is the opposite. The cyclone sample shows consistently lower silica than the calculated one.

As stated earlier, there was some difficulty in sampling the iron product due to the inability to grind the cyclone and crucible materials, which made it difficult to

Figure 8.25 Silica analysis in the crucible material

Figure 8.26 Silica analysis in the filter fines

Figure 8.27 Silica analysis in the cyclone material

take a representative sample. In addition, the formation of a wustite-silica-calcium oxide phase and its apparent segregation from the bulk of the reduced ore resulted in a non-uniform distribution of the silica (and other impurities within the matrix of the main product). And given the amount of each product fraction and its form, it was not easy to get such a small sample (0.1-0.5 gm) that would be representative of the whole material.

The equilibrium relationship for the system $\text{FeO-SiO}_2\text{-CaO}$ is well understood and is available in the literature (104-106). It is widely believed that when ferrous slags are melted (in equilibrium with iron) the iron is mostly in the divalent state, but some trivalent iron is also present. Addition of silica to the melt decreases the Fe^{3+} and ferric iron becomes insignificant at silica content beyond $2\text{FeO}.\text{SiO}_2$. On the other hand, when lime is added to a wustite melt, the Fe_2O_3 content increases to about 20%. At steel-making temperature of 1600°C , wustite slags extend from pure wustite melt to compositions around CaOSiO_2 , and is bordered on the acid side by saturation with solid SiO_2 , and by solid CaO and $2\text{CaO}.\text{SiO}_2$ on the basic side.

Fayalite ($2\text{FeO}.\text{SiO}_2$) is soluble in CaOSiO_2 and $\beta\text{-}2\text{CaO}.\text{SiO}_2$, and upon cooling, olivines (the general composition $\text{Ca}_x.\text{Fe}_{2-x}.\text{SiO}_4$, $X>2$), $2\text{FeO}.\text{SiO}_2$, and $y\text{CaO}.\text{SiO}_2$ ($y=1,2$, or 3) are formed. These silicates and the main body of the uncrystallized combination of wustite, silica, alumina, and lime form a glassy matrix that serves as bonding medium between ore particles at a lime/silica ratio of 0-1. When this ratio increase to 1.2, devitrification of the silicate glass occurs with the separation of $2\text{CaO}.\text{SiO}_2$ crystallites and calcium ferrite ($\text{CaO}.\text{Fe}_2\text{O}_3$).

At the smelting temperatures employed in this research ($>1600^\circ\text{C}$ in the upper cylindrical section), almost all solid feed is melted and forms a liquid film on the wall. Given the

extended residence time of the film, it is possible that olivines could have formed as the melt passed down and it's temperature dropped. The continued cooling of the system at the conclusion of each experiment would allow further segregation of the olivines formed.

As mentioned previously, X-Ray diffraction revealed the presence of three phases in the processed ore. These phases are; metallic iron, wustite, and wustite-silica-lime (Figure 8.29). In addition, it was occasionally observed that a "white" material was formed on the graphite walls, specifically at the upper section. Four samples of this material were chemically analyzed for total silica, and the results are presented in Figure 8.28. These results clearly indicate that the silica composition in these samples is much higher than it's average one, and it is 2-4 times greater than that of the taconite feed. This is another indication that a CaO-FeO-SiO_2 phase was formed and that it separated out of the main body of the product.

Figure 8.29 Silica analysis in the "white material" collected from various experiments.

8.3.2 Impurity Elements

The composition of various elements in the reduced product and the taconite concentrate was determined using atomic absorption spectroscopy, after dissolving a known amount of the material in hot hydrochloric acid followed by oxidation with concentrated nitric acid. The solution was then filtered and diluted to 100 ml. In some cases, it was

Figure 8.29 Photograph of the cyclone product (EXP9).
White: α -Fe, grey: FeO, dark grey: $\text{Fe}_2\text{SiO}_4\cdot\text{CaO}$,
dark: porositles.

necessary to further dilute a given volume of the original solution by a factor of 2-5, particularly when analyzing for calcium and/or magnesium.

The elements analyzed for were; Mn, Co, Cr, Ca, Mg, and Cu. As can be seen in Tables 8.10-8.12, the ore itself does not contain any copper, but the copper composition ranged from 0.02% to 0.05% in the products. The copper in these samples resulted from the erosion of the plasma torch electrodes, mainly the front one. As expected, very little copper reported into the filter (0.02%), as compared to that in the cyclone and the crucible (0.03-0.05%).

Cobalt, manganese, and chromium seem to have similar analysis in most of the samples analyzed. Manganese

Table 8.10 Analysis of impurity elements in the filter fines

	Co	Cr	Ca	Cu	Mg	Mn
EXP21	0.012	0.026	0.0339	0.0	0.094	0.011
EXP24	0.018	0.023	0.082	0.018	0.084	0.017
EXP25	0.023	0.018	0.092	0.0	0.024	0.016
EXP26	0.010	0.024	0.112	0	0.133	0.110
EXP27	0.018	0.025	0.105	0.01	0.094	0.110
ORE	0.024	0.018	0.091	0.00	0.73	0.010

Table 8.11 Analysis of impurity elements in the crucible product.

