THE REDUCTION OF COMPOSITE IRON ORE-COAL PELLETS

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TO LIQUID IRON

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfilment of the Requirements for the Degree Doctor of Philosophy

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McMaster University April 1978

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ABSTRACT

An ironmaking process has been proposed in which composite iron ore-coal pellets are smelted to produce liquid iron. Studies have determined the manner in which individual composite pellets react, their compositional limitations and the chemical compositions of the resultant slag and iron.

Laboratory reduction experiments were performed on various composite pellets bonded with bentonite, cement or calcium carbonate. Ore-coal pellets bonded with bentonite reacted to form a fayalite-type slag high in iron oxide content and an iron melt low in carbon (2%) but high in sulphur (0.3%) contents. Ore-coal pellets which were made self-fluxing by being bonded with cement or calcium carbonate produced a basic slag low in iron oxide content and an iron melt containing over 3% carbon and below 0.05% sulphur. The off-gas from reaction of ore-coal pellets was found to be mostly carbon monoxide and hydrogen which in combustion with oxygen is to supply the heat required by the process.

A computer model of the process was constructed using heat and mass balance equations which illustrated the effects of changes in process variables on input material requirements. Indications from a process analysis are considered to be positive for an ironmaking process based on composite pellet smelting. However, the ultimate success of the process will depend on whether sufficient heat can be retained within the reaction vessel where it is needed. To this end, hot-model "pilot plant" experimental trials are recommended.

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CHAPTER 1

INTRODUCTION

1.1 Direct Reduction

Ironmaking techniques have developed over the years into two distinctly different process routes. Blast furnace smelting accounts for some 96% of the world's iron production, but advancing strongly in recent years are several techniques commonly known as direct-reduction processes. The most generalized definition considers direct reduction as any process that reduces iron ore to iron, other than blast furnace smelting. Some authors restrict direct reduction to those processes which reduce iron ore to sponge iron or metallized pellets, without melting. However one defines it, a direct-reduction process invariably seeks to be an alternative to blast furnace smelting as an ironmaking process.

Most of these alternative processes produce sponge-iron pellets of about 92% iron in one of two ways. Some reduce iron ore pellets or fines with hot hydrocarbon or hydrogen gases in retorts, shafts or fluidized beds. Others use rotary kilns with coal or char as reductant and fuel. After reduction, the sponge iron pellets, which are about 0.5 in. in diameter, or briquetted fines, are fed into electricarc furnaces to be melted and refined into steel. Short descriptions j of the major processes will be delayed until the next chapter; here, as an introduction, major reasons for considering direct reduction are presented.

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When one considers the productivity and low fuel consumption per ton of hot metal produced, blast furnace smelting is far in advance of other processes. If this is the case, then why should one spend considerable time and effort developing an alternative reduction technology? The answer, or perhaps reasons, are complex and usually depend on a variety of economic interactions between geography, size of available market, transportation, availability of raw materials (especially metallurgical coal), existing hot metal capacity, capital costs, the availability of energy and in what form (gas, oil, coal or electricity). With so many factors entering the equation, justifications for direct reduction will vary from one geographical location to another and from one type of process to another. Another pitfall, is that any analysis is time dependent because world-wide economic, technological or supply conditions can change rapidly.

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Originally, the most important reason for interest in direct reduction was the shortage of high-quality coking coal which is necessary for the operation of large modern blast furnaces. Regions with no suitable coking coal must import it and thus transportation costs and assurances of supply become substantial factors in the cost of operating blast furnaces. Regions with cheap natural gas or cheap electrical power have used alternative processes for quite some time. Directreduction processes have no need for coke and thus coke ovens and their pollution control accessories can be eliminated.

In order to take advantage of the increasing economy of largescale plants, in terms of dollars per ton of metal produced, the modern blast furnace with supporting facilities has become so large that an

immediate market expansion of an extra 2 to 4 million tons per year is needed for each new furnace. Equally distressing, is that such a blast furnace facility would need a capital investment of well over \$100 million. Also, the accompanying steelmaking facilities must be of matching large capacity; again involving very large capital costs. Substantial hazards in financing and marketing face all but the giant steel companies who wish to expand using the blast furnace route. On the other hand, direct-reduction processes using smaller, multiple units, can be geared to much smaller incremental increases and thus financing and marketing problems become more manageable. This is particularly important to the Canadian scene where companies and their markets tend to be in the medium to small range.

An increasing percentage of the world's steel is being manufactured in electric-arc steelmaking furnaces for which the major raw material is steel scrap. In many regions, scrap is in short supply and fluctuates so widely in price that the profitability of steel plants becomes very unpredictable. In order to dampen such wide swings in supply and price, directly reduced sponge-iron pellets can be melted as a scrap substitute, or more likely, mixed in varying proportions depending on their costs and availability. The major impetus to develop directreduction plants in the 1960's was to rid the electric-arc melt shop₃ of their total reliance on the scrap market.

Most direct-reduction processes use fuels and energy in a manner different from blast furnaces and moreover, they use fuels and energy that are not widely useful in blast furnaces. Lately, this is becoming a major consideration. The total energy consumption of the direct-

reduction route to produce a ton of steel will probably remain slightly higher than the blast furnace route. However, due consideration should be given to the sources and availability of energy, which in blast furnace smelting mainly comes from coking coals. Natural gas in the Middle East, Mexico and Venezuela, and non-coking bituminous coals in North America and Brazil, are now becoming the alternative sources of energy for iron production. Thus, the reduction processes to be used in future will be chosen accordingly. The use of electrical power or heat from a nuclear reactor to produce hydrogen, for direct-reduction plants, would seem to be (in Canada, at least) a twenty-first century development. It has become axiomatic that for each region wishing to begin or even to continue steelmaking, a complete ànalysis is most necessary, paying particular attention to energy sources, consumption, costs and availability.

Having discussed direct reduction generally, and shown where it has advantages over blast furnace smelting in terms of size, costs and energy, perhaps the best way to summarize would be to say that direct reduction merits consideration because of its great adaptibility to the prevailing conditions in a chosen region. Once a particular process is chosen (e.g., gaseous/shaft or coal/kiln) then the range of flexibility narrows scmewhat because input materials and operating parameters, which control productivity and product quality, become dominant.

1.2 Proposed New Direct-Reduction Process

To meet the competition offered by the high-performance standards of the blast furnace, any alternative reduction process must use iron oxide and fuel efficiently and under conditions in which the reduction reactions proceed rapidly. Sponge-iron reduction processes find it difficult to meet these conditions of high productivity because the reducing gas must diffuse to the pellet centres and because the operating temperatures must be kept low to prevent the pellets from fusing.

A process which increases the rate of reduction by intimately mixing reductant and iron ore, and which operates at high temperatures to produce liquid iron would have a distinct advantage over sponge-iron processes. Also, sponge-iron pellets are usually melted and refined in electric-arc steelmaking furnaces and it has been shown that operating costs increase substantially as the entrapped gangue content of the pellets increase. Thus, the iron ore concentrate from which the sponge iron pellets are produced, should have a very low gangue content (less that 4%) which cannot be met by many iron ore sources without undue penalties in cost and recovery. Lqw sulphur fuels and coals with the correct ash properties should also be used in sponge iron production. A process which produces liquid iron and slag does not have such stringent restrictions.

With the above reasons in mind, a new direct-reduction process is proposed which is radically different from any of the sponge-iron processes. Iron ore, coal and possibly lime are mixed intimately and formed into composite pellets which are then reacted at high temperatures, within a body of foaming slag, to produce liquid iron. The slag

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is foamed by the off-gases, very rich in carbon monoxide and hydrogen, which escape from the reacting pellets. Oxygen is lanced within the body of the foaming slag to cause direct combustion of the off-gases which provides the thermal energy needed for the reduction reactions. Also, the oxygen and combustion gas products further the course of foaming. The pellets, in turn, are buoyant within the slag and when reduction and heating are complete, the heavier iron droplets fall to the liquid metal bath below.

The slag normally acts as a holding medium for sulphur, phosphorus and gangue constituents, but also has the important function of transferring the heat from combustion to the reacting pellets and to the metal bath. This is possible because the combustion takes place within the body of the slag. This process has the possibility of being made continuous by adjusting the pellet feed rate and the tapping of both iron and slag. Figure 1.1, illustrates the pertinent aspects of the process and also shows some of the generalized chemical reactions. The combined reactions within an individual pellet are endothermic and need the heat supplied by the highly exothermic combustion reactions.

This process could lead the way towards continuous iron- and steelmaking; towards decreasing our dependence on blast furnaces and coke ovens, serious sources of pollution; and towards a source of virgin iron which is badly needed by the smaller Canadian steel companies who are unable financially to build blast furnaces. It is also perceived that this process could be more economical in that both capital and operating costs could be reduced and that it could be more efficient in its use of energy than conventional ironmaking. Lower ranked non-coking coals could be used as both reductant and energy sources.

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Figure 1.1: Illustration of proposed direct-reduction process.



The Canada Centre for Mineral and Energy Technology (CANMET), a branch of the Department of Energy, Mines and Resources, Ottawa, holds patent protection⁽¹⁾ on this process. This investigation was undertaken as part of a CANMET Research Agreement, 1972-74, entitled "Coal Energetics in High Temperature Iron Ore Reduction".

1.3 Objectives of Present Work

This project is undertaken as a technological investigation into a direct-reduction process in which liquid iron would be produced via the reduction of composite pellets of iron ore and coal. Since this process has no previous history, the project should begin, necessarily, as an overview to high-light difficulties and then to investigate some of the more prominent. In particular, reduction experiments must be performed on individual composite pellets of varying compositions in order to determine the manner in which the pellets react, the limitations of the process, the chemical composition of the resultant liquid iron and the composition of the off-gas which must be byrned to supply the process energy. Finally, computer charge calculations incorporating heat and mass balance equations will be used in an overall process analysis.

It is recognized that other, very important aspects will need to be investigated at some later date. Some of these are, oxygen lancing and foaming of slags, heat transfer from combustion to the reacting pellets, and the danger of re-oxidation of the metal droplets by the oxygen before they reach the metal bath. These aspects, although important, are beyond the scope of the present work as they can be investigated best under pilot-plant conditions. ちょう ちちちち かいちょう あましてい いろいう いっち ちょう

1.4 Structure of Thesis

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In order to set the proper tone for a presentation of this work, it should be emphasized that this is a laboratory investigation which seeks information about a process with accuracy sufficient to allow a move onward towards the next stage - a pilot plant.

This thesis is structured so that the four areas of immediate concern are presented sequentially, as follows.

- a) Reduction experiments on pellets of various compositions to find potential limitations of the process and the chemical composition of the resultant iron product.
- b) A metallographic examination of the internal microstructure of various partially-reduced pellets in order to obtain a clearer understanding of the reaction sequences taking place within each type of pellet during reduction.
- c) An analysis of the off-gas from pellet reduction in order to calculate how much heat may be made available from combustion of the offgas with oxygen.
- d) An analysis of the proposed process incorporating heat and mass balance equations in order to show the effects of process variables, such as temperature and product specifications, on materials input and output (liquid iron and slag).

A generous use of appendices has been made in order to house detailed calculations and explanations. These appendices are at the end of the thesis and are identified by their related chapter, e.g., A3.3 is the third appendix to Chapter 3.

CHAPTER 2

REVIEW OF IRON ORE REDUCTION PROCESSES

2.1 History of Ironmaking

Ironmaking has a long history, reaching back into antiquity some 3000 years. The deliberate reduction of iron ore to produce a material for tools, cooking utensils and weapons heralded the Iron Age of man. Iron was made by putting charcoal and iron ore in a shallow hearth and an intense heat was generated by directing air at the burning charcoal. The combustion of the charcoal created a reducing gas which removed oxygen from the iron oxide in the ore. The temperature was not high enough to melt the iron but some impurities in the ore did melt and the reduced iron became a hot pasty lump which when removed from the fire, was hammered into shapes. This was called sponge iron because the removal of oxygen from iron ore, without melting, leaves a honey-combed structure that resembles a sponge.

Over a long period of time, the primitive hearth was augmented with a stack which contained deeper beds of charcoal and ore, and the force of the air blast was increased. In this manner, the production of iron was increased and fuel consumption decreased because the gases which ascended the stack from the hot zone, preheated and prereduced the ore. Sometime during the 14th century, ironmakers found that when measures were taken to increase the temperature, the iron absorbed more

carbon and its melting point decreased. As a result, molten, carbonsaturated iron collected at the bottom of the shaft in the hearth, from which it could be tapped and run off at intervals. The oxide impurities, mainly silica, alumina and lime, formed a molten slag which floated on top of the liquid iron and was discarded after being tapped from the furnace. Charcoal as fuel eventually gave way to coke about the year 1700 and in 1824 a preheated air blast was first used which greatly increased the hearth temperature, ease of operation and productivity. This evolution, over some 500 years, led to the modern blast furnace which today is the predominant means of reducing iron ore.

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2.2 The Blast Furnace

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2.2.1 <u>Advantages</u>

During the past thirty years there has been some remarkable advances in ironmaking techniques, though the process itself has remained basically unchanged. The very high productive capacity of the modern blast furnace, 5000 - 12000 tons per day depending on its size, is attributed to its basic simplicity in both construction and operation. The furnace itself is a simple, vertical shaft through which the materials (ore, coke and limestone flux) move from top to bottom by only the force of gravity. Preheated air is blown into the bottom through tuyeres to burn the coke and provide the heat required for smelting. A relatively high thermal efficiency results from the countercurrent flow of ascending gases and descending solids. Carbon monoxide, hydrogen and nitrogen leaving the combustion zone at very high temperatures ascend through the furnace, transferring most of their sensible heat to the descending charge. A major portion of the ore is reduced by the carbon monoxide and hydrogen in the upper part of the shaft, but the final reduction and carburization of iron, some reduction of silica, and desulphurization of the iron by the slag, take place in the lower part of the shaft and in the crucible where higher temperatures prevail. The hot metal or molten pig iron usually contains about 4% carbon, 1% silicon and 0.030% subbur. This metal can then be refined into steel by oxidizing most of the carbon, silicon and other impurities from the iron melt. In providing the most economical source of molten iron, in very large quantities, the blast furnace has strengthened its position as a major supplier of iron for steelmaking.

The history and technology of ironmaking is well presented in the two-volume set, "Blast Furnace - Theory and Practice"⁽²⁾. Metallurgical principles and such topics as gas/solid reactions and slag/metal reactions are covered adequately in standard texts, e.g., "The Reduction of Iron Ores" by von Bogdandy and Engell⁽³⁾, and "The Physical Chemistry of Iron and Steel Manufacture" by Bodsworth and Bell⁽⁴⁾.

2.2.2 Energy Requirements

Many improvements in blast furnace technology such as larger furnaces, burden preparation, higher blast temperatures, oxygen and fuel injection through the tuyeres and high top pressure, have increased the production rate and decreased the fuel rate to a considerable degree. A coke requirement of about 1100 lb/ton hot metal (550 kg/tonne) is considered to be good practice when using high quality ore in the form of pellets and sinter and high temperature air blast. Hydrocarbon fuels, such as coal tar, oil, gas and powdered coal may be injected through the tuyeres and hence replace coke on a pound for pound basis up to say, 300 lb/ton hot metal (150 kg/tonne).

The number of papers and the amount of detail published in the past few years on energy requirements of different reduction processes has been overwhelming, and confusing. Advocates of particular processes advance supporting data at variance with others. This is not surprising since in the construction of a generalized energy balance, it is difficult to keep track of the many credits and debits which, in the case of the blast furnace, include such items as top gas, coke-oven gas and coke breeze.

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Elliott⁽⁵⁾ has used statistics from 1972, published by the American Iron and Steel Institute, to illustrate energy flow patterns in the production of steel. There is a wide variation throughout the industry in the amounts of energy used in each operation, principally because of the nature and availability of raw materials. Table 2.1 lists the average net energy requirements for different operations. The figures do not include energy used in the transportation of raw materials or products, nor the energy used for raw material preparation, e.g., ore beneficiation. However, the figures do include those items which are of a dual nature, such as coke oven gas, which is used for underfiring the ovens and augmenting blast furnace gas in the stoves, in addition to being exported to other areas of the steel plant. Firing to harden pellets (induration) was considered to consume about the same amount of energy as sintering, although this would depend on the type of ore and particular method employed. Undersized coke, known as coke breeze, was considered an output (credit) from the coking operation but an input to sintering (debit). It can be seen from Table 2.1 that the blast furnace operation by itself consumes about 14×10^6 Btu/ton hot metal. Basic oxygen furnace steelmaking requires very little energy and most of what is needed is electrical energy required to manufacture oxygen. Steelmaking via melting steel scrap in electric-arc furnaces consumes about 6.5 \times 10⁶ Btu/ton raw steel. The electrical power consumed in this case, 545 kWh/ton, was converted to an energy value after considering that it takes about 10,000 Btu to produce 1 kWh in a thermal electric plant (35% efficiency). For hydro-electric power, perhaps a straight thermodynamic conversion of 3412 Btu/kWh is best.

PROCESS	PRODUCT	10 ⁶ Btu/ton	10 ⁶ kJ/tonne
Agglomeration (Sinter or Pellets)	agglom.	2.3	2.4
Coking	coke	5.4	5.6
Blast furnace	hot metal	14.0	14.6
Basic Ox. Furn.	raw steel	0.65	0.68
ElectArc Furn.	raw steel	6.5	6.8

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Table 2.1: Average net energy requirements in 1972 for processes employed by the American steel industry⁽⁵⁾.

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The International Iron and Steel Institute has published a $study^{(6)}$ on energy usage in the steel industry using data from 1973-74. It also includes model steel plant studies utilizing the most up-to-date technology so that energy consumption figures from diverse plants, old and new, can be compared with the "target" or most desirable values. The Government, Energy and Minerals Committee of the Iron and Steel Society, AIME, has extracted data from this study and has published its findings⁽⁷⁾ in the form of two tables.

Table 2.2 shows the details of the energy consumption for a typical (American) blast furnace. Table 2.3 shows the type of energy efficiency that may be obtained according to the IISI model energy balance study. It can be seen that the net energy consumed using "best technology" is 19.48 x 10^6 Btu/ton hot metal (20.3 x 10^6 kJ/tonne) compared to 23.16 x 10^6 Btu/ton hot metal (24.2 x 10^6 kJ/tonne) which was the average for a typical 1973 American blast furnace.

Trends in blast furnace technology can be illustrated by comparing the itemized values in the two tables. For instance, blast furnaces will use very little or no direct shipping ore; a blend of pellets and sinter will prevail. The coke rate will decrease mainly due to increased tuyere injections of gas and oil, and oxygen enrichment of the air blast. Although not noted in Table 2.3, powdered coal also will be injected through the tuyeres. All things considered, there is very little doubt that blast furnace ironmaking will continue to improve and will remain the predominant iron ore reduction process for quite some time.

	Unit	Unit per net ton of product	10 ⁶ Btu per unit	10 ⁶ Btu per net ton of product
Consumption		· · · · · · · · · · · · · · · · · · ·		
Iron ore (sized)	net ton	0.408	0.725	0.30
Pellets	net ton	0.759	2.67	2.02
Sinter	net ton	0.459	2.47	1.13
Coke	net ton	0.597	31.50	18.81
Limestone	net ton	0.232	0.24	0.06
Refractories	1b	5.0	0.0125	0.06
Fuel oil	gal	4.93	0.150 ,	0.74
Natural gas'	10 ³ cu.ft	0.325	1.00	0.33
Coke oven gas	10 ³ cu.ft	0.121	0.50	0.06
Blast furn. gas	10 ³ cu.ft	28.57	0.095	2.71
Oxygen	10 ³ cu.ft	0.207	0.183	0.04
Electricity*	kwh	25.0	0.0105	0.26
Steam	10 ³ 16].2	1.00	1.20
		đ	Sub total	27.72
Production -	•			
Blast furn. gas	10 ³ cu.ft	48.04	0.095	-4.56
Net Energy Consumption	on			23.16
*Includes 10 kwh for	raw material	s handling		

Table 2.2: Details of energy consumption for a typical 1973 American blast furnace(7).

ł	Unit	Unit per net√ton of product	10 ⁶ Btu per unit	10 ⁶ Btu per net ton of product
Consumption				
Pellets	net ton	1.162	2.67	3.10
Sinter	net ton	0.498	2.47	1.23
Coke	net ton	0.400	31.50	12.60
Refractories	lb	5.0	0.0125	0.06
Fuel oil	gal	16.6	0.150	°2.49
Coke oven gas	10^3 cu.ft	71.305	0.500	0.65
Blast furn. gas	10 ³ cu.ft	16.039-7	0.085	1.36
Oxygen	10 ³ cu.ft	0.671	0.183	0.12
Electricity	kwh	120.0	0.0105	1.26
			Sub tota1	22.87
Production				
Blast furn. gas	10 ³ ∙cu.ft	39.9	0.085	-3,39
Net Energy Consumption				19.48

Table 2.3: Projected energy consumption in a modern blast furnace (7).

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2.3 Direct Reduction Processes

2.3.1 Historical Development

Developing parallel to the blast furnace, are other methods of ironmaking commonly known as direct-reduction processes. The earliest direct-reduction furnaces were of course, the sponge iron hearths which were in use before the advent of the blast furnace. One of the first deliberate attempts to challenge the Blast furnace was in 1869, when Siemens, in Northhamptonshire England, mixed crushed iron ore and coal in a rotating kiln. The resultant hot sponge iron fell into a bath of liquid pig iron which was then refined to steel in his newly developed open-hearth furnace. He had hoped to gain economy of fuel and a higher quality of steel but had to abandon his attempts because the costs were too high and the iron (steel) contained excess impurities of sulphur and phosphorus. He believed that his difficulties could have been avoided with richer and purer ores and fuels with less sulphur.

The next attempts were made in Sweden in the 1920's, where a very rich iron ore deposit, of low phosphorus content, provided favourable conditions for the solid-state reduction of fron by the Wiberg process. Iron ore was fed into the top of a vertical shaft and a hot reducing gas mixture of carbon monoxide and hydrogen was passed upward through the furnace. The sponge iron product was removed through a rotary discharge unit at the bottom of the shaft. The Swedish experience demonstrated that granules or pellets of sponge iron could be produced on a continuous basis but in order to make use of this material, it was necessary to melt it so that the entrapped gangue could be removed during refining and the steel could be poured into ingot molds. The blast furnace route still had the advantage because it produced liquid hot metal which could be converted readily to steel by oxidizing the carbon, silicon and other impurities from the melt. The extra cost to melt sponge iron curbed any general interest in direct reduction for some 25 years.

About 1950, electric-arc steelmaking became a major means of melting and refining solid steel scrap. Previously, this method had been confined to the more expensive alloyed steel, but with improvements in electric furnace technology, plain carbon steels made in large tonnages became possible. Within a few years it was realized that sponge iron pellets could be considered as a purer form of iron than scrap and the quest was on to develop direct-reduction processes which would produce a scrap substitute for electric-arc steelmaking.

The field of direct reduction has not been neglected by the world's metallurgical community; the reward for a successful process is high, but equally high is the casualty rate. More than 1000 processes have been patented; more than 300 have been experimentally tested; only about 50 reached the pilot-plant stage and of these only about 8 have reached large scale engineering or actual production. A comprehensive tabulation⁽⁸⁾ of the more durable processes was published in 1967 by the European Coal and Steel Community. The great speed with which new processes are introduced and accepted or, more usually rejected, can be gauged by the fact that the Midrex⁽¹¹⁾ process is not to be found on that list. In 1977, Midrex was the most successful with 7 plants producing sponge iron pellets at the rate of 2.7 million tons per year.

The many direct-reduction processes may be separated into a few generic classes. Processes which produce sponge iron or metallized pellets can be divided into two groups on the basis of the type of reducing fuel used; those that use gaseous hydrocarbons and those that use solid reductants, such as coal. Sub-groups also may be formed on the basis of the type of reduction vessel used. The vessels in which the reduction takes place may be retorts (static pellet bed), vertical shaft furnaces (continuous pellet feed), fluidized beds (continuous fine particle feed), and rotary kilns (continuous pellet feed).

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There are many papers and conference proceedings^(9,10) in the open literature which describe many of the different processes and hence a literature survey will not be attempted here. Pertinent references however, will be given.
2.3.2 Gaseous Shaft Reduction

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In gaseous shaft reduction, a hot mixture of carbon monoxide and hydrogen is usually obtained by taking a portion of the process off-gas containing carbon dioxide and water vapour and reforming it with natural gas (methane) at about 1000°C in the presence of a catalyst. Also, in recent years, there has been an increased interest in the use of coke oven gas and coal gasification to produce the reducing gas mixtures.

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Figure 2.1 illustrates the essentials of the Midrex process (11,12,13). There are three separate processes; the generation of reducing gas, the reduction of ore and cooling of the product. The top gas leaves the furnace at about 400°C and contains about 30% CO $_2$ and water vapour. It is washed and cooled to remove the water vapour by direct contact in a water scrubber, where the dust content is also reduced. The bulk of this gas is compressed, mixed with fresh natural gas and passed into the reforming furnace. Here it is catalytically converted to a reducing gas of about 95% CO and H_2 , which is then passed, at about 950°C, to the reducing shaft above the cooling zone. The remainder of the top gas, with additional fuel, is used for firing the reformer. Iron ore pellets, which had been indurated previously at a pelletizing plant, are introduced at the top of the shaft and descend counterflow to the reducing gases. Carbon dioxide and water vapour are produced in the reduction reactions which together with unreacted CO and H₂, leave the furnace as The passage of the ore pellets through the reduction zone top gas.





takes about 5-6 hours. The metallized pellets are cooled in the lowest part of the shaft, where gas, mostly nitrogen and some reducing gas, is passed countercurrent to the descending pellets. This gas enters at about 30°C and leaves at about 400°C. The pellets pass through the cooling zone in 5-6 hours and are discharged at about 40°C.

The product is a sponge iron pellet, containing 92% Fe and about 1% carbon, which is then conveyed to an electric-arc steelmaking shop. Two units at Sidbec, Contrecoeur, Quebec have a combined capacity of more than 1 x 10^6 tons per year. Energy requirements^(11,12) are given as 12.0 x 10^6 Btu/ton iron pellets (12.5 x 10^6 kJ/tonne) for natural gas and 140 kWh/ton (0.5 x 10^6 kJ/tonne)* for electric power. Hence, the total energy requirement is 12.5 x 10^6 Btu/ton iron pellets (13.0 x 10^6 kJ/tonne).

Other gaseous shaft reduction processes of significance are $Armco^{(14)}$ and $Purofer^{(15)}$ but these will not be described here as the principles are similar to Midrex.

* 1 kWh = 3412 Btu = 3600 kJ

2.3.3 Rotary Kiln Reduction

The SL/RN (Stelco, Lurgie/Republic Steel, National Lead) Process^(16,17,18) is a rotating kiln process which uses a solid reductant. A kiln capable of producing 400,000 tons of sponge iron pellets per year has been built by Stelco in north-western Ontario and will supply Stelco's electric-arc furnaces in Edmonton, Alberta and Contrecoeur, Quebec.

Figure 2.2 shows a schematic flow diagram of the SL/RN process. The charge to the kiln consists of indurated iron ore pellets, coal, recycled char and dolomite for sulphur control. These materials travel through the kiln countercurrent to the heating gases and discharge, about 5 hours later, into a rotating drum cooler through a gas-tight seal. The kiln is fired from the discharge end by any type of fuel, but in addition to the end burner, air, and natural gas when required, is blown into the freeboard area above the charge through burner tubes located along the length of the kiln. This is to maintain a controlled longitudinal temperature profile by burning CO from the reduction zone and volatiles from the coal. The charge materials reach a temperature of about 1000°C as they pass through the kiln and gases from the coal reduce the ore pellets to sponge iron. The hot products, consisting of sponge iron, unreacted coal char and gangue, exit the kiln via a transfer chute into a rotary cooler where they are cooled to about 100°C. The cooler discharges onto a combination of screens and magnetic separators which separate the metallized iron pellets, recycles the coal char and discards the waste.



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Data on energy requirements are lacking. A gross fuel consumption of 23 x 10^6 Btu/ton sponge iron was reported by Stelco⁽¹⁸⁾ as a tentative figure. This was achieved during start-up trials just before the kiln was shut down because of depressed market conditions. A recent review paper⁽¹⁹⁾ estimates that the energy consumption for SL/RN can be expected to be 19.9 x 10^6 kJ/tonne Fe (19.0 x 10^6 Btu/ton Fe) for coal and 60 kWh/tonne Fe. A rotary kiln process, very similar to SL/RN, has been developed by Krupp⁽²⁰⁾ in which it is claimed that the energy consumption amounts to 16.7 x 10^6 kJ/tonne sponge iron (16.0 x 10^6 Btu/ton). This value appears optimistic in light of Stelco's experience but it does indicate the potential energy consumption for a rotary kiln process.

Allis-Chalmers have developed $ACCAR^{(21)}$, a rotary kiln reduction process in which hydrocarbon fuels are injected beneath the charge materials along the length of the kiln; otherwise, it is also similar to SL/RN. A commercial operation is planned at Sudbury, Ontario.

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2.3.4 Smelting Reduction

There are a number of reduction processes which produce liquid iron rather than sponge iron pellets. One of these, electric pig-iron smelting, has been used in Norway since the 1920's and is called the Tysland-Hole process⁽²²⁾ after its two Norwegian developers. Iron ore sinter and coke are charged into the smelting furnace to surround large electrodes. In this type of submerged-arc reduction, the required heat is generated by the electrical resistance of the coke bed .ather than by an open arc. The process requires about 300 kg carbon as coke and 2000 kWh per tonne hot metal⁽²²⁾. Although the electric power required is substantial, it is produced by a hydro-electric generating station. Hence, using the thermodynamic conversion factor of 3412 Btu/kWh (3600 kJ/kWh), the net energy consumption is calculated to be 15.3 x 10^6 Btu/ton hot metal (16 x 10⁶ kJ/tonne). Electric pig-iron smelting is energy intensive and over the years, the desire for some preheating and prereduction of the ore, before charging, had led to several processes which combine a shaft, kiln or travelling grate with the electric smelting unit.

In order not to rely on electric power, and yet gain the advantages of producing liquid iron rather than sponge iron, other processes have been developed, although for various reasons, they have not progressed σ beyond the pilot-plant stage. It has been shown that it is possible to reduce ore and melt iron in one furnace using a solid reducing agent and oxygen. Iron ore was reduced by carbon and the emanating carbon monoxide was burnt with oxygen to supply the required heat. The leaders in developing this type of smelting-reduction process are the Swedes, who in

the 1960's extended the use of their rotating oxygen steelmaking furnace (Kaldo) to produce pig iron. Unfortunately, this new process, named $DORED^{(23,24)}$, was abandoned in 1970 because of excessive lining wear, mainly due to the high iron oxide content of the slag.

To overcome the refractory wear problems, the British Iron and Steel Research Association (BISRA) developed a process (25) whereby a kiln was rotated at very high speeds. Centrifical forces caused the liquid iron to spread evenly over the refractory surface and thereby protected it from the lighter iron oxide-rich slag. An Italian development, called ROTORED⁽²⁶⁾ proceeded in a similar manner except that the cylindrical vessel was vertical.

In Sweden, smelting-reduction has been studied and promoted by Prof. Sven Eketorp of the Royal Institute of Technology, Stockholm. The Eketorp-Vallik reactor, a stationary furnace, was the base of the EV-Process⁽²⁷⁾ in which iron ore concentrate was fed onto a bath of highcarbon iron. The reduction was carried out with the oxides in the molten state and the carbon in the bath was continuously replenished with oil, gas or powdered coal which was blown directly into the bath. Hydrogen and carbon monoxide which escaped from the bath were burnt with oxygen directly above the bath to supply the necessary heat. It was here that the operating problems lay. Far too much heat was created above the bath and not enough heat was transferred to the bath.

Eketorp has published a number of papers^(28,29,30) on the fundamentals of iron- and steelmaking processes which emphasize the advantages to be gained by smelting-reduction.

2.3.5 Ore-Carbon Pellet Reduction

There are many papers in the open literature on reduction aspects of iron oxide and carbon pellets. Most are of a fundamental nature and study reaction mechanisms and kinetics of the system. Unfortunately, there has been very little industrial application. Prereduced ore-coke⁽³¹⁾ and ore-coal⁽³²⁾ pellets suitable for blast furnace feed were investigated some years ago and lately, there have been a number of attempts to smelt ore-carbon pellets in cupolas^(33,34). Laboratory studies^(35,36) on the reduction of iron oxide-carbon composites to liquid iron have shown that reduction at high temperature is possible even in an atmosphere of pure oxygen. These studies also showed that should the carbon reductant contain sulphur, then most of that sulphur would transfer to the iron melt. The present investigation, outlined in Sections 1.2 to 1.4, will attempt to further the development and use of composite iron ore-coal pellets in ironmaking processes.

2.4 Summary - Alternate Routes to Steel

Eketorp $\binom{28}{2}$ combined the iron-oxygen and iron-carbon phase diagrams to illustrate the alternative routes which may be taken to obtain steel. In Figure 2.3, the blast furnace route is shown as the path ABCD. Iron ore pellets and sinter are reduced to iron which then melts and becomes carbon saturated. After being tapped from the blast furnace at C, the hot metal is converted to steel along path CD, usually by a basic oxygen steelmaking process. Direct-reduction processes which produce sponge iron pellets, AB, are usually linked to electric-arc steelmaking, BD. A route(37) from iron oxide to steel in which the oxide is melted, AE, and then deoxidized by the injection of carbon, ED, is direct steelmaking in its truest sense. However, the very great problem of holding molten iron oxide in a vessel has proven to be a formidable barrier to its development. Smelting-reduction and the reduction of composite iron ore-coal pellets as envisioned in the present investigation is shown as path ABC'. Conversion of the hot metal to steel, path C'D, by the basic oxygen process may be performed in the same vessel after decanting the primary slag, or in a separate steelmaking vessel.





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CHAPTER 3

LABORATORY REDUCTION OF PELLETS

3.1 Introduction

An investigation into a proposed process which has no previous history should begin by quantifying in a laboratory, those ideas put forward in more general terms. For instance, the very first stage of experimental work must identify major characteristics of the system and find the potential limitations of the proposed process. In this case, preliminary questions need to be answered about the optimum quantity of coal a pellet should contain, and about the chemical composition of the metal product when such pellets are reduced. In keeping with this modest approach to a rather complex process, simple tests on a laboratory scale were carried out, and as knowledge accumulated, new methods and ideas were tried. It can be appreciated that many experiments show what does <u>not</u> work, and although usually unreported, they nevertheless contribute to the knowledge of the process and to the success of the next experiment.

The concept that an ore-coal pellet, when heated, is self-reducing and has no need of a surrounding slag, greatly simplifies experimental techniques. In order to observe directly the making of iron, the pellets were dropped into an alumina crucible held within a furnace at 1500°C, to be reacted completely within a self-created reducing atmosphere. This atmosphere was created partly from the gasification of the coal in the pellets and partly from the reduction off-gases. After cooling, a metal button was available for chemical analysis. This procedure, to

be described later in more detail, was kept as routine as possible in order to lessen experimental variability and to determine effects specifically due to pellet composition.

The following sections will specify the raw materials used and will outline the experimental procedure. Then, the results from the reduction of bentonite-bonded pellets and self-fluxing pellets will be presented.

3.2 Raw Materials

3.2.1 Coal

The coal used in this investigation was prepared by powdering in a disc pulverizer, and all that passed through a 50 mesh sieve was considered satisfactory for pelletizing. This coal is classified as bituminous high volatile A, and the proximate analysis, on a dry basis, is as follows.

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Complete chemical and sieve analyses are given in Appendix A3.1.

3.2.2 Iron Ore

The iron ore concentrate, supplied by the Sherman Mine, Temagami, Ontario, was found to be finely ground magnetite; 73% minus 325 mesh. The chemical analysis of the concentrate is as follows!

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% Fe	% SiO ₂	% A1203	% MgO	% K ₂ 0	% S
68.1	5.23	0.3	0.3	0.05	0.063

The sulphur level was excessively high for this concentrate which was shipped wet in a barrel, and then oven-dried in open pans. Although the reason for the sulphur pick-up could not be traced, the sulphur content was uniform throughout the batch and thus was not considered prejudicial to experimental results. Indeed, since low sulphur coals are becoming more scarce, it was originally considered that, perhaps, raising the coal sulphur content to 1% by the addition of FeS would be advisable. This became unnecessary since the additional sulphur load from the ore achieved the same purpose. The origin of the small amount of extra sulphur within the pellet, i.e. from ore or coal, was considered to be immaterial to the resultant iron.

3.2.3 Bentonite

The Wyoming bentonite used as a binder for the ore-coal pellets was not chemically analysed. However, since the pellets contained a maximum of 2% bentonite, it was considered reasonable to use the following typical composition (38) for calculation and discussion purposes in this work.

65% SiO₂, 18% Al₂O₃, 3% Fe₂O₃, 3% (CaO + MgO), 3% (Na₂O + K₂O) 8% Loss on Ignition

The bentonite was analysed for sulphur, however, and was found to contain 0.38% S. $^{\setminus}$

3.3 Procedure

3.3.1 Furnace Design

A vertically mounted, molybdenum wound, tubular resistance furnace was used for this investigation, as illustrated in Figure 3.1. The furnace drew power from a proportional power controller (Barber-Coleman, Series 621) driven by a null balance millivoltmeter controller (Barber-Coleman, Model 377) which received the output from a Pt/Pt 10% Rh control thermocouple. The power controller limited temperature variation of the furnace to within $\pm 2^{\circ}$ C.

The working tube, which was fitted inside the furnace tube, was of recrystallized alumina (McDanel 997), 785 mm long, and had an internal diameter of 42 mm. It was closed at top and bottom with water-cooled brass heads which were sealed to the tube with "0" rings. The head at the top, had an off-gas outlet tube and a 20 mm diameter hole, through which pellets could be added. The hole was stoppered with a rubber bung which contained an optical flat so that pellets which were being reduced could be observed directly. The head at the bottom was fitted with a gas inlet tube and a central air-tight swage-lock fitting, through which a closed-end alumina thermocouple sheath was inserted. This sheath supported the crucible in the hot zone and also allowed monitoring of the crucible temperature. The crucibles were of recrystallized alumina, 64 mm high and 35 mm dia., which just fitted into the working tube and could be lifted up without tipping, into the hot zone by the thermocouple sheath.

The temperature variation of the hot zone at 1500° C was $\pm 2^{\circ}$ C over 25 mm. The experimental temperature was monistored at the bottom of the crucible by a Pt/Pt-13% Rh thermocouple, the output of which was "read with a null-point potentiometer.