	Co	Cr	Ca	Cu	Mg	Mn
EXP21	0.014	0.02	0.081	0.02	0.09	0.008
EXP24	0.014	0.014	0.079	0.016	0.082	0.069
EXP25	0.015	0.018	0.29	0.023	0.576	0.142
EXP26	0.013	0.027	0.094	-	0.111	0.103
EXP27	0.011	0.021	0.077	0.033	0.112	0.078

composition 0.10-0.15%, cobalt analyzed 0.012-0.02%, chromium was 0.013-0.025%. Calcium and magnesium composition was not uniform and, in some cases, differed significantly from that of the ore samples. This could be attributed to the formation of a fayalite phase, as discussed previously, incomplete oxidation of the two elements, or both. In addition, and as described earlier, the original solution was diluted by a factor of 2-5 in order to lower the concentration of Ca and Mg to within the detectable limit, as a result some inaccuracy was introduced.

Table 8.12 Analysis of impurity elements in the cyclone product.

	Co	Cr	Ca	Cu	Mg	Mn
EXP21	0.027	0.014	0.061	0.036	0.015	0.011
EXP24	0.031	0.015	0.076	-	0.861	0.139
EXP25	0.026	0.017	0.042	0.036	0.05	0.05
EXP26	0.012	0.025	0.111	0.034	0.114	0.100
EXP27	0.016	0.025	0.096	0.028	0.179	0.084

On the average, the ore samples contain a total of 0.35-0.40% of these elements, the fines contain 0.42%, the cyclone product has 0.46% and the crucible samples averaged 0.38%. It should be noted that there is a 10% absolute error in the analysis reported in this section.

8.4 Materials Balance

A mass balance on oxygen was performed by using the gas analysis measured with the IR analyzer, total inlet gas flowrate (argon-nitrogen plasma gas, argon carrier gas, and carbon monoxide-carbon dioxide reacting gas mixture), and finally the taconite feed rate and its average oxygen content. In these calculations, the following assumptions were made; first, the system total pressure is equal to one atmosphere and the ideal gas law applies. Second, no infiltrating air, that is, all excess oxygen in carbon monoxide and carbon dioxide leaving the reactor was extracted from the ore feed. Third, the measured CO-CO₂ composition represents their average value at the cyclone discharge. Fourth, once the product exits the reactor it does not react further with carbon monoxide-carbon dioxide gas. Finally, taconite fines are fed at a steady and unchanging rate.

A summary of the results is shown in Table 8.13. The first column in the table represents the percentage of oxygen removed from the concentrate feed based on the oxygen balance. Column 2 is the percentage of oxygen removal based on the iron analysis determined chemically and the assumptions made in section 8.1.3. The last entry in the table corresponds to the maximum relative error in the two methods.

Clearly, the results shown in Table 8.13 agree very well with each other, and a maximum variation of 8% is reasonably small given the complexity of the experimental

Table 8.13 Comparison between oxygen removal based on oxygen balance and that based on iron analysis.

EXP'T #	PERCENT OXYGEN REMOVAL		
	OXYGEN BALANCE	FROM IRON ANALYSIS.	ERROR
25	81.94	86.76	6.0
29	83.78	84.11	0.4
30	84.90	90.96	7.2

system employed, and the inherent error in the measurements of the flowrates of the gases and their analysis. For instance, the mass flowmeters employed have a maximum error of 1% of full scale, which corresponds to 0.1 SCFM of each gas. In addition, the error in the IR readings could be as high as 0.7% for carbon monoxide and 0.4% for carbon dioxide, due to the interference between the two components. The chemical procedure employed in determining the total iron has an average error of 3%. ~~Off~~^o course, the difficulty in sampling was also another source of error.

Another factor that contributed to the observed difference is the assumption made in calculating the weighted average of oxygen removal from the product (column 2). This weighted average was based on the weight of the product

fractions actually collected, and ignored the the fines that were always present on the chamber's walls, as well as those that were not trapped in the filter bag, and did not consider the solids that adhered to the cyclone wall.

8.5 Carbon Analysis

Several samples were sent to LECO CORPORATION (St. Joseph, Michigan) for the determination of total carbon. The procedure employed consisted of heating a sample to 1000 °C, reacting it with pure oxygen, and absorbing the evolved carbon dioxide using sodium hydroxide. The results obtained are presented in Table 8.14.

The carbon analysis in the filter powder is relatively high (0.41-0.76% C), and is believed to have resulted from the abrasion of the graphite lining while the reactor was being heated up to the desired temperature. This suggestion is supported by the observation that, during the plasma pre-heating experiments, black deposit was found on the chamber's walls and inside the filter. The crucible material contains 0.33-0.57% C, in comparison to 0.03-0.06% C in the cyclone product. The apparent higher carbon analysis in the crucible material could be due to two reasons; first, some carbon fines may have collected in the crucible during the heating period. Second, this material contained significant portion of the spherically-shaped particles that melted and passed out of

the reactor while the cyclone temperature was increasing and stabilizing at the desired point. In other words, these spheres spent extended periods of time in contact with the graphite, and given the operating temperatures employed, a relatively higher amount of dissolved carbon in these samples is not surprising. See carbon analysis in EXP 21 Crucible.

Carbon composition in the cyclone product can be considered to be very low and insignificant. Except for that portion in the immediate contact with the lining (see carbon analysis in the cyclone material for EXP21), the cyclone product is not expected to contain much carbon, particularly the fraction that forms the molten droplets entrained in the gas phase, and does not come in contact with the graphite.

Table 8.14 Carbon analysis in several product samples

	Filter	PERCENT CARBON Cyclone	Crucible
EXP 26	0.412	0.030	0.569
EXP 28	0.756	0.059	0.326
EXP 21	0.650	1.277*	3.800**

* sample taken from the material in direct contact with the wall

** sample taken from spherically shaped material

CHAPTER 9

THEORETICAL MODELING

9.1 General

Before the mathematical model is developed, the following experimental observations are emphasized:

I. Plexiglass cyclone (101, 102):

1. At any given vertical position, the axial velocity (u) tends to increase very little with the radial distance up to $r = 3.0-4.0"$, then it changes rapidly towards the center.

2. The tangential velocity (ω) reaches a maximum value at radial position of $2.1-2.5"$, decreases thereafter and reaches almost a constant value in the immediate vicinity of the wall. The limiting value of ω ranges from $0.4-0.6V_0$, where V_0 is the average inlet gas velocity.

3. Both u and ω tend to follow the same pattern, and change very little with the axial position. This is only true at positions away from the entrance and exit of the cyclone.

4. Most particles appear to follow a helical path very close to the cyclone wall. The distance between successive spirals seems to be constant and does not change with the gas flow rate. The spirals move at a faster rate with increasing gas feed rates.

5. The pressure drop in the axial direction is very

small, and does not change appreciably with the axial distance. The gas flow rate tends to affect the pressure drop, but not greatly.

6. In the meantime, there appears to be a significant pressure drop in the radial direction. The gas pressure increases almost linearly with the radial distance up to $r = 4.75$ ", then it begins to drop thereafter. The gas flow rate influences the radial pressure drop greatly.

II. Hot cyclone:

1. The temperature of the graphite lining (T_w) decreases with the axial distance (z). The dependence of T_w on z is nearly linear.

2. The temperature in the radial direction changes appreciably with the radial distance. It increases by 280-300 °C when moving from the graphite wall to 2" away from the center line, as measured at $z = 1.5'$ from the cyclone top.

3. The rate of energy transfer to the reactor walls changes significantly from top to bottom. This is due to several factors including: different cooling rates for each section, changing gas and wall temperatures, and decreasing gas velocities. Due to these factors, and others, the thermal resistance of the composite wall is not constant but varies with the axial distance.

4. On the average, the gas flow appears to be of laminar type. This conclusion is based on the properties of the gas

evaluated at an average reactor temperature of 1700°C , and an average gas velocity corresponding to twice it's axial component.

5. A uniform liquid film appears to have been established on the walls of the second cylindrical section only, that is at a vertical distance equals $L/2$, where L is the total height of the cyclone.

The mathematical treatment to follow takes these observations into account, whenever applicable. The model formulation proceeds as follows:

1. Develop the gas velocity profiles (u, v, ω).
2. Determine the velocity components of the particles (u_p, v_p, ω_p).
3. Develop the gas temperature profile (T).
4. Predict the particles' temperature and the degree of melting (T_p, X_m).
5. Estimate the concentration profile of reactant A (C_A).
6. Calculate the extent of the reduction of spherical particles (X_p).
7. Calculate the degree of conversion of the falling film (X_f).

9.2 Velocity Profiles

9.2.1 Gas velocity components:

I. Tangential component:

Following the approach described by Rietema (90), the

gas tangential velocity can be written as:

$$\frac{v}{r} \frac{\partial(r\omega)}{\partial r} = -v \frac{\partial\left(\frac{1}{r} \frac{\partial(r\omega)}{\partial r}\right)}{\partial r} \quad (9.1)$$

where ω and v are the tangential and radial velocity components, respectively, r is the radial position, and ν is the kinematic viscosity. Equation 9.1 assumes that ω is independent of the axial and tangential positions. To solve for ω , two boundary conditions are needed. These are:

$$\omega(r=R) = \omega_R \quad (9.2)$$

$$\frac{\partial\omega}{\partial r} - \frac{\omega}{r} = 0 \quad (9.3)$$

at $r = r_1$. Where R is the cyclone radius, ω_R is the tangential velocity in the vicinity of the wall, and r_1 is the radial distance at which the shear forces are zero ($\tau_{r\theta}(r = r_1) = 0$). By introducing the following groups:

$\lambda_1 = (V_0 R)/\nu$, $(\omega^n) = (r v)/(V_0 R)$, $n = r/R$, and $W = \omega/V_0$, and $W_R = \omega_R/V_0$, equations 9.1 through 9.3 can be written in dimensionless form as follows (assuming ν/V_0 is constant and incorporating it in λ_1):

$$\lambda_1 \frac{\partial(\eta W)}{\partial \eta} = - \frac{\partial\left(\frac{1}{\eta} \frac{\partial(\eta W)}{\partial \eta}\right)}{\partial \eta} \quad (9.4)$$

$$W(\eta=1) = W_R \quad (9.5)$$

$$\frac{\partial W}{\partial \eta} - \frac{W}{\eta} = 0 \quad (9.6)$$

$$\text{at } \eta = \eta_1.$$

Equation 9.4 can be integrated to give:

$$\eta W = C_2 - C_1 e^{(-\eta \lambda_1)} \left(\frac{1}{\lambda_1} + \frac{1}{\lambda_1^2} \right) \quad (9.7)$$

where;

$$C_1 = \frac{\lambda_1^2 W_R}{-e^{(-\lambda_1)} (1 + \lambda_1) + \left(\frac{\eta_1^2 \lambda_1^2}{2} + \eta_1 \lambda_1 + 1 \right) e^{(\lambda_1 \eta_1)}} \quad (9.8)$$

$$C_2 = W_R + C_1 e^{-\lambda_1} \left(\frac{1}{\lambda_1} + \frac{1}{\lambda_1^2} \right) \quad (9.9)$$

II. Radial Component:

The radial gas velocity can be estimated from:

$$v \frac{\partial v}{\partial r} - \frac{\omega^2}{r} + u \frac{\partial v}{\partial z} = - \frac{1}{\rho} \frac{\partial p}{\partial r} \quad (9.10)$$

The radial position is related to the axial distance by:

$$\partial t = \frac{\partial z}{u} = \frac{\partial r}{v} \quad (9.11)$$

Substituting equation 9.11 into 9.10, and assuming that the pressure drop in the radial direction is linear in r , equation 9.10 becomes:

$$2v \frac{\partial v}{\partial r} - \frac{\omega^2}{r} = - \frac{\Delta P_R}{\rho R} \quad (9.12)$$

Equation 9.12 is solved with the following boundary condition:

$$v(r=0) = 0 \quad (9.13)$$

In the above relations, v and u are the velocity components in the radial (r) and axial (z) directions, respectively, P is the gas pressure at r , and ρ is the gas density. Equations 9.12 and 9.13 written in dimensionless form become:

$$2V \frac{\partial V}{\partial \eta} - \frac{W^2}{\eta} = -\lambda_2 \quad (9.14)$$

$$V(\eta=0) = 0 \quad (9.15)$$

where:

$$V = v/V_0, \text{ and } \lambda_2 = \Delta P_R / \rho V_0^2$$

III. Axial component:

Assuming that u is independent of the vertical and tangential positions, and the pressure drop is negligible in the axial direction, the vertical gas velocity can be found from:

$$v \frac{\partial u}{\partial r} + v \left(\frac{1}{r} \frac{\partial (r \frac{\partial u}{\partial r})}{\partial r} \right) = -g \quad (9.16)$$

Expanding the second part in the left-hand side and ignoring the second-order term in u , equation 9.16 reduces to:

$$\left(v + \frac{v}{r} \right) \frac{\partial u}{\partial r} = -g \quad (9.17)$$

The boundary condition for relation 9.16 is :

$$u(r=R) = 0 \quad (9.18)$$

In dimensionless form 9.17 and 9.18 becomes:

$$\left(V + \frac{v}{\lambda_1} \right) \frac{\partial U}{\partial \eta} = -\lambda_3 \eta \quad (9.19)$$

$$U(\eta-1) = 0 \quad (9.20)$$

where:

$$U = u/V_0, \text{ and } \lambda_3 = Rg/V_0^2.$$

The tangential component of the gas velocity is shown in Figure 9.1 versus the radial distance and for several values of λ_1 . Observe that W_R was taken to be 0.5 and n_1 was assumed equal to 0.4. As can be seen, λ_1 has significant impact on the tangential velocity. λ_1 represents the Reynold's number based on the average radial velocity, as such it is the ratio of the momentum forces due to the flow in the radial direction to the viscous forces of the fluid. At low values of λ_1 , W increases steadily from the center to the wall. At higher values of λ_1 , the tangential velocity tends to go through a maximum value at intermediate radial positions before it starts to decrease as the reactor wall is approached. The locus of the maxima shifts towards the wall with decreasing λ_1 values.

Equations 9.14 and 9.19 were solved numerically using Runge-Kutta fourth order method, and the results are displayed in Figures 9.2 and 9.3. Figure 9.2 shows the radial gas velocity as a function of the radial distance and for several values of λ_2 (pressure force in the radial direction/momentum force of the inlet gas). The radial gas velocity tends to accelerate rapidly from the center to a radial distance of

Figure 9.1 Tangential gas velocity vs radial position.

0.1-0.2, then it drops slowly until a radial distance of 0.8-0.9 is reached, beyond which it decreases sharply. Figure 9.2 was plotted for $\lambda_1 = 2.5$, $n_1 = 0.4$. The effect of λ_2 is seen to increase V at a given radial position, and to shift the position where the maximum velocity is attained.

Figure 9.3 presents the axial velocity for several values of λ_3 (gravity forces/momentum forces). Here λ_2 is assumed to be 0.5. Notice that the axial velocity is nearly flat around the center position, drops rapidly at a radial distance of 0.2, then decreases to zero at the wall. At a given radial

Figure 9.2 Radial gas velocity versus radial position.