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Figure 3.1: Schematic cross-section of laboratory furnace.

3.3.2 Experimental Technique

A laboratory pelletizing wheel was constructed using a 400 mm dia. rubber tire which could produce 1000 gram batches of pellets. However, it was found that the crucible experiments needed only 20 to 30 grams and since the pellet composition changed with each experiment, it was far more convenient to mix the ore, coal and binder with just enough water to make a viscous paste and then form the pellets by hand. All spherical pellets throughout the investigation were 11 ±2 mm dia. after drying.

The following describes a typical experiment and, as mentioned previously, the procedure was kept as routine as possible so that results reflected differences due only to pellet composition. A crucible was held in the hot zone of the furnace at about 1520°C while the working tube was flushed with argon. Three pellets, of about two grams each, were dropped some 350 mm through the hole in the top head and into the crucible. The optical flat assembly was replaced in the hole and the argon flow was shut off. A large volume of off-gas and soot formed immediately, but after about 15 sec. the soot in the off-gas cleared and this allowed direct observation of the reduction process through the optical flat assembly. Since the pellets were cold when added to the crucible, the crucible temperature dropped some 20°C. Hence, during a typical run of about 6 min. duration, pellets were added each minute or so, at a rate which controlled the crucible temperature to 1500 ±5°C. After about twelve pellets were reduced and melted the crucible was lowered to the bottom of the furnace in 5 cm steps in order to minimize thermal shock and breakage of the working tube. The cooling rate of the crucible from 1500 to 1000°C was about 100°C per minute. After removal from the furnace, a metal button weighing about 10 grams was available for chemical analysis.

3.3.3 Chemical Analysis

The metal produced by the pellet reduction experiments was first pulverized with an impact mortar and then analysed for carbon, sulphur and in some cases, silicon.

The carbon determination was performed on a combustion gas analyser which is standard equipment supplied by Leco (Laboratory Equipment Corp., Michigan). The accuracy of determination is given by Leco as $\pm 1\%$ of the carbon present up to 4%C. However, in this investigation, if the first two determinations were within 0.10%C of each other, they were averaged; if not, then more determinations were performed. Hence, a wider range for carbon determinations would be more appropriate, e.g., 2.75 $\pm 0.05\%$ C.

The sulphur determination was performed on standard Leco equipment which uses the combustion - iodate titration method. As was the case for carbon, two determinations were averaged if the readings were within the estimated range; if not then a further pair of determinations were performed. Since the sulphur contents varied from near zero to 0.4%, ranges for low and high percentages are estimated as $0.020 \pm .002\%$ S and $0.385 \pm .010\%$ S respectively.

The silicon content was determined by the gravimetric-perchloric acid method in which duplicate, one gram iron samples we e dissolved, and SiO_2 precipitated, filtered and weighed. Details of this method are described in ASTM E350-73. The estimated range for the silicon contents encountered in this investigation is 0.26 ± 0.02% Si.

Analyses of duplicate samples were quite sufficient for the intended purposes of this investigation since the information sought was firstly, the levels of C, S and Si of each metal button and secondly, large changes in those levels resulting from differences in pellet composition from one experiment to another.

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3.4 Reduction of Bentonite-Bonded Pellets

3.4.1 Ore-Coal Pellets

It was found that 1.5% to 2.0% bentonite binder was necessary to give the ore-coal pellets enough strength so that they could be handled easily and dropped into the crucible without shattering. After drying at 120°C for one hour, pellets of 12 mm diameter, withstood loads of about 5 kg.

The theoretical amount of coal needed in a pellet for the reduction of the ore and for carbon dissolution into the resultant liquid iron , was calculated to be 27%. This calculation was based only on the fixed carbon content of the coal since the extent of reduction by the coal volatiles, under such conditions, was unknown. Reduction tests were performed at 1480°C* on pellets with coal contents varying from 20 to 30%.

Immediately upon entering the hot crucible, the coal in the pellets began to coke and the evolving hydrocarbon volatiles cracked, as was indicated by a great amount of soot in the off-gas for the first fifteen seconds. The off-gas cleared of soot when the pellet surface had become hot enough so that the hydrocarbons cracked within the pellet. Thus, carbon was left inside while hydrogen (and CO from reduction) escaped. After about 90 sec., off-gas ing ceased and 20 sec. later, the pellets melted.

*These were the first tests and were performed before it was realized that the crucible temperature dropped some 20°C when the cold pellets were introduced. All subsequent tests were at 1500°C.

It was found that pellets with coal contents above 24% left large amounts of powdery black residue; a mixture of tiny iron droplets and carbon. There was so much excess carbon that the iron droplets were prevented from coalescing. Pellets of 20% coal became sponge-iron with no carbon in solid solution and with entrapped slag and FeS in the ferrite matrix. This was because there had been just enough coal in the pellets to reduce the ore and not enough carbon was left over to dissolve into the iron and thereby cause it to melt. The best results were obtained with pellets of 23% coal which produced liquid iron of 2.0%C, 0.3% Si and 0.35% S. Small droplets of greenish glassy slag also were formed, but these were too small to analyse.

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These preliminary tests on bentonite-bonded pellets of 23% coal showed that nearly all of the sulphur was transferred from the coal to the liquid iron. Unfortunately, reduced Fe or FeO particles serve very efficiently as scavengers for sulphur. The silicon content of the metal was quite low, partly due to the slow reaction rate of silica reduction but mostly due to the tendency of silica to slag with other oxides available in the pellet. For these reasons, high silicon contents of the resultant iron, would be unlikely to occur. This leads one to anticipate that, under similar conditions, low silicon iron may be expected in the proposed direct-reduction process. The carbon content of the metal was lower than expected and seemed to reach an upper limit of about 2.0%, even though there was an abundant supply of coal in the pellet.

Two major problems were identified. Firstly, it had to be determined why the melt would not pick up more carbon than it did, and secondly, means had to be found to inhibit sulphur transfer from the coal to the iron.

3.4.2 Ore-Graphite-Sulphur Pellets

What was preventing the iron melt from absorbing more carbon? Since the iron droplets from which the melt formed had unusually high sulphur contents, the surface-active properties of sulphur in iron became the first suspect. Carbon transfer to the iron could be inhibited by sulphur which is adsorbed preferentially on the liquid iron surface and which could act as a barrier to mass transport through that surface. To test this supposition, pellets of 17% graphite, with and without sulphur additions (as FeS and elemental S), were reacted at 1500°C. All melts became nearly saturated with carbon at about 4%, in spite of having up to 0.47% sulphur. Clearly, sulphur in the melt did not inhibit carbon transfer to the melt.

3.4.3 Ore-Coke Pellets

Since it was found that sulphur did not inhibit carbon transfer to the iron melt, an attempt was made to narrow the possible causes by eliminating the hydrocarbons from the pellet and subsequent reduction. Thus, coal was coked at 900°C and then pelletized with iron ore to act as the carbon reductant instead of coal.

Reduction tests were performed at 1500°C on pellets made with 19% and even 21% coke with disastrous results. Almost no carbon was absorbed by the iron which at 1500°C had been only partially melted. During reduction there was an inordinate amount of foaming brown slag and coke dust was blown throughout the furnace by the reduction offgases. Although the iron ore was reduced, the coke was unreactive in its role of supplying carbon to the molten iron and circumstantial

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evidence pointed to the coal (coke) ash as the cause. It was reasoned that as a coke particle was consumed, the ash accumulated on its surface and by virtue of its low melting point, would form a slag coating on that coke particle and thereby insulate it from the iron.

At this stage of the investigation, the foregoing was considered to be the most likely cause, but as will be shown later, this conclusion was only partly right. Metallographic examination of the microstructure of a pellet which had been quenched before reduction was complete will be shown in the next chapter and will interpret clearly the cause of the carbon problem and its solution.

3.5 Reduction of Self-Fluxing Pellets

3.5.1 CaCO₃ Additions to Bentonite-Bonded Pellets

An undesirable feature of using coal as a reductant is the resulting high sulphur content of the iron melt. However, should a pellet form its own desulphurizing slag, the problem may be lessened. To this end, up to 9% powdered calcium carbonate was added to ore - 23% coal pellets bonded with 2% bentonite. Reduction tests were performed at 1500°C, the results of which were disappointing. Firstly, the pellets were weak; the bentonite seemed to lose its bonding properties at the higher carbonate levels. Secondly, at the maximum carbonate content (9%), desulphurization was only 25% effective, i.e., 75% of the sulphur input transferred to the iron while 25% was retained in the slag. Further investigation of self-fluxing pellets continued in the direction of using highly basic pellet binders, particularly cement and calcium carbonate, for the dual purposes of bonding and desulphurizing.

3.5.2 <u>Pelletizing and Bonding Procedure using Cement, Carbonate</u> and Hot Pressing

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A cement bonding process for iron ore pellets was developed commercially some years ago but when this type of pellet was used as a blast furnace feed, difficulties were encountered due to pellet swelling. However, swelling should not be a concern in the present investigation and thus using cement-bonded ore-coal pellets may be of some value.

Small additions of gypsum $(CaSO_4 \cdot 2H_2O)$ are added to commercial portland cement to prevent premature setting of the paste. Normally, this is beneficial but it does raise the sulphur content to about 1%. Thus, cement clinker (0.37%S) was obtained from a manufacturer before the addition of gypsum and was ground to 90% minus 325 mesh. The chemical analysis is given in Appendix A3.2.

Varying amounts of cement were added to ore-coal mixtures and although there was no difficulty in pelletizing the moistened blends, curing the pellets did present problems. When left to the open air, the pellets dried out before hardening, and steam curing caused the pellets to swell some 30%. In both cases the pellets remained quite fragile. Room temperature curing under moist conditions for three or more days did produce hard pellets but since this was time consuming, a curing méthod was devised for this study, wherein the pellets were placed into a pressure-tight, capped steel pipe, which then was held in an oven at 70°C for ten hours. Afterwards, the pellets were thoroughly dried at 120°C. Pellets with less than 10% cement (anhydrous) remained too fragile to be of much use.

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Carbonate bonding of pellets has been developed commercially $\binom{39}{2}$, but for 30 gram batches the following procedure was devised. Powdered lime was added to the ore-coal mixtures in varying amounts up to 8% and when pelletized with water, the lime slaked to Ca(OH)₂. The pellets were then partially dried and placed in a flask. Carbon dioxide was bled into the flask while it was held in an oven at 60°C for about 30 minutes. Afterwards, the pellets were dried at 120°C.

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Another method for agglomerating composite mixtures is that of, hot pressing. Since coal becomes plastic at about 377°C, it can serve as the pellet binder with the advantage that no water or CO₂ is used and thus the lime is not slaked or chemically changed to carbonate. A split mold of graphite, retained in a copper tube, and with a plug and plunger of steel, was constructed to produce hot-pressed cylindrical pellets 12 mm in diameter and in height. The mold was heated to 400°C while the mixture was pressed under a load of 500 to 600 kg. Reduction of hotpressed ore-coal-lime pellets allowed comparison with carbonate-bonded pellets.

3.5.3 <u>Reduction Tests</u>

Before proceeding with a presentation of results, it may be helpful to review the objective of these reduction experiments. When coal was used as a reductant for iron ore, the sulphur in the coal transferred to the resulting iron melt. The objective was to interfere with this transfer by having the pellet form its own desulphurizing slag and thereby scavenge the sulphur internally to the pellet during reduction and melting. Should most of the desulphurization be performed by the internal pellet slag before it joins the foaming process slag, the time required to obtain low sulphur contents of the metal bath would be lessened. The major concern here, is the reduction of individual selffluxing pellets and the slag/metal distribution of sulphur between the internal slag and iron droplets formed during reduction and melting of these pellets.

Reduction tests were performed at 1500°C on ore-coal pellets, bonded with various amounts of cement (K series) and calcium carbonate (L series), and on hot-pressed ore-coal-lime pellets (M series) in much the same manner as described previously in Section 3.3.2. In these experiments, four pellets (approx. 10 g) were dropped into the crucible at the same time. After the pellets were reacted, the molten slag and iron, which were partially separated in the bottom of the crucible, were cooled quickly. The reduced slag/metal contact area after complete collapse of the pellets and the high rate of cooling at the end of the experiment, allowed minimal opportunity for any further slag/metal reaction to take place. Thus, the results presented in this section reflect, as closely as possible, the conditions which existed between the iron droplets and internal pellet slag at the time of their separation.

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3.5.4 <u>Results and Discussion</u>

The percentages of the pellet constituents and the chemical analysis of the resultant metal for each of twenty experiments are tabulated in Table 3.1. Some experiments were repeated with a portion of the cement or lime flux replaced by magnesia (in one case, by magnesia + alumina) in order to lower the liquidus temperature of the pellet slag formed during reduction.

In order to show the effect of pellet composition on desulphurization of the resultant iron, the data were treated in the following way. Each lot of pellets with a specified flux/binder addition was reacted and the sulphur content of the iron, [%S], was measured. Also, the theoretical sulphur content of the iron that would have resulted had no desulphurization taken place, $[\%S]_{max}$, was calculated from the weight of metal produced and the total sulphur input, assuming all sulphur had entered the iron. Thus, the actual sulphur content of the iron and its theoretical maximum for each experiment, were used to calculate percentage desulphurization, % DeS.

Further, the data from each experiment allowed calculation of the theoretical slag/metal distribution of sulphur, based on equilibrium thermodynamics, weights of input materials and metal analysis. This distribution may not have been achieved but it shows what could be expected should the pellet slag and iron droplets be in equilibrium when the pellets collapse from melting after reaction. Arising from these calculations is a value for the equilibrium sulphur content of the iron, [%S]_{eq}, which is then used to calculate an equilibrium percentage desulphurization value, % DeS_{eq}. The actual desulphurization obtained, % DeS,

can then be compared with the equilibrium value. A detailed representative calculation for the complete treatment of the data is presented in Appendix A3.3. Table 3.2 presents the calculated desulphurization values and slag properties, such as weight, basicity and liquidus temperature, for each experiment.

In order to show graphically the effect of pellet composition on desulphurization of the pesultant iron, Figure 3.2 was constructed using the tabulated data. Percentage desulphurization, % DeS, was chosen as \sim the more correct parameter to plot against flux addition, since the sulphur input varied somewhat with each experiment. The variation was small however, and thus the ordinate on the right-hand side of the diagram depicting sulphur content of iron, [%S], is fairly accurate. It also illustrates more clearly that adequate additions of basic flux (as binder) to the pellets can desulphurize the iron from about 0.4% S down to the/0.04% S range.

Bonding pellets with cement can achieve the desired desulphurization but note that it takes considerably more cement to equal the performance of lime as either desulphurizing or bonding agent. An estimate of the slag weight per tonne of iron, for each lot of pellets, is placed along the top of the diagram. The bonding ranges placed on the diagram for both carbonate and cement are for general guidance only. Below the suggested minimum, it was found that the pellets did not harden very well and considerable breakage or dusting could be expected during handling in an industrial manner. Above the suggested maximum, it was found that the pellets contained such an excess of lime that during reduction and melting, it could not be dissolved into the molten slag.

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Ídent.	Hardened Pellet		Calcined Flux		Metal Analysis		
	% Ore	% Coal	% Cement	% Mg0	% C	% S	<u> </u>
К4	71.3	22.5	5.0	0.0	2.22	. 281	-
КЗ	65.8	22.0	9.8	.0.0	2.90	.176	.28
к1	62.8	22.0	12.2 -	0.0	3.47	.086	.35
K2	61.4	20.5	14.5	0.0	3.34	.138	-
K2-1	61.2	20.5	12.9	1.6	4.40	.016	• .19
			% CaO	% Mg0		·	
L5	7415	23.5	1.1	0.0	2.18	. 300	-,
L1 `	73.2	23.2	2.0	0.0	2.08	.296	-
L8	69.5	23.2	4.1	0.0	2.75	.210	.26
L9	66.1	23.3 `	6.0 `	0.0	2.86	.137	-
L9-1	66.0	23.2	4.7	1.2	3.90	.080	<u> </u>
L9-2	65.8	23.1	4.1	1.8	3.76	.052	.16
L9-3	65.7	23.1	3.6	2.4	3.60	.080	-
L3	,64.6	21.8	7.6	0.0	2.94 -	.085	-
L3-1	64.1	21.9	5.9	1.7	3.68	.040	.10
L3-2	64.4	22.0	5.1	1,7+	3.77	.044	-
				.9 A1 ₂ 03			
MI	77.0	23.0	0.0	0.0	1.95	.318	.20
M2`	74.3	23 [.] .5	2.2	0.0	2.38	.296	-
M3 (72.8	23.0	4.2	0.0	2.35	.225	-
M4	70.3	23.5	6.2	0.0	3.00 .	.128	.26
M5	68.9	23.0	8.1	0.0	2.87	.037	-

Table 3.1: Pellet constitution and chemical analysis of reduced metal

[Metal			Slag			
	Exp't Ident:	^{%S} max	^{%S} eq	calc. ^{%DeS} eq	actual %DeS	Weight kg/tonne	Basicity Ratio B	Liquidus oc
Cement-bonded	К4	.452	. 367*	19.*	38.	(195)	0.66	1350
	КЗ	.512	. 122	76.	[.] 66.	300	1.12	1425
	К1	.715c	.052	93.	88.	360	1.31	1450
	К2	.535	.024	95.	74.	416	1.48	1675
	K2-1	.542	.007	99.	97.	416	1.56	1500
		c - co ce	mmercia ment	l 		、 、		
Carbona te~bònded	L5	.417	. 400*	4.*	28.	(125)	0.29	(1250)
	LI	.418	. 387*	7.*	29.	(142)	0.51	1325
	L8	. 433	.188	57.	52.	187	1.04	1450
	L9	.453	.043	90.	70.	233	1.57	1800
	L9-1	. 447	.023	95.	82.	228	1.45	1550
	L9-2	.447	.029	94.	88.	230	1.42	1500
	L9-3.	. 448	.034	92.,	82.	233	1.40	1575
	L3	.438	.008	98.	80.	272	2.04	1950
	L3-1	. 440	.006	98.	91.	270	1.92	1675
	L3-2	. 438	012	<u>9</u> 7.	.90	270	1.64	- 1500
pressed with Lime	MI	. 402	. 398*	·].*	21.	(102)	0.04	(1225)
	M2	.417	.366*	12.*	29.	(145)	0.55	1375
	M3	.417	.235	44.	45.	185 -	1.03	1425
	M4	. 412	.037	91.	69.	230	1.54	1800 .
Hot-	M5	.433	.008	98.	92 . -	270	2.04	1950

* - calculations in these instances are not valid as the slag contained appreciable amounts of FeO; brackets infer approx. values

Table 3.2: Calculated desulphurization values and slag properties.





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The desulphurization behaviour of hot-pressed ore-coal-lime pellets was very similar to that of calcium carbonate bonded pellets. Indeed, this was to be expected since during reaction the calcium carbonate within the pellets would be calcined to lime prior to its role in desulphurizing the iron.

A cursbry look at the primary desulphurization data (open symbols on Figure 3.2) shows that there seems to be a direct relationship between desulphurization and lime flux additions; not altogether unexpected, since the more lime added, the more desulphurization to be gained. However, this simple explanation became far more complicated as it was more closely examined. The rest of this section will focus on the formation and role of the internal pellet slag. Some of the symbols used in Figure 3.2 will be explained later in this section and will tie in to other diagrams.

The primary desulphurization data showed that even at the maximum lime addition, the sulphur content of the iron was still higher than expected. As a first step towards understanding the data, the equilibrium slag/metal distribution of sulphur, at the time of melting, was calculated for each reduction experiment, as detailed in Appendix A3.3. Briefly, the stag composition was calculated from input materials and used to obtain the basicity ratio and sulphide capacity of the slag Using both metal and slag parameters, 'equilibrium thermodynamic equations allowed calculation of the slag/metal distribution of sulphur and, in turn, equilibrium percentage desulphurization values, % DeS_{eq}. The calculated equilibrium reference curves on Figure 3.2 represent these

*Background information and definitions of these terms may be found in Chapter 6 - Applied Metallurgical Thermodynamics (Section 6.5).

values.

The experimental data have been replotted in Figure 3.3 to show percentage desulphurization verses an empirical slag basicity ratio, B. The reversed S-shaped curve is the locus of the calculated equilibrium values and represents the theoretical goal for desulphurization of iron reduced from self-fluxing pellets. Below B = 1.0, the iron melts were desulphurized more than what is indicated by the calculated reference curve. When the amount of slag produced by an individual pellet is small because of little or no lime addition, then minor constituents not hitherto considered, such as alkali impurities from ore and coal, should be included in the calculations. A more important factor is that an insufficient lime addition allows the formation of a silicious iron oxide slag (e.g., fayalite) which alters the desulphurization properties of the pellet slag in a positive manner, not considered in the theoretical treatment. In short, the slag/metal distribution calculations used to obtain the reference curve are not valid when applied to silicous slags containing appreciable amounts of alkalies or iron oxide. Providing that enough information is available, the theoretical treatment could be extended to include these types of slags but since the major interest was to desulphurize the iron by using self-fluxing pellets, this was not considered worthwhile.

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The primary desulphurization data, represented by open symbols in Figures 3.2 and 3.3, show that the iron reduced from pellets of higher basicity (B >1.4) was not desulphurized to the extent indicated by the reference curve. When the products of these reduction experiments were examined, it was observed that the crucibles contained large drops of iron, greyish slag, some carbonaceous residue and some white powdery lime.

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Also, it was found that the liquidus temperatures of the calculated slag compositions were far in excess of 1500°C, the experimental reduction test temperature. Clearly, the internal pellet slag should be in a fully molten state in order to obtain better desulphurization of the molten iron droplets formed during reduction and melting.

As a measure to reduce the liquidus temperature of the slag, reduction experiments were performed wherein 20, 30 and 40% of the lime in the carbonate-bonded pellets was replaced with magnesia; the total flux weight being kept constant. The effect of this measure on desulphurization is shown by arrows labelled L9 in Figures 3.2 and 3.3. The results from 20 and 40% replacement were about equal and showed some improvement. The point nearest to the reference curve and showing the best desulphurization, was for pellets wherein 30% of the lime was replaced with magnesia. In order to understand these new results, from a slag liquidus point of view, a portion of the phase diagram in the 5% Al_2D_3 plane of the system CaO-MgO-SiO₂-Al₂O₃ is reproduced from Muan and Osborn(40) as Figure 3.4. In this diagram the phases have been left unidentified to avoid clutter, while the isotherms map the contours of the liquidus surface. The objective was to move the composition of the slag from pellets L9 into a liquid region at 1500°C by replacing lime with magnesia. Path L9, -1, -2, -3 shows that the slag compositions moved into the fully liquid zone at 2 (best results) but continued too far, for at 3, some of the MgO could not be dissolved into the slag and this led to somewhat poorer results.

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Figure 3.4: A portion of the phase diagram for the system $CaO-MgO-SiO_2-5\%A1_2O_3$ showing the liquidus temperatures of selected pellet slag compositions.

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Applying the above to pellets L3, replacement of lime with magnesia moved the slag composition into the trough position, L3-1. Here it can be seen that more magnesia would not produce a liquid slag. Upon examining phase diagrams in the 10% and 15% Al₂O₃ planes of the same oxide system, it was decided to increase the alumina content from 5% to 12% in order to obtain a liquid slag at 1500°C. When this new set of pellets were reduced there was no improvement in desulphurization; the beneficial effect of having a fully liquid slag was off-set because its basicity and thus its sulphide capacity was impaired by the higher alumina content. This is shown by the arrow labelled L3 in Figure 3.3.

Reduction of pellets containing 14.5% cement presented the same problem in that the slag liquidus temperature was in excess of the reduction test temperature. This was resolved by replacing about 10% of the cement with MgO and is illustrated by the arrows labelled K2 in Figures 3.2 and 3.3. The attainment of near equilibrium desulphurization, 97%, resulting in 0.016% S content of the iron melt, must be tempered by the observation that the slag weight from so much cement would be a very heavy burden for a process to carry.
A clearer picture of the effect of liquidus temperature of the internal pellet slag on desulphurization can be gained by examining Figure 3.5. Desulphurization of iron by a slag is a function of slag weight as well as basicity and in order to remove weight as a variable, percentage desulphurization was divided by slag weight (kg/tonne) for those experiments in the carbonate-bonded series. This new parameter, which introduces no new concept and is merely a measure of desulphurization obtained per unit of slag weight, was plotted against liquidus temperatures of the internal pellet slags, as calculated from input materials.

The extended arrows L9 and L3 correspond to those in previous diagrams and show that desulphurization rose to a peak when the internal slag was able to become fully liquid at the reduction test temperature. The datum point with basicity ratio 1.64 is perhaps an anomaly because it represents experiment L3-2 wherein alumina was added to lower the slag liquidus to 1500°C. In doing so, the slag weight was increased and the basicity decreased, both negative factors but with weight a more negative influence on this type of plot, then basicity. Although the basicity ratios are listed for each experiment, it should be remembered that they are valid only if the slag was fully liquid. Partially melted slags left undetermined amounts of lime or magnesia powder undissolved and thus the basicity ratios of the liquid portions that did form, could be significantly lower than the ratios calculated from input materials.



One solution to the above problem, would be to introduce the concept of an "active slag" which would be defined as that portion of the total slag which was liquid at the reduction test temperature of 1500°C. It will be recalled that for each reduction experiment, a slag composition was calculated from input materials (Appendix A3.3) and its liquidus temperature was found from the appropriate phase diagrams (e.g., Fig. 3.4) compiled by Muan and Osborn⁽⁴⁰⁾. For those slags which had a liquidus in excess of 1500°C, the composition of the liquid portion or "actual slag" can be estimated from the same diagrams and used to calculate an active slag basicity ratio, B_A .

The weight of the active slag can be estimated by dividing the active slag silica content into the total silica input. This assumes that all of the silica was dissolved into the liquid portion of the slag. Here, perhaps it is best to digress for a moment in order to consider the sequence of slag formation. Silica enters the pellet mostly as a constituent of the ore, usually as discrete silicate particles containing some alumina, magnesia, and in many cases, some iron oxide. After the ore and coal are formed into a pellet, the splicate particles would be surrounded by carbonate or cement as the bonding material. When introduced into the hot zone of a furnace, the temperature of a pellet would rise very quickly and several steps in slag formation would happen sequencially. The bonding material would calcine and some lime (and magnesia, if present) would react with, and diffuse into, the surfaces of the still-solid silicate particles. Events would soon overtake solidstate diffusion for as soon as the temperature rose above, say 1400°C, the silicate particles would begin to melt and the small molten droplets of slag would then dissolve as much lime and magnesia as possible.

Should there be excess lime in the pellet then the molten slag would become saturated with lime, the amount being controlled by the reduction test temperature. Lime may continue to enter the slag but solid phases such as 2Ca0.SiO₂ (dicalcium silicate) or 3CaO.MgO.2SiO₂ (merwinite) would form. Should this happen, the composition of the liquid portion would change slightly and the amount of liquid would decrease. Since the time available to form a liquid slag would be very short, perhaps 30 to 60 seconds, the amount of silica removed from solution by this type of phase formation would be expected to be small. Hence, the assumption that most, if not all the silica is dissolved in the liquid slag appears to be the most likely (and perhaps, only) way of estimating the weight of the "active slag".

Using the newly obtained values of basicity and weight, the active slag/metal sulphur partition and equilibrium percentage desulphurization equations were recalculated in the same way as outlined in Appendix. A3.3. Table 3.3 lists the pertinent data with the experiments prefixed by the letter "A", recalculated according to the "active slag" concept. The data for the other experiments, i.e., those with slag liquidus temperatures of 1500°C and below, remain unchanged but are included for completeness. The actual percentage desulphurization for each experiment has been plotted against the active slag basicity ratio, B_A , in Figure 3.6. This figure should be compared directly to Figure 3.3. It can be seen that the calculated reference curve has changed very little in either shape or position. As discussed previously, the slag/metal sulphur distribution calculations used to obtain the reference curve below $B_A = 1$ are not valid when applied to siliceous iron oxide slags and thus the melts were desulphurized more than what is indicated by the reference curve.

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	Active Slag Concept			Actual		Active
Exp't Ident.	Basicity Ratio, B _A	^{%S} eq	%DeS _{eq} .	% S	%DeS	Slag Liquidus ^O C
К4	0.66	.367*	19.*	.281	38.	1350
К3	1.12	. 122	76 . ·	.176	66.	1425
КI	1.31	.052	93	.086	88.	1450
A-K2	1.34	.038	93	.138	74.	1500
K2-1	⁻ 1.56	.007	99	.016	97.	[`] 1500
L5	0.29	. 400*	4.*	. 300	28.	(1250)
LÌ	0.51	. 387*	7.*	.296	29.	1,325
L8	1.04	.188	57.	.210	52.	[•] 1450
A-L9	1.27	.106	77.	.137	70.	1500
A-L9-1	1.37	.030 .	93.	.080	82.	1500
L9-2	1.42 [·]	.029	94.	.052	88.	1500
A-L9-3	1.34	.042	91.	.080	82.	· 1500
A-L3	1.30	.090	80.	.085	80.	1500
A-L3-1	1.36	.038	91.	.040	91.	1500
L3-2	1.64	.012	97.	.044	90.	1500
M] M2	0.04		.].* 12 *	.318	21:	(1225) [·]
1.15	1 0.55	. 500 "	14."	• 230	23.	1373

 * - calculations in these instances are not valid as the slag contained appreciable amounts of FeO; brackets infer approx. values

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80.

79

.225

.128

.037

45.

69.

92

1425

1500 .

1500

.235

.085

.093

1.03

1.27

1.30

M3

A-M4

A-M5

Table 3.3: Calculated desulphurization values fusing the active slag concept.





The major observation to be seen when comparing Figures 3.3 and 3.6 is that when the active slag concept is applied and only the liquid portion of the pellet slag is considered to take part in the reactions, desulphurization was much closer to the theoretical goal, as represented by the calculated reference curve. This substantiates an earlier observation that the internal pellet slag should be in a fully molten state in order to obtain better desulphurization of the molten iron droplets formed during reduction and melting. It also shows that should this condition be met, the reacting pellets can approach equilibrium with respect to sulphur in under two minutes which suggests that there are no large kinetic hindrances to desulphurization in this manner.

The active slag concept has been useful in explaining the experimental results when the slag was only partially molten but the reverse side of the coin needs to be challenged, i.e., the assumption that the lime powder not dissolved into a liquid slag is "inactive". The recalculated data from experiment M5 (A-M5 in Table 3.3) shows that the actual desulphurization was considerably more than the calculated "equilibrium" value. These pellets were hot-pressed and contained 8.1% lime powder but only about half would have been dissolved into a liquid slag. This large amount of "excess" lime powder available within the pellet probably desulphurized the coal volatiles by gas-solid reaction and therefore cannot be considered inactive. Although the active slag concept has been useful in explaining results, its assumptions should be kept in mind and it should not be applied too rigorously.

It will be recalled from Section 3.4 that two problems were identified in the reduction of bentonite-bonded pellets. Firstly, the carbon content of the resultant iron remained at about 2.0% in spite of an excess of coal in the pellets, and secondly, means had to be found to inhibit sulphur transfer from coal to iron. In attempting to solve the sulphur problem by testing self-fluxing pellets, as described in this section, it was noticed that the carbon content of the iron rose appreciably with each new attempt to desulphurize. This effect is shown in Figure 3.7 wherein the carbon content of the iron has been plotted against slag liquidus temperature. The peak in carbon content at 1500°C indicates that the slag should be fully liquid, or nearly so, in order to allow the small iron droplets enough mobility to contact and absorb carbon particles within the reacting pellet. More important, it will be observed that due to an increase in the basicity of the internal pellet slag, the carbon content rose from 2% (Bentonite-bonded pellets) to over 4% (carbonate and cement-bonded pellets).

In response to this significant observation it was decided to investigate more closely the effect of lime and magnesia on reduction mechanisms within iron ore-coal pellets. This new investigation will be described in the next chapter where the internal microstructure of partially reduced pellets will be examined metallographically.



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Effect of pellet slag liquidus temperature on carbon content of iron. Figure 3.7:

3.6 Summary

Composite iron ore-coal pellets were reduced to iron by performing a series of small crucible experiments. It was found that such pellets are capable of very fast reduction; from cold pellet to reduced iron at 1500°C in 110 sec. From this it can be reasoned that the rate at which the pellets react probably would depend on the rate at which they could be heated and not on any internal constraints.

A pellet containing about 23% coal was found to have sufficient coal to reduce and carburize the resultant iron. Too much coal weakened the pellets and left a carbonaceous residue, while too little coal produced sponge irom.

Reduction of ore-coal pellets bonded with 2% bentonite produced iron melts containing about 2%C, 0.3% Si and very high sulphur at 0.3%. Limestone additions to the ore-coal mixtures produced very weak pellets and the sulphur content of the iron remained high.

Three techniques for bonding composite pellets containing basic flux additions were investigated. Carbonate bonding was the preferred method in the laboratory but hot pressing or briquetting may have economic advantages in an industrial context. Cement bonding produced hard pellets only above 12% cement (anhydrous) which would increase considerably the slag loading to the process.

The reduction of self-fluxing pellets showed that desulphurization and carburization were at maximum levels when the internal pellet slag was fully liquid at the reduction test temperature. These conditions produced iron melts containing about 3.76% C, 0.16% Si and 0.052% S.

In order to gain a clearer understanding of composite pellet reduction, it was proposed to examine the internal pellet microstructure of partially reduced pollets.

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CHAPTER 4

METALLOGRAPHIC INVESTIGATION OF PARTIALLY REDUCED PELLETS

4.1, Introduction

The pellet reduction experiments described in the previous chapter showed that the problems of high sulphur and low carbon contents of the iron from bentonite-bonded pellets could be alleviated by reducing self-fluxing pellets. Composite pellets of known composition were observed during their reduction and later, a chemical analysis of the resultant iron was obtained. This analysis, coupled with calculations of slag composition and slag/metal distribution of sulphur, allowed the reduction behaviour of the pellets to be described. The discussion centred mainly on the properties of the internal pellet slag. However, in order to obtain a clearer understanding of the reduction mechanisms within a pellet, these macro-observations need to be substantiated by observing the changes of the internal pellet microstructure during reduction. It was considered that the best approach would be to interupt the reduction reaction and attempt to preserve the microstructure at that point by cooling the pellets quickly. Then, from an examination of the microstructure from centre to surface, one should be able to follow the reduction of individual iron ore particles and the formation of the internal perlet slag.

4.2 <u>Procedure</u>

4.2.1 Pellet Compositions

The pellets used for the partial reduction experiments were from lots prepared for the previous reduction experiments and hence had the following compositions.

75% ore, 23% coal, 2% bentonite

79% ore, 19% coke, 2% bentonite

81% ore, 17% graphite, 2% bentonite

63% ore, 22% coal, 12% cement (anhydrous)

66% ore, 23% coal, 11% carbonate (4.7% CaO + 1.2% MgO)

4.2.2 Experimental Technique

An alumina crucible was held in the hot zone of the furnace at. 1500°C while the working tube was flushed with argon. One pellet was dropped into the crucible through the hole in the top head; then after the optical flat assembly was replaced in the hole, the argon flow was shut off. After about 15 seconds, the off-gas from the reacting pellet cleared of soot and the pellet could be observed directly. After about 50 seconds the crucible was lowered quickly to the bot+om of the furnace tube, where a strong stream of argon quenched the crucible and pellet.

Several trials with each type of pellet were necessary in order to obtain the correct timing. Too long at temperature resulted in a partially melted and collapsed pellet, while too little time did.not allow the ore at the pellet surface to be fully reduced. The alumina working tube in the furnace cracked from thermal shock, but it could still be used for a number of tests as there was very little air leakage due to positive pressures within the tube. The alumina crucibles also cracked during the severe argon quenching but most of them could be reused several times.

The above procedure produced pellets which were fully reduced and partially melted at their surfaces, but nearer their centres, reduction had just begun. Although this procedure allowed observation of ore particles in different stages of reduction, no direct information could be obtained on temperatures within the pellet, other than surmising that the surface reached about 1450°C. After metallographic observations, it was estimated that the pellet centres reached about 900°C, depending on the type of pellet and its residence time in the hot zone.

4.2.3 Metallography

The partially reduced pellets were sectioned through their centres with a fine jeweller's saw and mounted in clear, cold-setting resin (Quick-Mount). Since the pellets were very porous, they were impregnated fir $e^{i\theta}$ with the liquid mounting resin while in an evacuated desiccator, and then mounted in air in the prescribed manner.

The mounted specimens were polished first on silicon carbide papers, then on metallographic polishing wheels using 6 and 1 micron diamond pastes on silk, and finally, finished using a gamma alumina slurry on "Microcloth". The microstructure was viewed usually in the unetched condition but to check the carbon content of iron droplets, the specimens were etched with 2% nitric acid in ethanol (2% nital). Partially reduced iron oxide particles (wustite) were etched with ethanol saturated with SnCl₂ or with an aqueous solution of SnCl₂. Photomicrographs were taken with Reichert and Leitz metallographs using Kodak Tri-X film.

In order to verify metallographic observations of slag and wustite grains formed during reduction, electron-probe microanalyses were performed on selected specimens using a JEOL, Type JXA-3 $(modified)^{(102)}$ microprobe. This microprobe is equipped with an ORTEC energy dispersive x-ray detector and the analyses were performed using this method rather than using wavelength spectroscopy. A computer program was used to correct the data and to calculate the weight percentages of the elements and their oxides (except sulphur) in the specimen. Further details and the accuracy to be expected for this type of analysis can be found in Appendix A4.1.

4.3 <u>Results and Discussion</u>

4.3.1 Ore-Coal Pellets Bonded with Bentonite

A series of photomicrographs showing the internal pellet microstructure, from centre to surface of partially reduced 75% ore - 23% coal pellets bonded with 2% bentonite is presented as Figure 4.1a to h. The pellets originally had a radius of about 6 mm but after being partially reduced, most had shrunk to a radius of about 5 mm. Upon examination of the photomicrographs, it will be noticed that at the centre of the pellet, (Fig. 4.1a), the iron oxide particles had been reduced from magnetite to wustite and the wustite has been partially reduced to iron. When particles of coal are heated, they soften and fuse together to form a tar-like mass which, in a pellet, would surround the iron oxide particles. As heating continues, the volatile hydrocarbons are driven off; the coal "boils" to form a cellular structure and hardens into coke. The mottled, grey, web-like material in the photomicrograph is coked coal. The background matrix material is mounting resin and aptly illustrates just how highly porous the pellets become after coking.