$S=0.4, L1=2.5, L2=0.5$

Figure 9.3 Axial gas velocity vs radial position.

position, the axial velocity increases rapidly with λ_3 .

9.2.2 Velocity components of solid particles:

The path that a particle follows in a given gas flow field can be deduced by considering the forces that act upon it. In the treatment to be presented, it is assumed that interactions among particles do not exist (dilute solid phase), the relative Reynold's number is nearly constant, and the friction forces between the particle and the cyclone walls are negligible.

Following the procedure developed by Hou (101), the particle's axial velocity can be shown to be:

$$\frac{du}{dt} = g - \frac{9\mu(u_p - u)}{2\rho_p R_p^2} \quad (9.21)$$

Boysan, et. al, (81) used the following expressions for the radial and tangential velocities, respectively:

$$\frac{dv_p}{dt} = -\frac{\omega_p^2}{r_p} - F(v_p - v) \quad (9.22)$$

$$\frac{d\omega_p}{dt} = -\frac{v_p \omega_p}{r_p} - F(\omega_p - \omega) \quad (9.23)$$

where; u_p , v_p , and ω_p are the particle's velocity in the axial, radial, and tangential directions, respectively, ρ_p and R_p are it's density and radius, g is the gravitational acceleration, μ is the gas viscosity, and r_p is the radial position of the particle at time t . The drag force F is given by:

$$F = \frac{9\mu}{2\rho_p R_p^2} (C_D \frac{Re_R}{24}) \quad (9.24)$$

Here Re_R is the relative Reynold's number and C_D is the drag coefficient.

Equations 9.21 through 9.23 can be integrated directly (81) to yield:

$$U_p = U_{p,0} + \frac{\lambda_4 - \lambda_5 U}{\lambda_5} [1 - e^{-\lambda_5 \lambda_8 \frac{z}{U}}] \quad (9.25)$$

$$V_p = V + \frac{\lambda_7}{\lambda_6} \frac{W_p^2}{\eta_0} + (V_0 - V - \frac{\lambda_7}{\lambda_6} \frac{W_{p,0}}{\eta_0}) e^{-\lambda_6 S} \quad (9.26)$$

$$W_p = W - \frac{\lambda_7}{\lambda_6} \frac{W_{p,0}^2}{\eta} + (W_{p,0} - W - \frac{\lambda_7}{\lambda_6} \frac{V_{p,0} W_{p,0}}{\eta}) e^{-\lambda_6 S} \quad (9.27)$$

Where:

$$\begin{aligned} U_p &= u_p/V_0, & V_p &= v_p/V_0, & W_p &= \omega_p/V_0, & \lambda_4 &= gt/V_0 \\ \lambda_5 &= (9\mu t)/(2\rho R_p^2), & \lambda_6 &= t F, & \lambda_7 &= V_0 t/R, & \lambda_8 &= L/(t V_0) \\ \text{and } S &= (n - n_0)/(\lambda_6 V). \end{aligned}$$

Subscript 0 pertains to the conditions at the beginning of the time interval ($t_0 = n_0/(\lambda_6 V_0)$), and t is the average gas residence time.

The particle's axial velocity is plotted versus the vertical distance in Figure 9.4. The inlet particle velocity was assumed to be zero. Figure 9.4 indicates that at high λ_5 (small particles or highly viscous gas), the particle reaches its terminal velocity at distance of $0.6*L$, but at lower values of λ_5 the particle may never reach the terminal velocity in the reactor, and that it will continue to accelerate with the axial distance.

Figure 9.5 shows the particle's tangential velocity as a function of the radial distance and for various values of λ_6 . It can be deduced that the particle's tangential velocity approaches a finite value as λ_6 approaches infinity. At the wall, the particle will travel with the same tangential velocity as that of the gas.

The radial component of the particle's velocity is shown in Figure 9.6 versus the radial distance and for various values of λ_6 . Comparing Figure 9.6 and 9.2, it could be concluded that the particle's radial velocity follows the same

Figure 9.4 Particle's axial velocity vs vertical distance.

Figure 9.5 Particle's tangential velocity vs radial position.

pattern as that of the gas. The effect of λ_6 on the radial velocity is similar to its effect on the tangential component. In the previous Figures the following were kept constant; $\lambda_1 = 2.5$, $\lambda_2 = 0.5$, $\lambda_3 = 0.25$, $n_1 = 0.4$, $W_R = 0.5$, and $\lambda_7 = 10$.

Figure 9.6 Particle's radial velocity vs radial position

9.3 Energy balance:

I. Gas phase:

Assuming that the conduction terms are negligible in comparison with the convection terms, and ignoring the heat of reaction, the energy balance equation takes the form:

$$u\rho C_p \frac{dT}{dz} = \frac{1}{R} [h(T_{r,m} - T_w) + \epsilon\sigma(T_{r,m}^4 - T_w^4)] \quad (9.28)$$