At a radius of about 2 mm (Fig. 4.1b), silica particles (dark grey) have reacted with wustite (light grey) to form a liquid iron silicate slag (intermediate grey). At a radius of about 3 mm (Fig. 4.1c), which also implies an increase in temperature, it can be seen that there has been considerable agglomeration of the original wustite grains, reduced iron and liquid iron silicate. This agglomeration is the probable cause of the pellet shrinkage.

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At a radius of about 4 mm (Fig. 4.1d) the solid iron grains have continued to grow because of continued reduction, but now they have been surrounded completely by liquid iron silicate slag. Secondary wustite can be seen to have precipitated from the silicate melt during solidification.

Just beneath the pellet surface at a radius slightly more than 4 mm (Fig. 4.1e), the iron silicate slag has solidified into unique elongated crystals identified mineralogically (43,44) as fayalite $(2Fe0\cdotSi0_2)$. The small white globules in the interdendritic spaces between the crystals are actually yellowish in colour and are identified as FeS. Figure 4.1f shows the same area but at a lower magnification of 100X in order to show how extensive the fayalite slag had become relative to the white grains of reduced iron.

The microstructure at the pellet surface, which was on the verge of collapse at about 1450°C, is shown in Figure 4.1g. This photomicrograph is also at the lower magnification of 100X. The microstructure has been etched with 2% nital to show the carbon content of the iron phase. The iron on the left, at the pellet surface, has a very fine pearlitic microstructure which indicates that its carbon content is about 0.8%, while the white grains of iron just beneath the surface contain little or no carbon.

Although the iron and slag at the pellet surface were molten, the various reduction reactions were continuing. Internally, iron oxide was being reduced and the off-gases were escaping through to the surface; the high-FeO slag, in contact with coke, was being reduced; and the iron near the surface, also in contact with coke, was absorbing carbon. From previous experiments, described in Section 3:4.1, it was found that bentonite-bonded pellets produced an iron melt containing about 2.0%C. In order to view the end products, slag and metal, a pellet which had been reduced and melted was prepared for metallographic examination and is shown in Figure 4.1h. Most of the iron in this specimen was pearlitic (0.8%) as shown in the lower right-hand corner of the photomicrograph, but a few high-carbon (~4%C) "white iron" droplets were evident also. The white phase in the droplet is cementite and the dark phase, pearlite. There did not seem to be enough high-carbon iron to produce an "average" melt containing about 2.0%C which leads one to suspect that the molten iron of previous experiments picked up additional carbon from coke particles after the melting of the pellets.



Figure 4.1a: Centre of pellet. The wustite grains were partially reduced to iron. The mottled, web-like material is coked coal. Unetched. Magnification 300X or ______30 µm.



Figure 4.1b: At radius of ~2mm, silica particles (dark grey) have reacted with wustite (light grey) to form a liquid iron silicate slag (intermediate grey).Unetched.Magnification 300X.

Figure 4.1a to h: Illustrations of the microstructure from centre to surface of partially reduced 75% ore-23% coal pellets bonded with 2% bentonite.



Figure 4.1c: At radius of ~3mm, there has been considerable agglomeration of the original wustite grains, reduced iron and liquid iron silicate slag. Unetched. Magnification 300X.



Figure 4.1d: At radius ~4mm, the reduced³iron grains have been surrounded by liquid iron silicate slag. Secondary wustite has precipitated from the silicate melt during solidification. Unetched. Magnification 300X.



Figure 4.le: Subsurface at radius of ~4mm. Fayalite crystals and interdendritic eutectic glass have solidified from the iron silicate slag. Unetched. Magnification 300X.



Figure 4.1f: Subsurface at radius of 4mm. Same area as above. Unetched. Magnification 100X or Land 100 µm.



Figure 4.1g: Surface at radius $\sqrt{5}mm$ showing "Slag A" with iron of $\sqrt{0.0\%}$ on the right and "Slag Al" with iron of ~0.8%C on the left. Nital etch. Magnification 100X.



Figure 4.1h: Final products, iron and "Melt Slag B". Some iron droplets contained ~4%C but most contained ~1%C (lower right). Nital etch. Magnification 100X.

The fayalite crystals (\sim 90%) and intercrystalline eutectic glass (10%), shown in Figure 4.1e, were analysed with an electron microprobe. Also analysed were three types of slag, two of which are shown in Figure 4.1g; "Slag A" associated the iron (ferrite) grains and "Slag Al" associated with iron of about 0.8%C content, at the pellet surface. A further specimen "Melt Slag B" was obtained from a fully reduced and melted pellet, Figure 4.1h. This slag was associated with the high-carbon iron droplet and would represent the most reduced slag or "best case" to be expected from the reduction of ore-coal pellets bonded with bentonite. Data from each specimen analysis are presented in Appendix A4.2 in the form of computer print-out sheets, while Table 4.1 summarizes the chemical composition for each phase. Four separate areas were averaged for the fayalite and eutectic glass while Slag A, Slag Al and Melt Slag B are averages of three separate areas. Microprobe analyses of solidified slags are sometimes difficult because when cooled, the slags are no longer single-phased. For instance, the high-silica slags may have precipitates of tridymite (SiO_2) . Also, the larger FeS globules were avoided whenever possible in order to obtain a more representative overall composition.

A pure fayalite crystal $(2\text{Fe0}\cdot\text{Si0}_2)$ contains, by weight, 70.6% FeO and 29.4% SiO₂. From Table 4.1 it can be seen that MgO is a sulstitute constituent for FeO in the fayalite crystal and it is known that it forms a solid solution with FeO and SiO₂ (45). It would be more correct to call this phase an olivine $(2(Mg, \text{Fe})0\cdot\text{SiO}_2)$ but since the MgO content is small, fayalite is preferable. Sulphur (as FeS), Al₂O₃, CaO and K₂O have been segregated to a eutectic glass consisting mostly of and FeO

			•
alite Eutectic S	lag A	Slag Al	Melt Sl

	Fayalite wt %	Eutectic wt %	Slag A wt %	Slag Al wt %	Melt Slag B wt %
Mg0	2.0	0.2*	0.5	2.3	3.7
A1203	1.1	11.9	4.8	7.3	10.1
si0 ₂	30.1	44.3	36.5	52.8	66.4
S.	0.1*	0.9	1.8	· 0.3	0.1*
к ₂ 0́	0.0*	0.4	0.1*	, 0.5	0.8.
Ca0	0.1*	2.1	1.2	1.3	Ż.2
Fe0	66.4	42.4	51.1	32.3	13.6
Total	¢ 99. 8	102.2	96.0	96.8	96.9
* - tra	ce amounts				,

Table 4.1: Electron-microprobe analyses of slags formed during reduction of ore-coal pellets bonded with 2% bentonite

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The three slags A, Al and B show progressively lower FeO contents as they become associated with iron of rising carbon content. They are, of course, the same slag at different stages of reduction. Also, the decreasing amount of sulphur in the slag can be related to previous experiments wherein most of the sulphur transfers to the iron melt; an expected result since the slag basicity is extremely low. Should large melts of iron be produced from ore-coal pellets bonded with bentonite, it would be reasonable to expect, from the analysis of Melt Slag B, that the slag produced would contain at least 15% FeO.

The formation of a fayalite-type slag and the reduction of wustite and slag, as shown in the photomicrographs of Figure 4.1a to h, can be illustrated further with the help of a binary FeO-SiO₂ phase diagram ⁽⁴⁶⁾, where the oxides are in equilibrium with metallic iron. From an examination of the phases depicted in the photomicrographs, an approximate temperature and phase field have been deduced and superimposed upon the phase diagram in the form of a dashed curve, as shown in Figure 4.2. Along the curve are points lettered a to h which correspond to the photomicrographs of Figure 4.1. Also, for the purpose of illustration, the slag compositions A, A1 and B have been simplified to a binary system wherein Al₂O₃ was added to SiO₂ and the small amounts of MgO and CaO were added to the FeO content. Solidification of those areas which are in the liquid regions, would then correspond to those phases found in the photomicrographs.



Figure 4.2: Binary phase diagram for the system FeO-SiO₂ in equilibrium with metallic iron (after Muan and Osborn).

A similar slag formation and reduction path can be devised by plotting an estimate of the phase fields from the photomicrographs and slag compositions on an $Fe0-Si0_2-A1_20_3$ phase diagram ⁽⁴⁷⁾. As shown in Figure 4.3, the dashed line is the approximate reduction path and the points lettered a to h correspond to the photomicrographs of Figure 4.1. As in the case for the binary illustration, MgO and CaO were added to the FeO content and the approximate slag analyses A, Al and B are plotted on the diagram.

Each point on the phase diagram is consistent with what is seen in the corresponding photomicrograph and with its chemical analysis, when available. For example, the position of point "e" was found by noting from the photomicrograph (Fig. 4.1e) that fayalite crystals (\sim 90%) precipitated from the slag melt and left an interdentritic eutectic glass (10%), and then performing a mass balance using the chemical analysis of each phase. The position of the eutectic glass can be found on the diagram at the lower end of the iron cordierite phase field. A check of the chemical composition of the eutectic from Table 4.1 will confirm this; the silica being too high by 4% due to the presence of precipitated tridymite. The slag formation and reduction path was found to be a curve rather that a straight line because, it is reasoned, most of the silica, as a constituent of the ore, was available immediately to form fayalite, early and at lower temperatures, whereas dissolution of alumina into the slag would be delayed. About 40% of the alumina input was in the form of bentonite clay and a further 40% would come from the coal ash. Hence, a large portion of the alumina was not available for dissolution until later in the slag formation and reduction sequence.

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Figure 4.3: Phase diagram for the system $\text{FeO-SiO}_2-\text{Al}_2\text{O}_3$ in contact with metallic iron (47).

The formation and decomposition of fayalite under a nitrogen atmosphere have been investigated by Baldwin ⁽⁴⁹⁾. His conclusions were:

- (i) Fayalite can form from an intimate mixture of FeO and SiO₂ above
 800°C by solid-state diffusion; well below its fusion point of
 1175°C.
- (ii) Fayalite forms more readily when alumina is present and when above 1050°C.
- (iii) Formation of fayalite occurs less readily in the presence of magnesia and is completely suppressed by lime; also lime decomposes fayalite.
- (iv) With small amounts of lime (lime/silica ratios < 1), FeO is held in the form of complex iron-calcium silicates. With large amounts of lime (lime/silica ratios > 2), FeO is completely eliminated

from all silicate complexes.

Although Baldwin was investigating pure fayalite, his conclusions help to explain the formation of the "fayalite" in the present work and show that lime and/or magnesia should be used to prevent its formation.

The kinetics of reduction of fayalite by H_2 , CO and CO + H_2 mixtures have been investigated by Gaballah et al. ⁽⁵⁰⁾. They found that it takes about 10 minutes to attain 70% reduction at 1000°C using pure H_2 ; that fayalite is practically irreducible in pure CO, and mixtures of CO + H_2 produced intermediate results, measured in hours (at 950°C). Clearly, in the present work, where a pellet is reduced and melted in under 2 minutes, it can be said that gaseous reduction of a fayalite-type slag is negligible. L. von Bogdandy and Engell⁽⁵¹⁾ describe an investigation by Krainer et al. ⁽⁵²⁾, in which molten slags containing iron oxide were reduced by coke and graphite. They found that slags with 70% FeO and a CaO/SiO_2 ratio of 1:1 were reduced about 7 times as quickly as fayalite (70.5% FeO). No times are given as the slags were trickled through a coke bed.

Three major points need to be emphasized. Fayalite is very easy to form and very difficult to reduce. Reduction by carbon, either as coke or as carbon in liquid iron seems to be the only way to reduce a fayalite slag. The best way to solve the problem is to prevent fayalite from forming in the first place by adding sufficient lime and/or magnesia.

Reduction of ore-coal pellets bonded with bentonite would be expected to produce a slag having a low melting point and a high FeO content. This fayalite-type slag would have a tendency to limit the carbon content of the resultant iron melt to less than 2.0%. Increasing the percentage of coal in the pellet would not raise the carbon content of the iron melt to any appreciable extent. In fact, as discussed in Section 3.4.1, not only was it found that there seemed to be an upper limit of about 2.0%C but raising the coal content of the pellets from the 22-23% range to above 24% was found to be detrimental in that no iron melt was formed at all. After reaction, the pellets disintegrated into a powdery mixture of tiny iron-slag droplets and carbon, because it was reasoned, the excess carbon prevented the droplets from coalescing.

The slag is considered to hinder carbon transfer to the iron melt-in two ways. Firstly, since the slag forms and melts at a temperature below 1200°C, it can physically separate coke from iron by shielding the iron within the iron-slag agglomerates and thereby limit the opportunity for direct contact between coke and iron. Secondly, any high-carbon droplets which are formed, immediately would be engaged in a slag/metal reaction which would lower both the FeO content of the slag and the carbon content of the iron. The slag formed from bentonite-bonded pellets would have very little desulphurizing capacity because its basicity ratio would be extremely low. Also, slags of high FeO content are very corrosive to refractory linings. For these reasons, use of this type of pellet in the high-temperature process presently under consideration, is not recommended.

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4.3.2 Ore-Coke and Ore-Graphite Pellets Bonded with Bentonite

The microstructure at the surface of a partially-reduced 79% ore-19% coke, pellet bonded with 2% bentonite is illustrated in Figure 4.4. After etching the specimen with 2% nital, it was observed that the surface, to considerable depth, was covered with what had been molten iron oxide-iron silicate slag which contained a few patches of high-carbon iron (\sim 4%C). It can be noticed that the coke particles, large and small, touch neither the molten oxide nor the iron.

The microstructure at the surface of a partially-reduced 81% ore-17% graphite pellet bonded with 2% bentonite is illustrated in Figure 4.5. After etching the specimen with 2% nital, two major differences from orecoke pellets became apparent. Firstly, although both specimens contain droplets of high-carbon iron (~4%), the carbon in the iron from orecoke pellets is in the form of cementite, a hard white phase of Fe₃C, while the carbon in the iron from ore-graphite pellets is in the form of very small graphite flakes, imbedded in a pearlitic matrix. It would seem reasonable to assume that the reason for this difference is that graphite surfaces were available which nucleated the growth of graphite flakes in the liquid iron droplet. The second major difference is that the graphite particles in the pellet seemed to be physically attached to high-carbon iron droplets and also, in close proximity to the molten oxide slag.



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Figure 4.4: Microstructure at the surface of a partially reduced 79% ore - 19% coke pellet bonded with 2% bentonite. Nital etch. Magnification 100% or L_____ 100 µm.



Figure 4.5: Microstructure at the surface of a partially reduced 81% ore-17% graphite pellet bonded with 2% bentonite. Nital etch. Magnification 100X.

It will be remembered from the previous chapter (Section 3.4.2) that ore-graphite pellets produced iron which was nearly carbon-saturated, while ore-coke pellets (Section 3.4.3) produced iron with little or no carbon content. A possible explanation is as follows. Reduction of iron oxide in either coke or graphite pellets is delayed until the temperature rises above; say 900°C, because there is no coal, and thus very little hydrogen or hydrocarbon volatiles in the system to promote earlier and faster reduction. Also, since these same gases are absent, they can not cool the pellet surface as they pass through it, and thus the surface rises in temperature at a rate higher than that when using coal as the reductant. From the above and observing the microstructure at the surface of both types of pellets, it may be said that most of the ore melts before it is reduced to iron. When carbon and iron oxide react, the product gas /is CO, which in turn can reduce more oxide. However, in this case, gaseous reduction can be expected to be quite slow. A considerable portion of the molten $\boldsymbol{\omega}$ re can be seen to be an iron silicate or fayalite-type slag. About 15% of a molten ore could become iron silicate if the ore originally contained 5% SiO₂, but this proportion would increase as iron oxide is reduced. As discussed in the previous section, reduction of such an iron silicate slag by CO is negligible. Reduction by carbon or by carbon in liquid iron is considered the predominant mechanism.

From Figure 4.5, it can be seen that the graphite particles maintain contact with the molten iron droplets. It is reasoned that the graphite particles feed carbon to the iron droplets and in doing so, they are themselves dissolved by the iron. The carbon in the iron droplets, in turn,

reduces the molten ore and thus the iron droplet increases in size. The end result is a melt of high-carbon iron, in spite of the fact that the ore melted before it was reduced.

On the other hand, from Figure 4.4, it can be seen that coke particles are less likely to maintain contact with either molten iron or oxide. Some must be in contact, of course, or else there would be no droplets of high-carbon iron. The explanation, which seems the most likely, is that as carbon is removed from a coke particle by an iron droplet, a residue of molten ash builds up and coats the surface of the coke which causes the particle to lose contact with the iron droplet. However, the coke particle is still available for regeneration of CO_2 to 2CO, but in doing so, it finds itself within an envelope of gas, touching neither molten iron nor iron oxide slag. Reduction off-gases, mostly CO, then can blow the coke particles from the pellet and thereby decrease the carbon available for reduction. The carbon in the molten iron droplet is decreased accordingly by reaction with the molten iron oxide slag, and the end result is an iron melt with little or no carbon content.

Ore-coke and ore-graphite pellets had not been considered as feed material for the proposed reduction process. This investigation into their reduction behaviour was part of the inquiry to find reasons why bentonite-bonded ore-coal pellets produced iron of only 2%C content. Coke dust may be used as a reductant in direct-reduction processes operating at lower temperatures to produce sponge iron but it can not be recommended as a reductant in the high-temperature process presently under consideration.

4.3.3 Ore-Coal Pellets Bonded with Cement

A series of photomicrographs showing the internal pellet microstructure, from centre to surface of a partially reduced 63% ore-22% coal pellet bonded with 12% cement (anhydrous) is presented as Figure 4.6a to d. This particular pellet was left in the hot zone of the furnace for some 60 seconds before being cooled; about 10 seconds longer than the bentonitebonded pellet. As a result, reaction at the centre had progressed to the point where liquid slag had formed, while at the surface, the pellet had partially melted into large globules of iron and slag.

Figure 4.6a shows the centre of the pellet where the magnetite had been reduced to wustite and the wustite has been partially reduced to iron. The web-like grey material is coked coal. In some areas, especially in the upper-right corner, some of the calcined cement has been lost from the cut face during sample preparation. A major observation from this photomicrograph is that the wustite had begun to fuse with cement, presumably, to form a glass-like slag. Figure 4.6b is an enlargement of the area in the lower-right corner of Figure 4.6a. Calculations based on stoichiometry show that when hydrated cement is calcined, say during pellet reaction, the remaining constituents are, approximately, 60% 3Ca0.2Si0, (rankinite), 25% CaO and 15% complex calcium aluminates. During reduction, wustite and these phases most likely would react together to form a glass-like Ca-olivine slag, CaO·FeO·SiO₂. The photomicrograph shows this slag as part of the iron-wustite-slag agglomerate. The cellular-like structure probably was caused by off-gases from reduction which bubbled through the semi-liquid mass.





Figure 4.6b: Centre of pellet. Enlargement of lower-right corner of above. Wustite has fused with cement to form a glassy slag (Slag 1). Unetched. Magnification 600X.

Figure 4.6a to d: Illustrations of the microstructure from centre to surface of partially reduced 63% ore-22% coal pellets bonded with 12% cement (anhyd.).


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Figure 4.6c: Subsurface of pellet showing iron-"Slag 2" agglomerates and coke particles. Unetched. Magnification 300X.



Figure 4.6d: Surface of pellet. The iron-slag-coke mixture (right) coalesces upon melting into large drops of iron and "Melt Slag 3" (left). Nital etch. Magnification 100X.

Figure 4.6c shows that just beneath the surface, most of the wustite had been reduced and the iron-slag agglomerate still was in a pasty semifluid state. Figure 4.6d shows the pellet surface at a lower magnification (100X), where the iron-slag-coke mixture collapses upon melting to form large globules of high-carbon iron and slag. The microstructure has been etched with 2% nital in order to show the carbon contents of the iron phases. The iron on the right of the photomicrograph in the iron-slagcoke mixture has very little or no carbon dissolved in it, while the large iron globule on the left contains about 2%C. The white phase within the iron globule is cementite, the dark, pearlite.

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The glass-like material, "Slag 1", tentatively identified as Caolivine, shown in Figure 4.6b, and "Slag 2" from the iron-slag agglomerate shown in Figure 4.6c, were analysed with an electron microprobe. Slag associated with high-carbon globules, which was considered representative as "melt slag" and similar to that shown in Figure 4.6d, was also analysed. Data from each specimen analysis are presented in Appendix A4.2 in the form of computer print-out sheets while Table 4.2 summarizes the chemical composition for each phase. Four separate areas for each of the three phases were averaged.

As a pure compound, Ca-olivine contains by weight, 38% FeO, 30% CaO and 32% SiO₂. From Table 4.2 it can be seen that the wustite-cement reaction product, Slag 1, is in fact Ca-olivine. Slag 2 and Melt Slag 3 show progressively lower FeO contents which implies that the Ca-olivine slag was reduced progressively until the final melt slag composition was %reached. It can be seen that the melt slag holds more sulphur than that

from reduction of bentonite-bonded pellets, mainly due to its increased basicity ratio. Also, the melt slag contains very little FeO.

The formation of Ca-olivine and the reduction path of wustite and slag, can be illustrated by plotting the slag compositions on a CaO-FeO-SiO₂ phase diagram⁽⁴⁸⁾. As shown in Figure 4.7, the dashed line is the approximate slag formation and reduction path and the points numbered 1, 2 and 3, correspond to the slags shown in the photomicrographs of Figure 4.6. The compositions from Table 4.2 were simplified somewhat by adding the small amounts of Al_2O_3 and MgO to SiO_2 and CaO respectively which may shift slightly the phase boundaries and liquidus isotherms, but not enough to upset the illustration.

	Slag 1 wt %	Slag 2 · wt %	Melt Slag 3 wt %				
MgO AlaOa	2.9 0.4	2.3 3.7	4.1 5.4				
Si0 ₂	32.5	31.4 .	38.3				
S KoQ	0.1*	0.4 0.0*	0.8 0.1*				
CaO	32.4	45.1	. 46.7				
Fe0	33.8	14.9	, 2.1				
Total	102.1	97.8	97.5				
* - trac	* - trace amounts						

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Table 4.2: Electron-microprobe analyses of slags formed during reduction of ore-coal pellets bonded with cement



Figure 4.7: Phase diagram for the system CaO-FeO-SiO₂ in contact with metallic iron (48).

The path from FeO to Slag l is unknown and hence was drawn as a straight line. The wustite-cement reaction forming Ca-olivine most likely started through solid-state diffusion at a temperature somewhat below the melting point of any of the phases involved. After the temperature rises sufficiently to allow the Ca-olivine to melt, the reaction would proceed much faster with both wustite and cement phases feeding the slag melt. Another point to remember, is that while Ca-olivine slag is being formed other wustite grains are being reduced by C, CO and H_2 .

In Section 4.3.1, a discussion point was that Krainer et al.⁽⁵²⁾ found that slags with a CaO/SiO_2 ratio of 1:1 were reduced 7 times as quickly as a fayalite slag. The present work seems to be in agreement, for the melt slag from cement-bonded pellets carries very little FeO while the reduction time is about the same as for bentonite-bonded pellets.

Reduction of ore-coal pellets bonded with cement would be expected to produce a slag with a low FeO content as well as a high-carbon iron melt which would be desulphurized to a considerable extent. However, such pellets would carry a heavy penalty in that they would produce slag weights of the order of 350 kg/tonne of iron.

4.3.4 Ore-Coal Pellets Bonded with Carbonate

A series of photomicrographs showing the internal pellet microstructure, from centre to surface of a partially reduced 66% ore-23% coal pellet, bonded with 11% calcium-magnesium carbonate (4.7% CaO + 1:2% MgO, as calcined flux), is presented as Figure¹⁴.8a to f. The pellet maintained its original radius of about 6 mm, but cracked somewhat during reduction. Also, this pellet was left in the hot zone of the furnace for some 40 seconds before being cooled; about 10 seconds shorter than for the bentonite-bonded pellet.

At the centre of the pellet (Fig. 4.8a) it can be seen that iron had not yet nucleated on the wustite particles. In fact, etching of the specimen in an aqueous solution of SnCl₂ revealed that some of the larger particles had centres which were still magnetite (Fig. 4.8b). The weblike grey material is partially coked coal and upon closer examination some carbonate or perhaps lime can be seen, but most seems to have been lost during sample preparation. In both upper and lower right-hand corners of Figure 4.8a, large silica particles can be identified.

At a radius of about 3 mm (Fig. 4.8c) iron had begun to nucleate and grow on the wustite grains and at 5 mm (Fig. 4.8d) each wustite grain had an envelope of very porous iron. It can be noticed also, that the silica particles, for the most part, had been constrained by the presence of lime to maintain their integrity and not form large amounts of iron silicate slag. At the pellet surface (Fig. 4.8e), all of the individual wustite grains have been reduced fully into rosettes of iron. Interwoven with the iron rosettes are particles of coke and areas of slag.

The pellet described above had been left in the hot zone of the furnace for only 40 seconds before being cooled and therefore, the pellet surface had not yet begun to melt. Another pellet of similar composition was allowed to remain in the hot zone for 60 seconds before being cooled. Melting was nearly complete and the end products, slag and iron, are shown in Figure 4.8f. Coalescence of iron and coke into drops of iron of about 4%C content was extremely fast and no evidence of an intermediate stage was found. The melt slag was opeque and greyish in colour and is shown on the left of the photomicrograph. Etching of the specimen with 2% nital in order to show the carbon content of the iron also etched the slag which revealed a dendritic solidification pattern.

The reduction of iron oxide grains into iron rosettes within a carbonate-bonded pellet is so radically different from that which happens in a bentonite-bonded pellet, that it bears closer examination. During the reduction of bentonite-bonded pellets, a low melting point fayalite slag was formed which coalesced into an iron and liquid slag agglomerate. The end products were a slag which had a high FeO content and an iron melt which had low carbon and high sulphur contents. On the other hand, during the reduction of carbonate-bonded pellets, each iron oxide grain was reduced individually into an iron rosette by H_2 and CO gases. There was no evidence of a low melting point slag nor any agglomeration. The end products were a slag containing little or no FeO and an iron melt of high carbon and low sulphur contents. Success seems to be tied to two things; reduction of iron oxide while in contact with lime, and the reaction of silica with lime which prevents the formation of an iron silicate slag.



Figure 4.8a: Centre[>] of pellet. Wustite grains and large silica particles (upper and lower right corners). Web-like material is coked coal. Unetched. Magnification 300X or _____ 30 µm.



Figure 4.8b: Centre of pellet. Many wustite grains still had centres of magnetite. Etched. Magnification 500X.

Figure 4.8a to f: Illustrations of the microstructure from centre to surface of partially reduced 66% ore - 23% coal pellets bonded with 11% (calcium + magnesium) carbonate. 1



Figure 4.8c: At radius of $\sqrt{3}$ mm. Iron had begun to nucleate and grow on the wustite grains. Unetched. Magnification 300X.



Figure 4.8d: At radius of ∿5mm. Each wustite grain developed an envelope of porous iron. Very little reaction between silica (upper centre) and wustite. Unetched. Magnification 300X.



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Figure 4.8e: Surface of pellet. Individual wustite grains have been reduced into rosettes of iron. Unetched. Magnification 300X.



Figure 4.8f: Final products, iron containing ~4%C and "Melt Slag C" (left). Nital etch. Magnification 100X.



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Figure 4.9a: Partially reduced wustite grains. Unetched. Magnification 600X or $13 \mu m$.

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Figure 4.9b: Partially reduced wustite grain. Etched. Magnification NOOX or ____10 µm. Depicted in Figure 4.9a are partially reduced wustite grains in the unetched condition, while Figure 4.9b shows, at a magnification of 1000X, one wustite grain which had been etched with SnCl₂ in ethanol. The Widmanstatten-type microstructure is typical of all of the partially reduced wustite grains and indicates that at the higher temperatures during reduction these grains, tentatively identified as calcio-wustite, were single-phased, but when cooled, calcium ferrite, most likely, precipitated onto the crystallographic planes of the wistite.

Analyses of a number of the partially reduced wustite grains were performed with the electron microprobe. Also analysed, were specimens of the greyish "Melt Slag C" from the partially melted pellet shown in Figure 4.8f. Since the slag can be seen to have primary dendrites and an average chemical analysis was desirable, the specimens were moved slowly over distances of about 500 microns during each 200 second analysis. Data from each specimen analysis are presented in Appendix A4.2 in the form of computer print out sheets while Table 4.3 summarizes the chemical composition of "Melt Slag C" (an average of four separate areas) and seven separate grains of calcio-wustite.

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	Melt Slan C		Calcio-wustite Grains wt %						
	wt %	1	2	3	4	5	6	7	
MgO	11.6	0.0* \							
A1203	4.1	0.2*							
si0 ₂	38.1	0.4	<pre>average of 7 grains * - trace amounts</pre>						
S	0.8	0.1*							
к ₂ 0	0.1*	0.0*		,					
Ca0	40.3	11.5	8.2	5.6	7.2	5.6	1.9	2.4	
Fe0	0.8	85.0	91.8	90`. 4	87.7	92.4	95.1	95.9	
Total	95.8	97.2	100.7	96.7	95.6	98.7	97.7	99.0	

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Table 4.3: Electron-microprobe analyses of slag formed by the reduction of carbonate-bonded ore-coal pellets, and of partially reduced calcio-wustite grains.

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The carbonate-bonded pellets used in these partial reduction experiments were from the lot identified as L9-1. From an input material balance the expected slag composition was calculated to be

12.7% MgO, 5.4% A1₂O₃, 37.8% SiO₂, 44.1% CaO

and was plotted on the phase diagram of Figure 3.4 in Chapter 3. Comparing the composition of "Melt Slag C", listed in Table 4.3 with the calculated values above, it can be seen that there is one minor but explainable difference. The actual lime content falls short of the calculated value by a small amount. The explanation is that the liquidus temperature of the calculated slag was about 1550°C whereas the reduction test temperature was 1500°C. Thus a small amount of lime did not dissolve into "Melt Slag C" and was left as a powder. The microprobe analyses were performed only on the large drops of solidified slag found in the specimen. In any case, most of the powder would have been lost during specimen preparation. These results, especially the minor difference between calculated and actual lime contant of the internal pellet slag, confirm the arguments put forward in Section 3.5.4 of the previous chapter; viz., in order to be effective, the slag should be molten and all lime and magnesia should be dissolved in it.

The seven wustite grains which were analysed with the microprobe were typical of all the partially reduced grains in the specimen and as shown in Table 4.3, they contained CaO in amounts varying from 1.9 to 11.5%. The grains were chosen at random and were unetched at the time of the analyses. In a recent publication by Schurmann and Kraume⁽⁵³⁾, the phase diagram FeO-CaO, at iron saturation, has been defined and is shown as Figure 4.10. It would seem that during reduction the carbonate bonding material was calcined and the resulting lime diffused into the iron oxide (now wustite) grains. At 1100°C, wustite can be seen to accommodate up to 12 wt % CaO. If, as in the present work, the calcio-wustite was cooled quickly, calcium ferrite, $2CaO \cdot Fe_2O_3$, would precipitate and as shown in Figure 4.9b, it takes a habit parallel to the crystallographic planes of the calcio-wustite.

A significant observation and one with no satisfactory explanation is that the partially reduced calcio-wustite grains analysed by the microprobe, contain little or no MgO. This was unexpected because 20% of the calcined flux (CaO + MgO) addition was MgO. Further investigation into this anomaly is indicated.

Normally, during the reduction process, the calcio-wustite grains are not cooled but increase in temperature and are reduced completely into individual iron rosettes before melting. Over the past several decades, many researchers have investigated the beneficial effects of calcium compounds on the reducibility of iron oxides (54 to 58). A detailed review of the various reduction mechanisms for calcio-wustite postulated by these researchers is beyond the scope of the present work.



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Briefly, Seth and Ross⁽⁵⁴⁾ put forward the view that calcio-wustite is unstable and dissociates into metallic iron and dicalcium ferrite. Furthermore, upon reduction, dicalcium ferrite yields iron and lime, the lime being available to react again with more wustite. The authors admit that this explanation is probably an over-simplification. Khalafalla and Weston(55) found that small additions of alkali and alkaline earth metal oxides exert a strong accelerating effect on reduction of wustite to iron. The extent of the reaction rate enhancement was found to be proportional to the ionic radius and electronic charge of the accelerating additive. The increase in rate was attributed to lattice distortion of the wustite caused by the addition of small amounts of relatively large interstitial ions (Ca⁺⁺). This lattice distortion affects the wustite surface thereby activating it to reducing gases. It would also enhance the diffusion of Fe⁺⁺ ions from the gas/solid reaction surface to the nucleated iron⁽⁵⁶⁾. A treatise by E1-Kasabgy⁽⁵⁹⁾ reviews this area in detail and provides further evidence that lime as a solute in magnetite or wustite increases the rate of reduction of iron oxide.

In order to recapitulate events that occur when carbonate-bonded pellets are reduced, it is best to return to the beginning. When such pellets enter the hot zone of the furnace, the coal starts immediately to volatilize (above 400°C), but the carbonate bonding within the pellet is somewhat slower to react. Appreciable amounts of carbon dioxide would evolve from the carbonate bonding only above 800°C. Pressures may build within the pellet which could cause cracking; a concern which should be investigated at a later date. Sulphur is both an organic and mineral constituent of coal. During volatilization, the organic sulphur is evolved, perhaps as H₂S, which can react with many constituents of the pellet, e.g., CaO, MgO, FeO or Fe. The mineral form of sulphur, mainly FeS, would remain relatively inert at lower temperatures and would react with the basic slag at a later time.

Hydrogen, carbon monoxide and carbon reduce the iron oxide particles; wustite and lime react to form calcio-wustite which in turn is reduced very quickly by the gaseous reductants.

Lime and magnesia react with the silica and alumina of the ore and with the coal ash to form a basic slag and thereby prevent the formation of fayalite, olivine, or other iron silicate slags.

The carbon left as coke after volatilization of the coal, acts mainly to regenerate the reduction off-gases H_20 and CO_2 into more H_2 and CO. When reduction is complete, the coke particles are entrapped within a mesh of reduced iron and during the melting stage, they supply carbon to the incipient iron melt.

Reduction of ore-coal pellets bonded with carbonate would be expected to produce a slag with a low FeO content, as well as a highcarbon melt. Also, the melt would be desulphurized to a considerable degree. For these reasons, this type of pellet should be considered as feed material for the high-temperature reduction process presently under consideration.

4.4 Summary

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Composite pellets of iron ore and coal bonded with bentonite, cement and carbonate were partially reduced and examined metallographically and by microprobe analysis in order to obtain a clearer understanding of the reaction mechanisms within each type of pellet.

Reduction of ore-coal pellets bonded with bentonite produced an agglomerate of fayalite slag and iron which when melted completely resulted in an iron melt containing less than 2%C and high sulphur content. The slag formed from such pellets would be expected to have a high FeO content. This type of pellet is not recommended for the process under consideration.

Ore-coke and ore-graphite pellets bonded with bentonite are also not recommended mainly because there is insufficient gaseous reduction of the iron oxides within the pellets and the ore melts before it is reduced.

Reduction of ore-coal pellets bonded with cement produced an agglomerate of Ca-olivine slag and iron, but the initial high FeO content of the slag was reduced quickly. The final products would be expected to be a slag with a low FeO content and an iron melt of high carbon content which would be desulphurized to a considerable extent. Cement-bonded pellets would carry a penalty in that they would produce a large amount of slag and therefore can be considered a second choice, at best.

During the reduction of ore-coal pellets bonded with carbonate, each iron oxide particle reacted with lime to form a calcio-wustite grain which was reduced individually into an iron rosette. No intermediate slag of high FeO content was formed. The final products would be expected to be a slag with a very low FeO content and an iron melt of high carbon and low sulphur contents. This type of pellet should be considered as the feed material for the high-temperature reduction process presently under study.

CHAPTER 5

ANALYSIS OF THE OFF-GAS FROM PELLET REDUCTION

5.1 Introduction

The overall reaction of pellet reduction, which is a summation of several chemical reactions, is endothermic. Hence thermal energy must be supplied to the process. One way to do this is to burn the off-gas from reduction with oxyger, within the reactor. In order to calculate how much heat would be made available by combustion, the chemical composition of the off-gas must be known. To this end, pellet reduction experiments were performed wherein the cumulative volume of the off-gas was measured and concurrently, gas samples were taken for chemical analyses by gas chromatography.

The pellets used in these experiments were from the lot identified in Chapter 3 as K1 and were composed of 62.8% ore, 22.0% coal and 12.2% cement (anhydrous). After hydration and drying the rement proportion rose to 15.2%, the increase in weight being water of hydration. These off-gas analysis experiments were performed concurrent to the K series (cement bonding) and prior to the L series (carbonate bonding) of experiments on the reduction of self-fluxing pellets. The high water loading from cement-bonded pellets represents, as will be discussed later, the worst case when seeking a highly combustible off-gas from pellet reduction.

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5.2 Experimental Procedure

An alumina crucible was held in the resistance tube furnace at 1500°C. Two pellets, totalling about three grams were held by a small cotton thread within the furnace, at the top where the temperature was about 100°C. The furnace was purged first with argon, then simultaneously, a very small piece of pellet (about 0.1 g) was dropped into the crucible to react and the flow of argon was shut off. This procedure displaced most of the argon from the furnace and subsequent gas train and replaced it with a gas of roughly the same composition as that which would be measured. After resetting the volume meter to zero, the test pellets were allowed to drop into the crucible to react.

A large volume of off-gas and soot formed immediately and this passed through a heated furnace cap, a glass wool filter, a dew-point indicator, and lastly, a wet test meter where the cumulative volume was measured at ten-second intervals. A small section of polyethylene tubing between the furnace cap and the dew-point indicator allowed syringe sampling of the off-gas. The sampling times during the 120 sec. runs, were approximate but could be grouped into samples taken at 15, 20, 30 and 40 seconds. After several preliminary trials, five test runs were carried out. On two runs, high pressure during the first few seconds caused some leakage from the furnace cap and thus they could not be used for volume data, but the remaining three were averaged for a volume verses time plot. Syringe samples of the off-gas from all five test runs

5.3 Chemical Analysis

Gas analyses were performed using an F & M Scientific 700 Laboratory Chromatograph, manufactured by Hewlett-Packard. Two separating columns were used; a column of silica gel for CO_2 analysis and molecular sieve 5A for H₂, O₂, N₂ and CO. The columns were kept at 40°C while an argon carrier gas was used at a flow rate of 20 ml/min. The filament current of the thermal conductivity detector was 120 mA while its temperature was kept at 80°C. Operating techniques for gas chromatography vary according to equipment and columns used, and to the gases being analysed. Hence the reader is referred to the literature^(60,61) for detailed chromatograph techniques.