Where u , ρ , and C_p are the velocity (axial), density, and heat capacity of the gas, respectively, h is the heat transfer coefficient, ϵ is the emissivity, σ is Boltzman constant, T is the gas temperature at $r = 0$, and $T_{r,m}$ is it's average temperature in the radial direction (at a given z). $T_{r,m}$ can be estimated from the following (assuming fully developed laminar flow, and the temperature distribution follows the velocity profile in the radial direction):

$$\frac{T_{r,m} - T_w}{T - T_w} = \frac{\int_0^R [1 - (\frac{r}{R})^2] r dr}{\int_0^R r dr} \quad (9.29)$$

or:

$$T_{r,m} = \frac{T + T_w}{2} \quad (9.30)$$

Substituting for $T_{r,m}$ and writing equation 9.29 in dimensionless form, the gas temperature profile becomes:

$$\frac{d\theta}{dZ} = \lambda_9 (\theta - \theta_w) + \lambda_{10} \left[\left(\frac{\theta + \theta_w}{2} \right)^4 - \theta_w^4 \right] \quad (9.31)$$

Here;

$$\theta = T/T_0, \quad \theta_w = T_w/T_0, \quad \lambda_9 = (hL)/(\rho C_p R U),$$

$\lambda_{10} = (\epsilon \sigma T_0^3 L)/(\rho C_p R U)$, T_0 is the inlet gas temperature, R and L are the cyclone radius and length, respectively.

II. Particle's heating and melting:

Assuming that the particle's internal resistance to heat conduction is negligible, it's temperature profile can be written as:

$$\frac{dT_p}{dt} = \frac{3h}{R_p C_{p,p} \rho_p} (T_{r,m} - T_p) + \frac{3\epsilon_p \sigma}{R_p C_{p,p} \rho_p} (T_{r,m}^4 - T_p^4) \quad (9.32)$$

Where R_p , $C_{p,p}$, and ρ_p are the particle's radius, heat capacity, and density, respectively, h_p is the heat transfer coefficient to the particle surface, ϵ_p is the emissivity of the particle, and T_p is it's temperature. $T_{r,m}$ is given by equation 9.30. In dimensionless form, equation 9.31 becomes:

$$\frac{d\theta_p}{dZ} = \lambda_{11} (\theta_{r,m} - \theta_p) + \lambda_{12} (\theta_{r,m}^4 - \theta_p^4) \quad (9.33)$$

Where;

$\theta = T_p/T_0$, $\theta_{r,m} = T_{r,m}/T_0$, $\lambda_{11} = (3h_p L)/(\rho_p C_{p,p} R_p U_p)$,
 $\lambda_{12} = (\epsilon_p \sigma T_0^3 L)/(\rho_p C_{p,p} R_p U_p)$, T_0 is the inlet gas temperature, and
 R_p is the particle radius.

Once the particle's temperature reaches it's melting point (T_m), it is assumed that it will remain at this temperature and all the energy arriving at the surface is used for melting only. In addition, it is further assumed that the particle size remains constant during melting, that is, the molten portion forms a liquid film surrounding the remaining solid fraction. With these assumptions, the degree of melting can be determined from:

$$-\frac{dr_p}{dt} = \frac{h_p}{\rho_p H_f} \left(\frac{R_p}{r_p}\right)^2 (T_{r,m} - T_m) + \frac{3\epsilon_p \sigma}{\rho_p H_f} \left(\frac{R_p}{r_p}\right)^2 (T_{r,m}^4 - T_m^4) \quad (9.34)$$

Where r_p is the particle's radius at time t , and H_f is it's latent heat of fusion. In terms of the following groups:

$\theta_m = T_m/T_0$, $\theta_{r,m} = T_{r,m}/T_0$, $\lambda_{13} = (h_p L)/(\rho_p H_f R_p U_p)$,
 $\lambda_{14} = (\epsilon_p \sigma T_0^3 L)/(\rho_p H_f R_p U_p)$, $\eta = r_p/R_p$, and $dz = u_p dt$
equation 9.34 becomes:

$$-\frac{d\eta_p}{dZ} = \frac{1}{\eta_p^2} \lambda_{13} (\theta_{r,m} - \theta_m) + \lambda_{14} (\theta_{r,m}^4 - \theta_m^4) \quad (9.35)$$

Equations 9.33, 9.34, and 9.35 are solved with the following initial conditions, respectively:

$$\theta(Z = 0) = 1.0, \theta_p(Z = 0) = \theta_{p,0}, \text{ and } n_p(Z = Z_1) = 0$$

Where Z_1 is the axial position at which the particle reaches it's melting point.

The gas temperature profile is shown in Figure 9.7 and 9.8. Figure 9.7 shows the effect of λ_9 on the center line temperature. (λ_9 = rate of energy convection to the wall/ rate of energy carried out by flow). At low convection rates to the walls, the gas temperature does not change very much with the axial distance, but it may approach the wall temperature as λ_9 increases to infinite values. Figure 9.7 assumes a λ_{10} of 0.2. Similar conclusions can be drawn on the effect of λ_{10} on the gas temperature (Figure 9.8).

The particle's temperature is presented in figure 9.9 for several values of λ_{11} (rate of energy convection to the particle's surface/rate of energy storage within the particle). λ_{12} is assumed to be zero in Figure 9.9. The figure assumes that the melting point of the solid phase is equal to $0.6T_0$. With high λ_{11} , the particle will reach it's melting point in very short distance, that is, when the rate of energy convection to the surface far exceeds the particle's ability to store energy, the particle will be heated up to it's melting point in a very short period of time, and vice versa. Although not shown, λ_{12} would have similar effect on

Figure 9.7 Gas temperature vs axial distance and λ_9 .

Figure 9.8 Gas temperature vs axial distance and λ_{10} .

the particle's temperature, but to a lesser extent.

Figure 9.10 shows the degree of melting versus axial distance for several values of λ_{13} (average residence time/time for complete melting). When the time for complete melting is very high relative to the particle's residence time (low λ_{13}), the particle will only be partially melted before exiting the reactor. But with higher residence time, the particle may be melted in a short distance from it's entrance. The previous figures assume that the wall temperature at the top is equal to $0.6T_0$, and changes linearly with axial distance to a value of $0.5T_0$ at the discharge end of the reactor.

Figure 9.9 Particle's temperature vs axial position.

Figure 9.10 Degree of melting of solid particles vs axial distance.

9.4 Mass balance:

I. Gas phase:

Here it will be assumed that the diffusion rate of carbon monoxide (component A) is much smaller than its bulk convection rate, and that the reaction rate of A follows first order kinetics. Then, a material balance on A gives:

$$v \frac{\partial C_A}{\partial r} + u \frac{\partial C_A}{\partial z} = -K_c C_A \quad (9.36)$$

where K_c is the reaction rate constant, and C_A is the concentration of A in the gas phase. As can be seen, equation 9.36 assumes that C_A is independent of the tangential position. Substituting for ∂r from equation 9.11, the concentration profile becomes:

$$2u \frac{\partial C_A}{\partial z} = -K_c C_A \quad (9.37)$$

Assuming ideal gas, equation 9.37 becomes (in terms of the partial pressure of A and the average temperature):

$$\frac{\partial P_A}{\partial z} = P_A \left(\frac{1}{T} \frac{\partial T}{\partial z} - \frac{K_c}{2u} \right) \quad (9.38)$$

In dimensionless form, relation 9.38 becomes:

$$\frac{\partial P_A^*}{\partial Z} = P_A^* \left(\frac{1}{\theta} \frac{\partial \theta}{\partial Z} - \lambda_{15} \right) \quad (9.39)$$

Substituting for $\partial \theta / \partial Z$ from 9.31:

$$\frac{\partial P_A^*}{\partial Z} = \lambda_9 \frac{P_A^*}{\theta} (\theta - \theta_w) + \lambda_{10} \frac{P_A^*}{\theta} \left[\left(\frac{\theta + \theta_w}{2} \right)^4 - \theta_w^4 \right] \quad (9.40)$$

Where;

$$P_A^* = P_A / P_{A0}, \quad \lambda_{15} = K_c L / 2U.$$

The dimensionless concentration is found from:

$$C_A^* = \frac{P_A^*}{\theta_{x,m}} \quad (9.41)$$

II. Conversion of spherical particles:

When the surface chemical reaction is rate controlling, the extent to which a solid particle has reacted can be found from the following:

$$\frac{\epsilon}{\frac{4}{3}\pi R_p^3} \frac{d(\frac{4}{3}r_p^3 \rho_p)}{dt} = -bK_c C_A \quad (9.42)$$

Where ϵ is the volume fraction of solids; b is the stoichiometric coefficient, and r_p is the particle radius at time t . Separating variables and integrating (assuming C_A is constant), equation 9.42 becomes:

$$X_B = \lambda_{16} C_A^* Z \quad (9.43)$$

Where;

$$X_B = 1 - (r_p/R_p)^3, \quad \lambda_{16} = bK_c C_A^0 / 3\epsilon \rho U_p$$

Figure 9.11 presents the effect of λ_{15} on the concentration profile along the reactor height. With very high reaction rates, the concentration drops sharply with the axial distance, but changes very little at low values of λ_{15} . Notice that when the reaction rate is zero ($\lambda_{15} = 0$), the concentration of carbon monoxide increases with height due to

Figure 9.11 Concentration profile of reactant A along the cyclone height.

the lowering of the temperature.

The effect of λ_{16} on the degree of conversion of the particles is shown in Figure 9.12 as a function of the axial position and for various values of λ_{16} (residence time/time for complete reaction). When λ_{16} becomes small, little conversion will be achieved within the reactor, and the conversion will increase with higher average residence time relative to the time required for complete reaction. Notice that the previous two figures assume that $\lambda_9 = 0.2$ and $\lambda_{10} = 0.03$. Figure 9.12 also assumes a λ_{15} value of 1.0.

Figure 9.12 Degree of conversion of spherical particles along the cyclone height.

III. Falling film reactor:

In the following derivations, it is assumed; fully developed laminar flow, Newtonian fluid, pressure forces on the film are insignificant, the film moves downward with no tangential velocity, and finally, it's reaction with carbon monoxide follows a first order kinetic model.