Preliminary analysis showed that immediately after dropping the pellets into the hot crucible, the off-gas from coal gasification contained about 0.2 vol.% CH_4 and a trace of H_2S at a level near the detection limit (0.1 vol.%). These amounts were deemed to be insignificant and thus the five gases mentioned previously, along with water \checkmark vapour, were considered to be the constituent gases. which were to be analysed. At no time during the reduction tests did the amount of sulphur in the off-gas rise above the detection limit of the analysis.

Calibration curves were obtained by injecting various known amounts of air $(O_2 \text{ and } N_2)$, H_2 , CO and CO_2 into the columns and then measuring the areas under their respective response peaks with a planimeter. This resulted in a graph of area verses volume percentage for each of the gases. The 2 ml syringe samples from the reduction experiments were injected into the columns and the areas of the response peaks were calculated and compared to the calibration curves. Since the pellet reduction tests took place in an air-free atmosphere, and in the presence of carbon, no detectable free oxygen was expected in the off-gas. When oxygen was detected, it was assumed to come from air leakage into the syringe at the time of sampling and so, an equivalent amount of nitrogen was subtracted from the nitrogen values. Two out of a total of fourteen samples were rejected because of excessive air leakage; the rest had $0.6\% 0_2$ or less. The water vapour content was calculated from the dewpoint measurements.

It should be emphasized here that a highly accurate chemical analysis was not necessary in view of the objective. In order to calculate heats of combustion, it was necessary only to identify the off-gas constituents along with their approximate volume percentages. For example, at low percentage levels, i.e. at 1.5% CO₂, the estimated accuracy is $\pm 0.3\%$ CO₂. When reporting CO (or H₂) values at the higher percentage levels, e.g. at 54% CO, the estimated accuracy is $\pm 3.0\%$ CO. These stimated accuracies were quite sufficient to allow combustion calculations and graphical representation of the chemical analysis. The first decimal place is used only to show the most probable composition and thus no attempt was made to have the gas percentage total 100%.

5.4 <u>Results</u> and Discussion

5.4.1 <u>Cumulative Volume and Rate of Gas Evolution</u>

The cumulative volume in litres, of the off-gas from reaction of ore-coal pellets bonded with cement was measured at 28°C and at an atmospheric pressure of 749 mm Hg. Three separate runs were averaged; then the volumes were converted to litres per gram of pellets and corrected to STP (0°C and 760 mm Hg). Table 5.1 lists the data. The corrected values were plotted versus time to obtain the curve labelled "Cumulative Volume" in Figure 5.1. This shows that there was about 0.44 litre of gas produced per gram of pellets. Also, a "Rate of Gas Evolution" curve was determined graphically by plotting the instantaneous slopes of the volume curve (dV/dt at time t). These rate values, labelled "R" are listed in the last column of Table 5.1. From Figure 5.1, it can be seen that after an initial induction period of about one second, the off-gas evolved at a very high rate due to the rapid gasification of coal, decomposition of cement and iron ore reduction. This was followed by a sharp decrease in evolution rate and after about 90 sec., off-gassing stopped. The pellets took a further 20 sec. or so before collapsing into a molten iron droplet.

Time	Cumul litr anc Run 2	ative Vo res at 28 1 749 mm Run 4	olume 30C Hg Run 5	Volume Average ≬∕a	Volume at STP	Evolution Rate, R x10 ³
				~/ 9	~/9	~795
	0.00	0.00	0.00	.000 、	0000. ز	19.5
`10	0.50	0.41	0.43	. 144	. 129	13.0
20 -	0.95	0.72	0.75	.258	.231	8.4
30.	1.20	0.97	0.98	. 338	. 30 2	5.6
40	1.45	1.10	1.13	.393	.351	4.4
50	1.60	1.21	1.25	. 433	.387	2.9
60	1.70	1.28	1.33	. 460	.411	2.0
70	1.80	1.31	1.37	.477	. 426	1.2
80	1.85	1.32	1.38	.483	. 432	0.5
90	1.87	1.33	1.39	. 488	.436	0.0
Weigh	t of Pel	llets rea	acted, g			
	3.98	2.75	2.73	_		

Table 5.1: Cumulative volume data of the off-gas from reaction of cement-bonded ore-coal pellets.

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5.4.2 Chemical Composition of the Off-gas from Cement-bonded Pellets

The instantaneous chemical analyses of the off-gas measured at various times during pellet reaction, are given in Table 5.2. The data in the table labelled "e", were estimated by taking cognizance of experimental conditions and thermochemistry. Detailed calculations and explanation are given in Appendix A5.1.

The rate curve of the total gas mixture can now be partitioned according to chemical composition so as to obtain the corresponding rate curves for the individual components of the mixture during reaction. Firstly, the rates of gas evolution (R = dV/dt) for the total gas mixture were obtained from the graph of Figure 5.1 at 1, 15, 20, 30 and 40 seconds. Then the rates were apportioned according to the chemical composition of the off-gas which had been sampled at those pertinent times. By way of example, the off-gas at 15 sec. evolved at a rate $R = 10.5 \times 10^{-3} \text{ k/gs}$. Since the hydrogen content of this gas at that time was found to be 47%, then hydrogen evolved at (10.5×10^{-3}) $\times 0.47 = 4.9 \times 10^{-3} \text{ k/gs}$. The evolution rate $R_i = dV_i/dt$ (at time t) has been calculated in this manner for each component "i" of the off-gas mixture and listed in Table 5.3. Hence, it has become possible to plot the evolution rate curves for H₂, C0, H₂0, C0₂ and N₂ as shown in Figure 5.1.

It can be observed from the gas evolution curves that the gasification of coal and the cracking of the hydrocarbons produced hydrogen (and perhaps some methane) at a very high rate at the beginning, then tapered off, while carbon monoxide from the combined ore-carbon reactions, increased. After about 50 sec., the coking of the coal in the pellets seemed to be completed since hydrogen evolution ceased and the off-gas

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	Chemical Analysis, Vol. %							
Gases	l sec.	15 sec.	[•] 20 sec.	30 sec.	40 sec.			
H ₂	86.e	47.	39.	15.5	9.0 .			
со	6.e	46.	54.	81.	88.			
H ₂ 0 .	3.4e	3.4	2.8e	0.8e	° 0.4e			
. ^{C0} 2	1.5e	1.5	1.5	1.4	1.2			
N ₂	3.0e	2.5	1.8	1.1	1.1			

e - estimated

Table 5.2: Chemical analysis of the off-gas sampled at various times during pellet reaction.

		1 s	ec.	· 15	sec.	20	sec.	30	sec.	40	sec.
		vo1%	$R \times 10^3$	vo1%	R x10 ³	vol%	R x10 ³	vol%	R x10 ³	vol%	R x10 ³
OFF	-GAS	100.	19.5	100.	10.5	100.	8.4	100.	5.6	100.	4.4
	H ₂	86.e	16.7	47.	4.9	39.	3.2	15.5	0,9	9.0	0.4
6	со	6.e	1.2	4Ġ.	4.7	54.	4.6	81.	4.5	88.	3.9
ENT:	H ₂ 0	3.4e	0.7	3.4	0.4	2.8e	0.3	0.8e	0.1	0.46	0.0
NDGM	с0 ₂	1.5e	0.3	1.5	0.2	1.5	. 0 . 1	1.4	0.0	1.2	0.0
22	N ₂	3.0e	0.6	2.5	0.3	1.8	0.1	1.1	0.0	1.1	0.0

e - estimațed

units of R - litre/gram-second at STP

Table 5.3: Partition of R, the rate of gas evolution from pellet reaction, according to the chemical composition of the off-gas.

became mostly carbon monoxide. It should also be noted that there were no significant amounts of H_2O , CO_2 or N_2 in the off-gas at any time during the reaction.

In an industrial process, it is most likely that pellets would be fed continuously into a reduction vessel. The chemical composition of the off-gas to be burned within the reactor would be, in essence, the average composition of the off-gas from an individual pellet. In Figure 5.1, the area under the "Rate of Gas Evolution" curve represents the total volume of gas evolved per gram of pellets reacted. Simifarly, the area under the rate curve for each off-gas constituent represents its volume component of the total gas volume. Hence, by comparison of the areas under the curves (volumes), the component percentages of the total gas volume (average off-gas composition) were calculated and listed in Figure 5.1 and Table 5.4. The major observation is that 94% of the off-gas was composed of hydrogen and carbon monoxide, in nearly equal proportions.

OFF-GAS COMPONENTS	:	VOLUME PERCENTAGE
H ₂		41. ± 3.
. CO	,	53. ± 3.
H ₂ 0	•	2.7± 0.6
^{C0} 2	, ^x ,	1.2± 0.3
N ₂		2.1± 0.5

Table 5.4: Average chemical composition of the off-gas from reaction of ore-coal pellets bonded with cement.

The reaction of cement-bonded pellets produced an off-gas which was highly combustible in spite of the high water content of the cement. The release of water upon the heating of Portland cement is very complex $^{(62)}$ but most of the combined water will have been driven off by the time the cement reaches 600°C. In the present case, where a pellet was being heated from its surface towards its center, water vapour was being continuously supplied to the off-gas. If this water vapour had escaped unreacted, there would have been about 11% in the off-gas instead of 2.7%. Since there was an abundance of CO in the off-gas, the water vapour most likely reacted with CO (water-gas shift reaction) to produce H_2 and CO_2 . Also, hot carbon particles within the pellet would be available for reaction with water vapour (water-gas reaction) to produce H₂ and CO. Carbon and iron also act as catalysts for the shift reaction $^{(63)}$ which would help to lower the water vapour content of the off-gas at lower temperatures. These reactions have been discussed more fully in Appendix A5.1.1; the main point of discussion here is that the water vapour emanating from the cement had ample opportunity to react with either CO or carbon within the pellet.

One problem which has not yet been pursued is an ϵ -timate of the amount of carbon soot entrained in the off-gas. This problem can be approached by considering coke-oven gas, in which about 60% by weight of the hydrogen content of the coal evolves during coking in the form of hydrocarbons, mostly methane (CH₄). This same ratio should apply to the volatilization of the coal in the outer regions of a pellet. Carbon soot was formed as the off-gas emerged from the pellet surface during the first 15 sec. of a test run. From the hydrogen curve of Figure 5.1, this corre-

sponds to about 75% of the coal in the pellet having been coked or in the coking stage. Hydrocarbon volatiles from coal nearer the pellet's centre cracked within the hot pellet and as a result, only hydrogen escaped.

The cement-bonded ore-coal pellets (K1) used in these experiments contained 22.0% coal of which 5.4 wt % was hydrogen. The weight of hydrogen input from the coal per gram of pellet was

 $0.22 \times 0.054 = 0.012 \text{ g H}$

Hence, the amount of carbon soot entrained in the off-gas was

0.012 g H x 0.60 x
$$\frac{12}{4} \begin{pmatrix} C \\ H_4 \end{pmatrix}$$
 x 0.75 = 0.016 g C

in 0.44 L of gas. Thus, it is estimated that in one cubic metre of offgas there was $(0.016/0.44) \times 1000 = 37$ g of carbon soot. In a later section, this value will be used in calculating the heat of combustion of the off-gas. The contribution to the heat of combustion by the soot was found to be about 10% of the heat value, and thus, even a large error of say 30% in the estimate of soot in the off-gas would affect the overall heat value by only ±3%. However, since a large amount of soot was observed during the first 15 sec. of pellet reaction, it would be a serious oversight not to consider it in the calculations.

5.4.3 Off-gas from Carbonate-bonded Pellets - Estimates of

Volume and Composition

In previous chapters it was shown that reduction of carbonatebonded pellets produced a melt with the desired carbon and sulphur levels. Hence, it would be of interest to know the approximate off-gas composition from reaction of this type of pellet.

A major difference between carbonate-bonded and cement-bonded pellets is that during reaction there would be a continuous supply of carbon dioxide from the carbonate bonding material instead of water vapour from the cement. However, appreciable amounts of carbon dioxide evolve from carbonate only above 750°C. Also, there would be an abundant supply of carbon from soot and coal (now coke particles) in excess of say, 900°C with which the carbon dioxide would react before it could leave the pellet, i.e.,

 $CO_{2(q)} + C_{(S)} = 2CO_{(q)}$ (Boudouard reaction)

The standard free energy change for this reaction is

ΔG° = 40,800 - 41.7 T cal/mol

which has been obtained from Kubaschewski et al.⁽⁶⁴⁾.

The equilibrium constant K, for this reaction can be found from the free energy equation, $\Delta G^\circ = -RT \ln K$.

 $\log K = \frac{-\Delta G^{\circ}}{4.575 \text{ T}} = \frac{-8920}{\text{T}} + 9.11$

Hence

At 900°C (1173°K), K = 32, but also by definition

$$K = \frac{p_{co}^2}{a_c \cdot p_{co_2}} = \frac{p_{co}^2}{p_{co_2}} = 32$$

where the activity of carbon $a_c = 1$ and p_{co} and p_{co_2} are the partial pressures of CO and CO₂ respectively. If $p_{co} + p_{co_2} = 0.70$; the remainder of the gas being mostly hydrogen, then substition of $p_{co_2} = 0.70 - p_{co}$ gives

 $p_{co}^2 + 32 p_{co} - 22.4 = 0$

whence $p_{co} = 0.685$ and $p_{co_5} = 0.015$ (equiv. to 1.5 vol % CO_2).

From the above calculation, it can be seen that should the gases approach the Boudouard equilibrium, which is most likely, then the carbon dioxide content of the off-gas would be controlled to a very low level, especially if the reaction temperature was above 1000°C. Indeed, this is so even in cement-bonded pellets because iron ore reduction has been shown to be a set of sequential reactions, viz:

> $Fe_3 0_4 + C0 = 3 Fe_0 + C0_2$ Fe_0 + C0 = Fe + C0_2

 $GO_2 + C = 2 CO$ (Boudouard reaction)

Thus, it can be reasoned that since the Boudouard reaction plays a major role in both cases, the average carbon dioxide content of the off-gas from carbonate-bonded pellets should be about the same as that from cementbonded pellets, i.e., 1 to 2%. In order to obtain the volume and composition of the off-gas from carbonate-bonded pellets, the following calculations are considered sufficient when the objective is to obtain an approximate heat of combustion term. Moreover, calculations of this type alleviate needless repetition of difficult and time-consuming experiments. Pellets from lot L9-2 (Chapter 3) were chosen as input material to an assumed reduction experiment because their composition was shown to be one of the more promising of the carbonate-bonded pellets which were reduced to metal.

Pellet Analysis

66% ore of 94% magnetite and 6% gangue

23% coal of 5.4% H, 5.2% O, 82.4% C and 4.7% ash

7.4% CaCO₂ of 56% CaO, 44% CO₂

3.7% MgCO3 of 48% MgO, 52% CO2

Basis for calculation -- 1 gram of pellet (dry)

Input of hydrogen (H): .

from coal: 0.23 × 0.054 = 0.0124 g

Input of oxygen (0): from ore: $0.66 \times 0.94 \times 64/232 = 0.171$ g from coal: $0.23 \times 0.052 = 0.012$ from CaCO₃: $0.074 \times 0.44 \times 32/44 = 0.024$ from MgCO₃: $0.037 \times 0.52 \times 32/44 = 0.014$ Total oxygen input = 0.221 g

In order to keep the calculations from becoming too cumbersome an approximate total off-gas volume may be obtained by summing the input hydrogen as H_2 and the input oxygen as CO. This manoeuvre is possible and would

cause little error because from the experience gained in measuring the off-gas from cement ponded pellets, 95% of the off-gas would be expected to be a mixture of H_2 and CO. The minor constituents of the off-gas would be expected to be 1% H_2O , 2% CO_2 and 2% N_2 . <u>Approximate volume</u> of the off-gas:

as H_2 : 0.0124(g x 11.1 ℓ/g = 0.138 ℓ as CO : 0.221 g x 0.80 ℓ/g x 28/16 = 0.309 Approx. total volume = 0.447 ℓ

Individual percentages may now be calculated while recalling that the volumes of the major constituents should be reduced by 5% to allow for the minor constituents. Thus the expected off-gas composition from carbonate-bonded pellets is as follows.

 $H_2 : 0.138 \times 0.95/0.447 = 30\% (vol.)$ CO : 0.309 x 0.95/0.447 = 65% $H_20: = 1\%$ CO₂: = 2% $N_2 : = 2\%$

This calculated analysis is approximate but reasonable. Replacing cement with carbonate as pellet binder lowers the water input and therefore lowers the H₂ content of the off-gas but increases the CO_2 input which in turn, increases the CO content of the off-gas. This analysis, though limited by the very nature in which it was calculated, is quite sufficient to estimate a heat of combustion value of the off-gas from carbonate-bonded pellets. It is expected that the amount of carbon soot carried by the gas would be about the same as for cement-bonded pellets, i.e., 37 g/m^3 .

5.4.4 Heats of Combustion and Flame Temperatures

In order to provide heat for the overall reduction reactions, which are endothermic, and to compensate for heat losses to the surroundings, it is proposed to burn the off-gas and entrained carbon soot with oxygen which would be lanced into the reduction vessel. It is reasonable to assume that in the proposed process, the off-gas emerging from the reacting pellets would be at the process temperature (about 1500°C) just prior to combustion with oxygen (25°C). A heat balance of the overall process, to be presented later, will account for this sensible heat along with other considerations. Here, the heat of combustion of the off-gas will be calculated at 25°C in order that the net heating value so obtained may be compared with those of other fuels.

The average chemical composition of the off-gas from cement-bonded pellets was found to be, by volume,

41% H_2 , 53% CO, 2.7% H_2O , 1.2% CO_2 and 2.1% N_2 . The entrained carbon soot was estimated to be 37 g per cubic metre of off-gas at STP. The heats of reaction⁽⁶⁴⁾ for burning hydrogen, carbon monoxide and soot with oxygen are:

 $H_{2(g)} + \frac{1}{2} O_{2(g)} = H_{2}O_{(g)}; \Delta H_{298K}^{\circ} = -57.8 \text{ kcal/mol}$ $CO_{(g)} + \frac{1}{2} O_{2(g)} = CO_{2(g)}; \Delta H_{298K}^{\circ} = -67.65 \text{ kcal/mol}$ $C_{(s)} + O_{2(g)} = CO_{2(g)}; \Delta H_{298K}^{\circ} = -94.05 \text{ kcal/mol}$

The basis for calculation will be one cubic metre of off-gas at STP, carrying 37 grams of carbon soot. Also, since the chemical composition of the off-gas is given as a volumetric percentage, it will be
recalled that the volume of 1 g mol. of an ideal gas occupies 22.4 litres (0.0224 m^3) at STP. The heat evolved is,

from H₂: $(0.41/0.0224) \times 57.8 = 1060 \text{ kcal}$ from CO: $(0.53/0.0224) \times 67.65 = 1600$ from C : $(37/12) \times 94.05 = \underline{290}$ Total heat evolved = 2950 kcal

(12350 kJ)

The net heating value, sometimes called calorific power, of the off-gas from cement-bonded ore-coal pellets is 2950 kcal/m³ (12350 kJ/m³) or (330 Btu/ft³). Similar calculations for the off-gas from carbonate-bonded pellets yield a net heating value of 3030 kcal/m³ or (340 Btu/ft³). The off-gas analyses and heating values for the two types of pellets are summarized in Table 5.5. For comparison, the net heating values of blast-furnace gas is about 95 Btu/ft³; of coke-oven gas, about 510 Btu/ft³ and of natural gas, about 930 Btu/ft³.

The energy liberated in a flame can be represented by the adiabatic flame temperature which is the maximum temperature theoretically attainable when a stoichiometric mixture of fuel-oxygen is reacted. This temperature is roughly proportional to the heat of reaction up to about 2000°C, but at higher temperatures, the dissociation of the products into free atoms and radicals becomes important and the energy is shared by the enthalpy of the exhaust gases and the increasing amount of energy used in the dissociation. Gaydon and Wolfhard ⁽⁶⁵⁾ tabulate data giving the adiabatic flame temperature for a stoichiometric mixture of H₂ and O₂ as 2810°C and for a mixture of CO and O₂ as 2700°C. Under controlled conditions, actual flame temperatures approach 90-95% of these values.

PELLET TYPE							
Cement-bonded (measured date	d a)	Carbonate-bonded (calculated data)					
63% ore 22% coal 15% cement		6 . 2 1	66% ore 23% coal 11% carbonate				
0.44 %/g	OFF VOL	-gas ume	0.45 e/g				
41.	^{%H} 2 🖏		30.				
53.	%CO		65. *				
2.7	`, %н ₂ 0		- 1.				
1.2 •	. %C0 ₂		2.				
2.1	%N ₂		2.				
37 g/m ³	C (est.)		37 g/m ³				
Net Heating Value							
2950	kcal/m ³		3030				
12350	kJ/m ³		12670				
330	Btu/ft ³		, 340				

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Table 5.5: Comparison of the composition and net heating values of the off-gases from cement-bonded and carbonate-bonded one-coal pellets.

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A major question arises as to whether the above information can be used to obtain a flame temperature when an oxygen jet is lanced into gaseous fuel. The short answer is that it can not, mainly because the above applies to premixed flames wherein the fuel and oxidant gases react immediately. An oxygen jet would form a turbulent diffusion flame which would depend on the rate of mixing rather than on the rates of the chemical processes involved. Also, a flame from an oxygen jet would be much less concentrated spatially than measured experimental flames and hence it would be further away from adiabatic conditions. Due to the lack of published data (not surprising considering the uniqueness of the case) it can only be surmised that the flame temperature would be several hundred degrees lower than the calculated values stated above. A lower flame temperature of, say 2200°C, would actually have an advantage, in be that there would/less dissociation of the combustion products and hence, the flame would have a higher combustion efficiency.

Another point to consider is that the off-gas contains a measure of carbon soot which when burned, would increase substantially the luminosity of the flame. A high temperature luminous flame represents one of the better methods to transfer heat to cooler surfaces, i.e., to slag and charge materials. Indeed, unless a foaming slag protects the furnace walls, overheating of the refractories may become a problem.

5.5 Summary

From an analysis of the off-gas from reaction of iron ore-coal pellets bonded with cement it was found that the total volume of gas evolved was 0.44 litre per gram of pellets reacted. When pellets were introduced to heat (1500°C), the coal began to gasify immediately causing a very high rate of hydrogen evolution during the first few seconds, then tapered off, while carbon monoxide from the combined ore-carbon reduction reactions increased. There were no significant amounts of H_2O , CO_2 or N_2 in the off-gas at any time during reaction. The off-gas from cement-bonded pellets contained, by volume, 41% H_2 and 53% CO, while the off-gas from carbonate-bonded pellets was calculated to contain 30% H_2 and 65% CO. Heat of combustion calculations showed that the off-gas from either type of pellet would have a net heating value of about 3000 kcal/m³ (12500 kJ/m³) or (340 Btu/ft³).

CHAPTER 6

APPLIED METALLURGICAL THERMODYNAMICS

6.1 Introduction

The previous chapters have dealt with reduction aspects of individual pellets. This chapter will give consideration to chemical and thermodynamic aspects of the process, outlined in Section 1.2, wherein composite pellets of iron ore, coal and lime are reacted at high temperatures within a body of foaming slag to produce liquid iron. In order to treat the proposed process in its entirety, computer charge calculations have been made in which a series of simultaneous heat and mass balance equations have been solved from given input data. These calculations are based on equilibrium thermodynamics and represent an overall view of the process. The purpose of this chapter is to present only the metallurgical data and reference sources which are relevant to the present work and to show how they are used. The theoretical basis for these calculations is thoroughly described in texts such as "Introduction to Metallurgical Thermodynamics"⁽⁶⁷⁾ by David R. Gaskell, and "Physical Chemistry of Iron and Steel Manufacture"⁽⁶⁹⁾ by Bodsworth and Bell.

The reduction process shall be viewed, for purposes of calculation, as one in which the reactants enter the vessel, are heated to the reaction temperature, and then are reacted. The reaction temperature was chosen as 1527°C (1800°K), a figure midway within the envisioned

process temperature range of 1450-1600°C. Iron ore reduction will be considered to be complete, i.e. all iron in the ore upon reduction will transfer to the iron melt. Slag/metal partition reactions will be used to calculate the silicon, sulphur and manganese contents of the iron.

Here, it may be worthwhile to review our understanding of the terms "pellet slag" and "process slag", for the two may be distinctly different in chemical composition. When an individual pellet reacts, an internal slag forms along with iron droplets and when the pellet collapses into molten iron and slag, the pellet slag would join the process slag in the vessel. As was seen in Chapters 3 and 4, the chemical composition of the internal pellet slag should be controlled within certain narrow limits in order to obtain the optimum sulphur and carbon contents in the iron. On the other hand, the process slag is not so restricted and through flux additions to the vessel, the slag composition can be adjusted to obtain, say, a higher basicity, or a more fluid slag. The slag/metal partition reactions considered in this chapter are reactions between the iron drop as it falls through the bulk of the process slag or between the metal bath and the process slag.

Most reference texts, research papers and compilations of thermodynamic data employ the calorie as the traditional thermochemical unit whereas S.I. dictates that the joule be the unit of energy. Rather than convert all the data before use, it has been decided to use the data in the traditional manner and afterwards, convert calories to joules, i.e., 1 cal. = 4.184 J.

6.2 Enthalpy Changes

The amount of heat required to raise the temperature of a reactant from $298^{\circ}K$ (25°C) to the process temperature T°K is given by

 $\Delta H = \int_{298}^{T} C_{p} dT$

where C_p is the molar heat capacity of the reactant. The heat capacity of a substance usually increases with increasing temperature and a convenient way of recording the data is by the use of an algebraic equation;

$$C_{p} = a + 2bT - cT^{-2}$$

the constants of which are derived from experimental data. Hence the enthalpy change or change in heat content becomes

 $\Delta H = H_T - H_{298} = aT + bT^2 + cT^{-1} + d$ cal/mol

Kelley⁽⁷⁴⁾ has compiled high temperature heat content and heat capacity data for most elements and inorganic compounds found in metallurgical systems and is used as the reference source for this study. As an example, the enthalpy change or heat required to raise oxygen from 298 to $T^{\circ}K$ is given by

$$H_T - H_{298} = (7.16T + 0.5 \times 10^{-3} T^2 + 0.4 \times 10^{-5} T^{-1} - 2313.)$$

cal/mol x 4.184/32 kJ/kg

In a similar manner, enthalpy changes as a function of temperature have been recorded for all process components, namely

 Fe_30_4 , $Si0_2$, $A1_20_3$, MnO, CaO, MgO, C, H₂, 0_2 , CO and $C0_2$.

6.3 Heats of Reaction

Enthalpy changes or heats of reaction for the formation of many compounds can be obtained directly from calorimetry⁽⁷⁵⁾, but for other more complicated reactions they can be found by applying the law of constant heat summation. Heats of reaction are temperature dependent and can be related to the base temperature through the difference in the heat capacities of reactants and products. The heat of reaction at temperature T°K is calculated by adding to the standard heat of reaction, ΔH°_{298} , the enthalpies of the products minus the enthalpies of the reactants;

 $\Delta H^{\circ}_{T} = \Delta H^{\circ}_{298} + \int_{298}^{T} \Delta C_{p} dT cal/mol$

Enthalpy changes arising from changes of state in any of the products or reactants, such as fusion, vaporization or dissolution into an iron melt, should also be included in the calculations.

It is possible, though laborious, to calculate heats of reactions in the above manner using heats of formation, heats of transformation and heat capacity data. However, compilations by Elliott and Gleiser⁽⁷⁶⁾ have made this unnecessary for they list the heats of formation at high temperatures for many compounds that are of interest in iron and steelmaking. As an example, the heat of reaction of the reduction of magnetite by carbon is calculated at the reaction temperature of 1800°K.

$$\frac{Fe_{3}O_{4}(s)}{4C_{(s)} + 2O_{2}} = \frac{4CO_{(g)}}{Fe_{3}O_{4}(s)} + \frac{4C_{(s)}}{4C_{(s)} + 2O_{2}} = \frac{4CO_{(g)}}{4C_{(s)} + 4CO_{(g)}} = \frac{\Delta H^{\circ}_{1800}}{\Delta H^{\circ}_{1800}} = \frac{4(-28,08b)}{\Delta H^{\circ}_{1800}}$$

adding $Fe_{3}O_{4}(s) + 4C_{(s)} = 3Fe_{(s)} + 4CO_{(g)}$

$$\Delta H^{\circ}_{1800} = 147,180 \times 4.184/232 = 2654 \text{ kJ/kg} (\text{Fe}_{3}0_{4})$$

A positive value indicates that the reaction must have heat supplied to it (endothermic) while a negative value indicates heat is evolved (exothermic).

In a similar manner, the heats of reaction for the combustion of CO, H_2 and C with oxygen have been calculated, along with the heats of reaction for the reduction of silicon and manganese oxides.

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6.4 Slag/Metal Partition of Silicon

6.4.1 Silicon Reduction Reaction

Silicon may be reduced from ore by carbon to a limited extent but mostly, the silicon content of an iron melt is determined by reaction between iron and a silicious slag according to the overall reaction,

 $(Si0_2) + 2[C]_{1 wt\%} = [Si]_{1 wt\%} + 2C0_{(g)}$ (1). wherein the squared brackets indicate that the carbon and silicon are dissolved in the iron melt, the standard states being 1 wt% solutions. The round brackets indicate a constitutent of the slag; the standard state, in this case, being solid silica. This overall reaction is comprised of several reactions which follow.

 $\Delta G^{\circ} = 227,700 - 48.7T$ cal (2) $\Delta G^{\circ} = -31,430 - 1.71T$ (3) $\Delta G^{\circ} = -56,400 - 40.32T$ (4) $\Delta G^{\circ} = -10,800 + 20.2T$ (5) $(SiO_2) + 2[C]_{1 \text{ wt}\%} = [Si]_{1 \text{ wt}\%} + 2CO_{(g)} \Delta G^\circ_1 = 129,070 - 70.53T \text{ cal} (1)$ The standard free energy change, ΔG° , applicable at 1800°K, for reaction (2) has been obtained from Kubaschewski et al.⁽⁷⁵⁾ and for reactions (4) and (5) from Elliott et al.(77). The standard free energy change for reaction (3), which changes the standard state from pure liquid silicon to 1 wt% silicon in iron was derived (68,70) using the activity coefficient of silicon in iron, as measured by Fruehan(78) in combination with the heat of solution of silicon in iron (at infinite dilution), as measured by Woolley and Elliott⁽⁷⁹⁾.

The equilibrium constant K, for reaction (1) can be found from the free energy equation; $\Delta G^\circ = -RT \ln K$.

Hence

$$\log K_1 = \frac{-\Delta G_1}{4.575T} = -\frac{28210}{T} + 15.42$$

but also by definition,

$$K_{1} = \frac{h_{\text{Si}} p_{\text{CO}}^{2}}{(a_{\text{SiO}_{2}})h_{\text{C}}^{2}} = \frac{f_{\text{Si}} [wt \% \text{Si}]}{(a_{\text{SiO}_{2}}) f_{\text{C}}^{2} [wt \% \text{C}]^{2}}$$
(7)

where h_{Si} and h_C are the Henrian activities of silicon and carbon in iron using 1 wt % as the standard state, a_{SiO_2} is the activity of silica in slag, the standard state being solid silica, and f_{Si} , f_C are the Henrian activity coefficients of silicon and carbon in iron, respectively. P_{CO} , the partial pressure of CO, may be set equal to one atmosphere as there is no other gas produced nor available at the slag/metal reaction site. After taking the logarithm and rearranging, equation (7) becomes

 $log[wt % Si] = log K_1 - log f_{Si} + log(a_{Si0_2}) + 2 log f_C + 2 log[wt % C]$

(8) The silicon content of the iron can be calculated from equation (8) when the reaction temperature, the carbon content of the iron and the composition of the slag are known. The reaction temperature allows calculation of log K_1 from equation (6); the carbon content of the iron allows calculation of the activity coefficients of silicon and carbon; and lastly, the slag composition allows the activity of silica to be calculated. These latter calculations, the activities of silicon and carbon in iron, and the activity of silica in slag are explored further in the following sections.

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(6)

6.4.2 Activities of Carbon and Silicon in Iron

The Henrian activity of solute "i" in iron is defined as

- h_i = f_i[wt % i]

 $f_{i} = f_{i}^{2} \times f_{i}^{3} \times \cdots$

 $\log f_i = \sum_{i=2}^{n} \log f_i^j$

where f_i is the Henrian activity coefficient and is itself a function of solute concentrations in the iron melt. In general, if iron is component l in an n-component system, then the activity coefficient of the ith element is

For each element i, $\log f_i$ can be expanded by a Taylor series as a function of the concentrations of the solute elements but since the solution is dilute, the second and higher ordered terms can be neglected; hence

 $\log f_{i} = \sum_{j=2}^{n} \frac{\partial \log f_{i}}{\partial wt \% j} [wt \% j] = \sum_{j=2}^{n} e_{i}^{j} [wt \% j]$

where e_i^j , the interaction coefficient of j on i, can be obtained from compilations by Elliott et al.⁽⁷⁷⁾, Bodsworth and Bell⁽⁶⁹⁾ and Sigworth and Elliott⁽⁸⁰⁾. A fuller explanation of the treatment, derived by Wagner⁽⁸¹⁾, may be found in the reference texts^(67, 69).

In the present case, carbon, silicon, manganese and sulphur are the major solutes to be considered in these calculations. Hence,

 $log f_{C}^{i} = e_{C}^{C}[wt \% C] + e_{C}^{Si}[wt \% Si] + e_{C}^{Mn}[wt \% Mn] + e_{C}^{S}[wt \% S]$ $log f_{Si} = e_{Si}^{Si}[wt \% Si] + e_{Si}^{C}[wt \% C] + e_{Si}^{Mn}[wt \% Mn] + e_{Si}^{S}[wt \% S]$

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The interaction coefficients, e_i^j , are valid only if all solute elements are in dilute concentrations and departures from Henry's law are small. This condition is met by all except carbon, which is envisioned as varying from 2 to 4%. In consulting the original research papers^(82,83) where, for example, log f_C was plotted against [wt % C] and the slope

d log f_C

d[wt % C] at infinite dilution defined e_C^C , it was found that at higher concentrations, this tangent line diverged from the curve and errors became substantial. In order to alleviate this difficulty, a line was drawn from 0%C to intersect the curve at the 3%C level which thereby ensured that when the slope of this line was multiplied by [wt % C], the correct value of log f_C at 3%C was obtained. Thus, for the present study, the interaction coefficients reflecting high carbon concentrations have been redefined as e_C^{3C} and e_{Si}^{3C} .

The interaction coefficients for carbon, silicon, sulphur and manganese in iron have been summarized in Table 6.1. Those for sulphur and manganese will be used in later sections. Since the manganese and sulphur contents of the iron are expected to be low, and since their effects on the activities of carbon and silicon/are very small, it can be seen that very little error would incur should their effects be neglected at this stage. Hence, carbon and silicon will be considered to be the only solutes contributing to h_C and h_{Si} . The activities thus can be calculated as follows.

	•			
` x	Solute j	Dilute Solution	Adapted to 3% C	References
e ^j C	C	0.22	0.18	77,82
	Si	P 0.08		80, 83, 87
	Mn	-0.012		80,84
	S	~ 0.046		80, 85
ej Si:	· Si 1	0.084		78, 83, 87
	С	0.20	0.24	83 .
	Mn	0.002		80
	S	0.055		80,85
ej S	S	-0,.028		85
	С	0.114	0.14	85
	Si	0.063	•	85 .
	Mn	-0.026		85
e ^j Mn	Mn	0.00	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	80
	С	-0.07	-0.07	80, 84
	Si	0.00		80
	S	-0.048		69,80

Table 6.1: Henrian interaction coefficients, e_i^j , for carbon, silicon, sulphur and manganese in iron.

For carbon, since $h_{C} = f_{C}[wt \% C]$ then $\log h_{C} = \log f_{C}^{C} + \log f_{C}^{Si} + \log [wt \% C]$ $= e_{C}^{3C} [wt \% C] + e_{C}^{Si} [wt \% Si] + \log [wt \% C]$ $= 0.18 [wt \% C] + 0.062 [wt \% Si] + \log [wt \% C]$ For silicon, since $h_{Si} = f_{Si} [wt \% Si]$ then $\log h_{Si} = \log f_{Si}^{Si} + \log f_{Si}^{C} + \log [wt \% Si]$ $= e_{Si}^{Si} [wt \% Si] + e_{Si}^{3C} [wt \% C] + \log [wt \% Si]$ $= 0.084 [wt \% Si] + 0.24 [wt \% C] + \log [wt \% Si]$

'6.4.3 Activity of Silica in Slag

The activities of silica in molten $CaO-MgO-SiO_2-Al_2O_3$ slags have been studied by Kay and Taylor⁽⁸⁶⁾. For the restricted range of blastfurnace slags, these results were represented by a graph of a_{SiO_2} against an empirical relationship R = % SiO_2 - (% CaO + % $Al_2O_3/2$ + % MgO/3). This relationship was replotted in a later publication by Taylor⁽⁸⁷⁾ and adopted by Bodsworth and Bell⁽⁷¹⁾ in their text, as

 $\log a_{Si0_2} = -0.032$ (% Ca0 + % Al₂0₃/2 + % Mg0/3 - % Si0₂) - 0.65 (at 1550°C)

The silica activity (86) was found to decrease by a factor of 0.89 for a 50°C rise in temperature from 1450-1500-1550°C and hence a temperature dependence equation was derived as

 $\log a_{SiO_2}^{TC} = 0.001(1550-TC) + \log a_{SiO_2}^{1550}$ where TC is the temperature in degrees Celsius.

In summary, $\log a_{SiO_2}$, corrected for temperature, can be obtained from the above relationships when the composition of the molten slag of blast-furnace type, is known.