The film velocity profile can be derived from a momentum balance written in cylindrical coordinate system as was presented in Chapter 6. The governing equation is:

$$\frac{d(r\tau_{rz})}{dr} = r\rho_f g \quad (9.44)$$

Here r is the radial position, ρ_f is the liquid film density, g is the gravitational acceleration, τ_{rz} is the shear force in the r -direction. Equation 9.44 is solved with the boundary conditions:

$$\tau_{rz}(r=R_f) = 0 \quad (9.45)$$

$$u_f(r=R) = 0 \quad (9.46)$$

where R is the cyclone radius, $(R-R_f)$ is the liquid film thickness, and u_f is it's velocity. Integrating 9.44 twice and substituting the boundary conditions, the film velocity as a function of r is obtained:

$$U_f = \lambda_{17} (1 - \eta_f^2) + 4\lambda_{17} \eta_f^2 \left[-\frac{\eta_f^2}{1 - \eta_f^2} \ln\left(\frac{1}{\eta_f}\right) - 0.5 \right] \quad (9.47)$$

Where;

$U_f = u_{f,a}/V_0$, $\eta_f = R_f/R$, $\lambda_{17} = \rho_f g R^2 / 8\mu_f V_0$, and $u_{f,a}$ is the average film velocity.

Once the film average velocity is calculated (based on the physical properties evaluated at the average film temperature), the extent of the reaction can be determined from:

$$\rho_f u_{fa} \frac{\partial r}{\partial z} = -r K_{cf} C_A \quad (9.48)$$

Integrating:

$$\frac{r}{R} = e^{-\frac{K_{cf}C_A}{\rho_f u_{f2}}(z-z_1)} \quad (9.49)$$

Here z_1 is the vertical distance in the reactor at which the film has developed. In dimensionless form, equation 9.49 becomes:

$$X_f = \frac{1 - [EXP(-\lambda_{18} C_A^* (Z - Z_1))]^2}{1 - \eta_f^2} \quad (9.50)$$

where:

$$X_f = \frac{1 - \left(\frac{r}{R}\right)^2}{1 - \left(\frac{R_f}{R}\right)^2} \quad (9.51)$$

and $\lambda_{18} = K_{cf} C_{A0} L / \rho_f U_f$.

X_f is shown in Figure 9.13 for several values of λ_{18} . In this figure Z_1 was taken to be 0.5, and $\eta_f = 0.9$. As the figure indicates, little reduction of the oxide film would be possible when λ_{18} is very small (Residence time of the film/time for it's complete reduction). And complete reduction is expected when λ_{18} is 0.5 or higher.

Figure 9.13 Fluid film conversion as a function of axial position.

CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

10.1.1 Experimental:

1. The influence of carbon dioxide on the reduction of taconite is insignificant. This is due to the very fast carbon gasification reaction.
2. The carbon monoxide inlet partial has little effect on the extent of the reduction.
3. The average reactor temperature has pronounced influence on the final degree of metallization.
4. Taconite interaction with the graphite lining contributed to the high degree of oxygen removal.
5. The flow behavior within the cyclone is essentially of plug flow type, with little back mixing.
6. The reduction of taconite with carbon monoxide is believed to be chemically controlled, although mass transfer may become important at high temperatures. The activation energy was 17.68 KCal/mole within the temperature range of 1400-1500 °C, and 10.42 KCal/mole at higher temperatures.

7. The apparent activation energy of the Boudouard reaction is 13.40 KCal/Mole within the temperature range studied.

10.1.2 Theoretical:

1. A comprehensive mathematical model has been developed. The influence of the various parameters on the flow dynamics of gases and solids have been evaluated.

2. The temperature distribution of the gas is largely controlled by the rate of energy radiation to the cyclone walls. In the meantime, the particle's temperature and the degree of melting are influenced more by convection heat transfer.

3. The degree of reduction of both solid particles and the falling film is a complex function of the flow dynamics, and energy and mass transfer rates. It is greatly influenced by the average residence time in the cyclone, as compared to the complete reaction time.

10.2 Recommendations

10.2.1 Experimental:

1. Study the influence of the presence of hydrogen on the reduction of taconite.

2. Inject the taconite fines and gaseous reactants tangentially, and compare with axial injection.

3. Replace the plasma torch with a carbon monoxide (or coal) fired burner.

10.2.2 Design Modifications:

1. The energy losses through the cyclone system can be further minimized by: a) removing the inner lining and replacing it with insulating material, b) replacing the top cylindrical section with a new one having one tangential port only. The tangential port could be 8" in diameter and 5-6" long. The larger diameter would allow better insulation.

2. Replace the graphite lining with a non-reactive material, possibly magnesite, and perform experiments at a fixed CO/CO₂ discharge ratio.

3. Once a non-reactive material has been installed, coal fines could be injected to the reactor, along with the other reactants, and the effect of coal injection could be studied experimentally. This would also allow the evaluation of several coal sources and qualities.

4. In the existing system, most of the product accumulates on the surface of the conical section. To facilitate easier discharge of the melt, three changes could be made. First, the length of the conical section could be increased to 12-15". Second, the discharge diameter may be enlarged to 5-6". And finally, the discharge tube could be eliminated or reduced in length (from 8" currently to less than 4").

10.2.3 Other Applications:

1. Synthesis and formation of fine carbides, borides, and nitrides.
2. Reduction and melting of other oxides, such as chromium oxides, cobalt oxides, aluminum oxides, e.t.c.
3. Production of ferrochrome and ferrovanadium.

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