6.5 Slag/Metal Partition of Sulphur

The transfer of an element from iron to slag, or vice versa, has been shown to be an electrochemical reaction between an ionic solution of molten oxides and molten iron containing diverse solute elements. Sulphur is transferred according to the cathodic reaction,

$$[S]_{iron} + 2e^{-} = (S^{2-})_{slag}$$
 (10)

and in order to maintain neutrality, a number of anodic reactions can take place simultaneously; e.g.,

$$[Fe] - 2e^{-} = (Fe^{2+})$$
 (11)

$$(0^{2}) - 2e^{-} = [0]$$
 (12)

$$[Si] + 4e^{-} = (Si^{4+})$$
 (13)

Since the iron melt usually contains carbon, then the evolution of CO can result from

$$[C]_{iron} + [0]_{iron} = CO_{(g)}$$

Combining equations (10), (12) and (14) results in the ionic equation

$$[S]_{iron} + [C]_{iron} + (0^{2-})_{slag} = (S^{2-})_{slag} + CO_{(g)}$$
(15)

and the equilibrium constant is

$$K_{15} = \frac{(a_{S}^{2} -) P_{C0}}{(a_{0}^{2} -) h_{S} \cdot h_{C}}$$

The ability of a slag to hold sulphur, therefore, is dependent upon the activities of both 0^{2-} ions and S^{2-} ions in the slag. Combining other equations, such as for sulphur and silicon transfer, results in a similar dependency on oxygen and sulphur ions in the slag.

(14)

6.5.1 <u>Concept of Basicity</u>

Ionic concepts of slag constitution have been very successful in explaining slag/metal reactions, but still it is difficult to put such an ionic treatment of slags to practical use. Although related to slag composition, the properties of single ions cannot be expressed independently from a host of other ions in the slag. Mindful that slags are ionic in nature, many difficulties are alleviated by considering slags as if they were solutions of neutral oxide molecules. Then, the results of reactions, such as the desulphurization of iron, can be plotted against empirical numbers based on slag composition. Perhaps the most useful is the concept of basicity, developed before the ionic treatment of slags, but quite adaptable to it.

The oxides, e.g. SiO_2 , AI_2O_3 , P_2O_5 which form anion complexes in molten slags (network formers) are said to be acidic, while the oxides, e.g. CaO, MgO, MnO, FeO which break down the anion complexes (network modifiers) are said to be basic. The ratio of basic oxides to acidic oxides is called the basicity ratio, a rather loose term since there are numerous ratios representing industrial slags. Oldest is the simple "Vee ratio", equal to wt % CaO/wt % SiO₂ but more complicated ratios have been devised in order to characterize slags more fully. Blast-furnace ironmakers may use % CaO + % MgO/% SiO₂ + % Al₂O₃ while steeImakers may substitute P_2O_5 for Al_2O_3 . The proportions of each constituent in the ratio should be noted carefully, since ratios may be developed from research data on a molar basis (not necessarily equi-molar), then converted to wt %.

Kalyanram, Macfarlane and Bell $\binom{(88)}{}$ investigated the desulphurizing power of CaO-MgO-Al₂O₃-SiO₂ slags and found a correlation with the molar ratio

$$\frac{N_{Ca0} + \frac{N_{Mg0}}{2}}{N_{Si0_2} + \frac{N_{A1_20_3}}{3}} = \frac{(\% Ca0) + 0.7 (\% Mg0)}{0.94 (\% Si0_2) + 0.18 (\% A1_20_3)} \equiv B$$

It is the above wt % ratio, defined as "Basicity Ratio B", that has been used in the present work and is the basis on which the slags of Chapter 3 (and Appendix A3.3) have been described. In summary, the use of basicity ratios to describe slag characteristics is very practical, very useful and very empirical.

6.5.2 <u>Sulphide Capacities of Slags</u>

The slag/metal distribution of sulphur can be represented by the "molecular" equation

 $[S]_{iron} + [C]_{iron} + (CaO)_{slag} = (CaS)_{slag} + CO_{(g)}$ (16) where $(a_{CaS}) P_{CO}$

$$K_{16} = \frac{(-CaS) + CO}{(a_{CaO}) + S^{+h}C}$$

Here, should the activities of CaO and CaS in slag be known, then the partition of sulphur between slag and metal can be calculated. Unfortunately, data on CaS is available only for binary CaO-Al₂O₃ and CaO-SiO₂ slags; the more complicated blast-furnace slags have yet to be investigated.

In contrast to the lack of data on the activity of CaS, many investigations have determined the sulphide capacities of slags. A gas mixture with known sulphur and oxygen partial pressures is equilibrated with a liquid slag of known composition. Hence the reaction is

 $(CaO)_{slag} + 1/2 S_{2(g)} = (CaS)_{slag} + 1/2 O_{2(g)}$ (17) or in ionic form

$$(0^{2-})_{slag} + 1/2 S_{2(g)} = (S^{2-})_{slag} + 1/2 O_{2(g)}$$

for which the equilibrium constant is

$$\kappa_{17} = \frac{(a_{\rm S})_{\rm slag}}{(a_{\rm 0})_{\rm slag}} \left(\frac{p_{\rm 0_2}}{p_{\rm S_2}}\right)^{1/2} = \frac{\gamma_{\rm S}(N_{\rm S})}{(a_{\rm 0})} \left(\frac{p_{\rm 0_2}}{p_{\rm S_2}}\right)^{1/2}$$

0

Rearranging gives

$$\frac{K_{17} (a_0)}{n (\gamma_S)} = (wt \% S) \left(\frac{p_{02}}{p_{S2}}\right)^{1/2}$$

where η is a factor to convert atom fraction N_S to (wt % S) in the slag. ` The activity of oxygen ions in the slag (a_0) and the activity coefficient of sulphur in slag (γ_S) are unknown but both are functions only of temperature and slag composition. For a given temperature and slag composition, the sulphide capacity is defined as

$$C_{S} \equiv (wt \% S) \left(\frac{p_{0_{2}}}{p_{S_{2}}}\right)^{1/2}$$

Published data for many slags has allowed Venkatadri and Bell⁽⁸⁹⁾ to establish a correlation at 1500°C between C_S and the slag basicity ratio,

$$B = \frac{(\% \text{ Ca0}) + 0.7 (\% \text{ Mg0})}{0.94 (\% \text{ SiO}_2) + 0.18 (\% \text{ Al}_2\text{O}_3)}$$

The data were shown originally as a graph but Bodsworth and Bell(72) have established the equation of the best straight line through the data as

 $\log C_{S} = 1.39 (B) - 5.57$ (at 1500°C)

The sulphide capacity of a given slag was estimated $(^{(89)})$ to increase with temperature by a factor of about 1.3 for each 50°C rise; hence, a temperature dependence equation was devised as

$$\log c_{\rm S}^{\rm TC} = -2.25 \times 10^{-3} (1500 - TC) + \log c_{\rm S}^{1500}$$

where TC is the temperature in degrees Celsius.

In summary, log C_S , corrected for temperature can be obtained from the above relationships when the composition of the molten slag (of the type from blast-furnaces) is known.

6.5.3 Sulphur Distribution Reactions

The slag/metal distribution of sulphur may be determined according to the overall reaction,

$$[S]_{1 \text{ wt } \%} + [C]_{1 \text{ wt } \%} + (Ca0) = (CaS) + CO_{(g)}$$
(16)

wherein the squared brackets indicate that sulphur and carbon arepdissolved in the iron melt, the standard states being 1 wt % solutions. The round brackets indicate a constituent of the slag. This overall reaction is comprised of several reactions which follow.

$(Ca0) + 1/2 S_{2(g)} = (CaS) + 1/2 O_{2(g)}$ [S] = 1/2 S_{2(g)}	$\Delta G^{\circ} = 23,010 - 1.34 \text{ T cal}$ $\Delta G^{\circ} = 31,520 - 5.27 \text{ T}$	(17) (18)
$[C] = C_{(gr)}$ $C_{(gr)} + \frac{1}{2} O_2 = CO_{(g)}$	ΔG° = - 5,400 + 10.1 T ΔG° =28,200 - 20,16 T	(19) (20)
$[S] + [C] + (CaO) = (CaS) + CO_{(g)}$	$\Delta G_{16}^{\circ} = 20,930 - 16.67 T cal$	(16)

The standard free energy change, ΔG° , applicable at 1800°K, for reactions (18), (19) and (20) have been obtained from Elliott et al. (77); for reaction (17), ΔG° will be derived later in this section.

The equilibrium constant for reaction (16) can be found from the free energy equation, $\Delta G^{\circ} = - RT \ln K$. Hence

$$\log K_{16} = \frac{-\Delta G_{16}^2}{4.575} = \frac{-4570}{T} + 3.64$$

but also by definition,

$$K_{16} = \frac{\binom{a_{CaS}}{p_{C0}}}{\binom{a_{CaO}}{h_{s} \cdot h_{C}}} = \frac{Y_{CaS} \cdot n^{*} \cdot (wt \ \% \ S) \ p_{CO}}{\binom{a_{CaO}}{h_{s} \cdot h_{C}}}$$
(22)

where $\eta\star$ is a factor to convert mole fraction $N_{\mbox{CaS}}$ to (wt % S) in the

(21)

slag. Converting to logarithms and rearranging, equation (22) becomes

$$\log K_{16} = \log \frac{(\text{wt x S})}{h_{S}} + \log \frac{P_{C0}}{h_{C}} + \log \left(\frac{Y_{CaS} \cdot n^{*}}{a_{Ca0}}\right)$$
(23)

From the discussion in the previous section, it may be remembered that activity data on CaS and CaO in complex slags are insufficient, but that sulphide capacities are known and can be used instead. Reaction (17) is comprised of three reactions which follow.

$$(Ca0) + H_2S_{(g)} = (CaS) + H_2O_{(g)} \qquad \Delta G^\circ = -15,650 + 0.87 \text{ T ca} \qquad (24)$$

$$H_2O_{(g)} = H_2(g) + 1/2 O_2(g) \qquad \Delta G^\circ = 60,200 - 13.94 \text{ T} \qquad (25)$$

$$H_2(g) + 1/2S_2(g) = H_2S_{(g)} \qquad \Delta G^\circ = -21,540 + 11.73 \text{ T} \qquad (26)$$

$$(CaO) + 1/2 S_{2(g)} = (CaS) + 1/2 - \frac{\Theta_2(g)}{2(g)} \Delta G_{17}^{\circ} = 23,010 - 1.34 T cal$$
 (17)

The standard free energy change, applicable at 1800° K, for reaction (24) has been obtained from Rosenqvist⁽⁹⁰⁾; for reactions (25) and (26), from Elliott et al.⁽⁷⁷⁾.

The equilibrium constant/for reaction (17) is

$$\log K_{17} = \frac{-\Delta G_{17}^{\circ}}{4.575} T_{T} = \frac{5030}{T} + 0.29$$
(27)

but also, by definition

$$K_{17} = \frac{\binom{a_{CaS}}{a_{Ca0}}}{\binom{a_{Ca0}}{a_{S2}}} \left(\frac{\frac{p_{02}}{p_{S2}}}{\frac{p_{S2}}{a_{S2}}}\right)^{1/2} = \frac{\gamma_{CaS} \cdot \eta^* \cdot (wt \ \% \ S)}{\binom{a_{Ca0}}{a_{Ca0}}} \left(\frac{\frac{p_{02}}{p_{S2}}}{\frac{p_{S2}}{a_{S2}}}\right)^{1/2}$$
(28)

where n^* is a factor to convert mole fraction N_{CaS} to (wt % S) in the

$$\log K_{17} = \log (\text{wt \% S}) \left(\frac{p_{02}}{p_{S2}} \right)^{1/2} + \log \left(\frac{\gamma_{\text{CaS}} \cdot n^*}{a_{\text{Ca0}}} \right)$$
(29)

Since.

$$\log C_{S} = \log (wt \% S) \left(\frac{p_{0_2}}{p_{S_2}} \right)^{1/2}$$

then
$$\log \left(\frac{\gamma_{CaS} \cdot \eta^*}{a_{CaO}}\right) = \log K_{17} - \log C_S$$

which can be substituted into equation (23). Thus

$$\log K_{16} = \log \frac{(\text{wt \% S})}{h_{S}} + \log \frac{P_{CO}}{h_{C}} + \log K_{17} - \log C_{S}$$
(30)

Substitution of log K_{16} from equation (21) and log K_{17} from equation (27) allows equation (30) to be solved for the equilibrium wt % S contained in a slag for which C_S can be calculated. If $P_{CO} = 1$ and the carbon, silicon and sulphur contents of the iron melt are known or chosen, then

$$\log (wt \% S) = \left(\frac{460}{T} + 3.35\right) + \log h_{C} + \log C_{S} + \log h_{S}$$
 (31)

Calculation of C_S , the sulphide capacity of a slag was discussed in the previous section and calculation of h_C , the Henrian activity of carbon in iron was discussed in Section 6.4.2. In a similar manner, h_S , the Henrian activity of sulphur in iron can be calculated as follows. For sulphur, since $h_S = f_S$ [wt % S], then

$$log h_{S} = log f_{S}^{S} + log f_{S}^{C} + log f_{S}^{Si} + log f_{S}^{Mn} + log [% S]$$

= $e_{S}^{S} [\% S] + e_{S}^{3C} [\% C] + e_{S}^{Si} [\% Si] + e_{S}^{Mn} [\% Mn] + log [\% S]$
= - 0.028 [% S] + 0.14 [% C] + 0.063 [% Si] - 0.026 [% Mn] + log [% S]

The interaction coefficients e_S^S , e_S^{SC} , e_S^{Si} and e_S^{Mn} are listed in Table 6.1 in Section 6.4.2, and are taken from the work of Ban-ya and Chipman⁽⁸⁵⁾.

In summary, the slag/metal distribution of sulphur according to reaction (16) can be calculated using equation (31) wherein substitution of the reaction temperature, sulphide capacity of the slag and the Henrian activities of carbon and sulphur in iron will allow the percentage of sulphur in the slag to be calculated.

6.6 Slag/Metal Partition of Manganese

6.6.1 Manganese Reduction Reaction

The manganese content of an iron melt may be determined according to the overall slag/metal reaction,

$$(MnO)$$
 + $[C]_1$ wt $% = [Mn]_1$ wt $% + CO(g)$ (32)

wherein the squared brackets indicate carbon and manganese are dissolved in the iron melt; the standard states being 1 wt % solutions. The round brackets indicate that MnO is a constituent of the slag; its standard state being solid MnO. The overall reaction is comprised of several reactions which follow.

 $(Mn0) + [C]_1 wt \% = [Mn]_1 wt \% + CO_{(g)} \Delta G_{32}^\circ = 63,950 - 40.38 T cal$ (32) The standard free energy change, ΔG° , applicable at 1800°K, for reactions (33), (34), (35) and (36) have been obtained from Elliott et al⁽⁷⁷⁾.

The equilibrium constant for reaction (32) can be found from the free energy equation, $\Delta G^{\circ} = - RT \ln K$.

$$\log K_{32} = \frac{-\Delta G_{32}^{\circ}}{4.575} = \frac{-13,980}{T} + 8.83$$

Hence.

(37)

but also by definition,

$$K_{32} = \frac{h_{Mn} \cdot P_{C0}}{(a_{Mn0}) h_{C}} = \frac{f_{Mn} [\% Mn] P_{C0}}{\gamma_{Mn0} \cdot \eta (\% Mn0) h_{C}}$$
(38)

where f_{Mn} is the Henrian activity coefficient of manganese in iron, γ_{MnO} , is the activity coefficient of MnO in slag and n is a factor to convert mole fraction MnO to wt % MnO in the slag. Although n varies with slag composition, for blast-furnace type slags containing less than one perčent MnO, a mean value $\eta = 0.011$ may be taken. Bodsworth and Bell⁽⁷³⁾ estimate that $\gamma_{MnO} \approx 1.0$ at 1540°C for the type of slags being considered here. If $p_{CO} = 1$, then equation (38) can be rearranged as

$$\frac{[\% Mn]}{(\% Mn0)} = K_{32} \cdot \gamma_{Mn0} \cdot \eta \cdot \frac{h_{C}}{f_{Mn}}$$

The equilibrium constant K_{32} can be obtained from equation (37) while the calculation of h_{C} , the Henrian activity of carbon in iron was discussed in Section 6.4.2. In a similar manner h_{Mn} or f_{Mn} can be calculated as follows.

For manganese, since $h_{Mn} = f_{Mn}$ [wt % Mn] then

$$\log f_{Mn} = \log f_{Mn}^{Mn} + \log f_{Mn}^{C} + \log f_{Mn}^{Si} + \log f_{Mn}^{S}$$
$$= e_{Mn}^{Mn} [\% Mn] + e_{Mn}^{3C} [\% C] + e_{Mn}^{Si} [\% Si] + e_{Mn}^{S} [\% S]$$
$$= 0.0 [\% Mn] - 0.07 [\% C] + 0.0 [\% Si] - 0.048 [\% S]$$
$$= -0.07 [\% C] - 0.048 [\% S]$$

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(39)

The interaction coefficients are listed in Table 6.1 in Section 6.4.2. The wt % ratio of manganese in iron to MnO in slag can be obtained from equation (39) which when combined with a total MnO input to the system, can determine the slag/metal distribution of manganese.

6.7 Summary

Thermodynamic equations have been derived and presented which summarize enthalpies, heats of reaction, and slag/metal partition reactions for silicon, sulphur and manganese. These equations will be used in the next chapter in which computer charge calculations will be made using simultaneous heat and mass balance equations.

CHAPTER 7 PROCESS ANALYSIS - COMPUTER STUDY

7.1 Introduction

Computer charge calculations were made in which a series of simultaneous heat and mass balance equations were solved from given input data. These calculations are based on equilibrium thermodynamics, presented in the previous chapter, and represent an overall view of the process. The input data include iron ore and coal analyses, a chosen operating slag composition, operating and preheat temperatures, and the required carbon and sulphur contents of the molten iron.

In order to ensure that the process slag would indeed be liquid and present no viscosity problems at the operating temperatures, it was necessary to choose a slag composition beforehand and impose this restriction upon the computer-modelled system. Carbon, silicon and heat balance equations were chosen as those best able to describe the process. Once the unknowns, namely, coal weight, flux silica and excess heat were computed, other parameters, such as the slag weight required to carry the sulphur input, could readily be calculated.

The output (computer print-out) includes required charge weights, slag weight, the C, Si, Mn and S contents of the iron, heat generated, heat required and excess heat. All are given in kg or kJ per metric tonne of hot metal produced. The term "hot metal" usually refers to liquid iron produced by a blast furnace but can, by extension, be used to describe liquid iron produced by the proposed direct-reduction process.

The computer program presented in this chapter is quite modest; it is neither sophisticated nor all-encompassing. Its purpose is to show the effects of process variables such as temperature, hot metal carbon and sulphur, and slag weight on input materials required to produce a tonne of hot metal. The program is flexible in that most input data can be changed at will, but in order not to swamp the reader with a multitude of graphs, only particular cases are considered. The results presented may be considered as examples of the type of information which may be gained from such a program.

7.2 Description of Computer Program

The major areas of the computer program (written in FORTRAN IV for a CDC 6400 computer) will be described briefly and sequentially from input through to output. A compilation of variable names and data used in the program is presented as Appendix A7.2 while the program itself is presented as Appendix A7.3.

7.2.1 Input

The iron ore and coal analyses used in the program were essentially the same as those used in the laboratory experiments described in previous chapters. However, the alumina content of the iron ore seemed to be unusually low and thus was increased from 0.3% to 0.5% in order to satisfy slag requirements to be described later. Although there was little or no manganese oxide in the ore used in the experiments, 0.2% MnO was added artificially to the analysis in order to give the program flexibility in computing the manganese partition reactions between slag and metal. For purposes of simplification, all of the iron content of the magnetite ore was considered to be in the form of Fe_3O_4 and that all of the iron oxide from the ore was reduced into the iron melt, i.e., no iron losses to fume or slag were considered.

There were no changes to the coal analysis. The 5.2 wt % oxygen content of the coal was assumed to evolve as CO as part of the coal's volatile matter. In Chapter 5 it was estimated that about 8% of the total carbon content of the coal escaped from the composite pellet as soot and hence would not be available for chemical reaction within the pellet. To account for this carbon loss, a correction factor for effective carbon utilization (EFF = 0.92 for the base condition of maximum utilization) was used in the carbon balance equation.

The slag composition was selected beforehand, not only to ensure that it would be liquid at the operating temperature but also to ensure that the most basic slag possible (for desulphurization) was being used.

A complete list of input data can be found in Appendix A7.2.

7.2.2 Enthalpies and Heats of Reaction

Enthalpy changes as a function of temperature were recorded for all of the process components. Two formulae for each component were listed; the first to obtain the energy required to heat the material from 25°C up to the operating temperature; the second, to obtain the energy required to heat the same material from 25°C up to the preheat tempera-The difference between the two was the enthalpy requirement, ture. within the vessel, of that component. Enthalpy requirements of iron ore $(Fe_30_4, Si0_2, Al_20_3)$ were fairly straightforward, but coal and calcium, magnesium carbonate presented problems because they decompose well before reaching the operating temperature. As an approximation, these materials were treated as if they were assemblies of their components, i.e., coal was considered to be carbon, hydrogen and CO (oxygen), while the carbonates were considered to be CaO, MgO and CO_2 . The development of the formulae was presented in Section 6.2 while the appendices give a complete list of names (A7.2) and formulae (A7.3).

Heats of reaction for the combustion of CO, H_2 and C, the reduction of the oxides of iron, silicon and manganese, the Boudouard reaction (conversion of CO₂ to CO), the dissociation of carbonates, the formation of slag and the solution of carbon in iron are listed in Appendix A7.2. The heats of dissociation of the carbonates are applicable within the temperature range of 450-1150°K while all other heats of reaction were calculated at 1800°K (1527°C) as explained in Sections 6.1 and 6.3. The process may be viewed thermodynamically as one in which the reactants enter the vessel, are heated to the reaction temperature and then are reacted. In this way, the heat contents and volumes or weights of the reaction products are not necessary to the calculations.

7.2.3 Si, S and Mn Partition Reactions

The development of the thermodynamic equations for the slag/metal partition reactions was presented in Sections 6.4 (silicon), 6.5 (sulphur) and 6.6 (manganese). The equations were transferred directly into the program (A7.3) with no changes other than substituting FORTRAN variable names (A7.2). Using known values for operating temperature, slag composition and hot metal carbon content, the activity of silica in slag and the activity of carbon in iron were calculated. These, in turn, allowed the calculation of the hot metal silicon content.

The slag composition and its temperature were used also to calculate the sulphide capacity of the slag. This, along with the activity of sulphur in iron was used to obtain the percentage of sulphur the slag could carry under equilibrium conditions. Percentages, rather than weights, were calculated at this stage because the weight of coal required by the process had not yet been calculated and thus the slag weight required to carry the sulphur input was not yet known. The weight per cent ratio of hot metal manganese to MnO in the slag was calculated in a similar manner.

7.2.4 Solution of Simultaneous Equations

The heart of the computer program is the solving of the heat and mass balance equations. The approach or technique used was to formulate three independent linear equations in three unknowns and then solve the equations simultaneously using a library sub-routine (SIMQ for IBM users, MASOO5 for CDC users) which is based on matrix algebra. The three equations were obtained from carbon, silicon and heat balances of the process. By separating the variables, these equations were fitted into a matrix of the following form.

Carbon eqn: $A_{11}X_1 + A_{12}X_2 + A_{13}X_3 = B_1$ Silicon eqn: $A_{21}X_1 + A_{22}X_2 + A_{23}X_3 = B_2$ Heat eqn: $A_{31}X_1 + A_{32}X_2 + A_{33}X_3 = B_3$ where the unknowns are $X_1 = \text{coal Weight}$ $X_2 = \langle \text{Flux Silica Weight}$ $X_3 = \text{Excess Heat}$

Each of the three equations are derived and explained in detail in Appendix A7.1.

7.2.5 Slag Weight and Carbonate Requirements

The weight of coal required by the processy calculated from the simultaneous equations was then used to obtain the slag weight required to carry the sulphur input from that quantity of coal. This was done by a simple sulphur balance whereby sulphur "in" equals sulphur "out"; i.e.,

COALWT * CLSU/100 = SLWT * SLSU/100 + HMWT * HMSU/100

SLWT = COALWT * <u>CLSU</u> - HMWT * <u>HMSU</u> SLSU

where COALWT = Coal weight, kg

0r

° far

CLSU = Coal sulphur content, % HMWT = Hot metal weight, kg HMSU = Hot metal sulphur content, % SLWT = STag weight, kg SLSU = Slag sulphur content, %

Next, the required weights of lime and magnesia flux were calculated. This was possible because the slag composition was chosen beforehand and, the slag weight had just been calculated, as above.

In order to reduce the pellet variations which could be treated it was decided to illustrate the particular case wherein the flux requirements were met by carbonate-bonded pellets. That is, lime and magnesia were fed into the vessel as carbonates within the pellet. This introduced a complication because dissociation of the carbonate bonding material would produce CO_2 which had to be accounted for in both the carbon and heat balances (Boudouard reaction; $CO_2 + C = 2CO$). Thus, the weight of CO_2 produced was calculated from the carbonate requirements and used in an iterative recalculation of the simultaneous equations.

7.2.6 Output

The page following the program listed in Appendix A7.3 illustrates the form of the print-out page. On top are listed input data; iron ore, coal and slag compositions, operating and preheat temperatures and the hot metal carbon and sulphur requirements. Next are Fisted the computed slag parameters which include basicity, sulphide capacity, activity of silica and percentage sulphur and MnO contents.

The materials input, e.g., weights of iron ore, coal, lime and magnesia, required to produce a tonne of hot metal are listed next, along with the computed hot metal chemical analysis and slag weight. Finally, the results of the heat balance are printed which include heat created, heat needed and excess heat.

7.3 <u>Computing Procedure</u>

7.3.1 <u>Variable Slag Weight</u>

A complete listing of the computer program is presented as Appendix A7 3. Six sets of input data were provided. At two levels of coal sulphur content (0.7 and 1.0%S), the program was required to compute materials balances to meet three hot metal sulphur specifications (0.020, 0.040 and 0.060%S). Hence, the input data defined the hot metal sulphur content and the program computed the slag weight necessary to carry the remainder of the sulphur input from the coal. In all cases, the hot metal carbon content was varied from 2.0 to 4.0% in steps of 0.2% for each operating temperature of 1500, 1520 and 1540°C. Each time the carbon or temperature level was changed within the program (by virtue of iterative "D0 loops") a print-out data sheet was issued.

7.3.2 Variable Hot Metal Sulphur Content .

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For reasons which will be explained in the next section, it was decided to reverse the restrictions placed on the hot metal sulphur content and the slag weight. Hence, in a second running of the program the slag weight was defined beforehand at 200, 250 and 300 kg/tonne hot metal and the hot metal sulphur content was allowed to vary and seek its equilibrium yalue. Some minor changes were made to the silicon and heat balance equations wherein SLWT replaced Q1 * COALWT. These changes are indicated in Sections A7.1.2 and A7.1.3. Also, the sulphur partition and sulphur balance equations were moved to follow the calculation of the required coal weight. In this way the hot metal sulphur content was computed which was in equilibrium with a fixed weight of slag. The hot
7.3.3 Energy Considerations

The print-out data sheet issued for each "computer experiment" listed the heat created by combustion of the reduction off-gases, the heat needed to sustain the process and the excess heat. In order to assess the energy requirements of the process, a third running of the program was performed and two new topics were introduced.

The first was to show the effect on the heat balance of increasing the quantity of coal in the pellet feed material above the base or minimum chemical requirement. This was done by decreasing, in steps, the correction factor for effective coal utilization (EFF) from the base figure of 0.92 to 0.76.

The second topic was to show the effect on the heat balance of preheating/the input materials to 300°C. This was considered to be the maximum preheat temperature that a pellet containing coal could sustain without loss of volatile matter.

7.4 <u>Results and Discussion</u>

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The computer program was run and pages of computed data were issued for each change in input data, hot metal carbon content and temperature. Figure 7.1 (is an example of the output from the program. It can be appreciated that hundreds of such pages were generated, each containing data which were used to plot graphical illustrations showing effects caused by changes in process variables.

Figures 7.2 and 7.3 illustrate the slag weights needed to achieve specified hot metal sulphur contents at varying carbon levels. Figure 7.2 represents the case wherein the input coal contained 0.7%S, while in Figure 7.3 the sulphur content of the coal was raised to 1.0%. The compositions of both iron ore and slag were the same in each case.

The three curves in each of three sets show the effect of varying the operating temperature from 1500 (slag liquidus) to 1520 and 1540°C. Superimposed upon the curves are the hot metal silicon contents calculated at the indicated temperature and carbon levels.

The weight of slag, which was of fixed composition, needed to achieve the desired hot metal sulphur content was computed using slag/ metal partition and sulphur balance equations at each carbon and temperature level. Moreover, the slag weight was computed without considering the amount of input gangue materials from the ore and coal. Hence, in order to accommodate all of the gangue, there existed a minimum slag weight. The two lines crossing each set of curves represent zero additions of flux silica and alumina and define the minimum slag weights, below which the required additions of these fluxes become negative.

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]	IRON ORE CONCENTRATE	68.1 PCT	IRON AS MAGNETITE	
	• • • •	5.2 PCT	SILICA	
	• .	.5 PCT	ALUMINA	
	, <u></u>	.2 POT	MNO	
	<u>.</u>			
C	COAL COMPOSITION ###	82.4 PC1	TOTAL CARBON	•
<u>~</u>		PCT	FIXED CARBON	** **** - · ·
đ		5.4 PCT	HYDROGEN	
0		5.2 PCT	OXYGEN	
p		1.0 PCT	SULPHUR	
	· · ·	4.7 PCT	ASH	
		54.5 PCT	ASH SILICA	
		33.5 PCT	ASH ALUMINA	
			• • •	
·	SLAG COMPOSITION ***	42.0 PCT		
		34.0 PCI	S102	•
		10.0 PCI	· AL203	
		14.0 _. PCT	MĢO	¢ v
、	1220ESS TEMD 1500 (1 0	an an feilineage sam in tra	
\sim		ці,		
-+-'	EXERCAL LENE 22.1	<u> </u>		· · · · · · · · · · · · · · · · · · ·
*	UNT METAL SDEPS STAT			
<u></u>	HUT HETAL SPECS	7 00 0C	TCAPPON	· ··· · · · · · · · · · · · · · · · ·
	•		1 SULFHUR	
		 C7		
······	SLAS BASICITY RATIO I	775.07		·····
	SULPHIDE CAPACI	1 •37E-03	· · /	
	SULPHUR PUT 1.8	39	·····	
	MNO PCI .1	09		4
<u> </u>	ACTIV OF *SID2 .	068		· · · · · · · · · · · · · · · · · · ·
i	MATERIALS INPUT			
	DRE WT (G 1412	.9	•	
	COAL WT KG . 475	•5 ·		• •
	FLUX WI, KG		`	,
	CÁO 99.5 0	R AS CACO3	177.6	
	MGD 33.2 0	R AS MGCO3	77.0	
	SI 32 12.4			•
,	AL 203 9.1			
	DXYGEN WT KG 772.	8	· · ·	. :
		•		
	MATERIALS OUTPUT			· .
	SLAG HT KG 236	• 8		
	HOT METAL WT KG	1000.0		•
•	CARBON PCT 3	.00		•
	SILICON PCT	• 4.8	•	• • • • • • • • • • • • • • • • • • • •
.	MANGAN PCT	.20		2 . 1
·	SULPHUR PCT	.040		▶
······································	EXCESS HEAT .KILO-JOU	LES . 3138F	+D7 HEAT CREATED	.1280E+08
			,	

Figure 7.1: Computer print-out data sheet.



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In practical terms, the process must operate above both lines, a primary condition. An upper limit of about 300 kg/tonne is indicated. This amount is about the maximum allowable for the production of satisfactory composite pellets. Should higher slag weights (more flux) be desired, then the materials would need to be added to the vessel direct $\mathfrak{P}_{\mathbf{x}}$ rather than as constituents of the pellets.

Some trends which can be seen from a general overview of Figures 7.2 and 7.3 are

- (i) The hot metal carbon content has a major influence on desulphurization. As the carbon content of the metal increases, the slag weight needed, decreases. Conversely, a decrease in carbon content can be compensated for by an increase in slag weight and/or temperature.
- (ii) Less stringent hot metal sulphur specifications allow one to operate at lower carbon levels.
- (iii) An increase in the sulphur content of the coal requires a shift to higher hot metal carbon levels and/or an increase in slag weight in order to maintain the same hot metal sulphur level.
- (iv) The minimum operating slag weight is about 200 kg/tonne hot metal, but this depends on the amount of gangue input and operating temperature.

The results shown in Figures 7.2 and 7.3 are most useful in illustrating firstly, the slag weights required to desulphurize the hot metal under given conditions, and secondly, the minimum weights required to carry the input gangue. However, sometimes a mathematical model may escape reality when a tacit assumption cannot be realized. In this case, to achieve the desired desulphurization, the program assumes that any level of hot metal carbon can be chosen and achieved at will. In practice, such control would be extremely difficult, if not impossible. Hence, the program was modified by reversing the restrictions placed on the hot metal sulphur content and the slag weight. Having learned that the slag weights should be between 200 and say, 300 kg/tonne, it was decided to fix the slag weights at 200, 250 and 300 kg/tonne and compute the hot metal sulphur content which would be in equilibrium with that fixed weight of slag.

The results of this modification are shown in Figure 7.4, where the hot metal sulphur content in equilibrium with a fixed slag weight is plotted against the corresponding hot metal carbon content. This plot is for an operating temperature of 1500°C only; the shifting of the curves due to a change in temperature is illustrated in Figure 7.5. These latter two diagrams show the process in a more realistic manner since the operating slag weight is more likely to be known and more easily controlled by input materials than is the hot metal carbon content:

As an example, should an operation produce hot metal at 3.0%C and at 1500°C, and slag at 250 kg/tonne then, from Figure 7.4, the equilibrium hot metal sulphur content would be 0.038%. Figures 7.4 and 7.5 apply when the input coal contains 1.0%S. A lower sulphur input would require less slag or would result in a lower hot metal sulphur content. As in the previous diagrams, percentage values for hot metal silicon contents are placed along the curves, mainly to indicate what levels may be expected at different carbon contents and temperatures.



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As was mentioned previously, the slag composition was chosen beforehand in order to avoid liquidus and viscosity problems. Another consideration was to select a slag which had the highest basicity ratio (for desulphurization), consistent with input gangue levels. Had a slag with a lower basicity ratio been chosen, the curves would have been shifted upwards, i.e., the hot metal sulphur content would have increased. To maintain the lower sulphur levels, the slag weight and/or hot metal carbon content would need to be increased. Also, should a slag with a lower basicity ratio be used, then the hot metal silicon content would increase, although in the case of silicon, changes due to temperature dominate.

Each print-out data sheet from the many "computer experiments" contained values for coal required, heat created, heat needed and excess heat. In scanning these sheets over the carbon range (2.0 - 4.0%), temperature range $(1500 - 1540^{\circ}C)$ and slag weights (200 - 300 kg), it became apparent that there were no large changes in any of the above parameters.

In all cases, the values for the excess heat were within the range of $3.1 \pm 0.2 \times 10^6$ kJ. Table 7.1 lists the weights of coal required per tonne of hot metal over the carbon, temperature and slag weight ranges. The amount of coal required by the process, as computed by the program, is governed by the chemical requirements for carbon within the vessel. This includes the carbon needed for reduction, the carbon needed for solution into the iron, and the carbon needed to convert the CO_2 from the carbonate bonding material (flux addition) to CO within the pellet by the Boudouard reaction.

From Table 7.1, it can be seen that an additional 30 kg of coal was needed to increase the hot metal carbon content from 2.0 to 4.0%. This is approximate because at the higher temperatures and carbon contents, more silicon is reduced which in turn requires more coal. When the slag weight was increased from 200 to 300 kg, an additional 20 kg of coal was needed. Only 2 kg of coal was needed to increase the operating temperature from 1500 to 1540°C mainly because the calculations are based on chemical requirements. The rest of the heat required for this temperature increase came by way of a decrease of about 0.2 x 10^6 kJ in the excess heat value.

Temp. ^O C	%C .	\$1ag W.t, 200	kg/tonne h.m. 250 300
1500	2.0 3.0 4.0	456 468 484	465475478488494503
1520	2.0 3.0 4.0	456 470 489	466475480489499508
1540	2.0 3.0 4,0	457 473 497	467476482492507516

Required Coal, kg/tonne hot metal

Table 7.1:

Weight of coal required per tonne hot metal over the carbon, temperature and slag weight - ranges.

The coal requirements listed in Table 7.1 are based on the minimum chemical requirements for each computation. In order to assess heat requirements, additional coal was added to the base or minimum requirement, which was burned solely for heat and affected the chemical balance equations only because there was an additional sulphur input. A mid-range computation (3.0%C, 1520°C, 250 kg slag) was selected as the base on which to add the coal. Figure 7.6 illustrates the print-out data sheet for this base.

On the print-out data sheet is listed the required amounts of ore, coal and carbonates needed to produce a tonne of hot metal. Should these materials be combined as composite pellets, the pellets would have the following composition.

> 65.3% iron ore 22.2% coal 8.7% CaCO₃ (4.9% CaO) 3.8% MgCO₃ (1.6% MgO)

It is gratifying to find that an independently constructed mathematical model <u>requests a pellet composition nearly identical to that which was</u> found by experiment to be the most <u>successful</u> (Lot L9-2, see Table 3.1 and Appendix A3.3).

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IRON ORE CONCENTRATE	68.1 PCT IRON AS MAGNETITE
	5.2 PCT SILICA
	•5 PCT ALUMINA
	1.2 PCT HNO
COAL COMPOSITION ***	82.4 PCT TOTAL CARBON
	59.1 FCT FIXED CARBON
	5.4 PCT HYDROGEN
	5.2 PCT OXYGEN
	1.0 PC.T SULPHUR
	4.7 PCT ASH
	54.5 PCI ASH SILICA
	33.5 PUT ASH ALUMINA
SLAG COMPOSITION ***	1.2 0 DCT CAO
SERG CONTOSTITER	
	10-0 PCT AL203
	14.0 PCT MG0
í ,	
PROCESS TEMP 1520.0	C
PREHEAT TEMP 25.0	C
SLAG BASICITY RATIO 1.	53
SUL PHIDE CAPACITY	•41E-03
SULPHUR PCT 1.78	7
MNO PCT .08	8
ACTIV OF SIC2 .0	65
MATEDIALS INCHT	
ORF WT KG 1409	7
CCAL WT KG 479.	, 8
FLUX WT KG	
CA0 105.0 CR	AS CACO3 187.5
MGO 35.0 CR	AS MGC03 81.3
SI02 .14.3	
AL203 10.4	
OXYGEN WT KG 782.2	
MATERIALS OUTPUT	
SLAG WT KG 25C.	0
HOT METAL WT KG	1000.0
CARBON PCT 3.	00
SILICON PCT .	70
MANGAN PCT .	20
SULPHUR FCT .	033
EXUESS HEAT +KILU-JOLL	LS • J141E+U/
HEAT UREATED . 12967E	
NEAL NEEDED • 90258E	rų/
FEFECTIVE CARPON HITTH	TATION FACTOR
CITEDITAE ONKOUN UITET	LAILUN FAUIUR= •92
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Figure 7.6: Computer print-out data sheet for the mid-range base computation.

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Figure 7.7 illustrates the effect of additional coal on the energy balance within the vessel. It can be seen that additional coal increased considerably the heat generated, while the heat required remained nearly the same at about 10 x 10^6 kJ/tonne hot metal. An expanded version of the heat balance equation can be found in Appendix A7.1.3 which details the individual components of the equation. Here, it may be worthwhile to review some of the assumptions on which the calculations are based, some of which were discussed in Chapter 5.

Within an individual pellet, the gaseous products from iron ore reduction are H₂O and CO₂. Also, dissociation of the carbonate bonding material produces ω_2 . Since the pellets are hot and there is an abundance of carbon, the calculations assume 100% conversion of these gases to H₂ and CO within the pellet. This introduces very little error because by experiment (Chap. 5), it was found that 95% of the pellet offgas was a mixture of H_2 and CO. The next assumption considers that all of the H_2 , CO and C (from soot and extra coal) emerging from the pellet is burned to H₂O and CO₂ by oxygen lanced into the vessel.) Further, the heat energy released from this combustion is retained within the vessel by being transferred to the slag and reacting pellets. It will be recalled that heats of combustion were calculated at 1527°C, i.e., the reactants are heated to the reaction temperature prior to combustion. Hence the combustion off-gases leaving the vessel at 1527°C represent no additional loss of heat. This sensible heat of the off-gas could be recovered later in a steam generating plant but it does not enter the calculations here.

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Slag Wt. - 250 kg. Hot Metal - 1000kg Temp. — 1520 °C 4.7 % Ash 1 480 kg 0.70 % Si 0.035 % S 3.0 % C 5.4 % H 1.0 % S 82.4 % C Coal -No Preheat 300°C Retained in Vessel 100 % Min. Process Heat Required 201 600 . 65% 120 ADDITIONAL COAL, kg/tonne 001. COAL, kg/tonne hot metal 520 560 80 60 Heat Generated 6 20 Reduction and Required for Min. Carbon Solution 480 Base 0 <u>۲ م</u> × ا0e *۴* ۱ HEAT ENERGY , ω ω ဖ

Figure 7.7: Energy balance within the vessel. Effect of additional coal.

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The line labelled "Heat Generated, Retained in the Vessel - 100%" in Figure 7.7, is the theoretical maximum based on the above assumptions. It can be appreciated that terms such as "combustion efficiency" should be avoided as they are too restrictive and even ambiguous. It is recognized that a large percentage of the heat generated, calculated as a theoretical maximum, cannot be recovered within the vessel. Inefficiencies in pellet reactions, combustion reactions, physical supply of reactants, and heat transfer to slag, pellets and vessel walls, all combine to lower the heat available to the process. Hence the dashed lines labelled 75% and 65% represent those percentages of the theoretical heat generated which are more likely to be retained in the vessel.

Two lines in Figure 7.7 represent the minimum process heat required; the first, for the case wherein the composite pellets are not preheated and the second, wherein the pellets are preheated to 300°C. Preheating coal above, say, 350°C can cause a loss of volatiles and stickiness. The components of the heat balance equation which contribute to the process heat requirement (heats of reduction reactions and enthalpies) are detailed in Appendix A7.1.3.

It can be seen from Figure 7.7 that should 75% of the theoretical heat generated be retained in the vessel, then no extra coal would be needed. At 65%, there would be a need for 100 kg of additional coal. This is about the maximum amount of coal which should be incorporated in a composite ore-coal pellet (c.f., Section 3.4.1). Should there be a need for more than 100 kg of additional coal, then coal or coke could be added directly to the vessel rather than as a constituent of the composite pellets. A small saving can be effected by preheating the pellets,

but in practical terms perhaps ways and means to retain more heat within the vessel would show greater dividends.

Heat losses through the vessel walls and mouth have been estimated from basic oxygen furnace studies as being about 0.3×10^6 kJ/tonne hot metal or about 3% of the process heat required. This was not included in the heat requirement calculations, but as it is fairly small, perhaps it can be thought of as part of the unretained portion of the heat generated.

7.5 Summary

Computer charge calculations were made in which a series of heat and mass balance equations were solved from given input data.⁵ The purpose was to show the effects on input materials required and output metal produced of changes in process variables such as temperature, hot metal carbon and sulphur, and slag weight. Most important, the computer program functioned as a learning aid in which it showed what overall trends can be expected when one or more variables of the process are changed.

It was shown that the hot metal carbon content has a major influence on desulphurization. Higher carbon levels allow desulphurization to lower sulphur levels using less slag.

The minimum operating slag weight at the highest basicity ratio . was about 200 kg/tonne hot metal. This depends mainly on the type of iron ore used, the chosen composition of the slag and the operating temperature.

Operating at higher temperatures increases desulphurization and also increases the hot metal silicon content. These trends are all well known in a metallurgical sense, but the possession of graphs, percentage values and weights of materials required will prove to be valuable information on which to base pilot-plant trials.

The coal requirement of the process was found to be nearly insensitive to other parameters such as hot metal carbon, temperature and slag weight. However, if less than 75% of the theoretical heat generated by combustion is retained in the vessel, then additional coal or coke would be needed to satisfy the heat requirement (10 x 10^6 kJ/tonne hot metal) of the process.

The mid-range computation which was selected as a base or standard (Figure 7.6), required an input pellet composition nearly identical to that which was found by experiment to be the most successful.

CHAPTER 8

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GENERAL DISCUSSION

8.1 Raw Materials and Pelletizing Techniques

Although the present work made use of only one type of iron ore concentrate (magnetite) and one type of coal (bituminous, high-volatile A), nothing was found during the investigation to suggest that the process would be unduly sensitive to changes in raw materials. An iron ore concentrate from any iron ore deposit should be suitable. Also, very low silica and alumina contents of the concentrate are not necessary since an appreciable slag weight is required for desulphurization. Nearly any type of coal should be suitable because coal is used only as a source of carbon and hydrogen. Certainly, premium grade coking coals of low sulphur content are unnecessary. However, the use of coals with very high sulphur and ash levels would be governed by slag conditions during operation and upper limits would need to be determined. Fluxes and binders such as calcined lime and dolomite, mixed to obtain desired CaO/MgO ratios, are not seen to present serious problems in either grade or supply.

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An optimal pellet composition was found experimentally which resulted in iron of low sulphur and high carbon contents. At a later date, a computer model study of the process was constructed independently of the experiments, based on equilibrium thermodynamics and a slag composition which was best for desulphurization at 1500°C. The computer program requested input raw materials, as separate entities, in nearly the same proportions as the experimentally found optimal pellet composition;

i.e., 66% ore, 23% coal and 11% calcium/magnesium carbonate. Pellets of this composition were made successfully in the present work, but in very small quantities.

Composite pellets containing coal should not be heated above 350° C, but pelletizing on an industrial scale should present no serious problems as there are a number of cold-bonding techniques available. Carbonatebonding⁽³⁹⁾ has been developed commercially and should receive prime consideration. The Grangcold⁽⁹¹⁾ process, developed in Sweden, uses cement as a binder which is made from blast furnace slag, but portland cement would be suitable should cement-bonded pellets be desired. Two similar processes, $COB0^{(92)}$ and $MTU^{(93)}$ use a technique known as hydrothermal bonding in which pellets containing lime and silica flour as binders are placed in steam autoclaves at 205°C to form gels and mineral hydrosilicate bonds. Briquets may also be made. Coal will soften at about 370°C and could itself act as a binder in a number of hot-briquetting processes⁽⁹⁴⁾.

8.2 Process Slag

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The weight of slag produced by a blast furnace is usually in the range of 150-350 kg/tonne hot metal, depending on the amount of input gangue materials. An estimated slag weight of 200-300 kg/tonne for the process under consideration is comparable to blast furnace smelting. However, calculations of slag weights were based on slag/metal partition reactions for sulphur and an assumed slag composition which contained no FeO. Should iron oxide be dissolved in the slag, #desulphurization would be hindered to a considerable extent⁽⁸⁹⁾ and a larger slag weight would then be required. This is one of the reasons why considerable effect was made to inhibit fayalite formation within the pellet during reduction.

From the beginning, it has been recognized that the slag is perhaps the most important component of the process. Not only must it be a holding medium for sulphur, phosphorus and gangue materials, but it has the added function of transferring the heat from combustion to the reacting pellets and metal bath. In order to transfer the required heat, combustion should take place, wholly or in part, within the body of slag which is both turbulent and foaming. Creating these conditions in a university laboratory was not possible and these aspects have been left to a second program which would entail pilot-plant testing.

Foams and emulsions in steelmaking have been investigated extensively during the past decade (95.to~99). Steelmaking slags usually contain appreciable quantities of iron oxide which can react with carbon dissolved in the liquid iron droplets or bath. Carbon monoxide gas is produced from this reaction which, in turn; foams the slag. In the case under consideration, all conditions conducive to foaming are present; e.g., gas evolution from the reacting pellets, suspended solids (coke particles) and metal droplets in the slag, and surface active agents such as P_2O_5 and sulphur which lower interfacial tension.

It has been assumed that the process slag would contain very little FeO, but this may not be so. The oxygen jet can, and probably will, oxidize many small iron droplets before they can sink through the slag to the metal bath. On the other hand, excess carbon as coke particles, will join the slag and help to keep the FeO content at low levels. Unfortunately, there is no way of knowing the nature of the process slag and whether it will foam before experiments are actually performed.

8.3 Product - Liquid Iron

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Liquid iron as a product of ironmaking has a distinct advantage over sponge iron pellets in that very little energy is needed to convert it to steel. Sponge iron pellets are usually melted and refined to steel in electric-arc furnaces which are energy intensive and require about 600 kWh/tonne steel (2.2 x 10^6 kJ/tonne).

Blast furnace iron is usually saturated with carbon and as a result, kish graphite precipitates from the iron, floats in the air and becomes an environmental nuisance. This would be avoided in the process under consideration because the liquid iron product is not expected to be carbon-saturated.

A question arises as to why one should strive for high carbon levels in the iron when in order to convert it to steel, the carbon must be removed. In Section 6.5, it was shown that effective desulphurization depends not only on the sulphide capacity (or basicity) of the slag but also on the activity of carbon in the iron. Hence, the higher the carbon content, the easier it is for the slag to desulphurize the metal. Should the input materials contain very little sulphur, then indeed it should be possible to smelt⁶ directly to steel, but this is utopian. Desulphurization will remain a prime consideration in iron smelting processes which are based on coal.

Conversion of the liquid iron product to steel, by basic oxygen steelmaking, may be performed in the same vessel after decanting the primary slag, or the iron may be transferred to a second vessel and processed in the same manner as blast furnace hot metal.

8.4 Generation of Heat

It will be recalled that in Chapter 5, the off-gas from reacting pellets was analysed in order to calculate how much heat could be made available by combustion of the gas with oxygen. In Section 5.4.3 and 5.4.4, it was calculated that the volume (at STP) of the off-gas from reaction of carbonate-bonded pellets (L9-2) would be 0.45 litre/gram pellet and its chemical composition would be 30% H₂, 65% CO and 37 g/m³ soot. The net heating value of this gas was calculated to be 12670 kJ/m³. Also, calculations showed that there is very little difference between ΔH_{298K} and ΔH_{1800K} for a gas of this composition. These calculated values were based on experimental results from reaction of cement-bonded pellets (Table 5.5).

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As mentioned previously, the base composition requested by the computer program (Fig. 7.6) was found to be nearly the same as for the carbonate-bonded pellets which were found to be most promising and hence used for the heat of combustion calculations in Section 5.4.4. On the other hand, the heat values generated by the program were calculated from the overall heat and mass balance equations and were not based on experimental results. Since the pellet compositions were nearly the same, the volume and net heating value of the off-gas calculated in Chapter 5, should apply (approximately) to the conposition listed in Figure 7.6, and the heat generated values could then be compared.

From Figure 7.6, the total weight of ore, coal, $CaCO_3$ and $MgCO_3$ to be fed as pellets into the process vessel to produce one tonne hot metal is 2160 kg. The amount of gas which would be produced is

and hence the heat generated would be

972 m³ X 12670 kJ/m³ = 12.3 x 10⁶ kJ/tonne hot metal.

This value compares favourably to the program value (Fig. 7.6) of 12.9 x 10^6 kJ/tonne hot metal which is considered high by about 3% since it did not account for the minor amounts of H₂O and CO₂ already in the gas.

There are several ways in which to vary the overall heat supply to the process and to control the temperature at various locations within the vessel. Should the flame from the oxygen jet become too intense, the oxygen supply may be reduced. Also, if the operating temperature becomes too high, shredded scrap could be charged into the vessel. On the other hand, to increase the operating temperature of the process, the coal content of the pellets may be increased or carbon in the form of coal, coke or calcium carbide, may be added directly to the vessel. Perhaps, if an immediate action was needed to increase temperature, the oxygen lance could be lowered so that silicon and carbon could be oxidized directly from the melt. However, before doing so, it should be remembered that sulphur reversion from slag to iron may occur due to the lower carbon content of the iron and to higher SiO₂ and FeO levels in the slag.

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A discussion of heat generation should include the subject of radiation heat losses, at least in general terms. In order to do this, one needs a mental picture of the process vessel and a proposed production rate. It is envisioned that the size of the vessel be no larger than a top-blown 150 ton basic oxygen steelmaking furnace. The internal height and diameter would be about 9 m and 5 m respectively which would result in an internal surface area of about 160 m². Let the average refractory thickness be 0.5 m and let it consist of tar-bonded magnesite (96% MgO) bricks which have a thermal conductivity ⁽¹⁰⁰⁾ of about 13 kJ m/hr m² °K. By substitution, the heat loss through the refractory *fining* would be about 6.2 x 10⁶ kJ/hr.

The production rate of such a vessel is envisioned to be not more than 30 tonne/hr but not less than 20 tonne/hr; hence an average of 25 tonne/hr. This leads to a loss of 250,000 kJ/tonne hot metal through the refractory walls and bottom. Should the vessel be clear of fume and not in operation, it would lose heat by radiation through the mouth. A formula has been derived (100) to calculate this heat loss which incorporates the non-blowing time and the area of the vessel mouth,

i.e., $Q_r = 9000 A_m (t_{min})^{0.9} k cal. \pm 5\%$

In this case, if the area of the mouth is $4 m^2$ and 10 minutes of each hour is not utilized in blowing, then radiation through the mouth is calculated to be 1.2 x 10^6 kJ for that 10 min. period or 50,000 kJ/tonne hot metal. Hence, the total heat loss by radiation from the vessel is calculated to be about 0.3 x 10^6 kJ/tonne hot metal or about 3% of the total process heat required.

A topic which has not yet been discussed is the amount of oxygen required for combustion and the oxygen flow rate to be expected. It may have been noticed from Figure 7.6 that the weight of oxygen required for the production of one tonne of hot metal was about 800 kg. This seems to be very large especially when compared to BOF steelmaking which requires about 80 kg/tonne steel. Oxygen is normally lanced into a 150 ton basic oxygen furnace at the rate of about 12000 ft³/min. (340 m³/min.)⁷. In the present case, the amount of oxygen required is 800 kg/tonne X 0.70 m³/kg $i = 560 \text{ m}^3$ /tonne hot metal. Should iron be produced at the rate of 25 tonne/hr, then oxygen lancing at the rate of 230 m³/min. (8,000 ft³/min.) is required. Hence, at a production rate of 25 tonne/hr, the oxygen flow rate for the process under consideration would be about two thirds that normally used during operation of a 150 ton basic oxygen steelmaking vessel.

8.5 Energy Requirements

It has been discussed previously and shown in Figure 7.7, that a reasonable estimate of coal required to produce liquid iron from composite pellets is about 560 kg/tonne hot metal. The coal used for these calculations has a net energy value of about 33,000 kJ/kg (14,200 Btu/lb) and hence the fuel energy required is 18.5×10^{6} kJ/tonne hot metal.

The energy required for pelletizing composite pellets should be very little because the pellets would not need to be heat hardened (indurated). Elliott⁽⁵⁾ estimated that the energy required to calcine lime is about 0.52 x 10^6 kJ/tonne lime, and since about 150 kg lime and magnesia are needed as flux/binder materials, then the energy required for calcination is only about 0.1 x 10^6 kJ/tonne hot metal.

Calculation of the net energy requirement for oxygen is much more uncertain. The manufacture of oxygen (101) requires about 520 kWh/tonne O_2 and since the amount of oxygen required for combustion is about 800 kg/tonne hot metal, then the electric power required is 420 kWh/tonne hot metal or 1.5×10^6 kJ/tonne; a substantial amount. However, the process will generate after combustion, large volumes of off-gas at high temperatures which may be used to raise steam and thereby generate, through steam turbines, a large portion of the power required to manufacture the oxygen:

From a mass balance it can be shown that after combustion of the reduction off-gases, about 1580 kg CO_2 and 270 kg H_2O per tonne hot metal will leave the vessel at a temperature of at least 1900°K (1627°C). Enthalpy values ⁽⁷⁴⁾ for these gases at 1900°K are 1940 kJ/kg CO_2 and 3750 kJ/kg H_2O and hence the sensible heat of the process off-gas would be about 4.0 x 10^6 kJ/tonne hot metal.

The raising of steam in a boiler to generate electric power normally is not attempted in BOF operations because of its very intermittent nature, e.g., 15 minutes of high temperature off-gas in each hour. However, for the process under consideration, a steadier operation is envisioned which could be adapted to electric power generation. Thermal efficiencies in electricity generation are usually about 30-35%, but due to uncertainties, perhaps it is best to be conservative and estimate that 25% of the sensible heat of the off-gas can be converted to electric power through steam generation. Hence, 1.0×10^6 kJ/tonne hot metal as electric power may be recovered, which leaves 0.5×10^6 kJ/tonne (140 kWh/tonne) to be purchased or otherwise produced.

In summary, a combination of the net electric power and fuel requirements for the reduction of composite pellets yields an energy consumption estimate of 19.0 x 10^6 kJ/tonne hot metal.

A comparison of alternative routes to steel, with respect to energy consumption per tonne of liquid steel, is shown in Table 8.1 and Figure 8.1. Energy consumption data, brought forward from Chapter 2, have been modified somewhat in order that all unit processes are treated equally. Electric power is converted directly, i.e., 1 kWh = 3600 kJ, and scrap additions or other complicating factors are not considered. The objective is to show the cumulative effect of the unit processes on energy consumption rather than an exact analysis.

A major portion of the energy consumed in pellet preparation is that required for induration. An average value for the total energy consumed is about 2.0 x 10^6 kJ/tonne pellets and since about 1.5 tonnes are required to produce 1 tonne of iron, then 3.0 x 10^6 kJ/tonne iron is consumed in the preparation of pellets for the blast furnace, shaft furnace, and rotary kiln processes.

There is no information available on the energy requirements of making carbonate-bonded composite pellets but since induration is not required and calcination of the flux/binder material requires only 0.1×10^6 kJ/tonne hot metal, a reasonable estimate for the energy required would be 0.5×10^6 kJ/tonne pellets. Since 2 tonnes of composite pellets are required to produce 1 tonne of hot metal, then about \sim 1.0×10^6 kJ/tonne hot metal would be the energy required for the preparation of composite pellets.

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	Blast Furnace Smelting	Composite Pellet Smelting	Shaft Furnace Reduction	Rotary Kiln Reduction
STEELMAKING 🦯	0.3	0.3	3.0	3.0
IRONMAKING	15.5	19.7	14.0	18.0
COKING	3.2			
PELLETIZING	3.0	1.0	3:0	3.0
ø	22.0	21.0	20.0	24.0
	ENERGY C	ONSUMPTION, ×	10 ⁶ kJ/tonne	steel

Table 8.1: A comparison of alternative routes to liquid steel, with respect to energy consumption.



Figure 8.1: A comparison of alternative routes to liquid steel, with respect to energy consumption.

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A factor for the product yield should be considered when converting hot metal or sponge iron pellets to steel. For comparison purposes here, let the yield of steel be 94% if the iron is produced via blast furnace smelting, 96% if via composite pellet smelting, and 92% if via sponge iron processes. Hence the energy requirements of the coking and ironmaking unit processes should be increased as follows.

 $Coking^{(5)}$:

5.6 x 10^{6} kJ/tonne coke x 0.55 tonne x 1.06 = 3.2 x 10^{6} kJ/tonne steel Blast furnace smelting⁽⁵⁾:

14.6 x 10^6 kJ/tonne hot metal x 1.06 = 15.5 x 10^6 kJ/tonne steel Composite pellet smelting:

19.0 x 10^{6} kJ/tonne hot metal x 1.04 = 19.7 x 10^{6} kJ/tonne steel Shaft furnace reduction (Midrex⁽¹²⁾):

13.0 x 10^{6} kJ/tonne sponge iron x 1.08 = 14.0 x 10^{6} kJ/tonne steel Rotary kiln reduction (SL/RN, Krupp⁽²⁰⁾):

16.7 x 10^6 kJ/tonne sponge iron x 1.08 = 18.0 x 10^6 kJ/tonne steel

The net energy requirement for basic oxygen steelmaking is quite small and is estimated to be 0.3×10^6 kJ/tonne steel. Energy is required for auxiliary heating, calcination of lime flux and the production of a nominal amount of ferroalloys. Some heat recovery can be achieved by raising steam in an off-gas boiler system. Over half of the energy consumed is electric power which is required to manufacture oxygen. On the other hand, melting and refining sponge iron pellets in electric-arc steelmaking furnaces consumes a considerable quantity of electric power, i.e., 600 kWh/tonne steel, plus about 0.8 x 10^6 kJ/tonne steel for miscellaneous uses. The energy values for steelmaking used here differ from those given by Elliott⁽⁵⁾ and listed in Table 2.1 because the electric power required was converted directly to its kJ equivalent.

An in-depth energy analysis at this stage of the investigation is not necessary, and perhaps premature, but some approximate values are in order. It can be seen from Figure 8.1 that the energy requirements to produce steel via composite pellet smalling is not much different from the other ironmaking processes. Inducation of pellets and coking are not required by the proposed process and yet the total energy consumed to produce steel is nearly the same as that for blast furnace smelting. This is mainly because blast furnace off-gas bas a low sensible heat content and a high chemical (latent) energy content which allows for high efficiencies in energy recuperation. The situation is reversed for composite pellet smelting. However, benefits gained from adopting composite pellet smelting lie elsequere. For instance, there are economic advantages to be gained from adopting a process which can be installed in small units and in which neither metallurgical coke nor natural gas is required. These advantages, among others, were discussed more fully in Chapter 1.

To sum up, the net energy consumption for composite pellet smelting is estimated to be 19.0 x 10^{6} kJ/tonne hot metal (18.2 x 10^{6} Btu/ton). When the process is linked between pellet preparation and steelmaking, the energy required to produce liquid steel is about 21.0 x 10^{6} kJ/tonne steel (20.1 x 10^{6} Btu/ton) which is not much different from other iron- and steelmaking processes.

CHAPTER 9

SUMMARY AND CONCLUSIONS

An assessment of the proposed process in which composite iron orecoal pellets are reacted to produce liquid iron was found to be such a large task, that it was necessary to break the project into smaller, more manageable packages. Each of the four laboratory investigations, Chapters 3,>4, 5 and 7 were presented and discussed separately, but always they remained integral parts of the overall project. The areas of investigation were limited to those which could be studied best, within the confines of a university laboratory.

Laboratory Reduction of Pellets

Reduction experiments were performed with a laboratory furnace on pellets of various compositions under conditions in which the heat transfer to the reacting pellets was very fast. It was found that composite pellets are capable of very fast reduction, i.e., from cold pellet to reduced iron at 1500°C in 110 seconds. This leads to the conclusion that within a largescale process vessel, the rate at which such pellets would reduce would depend on the rate at which they could be heated and not on any internal constraints. Pellets containing 22-23% coal were found to have sufficient coal to reduce the iron oxide and carburize the resultant iron. Self-fluxing pellets were shown to produce an iron melt in which desulphurization and carburization were at maximum levels.

Metallographic Investigation of Partially Reduced Pellets

Bentonite-bonded Pellets

Reduction of ore-coal pellets bonded with 2% bentonite produced an agglomerate of fayalite slag and iron which when melted completely resulted in a slag of high FeO content and an iron melt containing less than 2% carbon and high sulphur content. This type of pellet is not recommended for the process under consideration. Also not recommended is the reduction of ore-coke pellets bonded with bentonite. These pellets produced iron with very little or no carbon content mainly because reduction was slower and the ore melted before it was reduced.

Cement-bonded Pellets

Reduction of ore-coal pellets bonded with 12% cement produced an agglomerate of Ca-olivine slag and iron but the initial high FeO content of the slag was reduced quickly. When melted completely, such pellets produced a slag with a low FeO content and an iron melt of high carbon content which was desulphurized to a considerable extent. However, cement-bonded pellets would produce a large amount of slag and therefore should be considered as second choice, at best.

Carbonate-bonded Pellets

Reduction of ore-coal pellets bonded with 11% carbonate produced a slag with a very low FeO content and an iron melt of high carbon and low sulphur contents. Each iron oxide particle reacted with lime and was reduced individually by H_2 and CO. In this way, the formation of a slag with an initially high FeO content was prevented. A beneficial effect

on desulphurization and carburization of the iron was shown when the liquidus temperatures of the internal pellet slags were lowered by the addition of magnesia to the lime (carbonate) bonding. Carbonate-bonded pellets should be considered as the feed material for the high-temperature reduction process presently under study. Under laboratory conditions it was found that such pellets can produce an acceptable product, i.e., an iron melt containing above 3.0%C, about 0.20%Si and below 0.05%S.

Analysis of the Off-gas from Pellet Reduction

From an analysis of the off-gas from reaction of cement-bonded ore-coal pellets, it was found that the total **vol**ume of gas evolved was 0.44 litre per gram of pellets reacted. When pellets were introduced to heat (1500°C), the coal began to gasify inmediately causing a very high rate of hydrogen evolution, at the beginning, then tapered off, while carbon monoxide from the combined ore-carbon reduction reactjons increased. There were no significant amounts of H_2O , CO_2 or N_2 in the off-gas at any time during reaction. The off-gas from cement-bonded pellets contained 41% H_2 and 53% CO, while the off-gas from carbonate-bonded pellets was calculated to contain 30% H_2 and 65% CO. Heat of combustion calculations showed that the off-gas from either type of pellet would have a net heating value of about 3000 kcal/m³ or 12500 kg/m³ (340 Btu/ft³).

Process Analysis and Energy Requirements

A computer model of the proposed metallurgical system was constructed in which a series of heat and mass balance equations were solved in order to illustrate the effects of changes in process variables on input material requirements and on the metallurgical system as a whole. It was shown that the hot metal carbon content has a major influence on desulphurization and, if at all possible, a carbon content of 3% or more should be maintained. A slag of maximum basicity at operating temperatures and of weight about 250 kg/tonne hot metal is recommended for adequate desulphurization of the hot metal. A carbonate-bonded composite pellet comprising 66% ore, 23% coal and 11% calcium/magnesium carbonate was found to be satisfactory, with respect to desulphurization and carbon content of the resultant iron melt.

A reasonable estimate of the energy requirements of the process are 560 kg coal and 420 kWh per tonne hot metal. Two thirds of this electric power, used to manufacture oxygen, may be generated on site through recuperation of the sensible heat contained in the process offgas. The net energy consumption for composite pellet smelting is estimated to be 19.0 x 10^6 kJ/tonne hot metal (18.2 x 10^6 Btu/ton). When the process is linked between pellet preparation and steelmaking, the energy required to produce liquid steel is about 21.0 x 10^6 kJ/tonne steel (20.1 x 10^6 Btu/ton).
Assessment

Laboratory studies have determined the manner in which individual composite pellets react, their compositional limitations and the chemical compositions of the resultant liquid iron and slag. Also determined were the composition and net heating values of the reaction off-gases which must be burnt to supply the required process energy. Indications from a process analysis, supported by the results of these studies, are considered to be positive for an ironmaking process based on composite pellet smelting.

However, of equal importance are problem areas which have been identified and introduced but not persued. Experiments should be performed to obtain information on combustion by oxygen lancing, foaming of slags, and heat transfer from combustion to the reacting pellets. The ultimate success of the process will depend on whether sufficient heat can be retained within the vessel where it is needed. To this end, hotmodel experimental trials are recommended. Carbonate-bonded pellets, as a first choice, should be prepared in quantity and of sufficient quality to withstand handling and thermal shock. A hot-model BOF "pilot-plant" facility of 100-200 kg hot metal capacity, may be adapted for continuous pellet feeding.

Theoretical and laboratory studies on the reduction of composite iron ore-coal pellets to liquid iron have been completed and should form the basis for a second experimental program, suggested above. Only after completion of hot-model BOF "pilot-plant" studies can one assess fully the future prospects for composite pellet smelting.

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APPENDIX A3

A3.1 Chemical and Sieve Analyses of Coal

The coal used in this investigation was supplied by the Canadian Metallurgical Fuel Research Laboratory, CANMET, Dept. of Energy, Mines and Resources, Ottawa. There, it is used as a reference coal in coking tests and is classified as bituminous, high-volatile A (Wharton #2, Pennsylvania). The complete chemical analysis, supplied by CANMET, Ottawa is as follows.

<u>Proximate</u> (dry basis)	<u>wt %</u>	- <u>Ash Analysis,</u>	<u>wt %</u>
Fixed carbon	59.1	SiO ₂	54.5 (±1.0)
Volative matter	36.2	A1203	33.5 (± .7)
Ash 3	4.7 (±.2)	Fe ₂ 03	6.2
		TiO2	1.3
<u>Ultimate</u> (dry basis)	<u>wt %</u>	$P_2 O_5$	0.1
Carbon	82.4 (±.3)	CaO	1.9
Hydrogen	5.4 (±.1)	MgO	1.0
Sulphur	.72(±.01)	SO3	0.2
Nitrogen ·	1.6	Na ₂ 0	0.6
Ash	4.7	ĸ,Ō	1.3
Oxygen (by difference)	5.2 .	L	

<u>Gross Calorific value</u> -- 14,730 Btu/lb. <u>Softening Temperature</u> -- 377°C

After disc pulverizing, the sieve analysis of the coal was

100% minus 50 mesh 49% plus 100 mesh 19% plus 200 mesh 32% minus 200 mesh

A3.2 Chemical Analysis of Portland Cement

Cement clinker was supplied by St. Lawrence Cement Co., Mississauga, Ont. and was ground to 90% minus 325 mesh. The chemical analysis of the cement clinker was given by the company as percentages of the mineral constituents, e.g., 55% C_3S (3CaO·SiO₂). This type of analysis has been converted to percentages of the separate oxides as follows.

	44	
	<u>Oxide</u>	<u>wt %</u>
	CaO	65.
•	SiO ₂	20.
	A1203	8.
	Fe_20_3	3.
~	MgÕ	0.5
	(K ₂ 0 + Na ₂ 0)	0.6
	Minor constituents	1.
	Loss on Ignition	2.

In addition, the ground clinker was analysed for sulphur and was

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found to contain 0.37% S.

A3.3 Calculation of Equilibrium Slag/Metal Distribution of Sulphur and

Percentage Desulphurization Values

The equilibrium slag/metal distribution of sulphur, at the time of melting, has been calculated for each pellet reduction experiment. Background information on applied metallurgical thermodynamics including derivations of basicity, sulphide capacity of slags, activities of sulphur and carbon in iron, and slag/metal distribution reactions are presented in Chapter 6, Section 6.5. In this section, the detailed calculations for experiment L9-2 have been chosen as representative.

Pellet Analysis

65.8% ore of 68% Fe, 5.2% SiO₂, 0.3%, M_2O_3 , 0.3% MgO and 0.063% S 23.1% coal of 4.7% ash and 0.72% S

coal ash of 55% SiO₂ and 34% Al₂ b_3

7.4% CaCO₃

3.7% MgCO₃

Melt Analysis

3.76% C, 0.16% Si, 0.052% S

Basis for calculation, 1 kg of pellets reduced at 1500°C

Input of sulphur

0.42 g from ore + 1.66 g from coal = 2.08 g total \$ load Weight of metal produced (assuming total reduction of iron oxide): 447. g Fe + 17. g C + 1. g Si = 465. g metal.

The maximum sulphur content of the metal assuming no desulphurization would be 2.08/465. $x \cdot 100 = 0.447\%$ S_{max}

Input of slag constituents:

Composition of slag:

37.4% SiO₂; 5.6% Al₂O₃; 38.3% CaO; 18.7% MgO

Phase diagrams (40) indicate that a slag of this composition would have a liquidus temperature of about 7500°C. The basicity ratio, B;(41) is calculated as

$$B = \frac{(\% \text{ Ca0}) + .7(\% \text{ Mg0})}{.94(\% \text{ Si0}_2) + .18(\% \text{ Al}_2 \text{O}_3)} = 1.42$$

and thus the sulphide capacity (42), C_s of the slag at 1500°C is

log $C_S = 1.39$ (B) - 5.57 = - 3.60 therefore: $C_S = 25.1 \times 10^{-5}$ <u>Metal</u> Henrian Activity of Sulphur in Iron, h_S : log $f_S = e_S^{3C}[%C] + e_S^{5i}[\%Si] = .14[3.76] + .063[.16] = .536$ therefore: $h_S = f_S[\%S] = 3.44 \times [\%S]$ Henrian Activity of Carbon in Iron, h_C : log $f_C = e_C^{3C}[\%C] + e_C^{5i}[\%Si] = .18[3.76] + .074[.16] = .688$ therefore: $h_C = f_C[\%C] = 4.88 \times [3.76] = 1863$

Slag/Metal Sulphur Partition:

Thermodynamic data have been used to combine the sulphide capacity of the slag with a sulphur partitioning equation between slag and iron^(41,42). Slag/metal sulphur distribution equations have been derived and presented in detail in Section 6.5.3.

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The final forms of the equation are:

$$\log (\%S)_{slag} = (460./T + 3.35) + \log h_{C} + \log C_{S} + \log h_{S}$$

or

$$(x_{S})_{s1ag} = 10.(460./T + 3.35) \times h_{C} \times C_{S} \times h_{S}$$

where T is the reduction test temperature in degrees Kelvin. Substitution of the known values reduces this equation to

$$(%S)_{slag} = 64.5[\%S]_{iron}$$
 -- (1)

Sulphur Balance:

Since the total sulphur input and the weights of both slag and iron have been calculated, a mass balance on sulphur, provides a second equation, vis.

$$\frac{107 \ (\%S)}{100} s \log_{+} \frac{465 \ [\%S]}{100} i ron = 2.08 \ g \ sulphur$$
(2)

Solving the two equations gives $(\%S)_{slag} = 1.84$ and

$$[\%S]_{iron} = [\%S]_{eq} = 0.029$$

Percentage Desulphurization:

The equilibrium percentage desulphurization can now be calculated. $\text{%DeS}_{eq} = 100 - \frac{[\text{\%S}]_{eq} \times 100}{[\text{\%S}]_{max}} = 100 - \frac{.029}{.447} \times 100 = 93.5\%$

Similarily the actual percentage desulphurization can also be calculated. Since [%S] = .052, then

Data from each experiment were treated in the above manner and Table 3.2 collates the resulting calculated values which were used to construct the desulphurization curves of Chapter 3.

APPENDIX A4

A4.1 - Electron-Microprobe Analyses - Correction Procedure and Estimation of Accuracy

These microprobe data have been processed by MYSTIC 4, a mineralogical version of MAESTRO (<u>Microprobe Analysis by Energy Dispersive Spec-</u> troscopy) by R.H. Packwood, Metal Physics Section, CANMET, EMR, Ottawa.

Spectra gathered by an ORTEC Si(Li) EDXA system, equipped with a pulse pile-up rejection, are processed first to remove low energy noise. Then, the peaks and background reference regions are smoothed; in this case with a 5-point least-squares fit. Background beneath the peaks are calculated by a variation on the method of C.E. Fiori et al. (Anal. Chem. vol. 48, #1, 1976, p 172), which allows for absorption in the sample, the crystal Be-window and the detector dead layer.

In the ZAF iterations, (atomic number, absorption, and secondary fluorescence corrections), overlaps between the supposedly Gaussian peaks are corrected together with peak "tailing", escape peaks and Beta line interferences. In the event of problems on the light elements, wavelength spectra can be included.

The oxides are reported as MgO, Al_2O_3 , SiO_2 , K_2O , CaO and FeO. Sulphur is reported as elemental S; the Ca or Fe associated with S are included with the oxides. A negative peak indicates that the theoretical background is greater than that actually observed. A query indicates that a peak centre exceeds its wings by less than two standard deviations, i.e., a decernable but indefinite and inaccurate peak.

The over-all accuracy of the final result is a function of counting statistics, the reliability of the theory involved, the distance a peak is from a background fitting region, and the stability of the JEOL microprobe. For background: Typical statistics for a 5-point, 200 sec. count range from $\pm 2-3\%$. The theory and its present calibration factors appear to be good to $\pm 5\%$. These lead to a background reading good to $\pm 7-8\%$ (L.E. to HE.).

For peaks: The corresponding figures for statistics and theory are $\nu \pm 1\%$ and $\pm 2\%$.

Drift in the electron beam current can be partially compensated for by using a reference material and noting the current digitizer reading. This is probably good to $\pm 1\%$. Other electronic instabilities have not been quantified.

In total, the order of accuracy for all elements above Mg is:

0.1 - 1.0 wt %, ±10% of reading 1.0 - 10 wt %, ±3% " " 10 - 100 wt %, ±1% " "

For Mg 0.1 - 1.0 wt %, ±20% " ". The detection limit is about 0.1 wt % for all elements.

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The output format of the computer program allows results to be printed to the fourth decimal place because some research projects may need and can obtain such accuracy. In the present case wherein slags are being analysed, only the first decimal place need be considered and even then the orders of accuracy stated above, apply.

A4.2 - Electron-Microprobe Analyses - Results

The following pages contain the results of electron microprobe analyses, as listed by the computer print-out.

Specimen	Number of Analyses
Bentonite-bonded Pellets	
Fayalite crystal	4
Fayalite eutectic glass	4
Slag A	3
Slag Al	3
Melt Slag B	3.
Cement-bonded Pellets(*)	
Slag 1, Ca-Olivine	4 . `
Slag 2	4
Melt Slag 3	4
Carbonate-bonded Pellets	
Melt Slag C	4
Ca-wustite	7
Standards- SiO ₂ , FeO, MgO, CaCC	P_3 and $A1_20_3$

(*) The cement-bonded pellets were analysed at a date later than the others and at a much higher beam current. This raised considerably the intensity and background counts, but otherwise the method and results of the analyses are comparable to those done earlier.

J INTENSITY	SE NPUT BG.	MPLE FA	YAL I T	E CPYSTAL DUTPUT WT PERCEN	77701/	17-1	
2.02 1.22 60.32 .72 ? 00 ? .07 ? 61.95 0.00	3.22 4.47 5.36 5.27 4.97 4.69 2.67 0.00 TDTALS	.00544 .00234 .09489 .00136 0.00000 .00019 .46875 .42704 1.00001 5 ITEP	MG AL SI F CA FE D ATION	1.3429 .4519 14.5075 .1779 0.0000 .0190 52.3516 31.1491 68.8509	2.2265 .8541 31.0316 .1779 0.0000 .0266 67.3766 0.0000 101.6933	•	;
				· •			
інтензіту І	ΥΑ NPUT BG.	IMPLE FA'	ALIT	E CPYSTAL DUTPUT WT PERCENT	77701×	17 2	
.71 1.04 28.82 .14 7 02 7 .24 7 30.33 0.00	1.74 2.38 2.80 2.62 2.33 2.15 1.02 0.00 TOTALS	.00374 .00391 .08885 .00054 0.00000 .00131 .44984 .45183 1.00001 5 ITEP(MG AL SI FE CA FE D ATION	.9177 .7505 13.5453 .0697 0.0000 .1329 50.4317 34.1523 65.8477 \$	1.5215 1.4184 28.9735 .0697 0.0000 .1859 64.9056 0.0000 97.0745	٥	
	SA	IMPLE FA'	YALIT	E CRYSTAL	77701/	1/ 3	
I TITENSITY	NPUT BG.	WT FTN		OUTPUT	T ONIDES	1	
.93 .47 7 28.94 .24 7 .12 7 .02 7 31.48 0.00	1.66 2.28 2.71 2.58 2.35 2.19 1.12 0.00 TOTALS	.00489 .00178 .08923 .00091 .00062 .00010 .46685 .43563 1.00001 5 ITEP	MG AL SI K CA FE D ATION	1.2109 .3443 13.6383 .1183 .0672 .0099 52.1574 32.4538 67.5462 S	2.0077 .6507 29.1723 .1183 .0809 .0138 67.1266 0.0000 99.1703		•
T	19 SA	MPLE FAY	ALIT	E CPYSTAL	77701×	1 < 4	•
INTENSITY	BG.	WT FTN		WT PERCENT			
1.90 2.13 60.96 .37 7 .14 ? .64 ? 60.85 0.00	3.52 4.83 5.70 5.45 4.91 4.56 2.31 0.00 TDTALS	.00511 .00408 .09590 .00070 .00039 .00175 .46045 .43162 1.00001 5.ITERF	MG AL SI S K CA FE D	1.2547 .7847 14.6574 .0920 .0421 .1782 51.5106 31.4803 68.5197	2.0803 1.4830 31.3523 .0920 .0507 .2493 66.2941 0.0000 101.6017		

ELECTPON-MICPOPPOPE ANALYSES

C. ADAMI 5 JULY 1977 DIPECT PEDUCTION SAMPLES

BEAM VOLTAGE 15.00 PV



	82	MPLE FA'	YAL I TE	E EUT.LIO.	777017	1 / Z	
TN				DUTPUT			
INTENSITY	B6.	WT FTN		WT PEPCENT	DXIDES		
.54 ?	3.34	.00146	MG	.3171	.5257	K.	
17.12	4.55	.03285	· AL	5.6673	10.7111		
86.60	5.06	.13623	51	20.3432	43.5141		
2.64	4.62	.00501	2	.6820	.6820		
.92	4.19	.00254	ĸ	.2866	.3453		
4.36	3.90	.01198	CA	1.2760	1.7851		
40.96	2.01	.30992	FE	35.7647	46.0292		x
0.00	0.00	.50002	0	35.6628	0.0000		
	TOTALS	1.00001		64.3372	103.5929		
		5 ITER	ATION	2			
		()			1		
	SB.	IMPLE 🔪 FA'	YALITI	E EUT.LIQ.	77701/	17.3	
11	IPUT			DUTPUT			
INTENSITY	PG.	HT-FTH		HT PEPGENT	DXIDES		
05 ?	3.21	0.00000	MG	0.0000	0.00nó		,
. SO.0S	4.36	.03840	AL	6.4356	12.1632	ł	probe beam
84.36	4.79	.13271	SI	19.6012	41.9269	. 1	antially bitters
6.77	4.36	.01284	2	1.7377	1.7377		partially mining
.97 ?	3.93	.00266	ĸ	.3024	.3644		a large tes
5.81	3.66	.01597	CR	1.7172	2.4024		Danticle
35.05	1.90	.26522	FE	30.8917	39.7576	1	
0.00	- 0.00	.53221	0	39.3143	0.0000 /	r	
1	TOTALS	1.00000		60.6857	98.3522		
		5 ITER	ATION	2			

TN	3A) PUT	MPLE FAY	YALITE	EUT.LIO.	77701× 1	/ 4	•
INTENSITY	B6.	ЫТ ЕТН		HT PEPCENT	DMIDES		
16 7 10.54 44.96 1.37 .43 2.78 18.62 0.00	1.60 2.18 2.39 2.14 1.96 1.82 .93 0.00 TOTALS	0.00000 .03961 .13861 .00511 .00231 .01495 .27615 .52325 1.00000 5 ITEP(MG AL SI CA FE D ATIONS	0.0000 6.6692 20.5919 .6974 .2625 1/6030 32.0918 38.0843 61.9157	0.0000 12.6047 44.0460 .6974 .3164 2.2425 41.3021 0.0000 101.20.2)	
	()	·					N
к . Т.N	DUT SA	MPLE FA'	YALITE	ELEUT.LIO. DUTPUT	77701/	1 5	
INTENSITY	BG.	WT FTN		NT PERCENT	CMIDES		• ,
.11 ? 19.82 89.22 .4.61 .95 5.80 35.16 0.00	3.26 4.44 4.88 4.43 4.04 3.77 1.99 0.00 TDTALS	.00029 .03803 .14036 .00874 .00262 .01594 .26606 .52797 1.00001 5 ITEP	MG AL SI S K CA FE D ATION	.0603 6.3667 20.7071 1.1914 .2982 1.7146 30.9879 38.6738 61.3262	.1000 12.0330 44.2925 1.1914 .3593 2.3987 39.8815 0.0000 100.2564		e.
				····	· · · ·		
INTENSITY	SA PUT BG.	MPLE FÁ' NT FTN	YAĻ I TE	E EUT.LIO. DUTPUT NT PEPCENT	77701/ • OXIDES	1× 6	
.28 ? 19.75 90.64 3.56 1.32	$3.20 \\ 4.37 \\ 4.81 \\ 4.37 \\ 4.00 \\ 4.00 $	\00074. .03789 .14258 .00675 .00362	MG AL SI S' K	.1573 6.4074 21.1770 .9244 .4112	.2607 12,1099 45.2976 .9244 .4955		
5.10 37.67 0.00	3.74 1.97 0.00 TDTALS	.01402 .28506 .50934 1.00001 5 ITER	CA FE D ATIONS	1.5044 33.0672 36.3512 63.6488	2.1047 42.5575 0.0000 103.7503		i,



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	58	MPLE MEL	T SL	86 B	77701/	12	1
· II	IPUT			OUTPUT			
INTENSITA	FG.	WT FTN		WT PEPCENT	DXIDES		
2.64	1.58	.01391	MG	2.3524	3.9004		
9.98	5.05	.03752	ĤL.	5.5084	10.4108		
77.69	2.16	.23954	2 I -	32.3387	69.1725		
.20 2	1173	.00076	S	.1093	.1093		
.87	1.56	.00470	k.	1.5605	.6754		
2.48	1.45	.01338	CA	1.5172	2.1225		
5.58	.72	.03270	FE	12.0305	12,9093		
0.00	0.00	.60750	0	47.5830	0.0000		
	TOTALS	1.00000		52.4170	99,3002		
		6 ITERF	ITION	2			
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7.4101	92	MPLE MEL	T SL	AG B	777017	17 2
INNI	91			DUTPUT		
INTENZITA	<u>~£5.</u>	WT FTN		WT PERCENT	DXIDES	
2.61	1.38	.01376	MG	2.4158	4.0054	
8.49	1.78	.03193	RL.	4.8254	9,1199	
72.08	1,92	22226	12	30.3002	64 9121	
27 2	1 57	00101	÷.	1444	1444	
• / :		.00101	 	- 1,994	• 1444	
	1.41	.00420	ĸ	.4969	.5987	
2.29	1.31	.01235	CA	1.3883	1.9422	
7.22	.65	.10701	FE	12.9104	16.6157	
0.00	0.00	.60751	n ⁻	47.5187	0.0000	
T	2.JATC	1.00001	-	52 4812	97 2294	
		5 17500	TION	° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° °	21.6004	

•	Se Se	MPLE MEL	T SL	AG B	77701/	1/	3
INTENSITY	B6.	NT FTN		UTPUT	DXIDES		
2.10 10.27 73.35 13 7 1.38 3.07 4.91 0.00	1.54 1.97 2.09 1.67 1.47 1.34 .62 0.00 TOTALS	.01105 .03862 .22615 .00050 .00745 .01654 .07279 .62692 1.00012	MG AL SI FE D	1.8694 5.6347 30.4385 .0706 .8842 1.8746 8.8444 50.3836 49.6164	3.0994 10.6496 65.1080 .0706 1.0655 2.6286 11.3827 0.0000 93.9984	÷	۲.)
•		5 ITEPA	TION	S			

	S F	AMPLE CA	-OUTV	/INE	77801/	1/1
1 THEFT THE TEN	1PUT		,	DUTPUT		
11116112114	Fip.	MT FTH		WT PEPCENT	I OMIDES	
2.39	4.03	.00576	MG	1.2296	2.0386	
.66 /	5.60	.00114	ĤL	.1962	.3709	
76.41	6.52	.10757	SΤ	15.0636	32.2210	•
.25 7	5.95	.00042	2	.0531	.0531	
15 ?	5,19	0.00000	к	0.0000	0.0000	
85.82	4.78	.21112.	CB	22,1386	20 9710	
34.98	2.25	.23693	FF	27 2016	25 7002	•
0.00	0.00	43706	'n	32 5174	0 0000	
	TOTAL	1.00000	U	22, 21(4) 22, 3002	0.0000	,
		5 ITEP	аттом	200,405 1000	101.4361	
-	, '	-		•		
	ĨĤ	IMPLE CA	עומר –	THE	77004 4	. . .
٩I	IPUT				67801×	17.2
· THTENSITY	EG.	HT FTN		UT PEPCENT		
	~				DVIDEZ	•
2.90	4.10	.00698	MG	1.4788	2.4518	
.68 7	5.68	.00417	FIL	.2013	3805	
75.56	6.61	.10639	ΣI	14.8616	31:7889	
.57 7	6.05	.00096	5	. 1212	1010	
14 7	5.28	0.00000	۰.	0.0000	8 0000	
94.12	4,87	.23153	ГВ	24,2857	22 9757	,
33.68	2.29	.22810	FF	26 8173	22.7127	
0.00	0.00	42487	'n	32 2342	27.J127 0.0000	
`	TOTALS	1.00000	C 7	67 7658	102 2210	
		5 ITEPP	AT LUN:	20001110	100.0015	
				-		`
	SA	MPLE CA-	- הו דעי	-	779.01	
ИІ	SAI PUT	MPLE CA-	OLIV	- INE - / DUTPUT	77801/	1/3
IN INTENSITY	SAI PUT BG.	MPLE CA- WT FTN	OLIV	- / OUTPUT WT PERCENT	77801	` 1⁄3
IN INTENSITY	SAI PUT BG.	MPLE CA- WT FTN	OLIV	- INE VOUTPUT WT PERCENT	77801 OXIDES	1∕3
IN INTENSITY 3.54	SAI PUT BG. <u>4.06</u>	MPLE CA- WT FTN .00852	OLIV Mi5	INE / DUTPUT WT PERCENT 1.7619	77801/ OXIDES 2.9212	1∕3
IN INTENSITY 3.54 .84 ? -	SAI PUT BG. 4.06 5.57	MPLE CA- WT FTN .00852 .00144	OLIV MG AL	- / DUTPUT WT PERCENT 1.7619 .2435	77801/ OXIDES 2.9212 .4602	1/ 3
IN INTENSITY 3.54 .84 ? .79.95	SAI PUT BG. 4.06 5.57 6.45	MPLE CA- WT FTN .00852 .00144 .11257	MIS AL SI	- / OUTPUT WT PERCENT 1.7619 .2435 15.5724	77801 OXIDES 2.9212 .4602 33.3093	1 × 3
IN INTENSITY 3.54 .84 ? .9.95 .45,7	SAI PUT BG. 4.06 5.57 6.45 5.82	MPLE CA- WT FTN .00852 .00144 .11257 .00076	MIS AL SI S	INE / OUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959	77801 OXIDES 2.9212 .4602 33.3093 .0959	1 × 3
IN INTENSITY 3.54 .84 ? .9.95 .45 ? .04 ?	SAI PUT BG. 4.06 5.57 6.45 5.82 5.82 5.03	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010	-OLIV MG AL SI S	INE / OUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109	77801- OXIDES 2.9212 .4602 33.3093 .0959 .0131	1/ 3
IN INTENSITY 3.54 .84 ? .9.95 .45 ? .04 ? .95.90	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591	-OLIV MG AL SI K CA	INE / OUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109, 24.8887	77801- OXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192	1/ 3
IN INTENSITY 3.54 .84 ? .99.95 .45 ? .95.90 29.58	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031	MG AL SI CA FE	INE / OUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109, 24.8887 23.6974	77801- OXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985	1 × 3
IN INTENSITY 3.54 .84 79.95 .45 .7 .95.90 29.58 0.00	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040	MG AL SI CA FE D	INE / OUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109, 24.8887 23.6974 33.7295	77801- OXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985 0.0000	1 × 3
IN INTENSITY 3.54 .84 79.95 .45 .7 .95.90 29.58 0.00	SAI PUT BG. 4.06 5.57 6.45 5.03 4.63 2.13 0.00 TOTALS	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000	MG AL SI K CA FE D	INE / OUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109, 24.8887 23.6974 33.7295 66.2705	77801- OXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985 0.0000 102.1173	1 / 3
IN INTENSITY 3.54 .84 ? .9.95 .45 ? .04 ? 95.90 29.58 0.00	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00 FDTALS	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA	MG AL SI S K CA FE D	INE / DUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705	77801/ OXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985 0.0000 102.1173	1 × 3
IN INTENSITY 3.54 .84 79.95 .45 .7 .04 7 95.90 29.58 0.00	SAI PUT BG. 4.06 5.57 6.45 5.03 4.63 2.13 0.00 TOTALS	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA	MG AL SI K CA FE D	INE / OUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705	77801- OXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985 0.0000 102.1173	1 / 3
IN INTENSITY 3.54 .84 79.95 .45 .04 795.90 29.58 0.00	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 (2.13 0.00 TOTALS SAN	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA	-OLIV MG AL SI K CA FE O TLONS	INE / DUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705	77801/ DXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985 0.0000 102.1173	1 × 3 4
IN INTENSITY 3.54 .84 79.95 .45 .04 795.90 29.58 0.00	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00 TOTALS SAN	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA	MG AL SI K CA FE D TLONS	INE / OUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705 NE OUTPUT	77801/ DXIDES 2.9212 .4602 33.3093 .0131 34.8192 30.4985 0.0000 102.1173	1 × 3 . 4
IN INTENSITY 3.54 .84 79.95 .45 .7 .95.90 29.58 0.00 INTENSITY	SAI PUT BG. 4.06 5.57 6.45 5.03 4.63 2.13 0.00 FDTALS SAN SUT BG.	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA WT FTN	OLIV MG AL SI K CA FE D TLØNS	INE WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705 NE OUTPUT WT PERCENT	77801- OXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985 0.0000 102.1173 77801- 0XIDES	1 × 3 4
IN INTENSITY 3.54 .84 79.95 .45 79.95 .04 7 95.90 29.58 0.00 INTENSITY 4.96	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00 TOTALS SUT BG. 4.18	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA MT FTN .01194	-OLIV MG AL SI S K CA FE D TLØNS OLIVI	INE / DUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705 NE DUTPUT WT PERCENT 2.5193	77801/ DXIDES 2.9212 .4602 33.3093 .0131 34.8192 30.4985 0.0000 102.1173 77801/ DXIDES 4.1769	1 3
IN INTENSITY 3.54 .84 79.95 .45 .7 95.90 29.58 0.00 INTENSITY 4.96 .60 7	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00 FOTALS SUT BG. 4.18 5.72	MPLE CA- MT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA MT FTN .01194 .00103	MG AL SI S K CA FE O TLØNS OL IVI MG AL	INE / DUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705 NE DUTPUT WT PERCENT 2.5193 .1780	77801/ DXIDES 2.9212 .4602 33.3093 .0131 34.8192 30.4985 0.0000 102.1173 77801/ DXIDES 4.1769 .3365	1 × 3 1 × 4
IN INTENSITY 3.54 .84 79.95 .45 .7 95.90 29.58 0.00 INTENSITY 4.96 .60 77.21	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00 TOTALS S.03 4.63 2.13 0.00 TOTALS S.72 6.65	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA MT FTN .01194 .00103 .10870	MG AL SI SK CA FE D TLØNS OLIVI MG AL SI	INE / DUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705 NE BUTPUT WT PERCENT 2.5193 .1780 15.3035	77801- OXIDES 2.9212 .4602 33.3093 .0131 34.8192 30.4985 0.0000 102.1173 77801- OXIDES 4.1769 32.7342	1 3
IN INTENSITY 3.54 .84 79.95 .45 7 95.90 29.58 0.00 INTENSITY 4.96 .60 77.21 .21 7	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00 TOTALS S.03 4.63 7.13 0.00 TOTALS S.72 6.65 6.06	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA MT FTN .01194 .00103 .10870 .00035	MG AL SI K CA FE D TLONS OLIVI MG AL SI S	INE / DUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705 NE DUTPUT WT PERCENT 2.5193 .1780 15.3035 .0445	77801/ DXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985 0.0000 102.1173 77801/ DXIDES 4.1769 .3365 32.7342 .0445	1 3 4
IN INTENSITY 3.54 .84 79.95 .45 7 .04 7 95.90 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 20.57 2	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00 TOTALS SAN SAN SAN SAN SAN SAN SAN SAN SAN SA	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA MT FTN .01194 .00103 .10870 .00035 0.00000	OLIV MG AL SI K CA FE D TLØNS OLIVI MG AL SI S K	INE / DUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705 NE DUTPUT WT PERCENT 2.5193 .1780 15.3035 .0445 0.0000	77801- OXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985 0.0000 102.1173 77801- OXIDES 4.1769 .3365 32.7342 .0445 0.0000	1 3 4 1 4
IN INTENSITY 3.54 .84 79.95 .45 7 .04 7 95.90 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00 TOTALS SAN PUT BG. 4.18 5.72 6.65 6.06 5.28 4*86	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA MT FTN .01194 .00103 .10870 .00035 0.00000 .20194	OLIV MG AL SI K CA FE D TLØNS OLIVI MG AL SI S K CA	INE / DUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705 NE DUTPUT WT PERCENT 2.5193 .1780 15.3035 .0445 0.0000 21.2542	77801- DXIDES 2.9212 .4602 33.3093 .0131 34.8192 30.4985 0.0000 102.1173 77801- DXIDES 4.1769 .3365 32.7342 .0445 0.0000 29.7347	1 3
IN INTENSITY 3.54 .84 79.95 .45 .04 79.90 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 29.58 0.00 20.59 20.59 20.59 20.59 20.59 20.59 20.00 20.59 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.00 20.	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00 FDTALS SIT BG. 4.18 5.72 6.06 5.28 4:86 5.28 4:86	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA MT FTN .01194 .00103 .10870 .00035 0.00000 .20194 .22819	OLIV MG AL SI K FE D TLØNS OLIVI MG AL SI S K CA FE	INE / DUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705 NE DUTPUT WT PERCENT 2.5193 .1780 15.3035 .0445 0.0000 21.2542 26.8315	77801- DXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985 0.0000 102.1173 77801- DXIDES 4.1769 1.3365 32.7342 .0445 0.0000 29.7347 34.5321	1 3
IN INTENSITY 3.54 .84 79.95 .04 79.95 29.58 0.00 29.58 0.00 29.58 0.00 29.58 7.21 .21 7 .21 7 .22 82.09 33.69 0.00	SAI PUT BG. 4.06 5.57 6.45 5.82 5.03 4.63 2.13 0.00 FOTALS SIT BG. 4.18 5.72 6.65 6.06 5.28 4:86 2.26 0.00	MPLE CA- WT FTN .00852 .00144 .11257 .00076 .00010 .23591 .20031 .44040 1.00000 5 ITEPA MT FTN .01194 .00103 .10870 .00035 0.00000 .20194 .22819 .44786	OLIV MG AL SI K CA FE D TLENS OLIVI MG AL SI S K CA FE D	INE / OUTPUT WT PERCENT 1.7619 .2435 15.5724 .0959 .0109 24.8887 23.6974 33.7295 66.2705 NE OUTPUT WT PERCENT 2.5193 .1780 15.3035 .0445 0.0000 21.2542 26.8315 .33.8690	77801- DXIDES 2.9212 .4602 33.3093 .0959 .0131 34.8192 30.4985 0.0000 102.1173 77801- DXIDES 4.1769 1.3365 32.7342 .0445 0.0000 29.7347 34.5321 0.0000	1 3

5 ITERATIONS

	1 8 1	, MPLE ILF	62		77801	17
11	łF'UT			DUTPUT		
INTENSITY	FG.	WT FTN		WT PEPCENT	DX1DES	
2.48	4.21	.00596	MG	1.1604	1,9240	
12.10	5.58	.02078	AL	3.3398	6.3123	
68.12	6.21	.09590\	1 E	13.2415	28.3237	
2.26	5.66	. 00383 ^Y	Ž	.4767	4767	
. 02 7	4.84	.00005	ĸ	.0050	.0060	
109.36	4.44	.26903	CA	28.6396	40.0668	
18.94	2.02	.12824	FE	15.4042	19.8252	
0.00	0.00	47621	D	37.7327	0.0000	
	TOTALS	1.00000		62.2673	96.9346	
		5 ITEPA	AT LON	2	ι.	

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77801/ 1/ 6 IAMPLE CLAG 2 DUTPUT INFUT **WT PEPCENT** DNIDES INTENSITY ЫT FTN EG. .00848 1.5661 2.5966 3.53 4.28 MG .5301 15.5530 1.0018 1.99 7 5.62 .00342 ĤL 84.87 ΞI 33.2678 6.42 .11949 . 2239 .2239 1.07 5.67 5 7 .00182 0.0000 -.16 7 r 0.0000 4.90 0.00000 1.A 51.6113 36.8915 140.13 4.51 .34474 10.3937 9.78 8.0759 FE 2.11 .06623 37.1595 ۵ 0.0000 0.00 0.00 .45583 1.00000 62.8405 99.0951 TOTALS 5 ITEPATIONS

*	SB.	MPLE ¹ 3LA	6.2		778014	1 < 7
11	IPUT		•	OUTPUT		,
INTERSITY	BG.	MT FTN		WT PEPCENT	DXIDES	
				, , , , , , , ,		
3.34	4.45	.00803	ru ₂	1.4948	2.4/84	
8.98	5.84	.01541	AL	2.4023	4.5403	
84.63	6.52	. 11915	SI	15.9418	34.0995	
1.15 ?	5.78	.00195	S	.2438	.2438	
33 7	4.97	0.00000	k.	0.0000	0.0000	
121.20	4.57	.29816	CA	32.0022	44.7710	
12.66	2.10	. 08574	FE	10.4039	13.3898	
0.00	0.00	.47156-	0	37.5113	0.0006	
	TOTALS	1.00000		62.4887	99.5228	
		5 ITEDA	TION	7		
				_}		

	2A	IMPLE CLA	16 2		77801-	$1 \le 8$
IN	PUT			OUTPUT		
THIEHZITA	FG.	HT FTN		MT PEPCENT	DXIDES	
2.93	4.56	.00706	MG	1.3446	2.2294	
6.01	6.01	.01033,	AL	1.6346	3.0894	
74.35	6.78	.10468	SI	14.0130	29.9739	
8.48	6.06	.01439	S	1.7729	1.7729	
17 ?	5.10	0.00000	ĸ	0.0000	0.0000	
118.98	4.67	29270	CĤ	31.3275	43.8272	
15.22	2.09	.10310	FE	12.4610	16.0373	
0.00	0.00	.46776	D	37.4464	0.0000	
Å	TOTALS	1.00000		62.5536	96.9301	
•		5 ITEPP	NOITE	S.		

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TA TNPHT	MPLE MELT	1186 3 047007	77801 1/9	
INTENSITY DE.	MT FTN	WT PEPCENT	DMI DE S	
6.24 4.33 10.14 5.54 98.97 6.12 4.11 5.26 .31 7 4.52 126.41 4.16 1.83 1.92 0.00 0.00 TOTAL S	.01501 M(.01741 A) .13934 S .00698 S .00076 P .31096 CP .01237 FP .49718 D 1.00001 5 ITEPATIO	5 2.5532 2.5766 I 18.0548 .8781 .0802 A 33.9671 E 1.5270 40.3630 59.6370	4.2331 4.8698 38.6193 .8781 .0967 47.5200 1.9653 0.0000 98.1822	``
1 1	MPLE MELT	SLAG 3	77801 - 1710	
INPUT INTEN⊈ITY BG.	WT FTN	DUTPUT WT PERCENT	DXIDES	
5.77 4.41 10.93 5.65 97.57 6.21 4.26 5.32 .38 4.51 127.26 4.13 2.42 1.84 0.00 0.00 TDTALS	.01388 M .01877 A .13737 S .00723 S .00093 K .31307 C .01642 F1 .49234 D 1.00001 5 ITEPATI	5 2.3740 2.7802 I 17.8528 .9086 .0978 9 34.1641 5 2.0244 39.7980 60.2020	3.9361 5.2546 38.1872 .9086 .1179 47.7956 2.6054 0.0000 98.8054	, [¹ -
\$ SF	MPLE MELT	SLAG 3	77801 < 1/11	
INPUT INTENSITY BG.	WJ FTN	DUTPUT	DMIDES	64
5.88 4.40 12.31 5.61 97.33 6.14 4.76 5.25 .31 7 4.43 121.05 4.05 2.71 1.78 0.00 0.00 TOTALS	.01415 M .02114 A .13703 S .00807 S .00076 K .29779 C .01836 F .50270 D 1.00001	5 2.4175 3.1329 I 17.8991 1.0192 .0807 A 32.5479 E 2.2624 40.6403 59.3597	4.0083 5.9212 38.2861 1.0192 .0972- 45.5345 2.9117 0.0000 97.7783,	
		2112	17	
ŢŔ INDUT	MPLE MELT	ILAG 3 OUTOUT	77801 - 1-12	•
INTENSITY BG.	NT FTH	WT PEPCENT	OX PDE S	,
5.98 4.38 11:60 5.58 97.89 6.11 2.65 5.21 .30 ? 4.41 122.49 4.03 1.03 1.78 0.00 0.00 TOTALS	.01439 M .01991 A .13782 S .00449 S .00075 K .30133 C .00698 F .51434 D 1.00001 5 ITERATI	5 2.4360 2.9322 I 17.8844 .5652 .0785 A 32.9383 E .8628 42.3027 57.6973	4.0390 5.5418 38.2547 .5652 .0946 46.0807 1.1104 0.0000 95.6863	Ê

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	5F	IMPLE	MELT S	LAG C	77701/	12	1
INTENSITY	Abûl Be		-N	DUTPUT	1 1 1 1 1 1 1 1 1 1	-	-
0.00		··· · ·	11	WI FEFCEN	UXIDE2		
8.87 4.52 45.46 2.36 .03 7 48.84 .79 0.00	1.78 2.15 2.41 2.12 1.36 1.73 .35 0.00 TOTALS	.0445 .0161 .1335 .0083 .0004 .2505 .0111 .5351 1.0000 6 IT	ia MG 9 AL 9 SI 5 S 9 CA 8 FE 0 ERATIO 8 ERATIO	7.3900 2.5197 17.9526 1.0751 .0512 27.6427 1.3798 41.9889 58.0111	$12.2525 \\ 4.7622 \\ 38.4007 \\ 1.0751 \\ .0617 \\ 33.6721 \\ 1.7758 \\ 0.0000 \\ 97.0002 \\ \end{array}$	•	
	۶a	A IAW	MELT ST	ac c	77701	, , , ,	
41	IPUT		NCCI 34	DUTPUT	77701Z	1/	2
INTENSITY	PG.	WT FT	Н	WT PEPCENT	OXTDES (
8.32 4.43 45,77 1.94 .04 ? 50.64 .23 , 0.00	1.34 2.22 2.47 2.15 1.35 1.70 .79 0.00 TOTALS	.0417 .0158 .1344 .0068 .0001 .2598 .0032 .5378 1.0000 5 IT	2 M& 6 AL 1 SI 6 S 7 K 3 CA 5 FE 9 D 1 EPATION	6.8828 2.4429 17.9275 .8789 .0207 28.6411 .4023 42.8037 57.1963	11.4117 4.6171 38.3469 .0249 40.0689 .5178 0.0000 95.8663		
	182 182	1PLE I	MELT SL	.AG C	77701/	1/	з
INTENSITY	* BG.	MT FTI	ч	DUTPUT WT PERCENT	NXINES	•	-
8.22 3.44 45.64 1.23 06 ? 52.78 .15 ? 0.00	1.81 2.20 2.46 2.12 1.82 1.67 .77 0.00 TBTALS	.04124 .01237 .13408 .00439 0.00000 .27079 .00219 .53510 1.00009 5 ITE	4 MG 2 AL 3 SI 5 S 6 FE 0 D 1 PATION	6.8319 1.9018 17.7771 .5543 0.0000 29.7754 .2707 42.8889 57.1111	$\begin{array}{c} 11.3272\\ 3.5944\\ 38.0251\\ .5543\\ 0.0000\\ 41.6559\\ .3484\\ 0.0000\\ 95.5053\end{array}$		
	182 Y	IPLE N	IELT SL	86 C	777012	1,2	А
Ini Inpensity	PUT RG.	MT FTM	4	DUTPUT		1	т
8.17 3.10 45.37 1.61 08 ? 51.45 .21 ? 0.00	1.92 2.31 2.58 2.21 1.85 1.69 .73 0.00 IOTALS	.04098 .01109 .13323 .00571 0.00000 .26399 .00300 .54202 1.00001 5 ITE	MG AL SI S K CA FE D	6.8028 1.7142 17.6456 .7274 0.0000 29.0378 .3705 43.7017 56.2983	11.2791 3.2397 37.7440 .7274 0.0000 40.6238 .4769 0.0000 94.0909		

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		IMPLE CA	-พบรา	ITE	77701/	14.5
INTENSITY	B6.	ыт ғтн		DUTPUT WT PEPCENT	OXIDES	
27 ? .13 ? .42 ? .58 .03 ? 16.62 43.18 0.00	1.87 2.62 3.14 3.33 2.88 2.65 1.25 0.00 TOTALS	0.00000 .00047 .00124 .00206 .00016 .08527 .60992 .30087 1.00000 6 ITEP	MG AL SI K CA FE D ATION	0.0000 .0975 .1978 .2462 .0164 8.2071 66.0302 25.2047 74.7953	0.0000 .1842 .4231 .2462 .0198 11.4818 84.9809 0.0000 97.3360	
-	SA	MPLE CA-	-NUST	ITE	77701/	1/ 6
ΙΗΤΕΗΣΙΤΥ	NPUT RG.	ыт ели		OUTPUT	DXIDES	
$\begin{array}{c} .07 & 7 \\ .30 & 7 \\ .61 \\02 & 7 \\03 & 7 \\ 11.92 \\ 47.21 \\ 0.00 \end{array}$	1.80 2.55 3.03 2.97 2.76 1.41 0.00 TDTALS	.00037 .00108 .00181 0.00000 0.00000 .06115 .66684 .26876 1.00000 6 ITEPf	MG AL SI SK CA, FE D ATION	.1019 .2283 .2918 0.0000 0.0000 5.8299 71.3557 22.1924 77.8076 \$.1690 .4315 .6241 0.0000 0.0000 8.1561 91.8347 0.0000 101.2154	
, INTENSITY	TAI NPUT RG.	MPLE CA- WT FTN	-MUST	ITE DUTPUT MT PERCENT	77701/	1/ 7
39? .17 .64 .10? .25? 8.10 46.33 0.00	1.75 2.47 2.96 3.16 2.77 2.55 1.24 0.00 TOTALS	0.00000 .00061 .00186 .00035 .00126 .04158 .65448 .29984 1.00000 6 ITEPF	MG AL SI FE D TTON:	0.0000 1276 3009 0423 1279 3.9731 70.2295 25.1987 74.8013	0.0000 .2411 .6436 .0423 .1541 5.5584 90.3854 0.0000 97.0250	
11		IPLE CA-	yust:		77701×	17 8
INTENSITY	BG.	WT FTN	(HT PEPCENT	DXIDES	
$\begin{array}{r} .04 \\ .22 \\ 1.14 \\ .11 \\ .10 \\ 10.43 \\ 44.73 \\ 0.00 \end{array}$	1.72 2.42 2.91 3.10 2.73 2.52 1.24 0.00 TOTALS	.00022 .00078 .00335 .00038 .00052 .05351 .63180 .30943 1.00000 6 ITEPA	MG AL SI K CA FE D	.0603 .1624 .5386 .0460 .0526 5.1335 68.1103 25.8962 74.1038	.1000 .3070 1.1522 .0460 .0634 7.1818 87.6580 0.0000 96.5082	

II INTENSITY 45 ? 37 ? 04 ? 19 ? 17 ? 7.80 45.26 0.00	51 BG. 1.78 2.50 3.00 2.79 2.57 1.20 1.00 TOTALS	AMPLE WT FT 0.0000 0.0000 0.0000 0.0000 0.0000 .0420 .6713 .2866 1.0000 6 IT	CA-WUS N 0 MG 0 AL 0 S 0 F 3 CA 4 FE 3 D 0 EPATION	TITE DUTPUT WT PEPCENT 0.0000 0.0000 0.0000 0.0000 3.9980 71.7906 24.2113 75.7887	77701/ DXIDES 0.0000 0.0000 0.0000 0.0000 5.5933 92.3946 0.0000 97.9878	1/13
IN INTENSITY 44 7 31 7 07 ? 25 ? 31 ? 2.70 46.81 10.00	EA BG. 1,99 2,79 3,36 3,58 3,11 2,86 1,35 0,00 TOTALS	MPLE (MT FTN 0.00000 0.00000 0.00000 0.00000 0.00000 .01452 .29115 1.00000 6 ITE	CA-WUST N MG AL SI SI K FE D RATION:	ITE DUTPUT MT PEPCENT 0.0000 0.0000 0.0000 1.3756 73.9195 24.7049 75.2951	77701/ DXIDES 0.0000 0.0000 0.0000 0.0000 1.9245 95.1344 0.0000 97.0588	1~14
INF INTENSITY 18 12 7 .24 7 34 7 23 7 3.42 47.25 0.00 T	2,AM B6. 1.94 2.73 3.28 3.50 3.06 2.82 1.35 0.00 DTALS	IPLE CI NT FTN 0.00000 0.00000 0.00074 0.00000 0.00000 01845 .70082 .27929 1.00000	A-WUSTI MG AL SI S K CA FE O	TE DUTPUT WT PERCENT 0.0000 0.0000 .1201 0.0000 0.0000 1.7463 74.5079 23.6257 76.3743	77701 / 1 OXIDES 0.0000 .2569 0.0000 2.4431 95.8916 0.0000 38.5916	/15

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	SA	MPLE SI	sc	,	77701/	12 9
11 Intensity	PUT RG.	WT FTN		UUTPUT WT PEPCENT	DXIDES	
.12 7 .14 7 98.23 .04 7 .12 ? .08 7 .06 ? 0.00	1.06 1.37 1.52 1.03 .93 .86 .42 0.00 TDTALS	.00078 .00067 .38831 .00019 .00086 .00057 .00113 .60749	MG AL SI S K CA FE D	.1169 .0862 45.1767 .0280 .1056 .0667 .1401 54.2799 45.7201	.1937 .1629 .96.6330 .0699 .1273 .0933 .1803 0.0000 .97.4604	•
T	S.P NPLIT	IMPLE FEI	٥	ΠΗΤΡΗΤ	77701/	1/10
INTENSITY	BG.	WT FTN		WT PEPCENT	OXIDES	
61 ? 13 .06 ? 01 ? .06 ? .04 ? 52.46 .0.00	1.91 2.68 3.23 3.44 2.99 2.75 1.28 0.00 TOTALS	$\begin{array}{c} 0.\ 00000\\ 0.\ 00000\\ .\ 00016\\ 0.\ 00001\\ .\ 00031\\ .\ 00023\\ .\ 74100\\ .\ 25830\\ 1.\ 00000\\ \end{array}$	NG AL SI K A FE D	0.0000 0.0000 0.0270 0.0000 0.0310 0.0217 78.1452 21.7751 78.2249	$\begin{array}{c} 0.\ 0000\\ 0.\ 0000\\ .\ 0578\\ 0.\ 0000\\ .\ 0374\\ .\ 0303\\ 100.\ 5728\\ 0.\ 0000\\ 100.\ 6983 \end{array}$,
11	SA NPUT	MPLE MG	כ	DUTPUT	77701×	1 / 1 1
INTENSITY	· B5.	WT FTN		WT PEPCENT	DXIDES	
86.36 10 ? .06 ? .20 ? .06 ? .05 ? .05 ? 0.00	1.68 1.19 1.44 1.56 1.37 1.27 .62 0.00	.43326 0.00000 .00019 .00070 .00033 .00024 .00078 .56450 1.00000	MG AL SI K CA FE O	58.5243 0.0000 .0359 .0981 .0400 .0275 .0959 41.1783 58.8217	97.0333 0.0000 .0767 .0981 .0482 .0385 .1235 0.0000 .97.4183	^
4I &	SA 1PUT ·	MPLE CAO	03	DUTPUT	77701/	1/12
INTENSITY	EG.	WT FTN		WT PEPCENT	DXIDES	
$\begin{array}{c}26 ? \\35 ? \\ .06 ? \\09 ? \\12 ? \\ 74.06 \\05 ? \\ 0.00 \end{array}$	1.61 2.15 2.44 2.37 1.88 1.69 .71 0.00 TOTALS	$\begin{array}{c} 0,00000\\ 0,00000\\ .00017\\ 0,00000\\ 0,00000\\ .37999\\ 0,00000\\ .61985\\ 1,00000\\ \end{array}$	MG AL SI K CA FE D	0.0000 0.0000 .0213 0.0000 0.0000 39.7344 0.0000 60.2443 39.7557	$\begin{array}{c} 0.0000\\ 0.0000\\ .0456\\ 0.0000\\ 0.0000\\ 55.5884\\ 0.0000\\ 0.0000\\ 55.6844\\ 0.0000\\ 55.6340\end{array}$,
41	SA IBUT	MPLE ALA	203	питрит	777012	1/13
INTENSITY	PG.	HT FTN		WT PEPCENT	OXIDES	·
12 ? 118.29 10 ? 24 ? 16 ? 01 ? 0.00	1.87 2.38 1.59 1.73 1.54 1.42 .67 0.00	0.00000 .42357 .00002 0.00000 0.00000 0.00000 0.00000 0.00000 .57641	MG AL SI K CA FE D	0.0000 52.9243 0046 0.0000 0.0000 0.0000 47.0711	0,0000 00270 00270 0.0028 0.0000 0.0000 0.0000 0.0000	

APPENDIX A5

A5.1 Chemical Composition of the Off-gas from Cement-bonded Pellets

A5.1.1 Chemical Analyses and Estimates of Moisture Contents

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The analyses for H_2 , CO, N_2 and CO_2 were straightforward measurements by gas chromatography. However, by the very nature of the dew-point indicator, the change of the moisture content of the gas with time, could not be measured; only the maximum value. The chemical analyses as measured are listed in Table A5.1. It will be observed that even the maximum value of the moisture content was small; the off-gas being mostly hydrogen and carbon monoxide.

The dew-point indicator was a simply constructed device wherein a closed-end polished copper tube was inserted vertically through a rubber stopper into a glass flask. Water was placed in the copper tube and its temperature controlled while the flask itself and the connecting tubes⁶ were kept warm. The off-gas was passed through the flask and the polished surface of the tube was observed for evidence of water condensation. Condensation was observed at 25.5°C but not at 26.5°C and it occurred about 15 seconds after the start of the runs. A dew point of 26°C is equivalent to 3.4% water vapour in the off-gas ⁽⁶⁵⁾. The source of most of the moisture was the water of hydration from the cement since the pellets had been dried previously at 120°C.

In order to provide a measure of thermochemical consistency when listing the off-gas composition at various times during reduction, the missing water vapour contents have been estimated by calculation using thermochemical data with the available measured chemical analysis.

Time	vol. % H ₂	vol. % CO	vo]. % N ₂	vol. % CO ₂	vol. % H ₂ 0
. 15	47.	46.	2.5		
∿lo sec.				1.5	3.4
	38.	54.5	. 2.3		
∿20 sec.	<u>41.</u>	<u>53.5</u>	<u>1.3</u>		
	avig 39.	avg 54.	avg 1.8	1.5	
	> 15.0	82.	0.7	• •	
∿30 sec.	~ <u>16.0</u>	<u>80.</u>	<u>1.5</u>		
	avg 15.5	avg 81.	avg 1.1	1.4	
	8.8	88.	1.1		
~40 sec.	. 9.1	88.	0.7		
	9.2	<u>87.</u>	1.6		
	avg 9.0	avg 88.	avg 1.1	1.2	
1.	1	1	1	1	1

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Table A5.1: Chemical analyses of the off-gas during reaction of cement-bonded ore-coal pellets.

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One difficulty that became apparent was the lack of measured temperatures of the reacting gases at the pertinent times. If it could be assumed that the gaseous reactions reached equilibrium as the gases passed through or were near the pellet surface, then an estimate of the pellet surface temperature would suffice for approximate calculations. From visual observation of the pellets during reaction, such an estimate was possible after the soot had cleared from the off-gas. The following will illustrate the type of calculation used.

The off-gas composition at 40 sec. was found to be 9% H_2 , 88% CO, 1.2% CO₂ and 1.1% N₂, while the moisture content was unknown. Also, by visual observation, the pellet surface temperature at 40 sec. was about 1350°C. First, let it be assumed that these gases reacted according to the water-gas shift reaction, the thermodynamic data for which is obtained from Kubaschewski et al.⁽⁶⁴⁾.

 $H_2^0(g) + C_2^0(g) = C_2^0(g) + H_2^0(g)$ $\Delta G^\circ = -8,600 + 7.65T \text{ cal/mol}$ The equilibrium constant (K) for this reaction is

$$\log K = \frac{-\Delta G^{\circ}}{4.575T} = \frac{1880}{T} - 1.67$$

At 1350°C (1623°K), K = 0.31 and thus

$$P_{H_20} = \frac{P_{C0_2} \times P_{H_2}}{K \times P_{C0}} = \frac{.012 \times .09}{.31 \times .88} = .00$$

Hence, the water vapour content is 0.4 vol %. Volume fractions may be substituted for partial pressures in these calculations because the

nitrogen content was low (1.1%) and it was the only constituent of the off-gas not taking part in the reaction. Similar calculations using the off-gas composition obtained at 30 sec. and an estimated temperature of 1300°C yield a moisture content of 0.8%. Again, calculations using the off-gas composition obtained at 20 sec. and an estimated temperature of 1200°C yield a moisture content of 2.8%. At 15 sec., where the complete gas analysis is known, calculations using the same thermodynamic equations yield a temperature of 1150°C. These calculated results are considered consistent and reasonable.

If it had been assumed that the gases reacted according to the watergas reaction;

 $H_2^0(g) + C(s) = H_2(g) + C_0(g);$ log K = $\frac{-7050}{T} + 7.44$

then at 15 sec. the temperature of the pellet surface would have had to be 790°C. This is an equilibrium value, theoretically possible, but in practical terms, it is too low. Firstly, the pellet had been exposed to an ambient temperature of 1500°C for 15 sec. leading one to expect a higher surface temperature, and secondly, by that time, CO generation from the combined reduction reactions had reached its maximum rate suggesting a higher temperature from a kinetic point of view. Calculations using the off-gas compositions at 20, 30 and 40 seconds and at temperatures above 1000°C show moisture contents becoming vanishingly small. In the absence of measured surface temperatures, the water-gas shift reaction was chosen as controlling because a gaseous reaction should be much closer to its final equilibrium than a heterogeneous reaction involving both gases and solids.
A5.1.2 Estimate of Initial Off-gas Composition

Due to limitations of experimental apparatus and procedure, samples of the initial off-gas from pellet reaction for chemical analysis could not be obtained. Nevertheless, when the composition data, gained at later stages, were being used to plot the "rate of gas evolution" curves of Figure 5.1, it was realized that in order to locate the high points of the curves, an initial off-gas composition was needed. Since there were no measured data, the following assumptions had to be made.

- a) An induction period of less than one second was observed before the pellet surface reached a temperature of about 500°C, at which time and temperature, rapid gasification of the coal occurred. Hence, a time of l sec. was chosen as the initial time for off-gas formation.
- b) Iron ore reduction could not have begun and thus the carbon monoxide content of the gas would be about the same as coke-oven gas, i.e., 6%.
- c) The cement would have begun to release its water of hydration almost immediately and from dew-point observations the off-gas reached its maximum moisture content of 3.4% at about 15 sec. Due to the lack of data, the moisture content of the off-gas at 1 sec. was assumed to be at its maximum value of 3.4%.
- d) The nitrogen content should be low and again, about the same as for coke-oven gas, i.e., 3%.
- e) The carbon dioxide content at 1 sec. was assumed to be at its maximum measured value of 1.5%.

f) Most of the remaining gas would be a mixture of hydrogen and hydrocarbons, mostly methane. Since the hydrocarbons would soon crack when carried a short distance from the pellet surface into hotter regions, it was assumed, for combustion purposes, that the remainder of the gas was composed only of hydrogen, ie., 86%.

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Thermochemical calculations were not attempted since there were doubts about controlling reactions, equilibrium, and the role played by methane and carbon soot on water vapour contents.

In summary, the instantaneous chemical analyses of the off-gas at various times during pellet reduction are given in Table A5.2. The data Tabelled e in the table were estimated, as outlined in this section, by taking cognizance of experimental conditions and thermochemistry.

Chemical Analysis, Vol. % Gases 1 sec. 15 sec. 20 sec. 30 sec. 40 sec. 9.0 H₂ 86.e 47. 39. 15.5 54. 81. 88. Ç0 6.e 46. H20 3.4e 3.4 2.8e 0.8e 0.4e °C0₂ 1.5 1.5 ľ.5e 1.4 1.2 3.0e 2.5 1.8 1.1 1.1 N2

e - estimated

Table A5.2: Chemical analysis of the off-gas sampled at various times during pellet reaction.

APPENDIX A7

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A7.1 Heat and Mass Balance Equations

Three independent linear equations in three unknowns were formulated using carbon, silicon and heat balances. By separating the variables, these equations were fitted into a matrix of the following form.

> Carbon eqn: $A_{11}X_1 + A_{12}X_2 + A_{13} = B_1$ Silicon eqn: $A_{21}X_1 + A_{22}X_2 + A_{23} = B_2$ Heat eqn: $A_{31}X_1 + A_{32}X_2 + A_{33} = B_3$

here the unknowns	are	х ₁	=	Coal Weight
	•	× ₂ .	=	Flux Silica Weight
		×3 .	=	Excess Heat

Derivations of each of the equations follow.

A7.1.1 Carbon Balance

The amount of coal required by the process is governed by the chemical requirements for carbon within the vessel. This includes the hot metal carbon content, the carbon needed to reduce the oxides of Fe, Si and Mn, the carbon needed to combine with the oxygen content of the coal so that it may evolve as CO, and the carbon needed to convert the CO_2 from the carbonate bonding (flux addition) to CO within the pellet. It will be recalled that about 8% of the total carbon content of the coal escaped the pellet as soot which was then unavailable for chemical reaction within the pellet. Hence, a correction factor for effective carbon utilization (EFF = 0.92 for max utilization) is introduced into the equation. The reduction reactions on which the carbon requirements are based, are included for clarity.

COALWT * COALC/100 * EFF = HMWT * HMC/100 + OREWT * FEOX/100 * 64/232 * 12/16 (Fe₃0₄ + 4C = 3Fe + 4CO)

> + HMWT * HMSI/100 * 2 * 12/28(SiO₂ + 2[C] = [Si] + 2CO)

+ HMWT * HMMN/100 * 12/55

(MnO + [C] = [Mn] + CO')

+ COALWT * COALCO/100 * 12/28 + CO2WT * 12/44

 $(CO_2 + C = 2CO)$

where COALWT = Coal weight, kg

COALC = Coal carbon content, % EFF = Effective carbon utilization HMWT = Hot metal weight, kg HMC = Hot metal carbon content, % OREWT = Ore weight, kg FEOX = Iron oxide content of ore, % HMS I = Hot metal silicon content, % HMMN = Hot metal manganese content, % COALCO = CO content of coal (from 0 content), % $CO2WT = Total weight of CO_2 from carbonates, kg$

The variables are separated to obtain the elements of the matrix equation wherein the unknown $X_1 = COALWT$.

- $A_{11}X_1 + A_{12}X_2 + A_{13}X_3 = B_1$ A(1,1) = (COALC * EFF - COALCO * 0.43)/100 A(1,2) = 0.0A(1,3) = 0.0

B(1) = (HMNT * (HMC + 0.858 * HMSI + 0.218 * HMMN)

+ 0.207 * OREWT * FEOX)/100 + (CO2WF * 0.273)

The variables which are separated into B(l), above, have been grouped together and defined as CNEED for ease of handling within the program, especially when used in the heat balance equation. Hence

CNEED = Weight of carbon needed to satisfy chemical.

requirements of reduction and solution, kg.

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and B(1) = CNEED

A7.1.2 Silicon Balance

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In formulating a silicon balance, the process vessel may be viewed as a theoretical box in which the silicon input equals silicon output. That is, silicon in the form of silica enters the system as a constituent of the iron ore and coal, and leaves as silicon dissolved in the hot metal and as silica in the slag. A complication arises, however, because the slag composition has been chosen beforehand and the slag weight is determined by a sulphur belance which, in turn, depends on the coal weight used. To regain the necessary freedom to balance, a provision is incorporated into the balance equation whereby an unknown quantity of silica can be added to the system as a flux material. Hence,

OREWT * ORSI02/100 * 28/60 + COALWT * CLSI02/100 * 28/60

+ FXSIWT * 28/60 = HMWT * HMSI/100

+)SLWT * SLSI02/100 * 28/60

 \rightarrow SLWT = $\frac{\text{CLSU}}{\text{SLSU}}$ * COALWT = Q1 * COALWT

(used in program because SLWT was[,]

unknown at this stage)

where	OREWT	= Ore weight, kg
	ORS 102	= Silica content of ore, %
	COALWT	= Coal weight, kg
	CLS 102	= Silica content of coal, %
	F XS IWT	= Flux silica weight, kg
	HMWT	= Hot metal weight, kg
	HMS I	= Hot metal silicon content, %
	SLWT	≈ Slag weight, kg
	SLS IO2	= Silica content of slag, %
	CLSU	= Sulphur content of coal, %
	SLSU	= Sulphur content of slag, %
	Q1	= Quotient used in program

The variables are separated to obtain the elements of the matrix equation wherein the unknowns X_1 = COALWT and X_2 = FXSIWT

 $A_{21}X_1 + A_{22}X_2 + A_{23}X_3 = B_2$ A(2,1) = (CLSI02 - Q1 * SLSI02) * 28./6000. A(2,2) = 28./60. A(2,3) = 0.0 B(2) = (HMWT * HMSI - OREWT * ORSI02 * 28./60.)/100.

A7.1.3 Heat Balance

In the proposed process, composite pellets of iron ore, coal and carbonate bonding material enter the vessel and react to produce liquid iron. This is endothermic; hence, thermal energy must be supplied to the reacting pellets. One way to do this is to generate heat by burning the off-gases from reduction with oxygen within the vessel. There are so many terms in the heat balance equation that perhaps it is best to list the terms in a manner which is believed to be self-explanatory.

(i) Heat Created = Heat Needed + Excess Heat

(ii) Heat of combustion of CO from all sources (Fe, Si, Mn oxide reduction, coal, CO₂ from carbonates)

+ Heat of combustion of H₂ (from coal)

+ Heat of_formation of slag

- + Heat of combustion of excess carbon above chem. needs (soot and extra coal)
- = Heats of reaction (Fe, Si, Mn oxide reduction, Boudouard)
- + Enthalpies (net) of Fe_3O_4 , SiO_2 , Al_2O_3 , MnO, C, H_2 , CO, CaO, MgO, CO₂

+ Enthalpy of Oxygen used for combustion of CO, $\rm H_2, \, C$

+ Heat of dissociation of carbonates

+ Heat of solution of carbon in iron

+ Excess Heat

+ ENTO2 * (COALWT * COALH/100) * $\frac{32/4}{2H_2(4)}$ + $0_2(32) = 2H_20$ + ENTO2 *[COALWT * (COALC/100 - COALCO/100 * 12/28) - CNEED] * $\frac{32/12}{C(12)}$ + $0_2(32) = C0_2$

+ HSC * HMVT * HMC/100

+ EXHT

Definitions of the variable names and the values assigned to the heats of reaction may be found in Appendix A7.2.

(iv) The variables are separated to obtain the elements of the matrix equation wherein the unknowns are

$$X_1 = COALWT$$
 and $X_2 = EXHT$ (Excess Heat)

 $A_{31}X_1 + A_{32}X_2 + A_{33}X_3 = B_3$ A(3,1) = 0XC0 * COALCO/100 + 0XH2 * COALH/100

- + HFSLAG * Q1 * SLSI02/100
- + OXC * (COALC/100 COALCO/100 * 12/28)
- (ENTSIHT ENTSILT) * CLSI02/100
- (ENTALHT ENTALLT) * CLAL03/100
- (ENTCHT ENTCLT) * (COALC COALCO * 12/28)/1CO
- (ENTH2HT ENTH2LT) * COALH/100
- (ENTCOHT ENTCOLT) * COALCO/100
- ((ENTCAHT ENTCALT) + HDCAO) * Q1 * SLCAO/100.
- ((ENTMGHT ENTMGLT) + HDMGO) * Q1 * SLMGO/100
- ENTO2 * COALCO/100 * 32/56

- ENTO2 * COALH/100 * 32/4

- ENTO2 * (COALC/100 - COALCO/100 * 12/28) * 32/12

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A(3,2) = 0.0A(3,3) = -1.0B(3) = HRFEOX * OREWT * FEOX/100 + HRSI02 * HMWT * HMSI/100 + HRMNO * HMWT * HMMN/100 + HRCO2 * CO2WT' + (ENTFEHT - ENTFELT) * OREWT * FEOX/100 + (ENTSIHT - ENTSILT) * OREWT * ORS102/100 + (ENTALHT - ENTALLT) * OREWT * ORAL03/100 + (ENTMNHT - ENTMNLT) * OREWT * ORMNO/100 + (ENTCO2H - ENTCO2L) * CO2WT + ENTO2'* OREWT '* FEOX/100 * 64/232 * 28/16 * 32/56 + ENT02 * HMWT * HMSI/100 * 2 * 28/28 * 32/56 +ENT02 * HMWT * HMMN/100 * 28/55 * 32/56 + ENTO2 * CO2WT * 2 * 28/44 * 32/56 - ENTO2 * CNEED * 32/12 + HSC * HMWT * HMC/100 - OXCO * OREWT * FEOX/100 * 64/232 * 28/16 - OXCO * HMWT * HMSI/100 * 2 * 28/28 . - OXCO * HMWT * HMMN/100 * 28/55 - OXCO * CO2WT * 2 * 28/44 + OXC * CNEED 💙

In the program, many of the above terms have been combined and fractions were condensed into single numbers. The expanded version given here allows one to follow individual heat terms more clearly.

A7.2 <u>Li</u>	sť	of Variable Names found in Computer Pro	gram. >
Input Variables			<u>Input Data</u>
FE .	=	Iron content of ore, %	68.1
ORS102	=	Si0, content of ore, %	5.2
ORAL03	=	$A1_20_3$ content of ore, %	0.5
ORMNO	=	MnO-content of ore, %	0.2
COALC	=	Total carbon content of coal, %	. 82.4
FIXC	=	Fixed carbon content of coal, %	59.1
COALH	=	Hydrogen content of coal, $\%$	5.4 .
COALO 🏹	=	Oxygen content of coal, %	5.2
CLSU	=	Sulphur content of coal, %	0.7, 1.0
ASH	=	Ash content of coal, %	4.7
ASHS 102	=	SiO ₂ content of coal ash, %	54.5
ASHAL03	=	$Al_2 \overline{Q}_3$ content of coal ash, %	33.5
SLCAO	=	CaO content of slag, %	42.0
SL\$102	=	SiO ₂ content of slag, %	34.0
SLAL03	=	Al ₂ O ₂ content of slag, %	10.0
SLMGO	=	MgO content of slag, %	14.0
SLWT	2 -	Slag weight, kg	200, 250, 300
EFF	=	Effective carbon utilization	0.92 (base) - 0.76 🌱
TEMPC	=	Operating temperature, °C	1500, 1520, 1540
PREHTC	=	Preheat temp. of input materials, °C	25, 300
HMWT	=	Hot metal (liquid iron) weight, kg	1000
HMC	=	Hot metal carbon content, %	2.0 - 4.0
HMSU	=	Hot metal sulphur content, %	0.020 - 0.060

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Variables defined within the program

FEOX	=	Iron oxide content of ore, %	
COALCO	=	CO content of coal (from oxygen content),	%
CLSI02	=	SiO ₂ content of coal, %	
CLAL03	` =	$A1_2\overline{0}_3$ content of coal, %	7

TK = Operating temperature in deg. K TPK = Preheat temperature in deg. K

The following enthalpies are in kJ/kg. Enthalpy formulae may be found in the program listing (A7.3).

250

ENTFEHT = Enthalpy of $Fe_{3}0_{4}$ to high (operating) temperature ENTFELT = Enthalpy of $Fe_{3}O_{4}$ to low (preheat) temperature ENTSIHT, ENTSILT = Enthalpy of SiO₂, high and low temp. ENTALHT, ENTALLT = Enthalpy of Al_2O_3 , high and low temp. ENTMNHT, ENTMNLT = Enthalpy of MnO, high and low temp. ENTCAHT, ENTCALT = Enthalpy of CaO, high and low temp. ENTMGHT, ENTMGLT = Enthalpy of MgO, high and low temp. ENTCHT, ENTCLT = Enthalpy of carbon, high and low temp. ENTH2HT, ENTH2LT '= Enthalpy of hydrogen, high and low temp. ENTCOHT, ENTCOLT = Enthalpy of CO, high and low temp. Enthalpy of CO2, high and low temp. ENTCO2H, ENTCO2L = = Enthalpy of oxygen to high (operating) temp. ENTO2

= Heat of combustion of C to CO₂ = 33022 kJ/kg C OXC \cdot = \cdot Heat of combustion of CO to CO₂ = 9956 kJ/kg CO OXCO = Heat of combustion of H_2 to $H_20 = 125,750 \text{ kJ/kg }H_2$ OXH2· · = Heat of reduction of FEOX to FE = 2654 kJ/kg FEOX HRFEOX Heat of reduction of SiO_2 to [Si] = 18885 kJ/kg [Si] HRSI02 = = Heat of reduction of MnO to [Mn] = 4770 kJ/kg [Mn] HRMNO = Heat of reaction (Boudouard), CO_2 to CO = 3666 kJ/kg CO_2 HRCO2 Heat of dissociation, $CaCO_3$ to CaO = 3007 kJ/kg CaOHDCAO = Heat of dissociation, $MgCO_3$ to MgO = 2917 kJ/kg MgO HDMGO = Heat of formation of slag = 14.75 kJ/kg SiO₂ HFSLAG Heat of solution of carbon in iron, kJ/kg [C] HSC =

w.

Silicon Partition Reaction

ACTLOG .	=	Logarithm of activity of SiO ₂ in slag at 1550°C
ACTLOGT	=	Logarithm of activity of SiO_2 in slag at operating temp.
ACTSI02	=	Activity of SiO ₂ in slag
SILOGK	=	Logarithm of Equilibrium constant, K _{Si}
HMS I	=	Hot metal silicon content, %
FSILOG -	í.	Logarithm of activity coeff. of Si in iron
HCLOG	=	Logarithm of activity of C in iron
НС	=,	Activity of C in iron
SILOG	=	Logarithm of Si in iron
SINEW	=	New value for hot metal silicon content, %

Manganese Partition Reaction

HMMN	= Hot metal manganese content, %
HMSU	= Hot metal sulphur content, % ·
.RDMNK	≓ _Equilibrium constant, K _{Mn}
FMNLOG	= Logarithm of activity coeff. of Mn in iron
FMN	= Activity coeff. of Mn in iron
ACTCMNO	= Activity coeff. of MnO in slag
Q2	= Quotient 2

Sulphide Capacity of Slag

BRAT10	=	Basicity ratio of slag
CSL0G15	=	Logarithm of sulphide capacity at 1500°C
CSLOGTC	=	Logarithm of sulphide capacity at operating temp.
CS ·	=	Sulphide capacity

Sulphur Partition Reaction

FSLOG	=	Logarithm of activity coeff. of S in iron
HS	=	Activity of sulphur in iron
SLSU	=	Sulphur content of slag, %
CLSU	=	Sulphur content of coal, %
Q1	=	Quotient 1

	Matrix for	three Simultaneous Equations
	OREWT =	Weight of ore, kg
	CNEED =	Weight of carbon needed to satisfy chemical requirements
		of reduction and solution, kg
	A(3,3), B(3)) = Matrix coefficients
	CALL MASO05	= Library sub-routine to solve sim. eqns.
	COALWT =	Weight of coal needed, kg
	FXSIWT =	Weight of silica flux needed, kg
•	EXHT =	Excess heat, kJ
	SLWT =	Slag weight, kg
	SLMNO =	MnO content of slag, %
	FXALWT =	Weight of alumina flux needed, kg
	CAOWT =	.Weight of lime flux needed, kg
	CAC03 _ =	Weight of CaCO ₃ , kg
	CO2WTCA =	Weight of CO ₂ from CaCO ₃ , kg
	FXMGWT =	Weight of magnesia flux needed, kg
	FXMGC03 ·=	Weight of MgCO ₃ , kg
	CO2WTMG =	Weight of CO ₂ from MgCO ₃ , kg
	CO2WT =	Total weight of CO ₂ , kg
		· .
	OXWT =	Weight of oxygen needed for combustion, kg
	HTCBCO =	Heat from combustion of CO, kJ
	HTCBH2 =	Heat from combustion of H ₂ , kJ
	HTCBC =	Heat from combustion of C, kJ
	HTFSLAG =	Heat from slag formation, kJ
	HTCREAT =	.Total heat generated, kJ
	HTNEED =	Total heat required, kJ
	EXHT =	Excess heat, kJ

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PROGRAM IST (INPUT, OUTPUT, TAPE5=INPUT, TAPE6=OUTPUT)
DIMENSION A (3, 3), B (3)
N=1 .
4 READ (5, 190) FE + ORSIO2, ORAL 03, ORMNO
READ(5,100) COALC, FIXC, COALH, COALO, CLSU, ASH
READ(5,100) ASHSIO2, ASHALO3
READ(5,100) SLCAO, SLSIOZ, SLALO3, SLMGO
READ(5,100) TEMPC, PREHTC
READ(5,100) HMWT, HMC, HMSU
100 EORMAT(SE10.0)
, , C
C CORRECTION FACTOR FOR EFFECTIVE CARBON UTILIZATION
EFF=0.92
CC
FEOX=FE#232./168.
COALCO = COALO * 28./16.
CLSIO2= ASH*ASHSIO2/100.
CLALO3= ASH*ASHALO3/100.
С
C START OF TEMP LOOP
DO 33 J=1500,1540,20
TEMPC=J
TK=TEMPC+273.
TPK=PREHIC +273.
С
C ENTHALPIES AND HEATS OF REACTION ARE IN KILD-JOULES PER KG
ENTFEHT=(48,0*TK -12650.)*4.184/232.
ENIFELT=(21.88*TPK +24.1E-03*TPK**2 -8666.)*4.184/232.
ENTSIHT=(14.41*TK +0.97E-03 *TK**2 -4455.)*4.184/60.
<u>ENTSILT=(11.22*TPK+4.1E-03*TPK**2+2.7E+05/TPK-4615.)*4.184/60.</u>
ENTALHT=(27.49*TK+1.41E-03*TK**2+(8.38E+05/TK)-11132.)*4.184/102.
ENTALLT = (27.49*TPK+1.41E+03*TPK**2+8.38E+05/TPK-11132.)*4.184/102.
ENIMNHT=(11.11*TK+0.97E-03*TK**2+0.88E+05/FK-3694.).*4.184/71.
ENTMNLT=(11.11*TPK+0.97E-03*TPK**2+0.98E+05/TPK-3694.)*4.184/71.
ENTCAHT=(11.67*TK+0.54E-03*TK**2+1.56E+05/TK-4051.)*4.184/56.
ENTCALT=(11.67*TPK+0.54E-03*TPK**2+1.56E+05/TPK-4051.)*4.184/56.
ENTMGHT=(10.18*TK+0.87E-03*TK**2+1.48E+05/TK-3609.)*4.184/40.3
ENIMGLT=(10.18*TPK+0.87E+03*TPK**2+1.48E+05/TPK-3609.)*4.184/40.3
ENICHT = {4.03*TK+0.57E-03*TK**2+(2.04E+05/TK)-1936.)*4.184/12.
ENTCLT=(4,03*TPK+0,57E-03*TPK**2+(2.04E+05/TPK)-1936,)*4.184/12.
ENTH2HT=(6.52*TK+0.39E-03*TK**2-0.12E+05/TK-1938.)*4.184/2.
ENTH2LT=(6.52*TPK+0.39E-03*TPK**2-0.12E+05/TPK-1938.)*4.184/2.
ENTCOHT=(5.73*TK+0.49E-03*TK**2+0.11E+05/TK-2105.)*4.184/28.
ENTCOLT=(6.73*TPK+0.49E=03*TPK**2+0.11E+05/TPK=2105.)*4.184/28.
-ENTCO2H=(10.37*TK+1.05E-03*TK**2+2.06E+05/TK-3936.)*4.184/44.
ENTCOPL=(10.57*TPK+1.05E-03*TPR**2+2.06E+05/TPK-3936.)*4.184/44.
ENTO2=(7.16*TK+0.5E-03*TK**2+(0.4E+05/TK)-2313.)*4.184/32.
, OXC = 33022.
OXCO≈9956.
OXH2=125750
HRFEOX=2654.
HRSI02=18885.
HRMN0=4770.
HRC02 = 3566.
HDCAO = 3007.
HDMGO = 2917.
HFSLAG=1475.

		254
0		• •
C	START OF CARBON LOOP	•
	DO 33 K=20,40,2	1
	С=К	
	HYC=C/10.	•
	HSC=(5400,+420;*HMC/2,)*4,184/12,	
C .		
<u> </u>	SILICUM PARTITION REACTION 10 CALCOLATE HIST ACTIOC-D 032#(SICAOISI ALO3/2 ISTACO/3 -SISTO2)=0.65	
•	ACTLOGI-0.001*(1550 -TEMPC)+ACTVOC	
	AGISTO2=10. **ACTLOGT	
C		. •
······································	SILOGK=-28210./IK +15.42	
	L=1 /	
	HMSI=1.0	
	40 F5ILOG=0.084*HMSI+0.24*HMC	٥
	HCLOG=0.18*HMC+0.062≈HMSI+ALOG10((HMC)	
	HC=(10,**HCLOG)	
•	SILOG=SILOGK-FSILOG+ACTLOGT+2.0*HCLOG	
	<u></u>	
•	IF (ABS(SINEW-HMSI).LE.2.E-3) GU IU 8	
١	1F {L=10/42943943 17 1-11	
, 1	43 WRITE(6.330)	
ir	330 FORMAT(32H1 HMSI FUNCTION DID NOT CONVERGE)	
	B HMSI=SINEW	·····
· C	·	
<u> </u>	MANGANESE PARTITION REACTION	•
	RDMNK= 10.**((-13980./TK)+8.83)	
į	EMNLOG=-0,070*HMC-0.048*HMSU	
i i	FMN= 10.**FMNLOG	• • • •
) r	, Q2- RUMAN ACTUMNU U. ULI 4 HUY FAM	1
<u> </u>	SUPHIDE CAPACITY OF SLAG	· · ·
· . •	BRATIO= $(SLCA0+0.7*SLMGO)/(0.94*SLSIO2+0.18*SLALO3)$	
*	CSL0G15=1, 39*BRATT0-5.57	
· · · · · ·	CSLOGTC=-0,00225*(1500TEMPC)+CSLOG15	
	CS=10.**CSLOGTC	
· <u>ĉ</u>	4. 	
	HMMN=0.5	
, .	CO24T=10].	
<u> </u>	M= 1	
• • •	SUI DADE DADITION DEACTION	
	12 ESLOG==0.028*HMSU+0.14*HMC+0.063*HUST=0.026*HMMN	
· · · · · · · · · · · · · · · · · · ·	HS=(10,**FSLOG)*HMSU	
	<pre></pre>	-
·		
C	MATRIX FOR THREE SIMULTANEOUS EQNS	•
/	OREWT=(100HMC-HMSI-HMMN-HMSU) *1.38*HMWT/FEOX	
• •	CNEED=(HMWT*(HNC+0.858*HMSI+0.218*HMMN)+0.207*OREWT*FE0)	()/100.
· · · · · · · · · · · · · · · · · · ·	<u>1</u> + (CO2HT*0.273')	
	A(1,1)=(COALC*EFF-COALCO*U.43)/100.	
1		

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:

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	(A(1,2)=0.0
) A (1, 3) = 0, 0
-	$\gamma B(1) = CNEED$
	A(2,1)=(CLSIO2-21*SLSIO2)*28./6000.
	A(2,2)=28./60.
	A(2,3)=0.0
	B(2)=(HYWT*HYSI-OREWT*ORSI72*28./60.)/100.
	A(3,1) = (OXCO*COALCO+OXH2*COALH+HFSLAG*Q1*SLSIO2
	1 +OXC*(COALC-COALCO*0.43)-(ENTSIHT-ENTSILT)*CLSIO2
	2 - (ENTALHT-ENTALLT) *CLALQ3- (ENTCHT-ENTCLT) * (COALC-COALCO*0.43)
	- 3 - (ENTH2HT-ENTH2LT)*COALH-(ENTCOHT-ENTCOLT)*COALCO
	4 = ((ENTCAHT-ENTCALT) + HDCAO) *Q1*SLCAO
	5 - ((ENTMGHT-ENTMGLT) + HDMGO) *Q1*SLMGO
	6 -ENT02#CDALCO#0.57-ENT02#COALH#8.0
	7 -ENTO2*(COALC*2.67-COALCO*1.14))/100.
	A(3.2) = 0.0
	A(3,3)=-1.0
	B(3) = (HREOX+(ENTFEHT-ENTFELT)+0.276*ENT02-0.483*OXCO)
	1 *DRFW1*FFDX/100.
	2 + (4RST02+1,14*ENI02-2,0*0XC0)*HMWT*HMST/100.
	3 + (HRMNO+D_29*FNTO2-0.51*OXCO)*HMWT*HMMN/100.
	4 + (HRCD2+(ENTCO2H-ENTCO2L)+9.73*ENTO2-1.27*0XCD)*CO2WI
	5 + (HSC) * HMNT*HMC/100.
	5 + (1 = NTSTHT = ENTSTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT
	$7 \pm (ENTMUHT-ENTMULT) \neq OPMUO) \neq OPEWT/100.$
	$8 \pm 10 \times c = 2 = 677 \times c \times$
	$\frac{0.110}{0.110} = 0.100 = 0.100 = 0.000 = 0.000 = 0.000 = 0.000 = 0.000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.0000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000 = 0.00000000$
	$T \in \{W_{n}^{(1)} \land 1, 1, 0\}$
	Q HOTTE/6, 3201
	320 FORMAT(15H SIMO HAS 0=7FRO)
Ŭ	10 COALNT=B(1)
	FYHT=B(3)
C C	
`	
	FXALWI=(SLWITSLALUS-UUALWITULALUS-UREW)TURALUSI/100.
:	CACO3= CAUNI*100./56.
	CO2WICA= CACJ3*44*/100*
	; + X MGWT = SLWT * SL MG0/100.
	F X MGCO 3 = F X MG V T * 8 4. 3/36.3
	CO2WING=FXMGC03#44./84.3
·	CD2NT=CD2WTCA+CD2N1MG
	1F (M-3)14,15,15
	<u>14 M=N+1</u>
	GO TO 12
•	15 DXWT+(COALNT*(2.67*COALC+8.0*COALH-0.571*COALCO)
	1 +0.276*OREWT*FEOX+HMWT*(1.14*HMSI+0.29*4MMN))/100.
	2 +0.727*C02WT-2.67*CNEED
C	
•	HTCBCO=DXCO*((OREWT*FEOX*0.483 +HMWT*HMSI*2.0 +HMWT*HMMN*0.51
	1 +COALCO*COALWT)/100. +CO2WT*1.27)
	. HTC8H2=9XH2*C0A1WT*C0A1H/100.

· · ·	
	256
4	
HTFSLAG=HFSLAG*SLWT*SLSI02/100.	
HTCREAT=HTCBC0+HTCBH2+HTCBC+HTFSLAG	i.
HINEED=HICREAI-EXHI	,
	·
WRITE(6,2JU)FE , URSIU2, URALU3, URANU	
ZUU FURMATIZZHI IRUN URE CUNCENTRATE FO. 1	CA 122V EQ 1
$\frac{1}{2} = \frac{1}{2} = \frac{1}$	CA /CCAJFOLI
	T02. 05H0103
210 ED2MAT/2240 COAL COMPOSITION ### _F8.1.17H PCT IN	TAL CARRON /
1 229.58.1.17H PCI FIXED CARBON / 228.58.1.13H PCI	HYDROGEN /
2 22X.F.8.1.11H PCT 0XYGEN / 22X.F.8.1.12H PCT SULPH	
3 22X FR 1. AH PCT ASH /22X FR 1.16H PCT ASH SILICA	/
4 22X.F8.1.17H PCT ASH ALUMINA)	
WRITE(6.220) SLCAD.SLSID2.SLALD3.SLMGD	
220 FORMAT(22HO SLAG COMPOSITION ***, F8.1, 8H PCT CAO	/ 22X,F8.1,
1 9H POT SIO2/22X, F8, 1, 10H PCI_AL203, /, 22X, F8.1, 8H	PCT MGO)
WRITE (6,240) TEMPC, PREHTC	
240 FORHAT (14HO PROCESS TEMP , F10.1, 3H C	
1 / 14H PREHEAT TEMP, F10.1, 3H C)	
WRITE(6,250) HMWT, HMC, HMSU 🗸	
250 FORMAT(22H0 HOT METAL SPECS ****, F7.1.4H KG / 25	Χ,
1 F5.2,12H PCT CARBON / 26X,F5.3,12H PCT SULPHUR	· · · · · · · · · · · · · · · · · · ·
WRITE(6,430) BRATIO,CS,SLSU,SLMNO,ACTSIO2	
430 FORMAT(22HD SLAG BASICITY RATIO , F4.2/6X, 18H SUL	PHIDE CAPACITY ,
1 E9.2/6X.12H SULPHUR PCT , F7.3/6X,12H MNO PCT	,F7.3/6X,
2 14H ACTIV OF SIO2 , F5.3)	
WRITE (6,440) OREWT, COALWT, CAOWT, CACO3, FXMGWT, FXMG	<u>;co3,</u>
1 FXSIWT, FXALWT, OXWT	
440 FORMAT(17HO MATERIALS INPUT /4X,* ORE WT KG *,F	8-1/
1 4X,* COAL WT KG *,F8.1/	
2 4X.* FLUX WT KG */6X.* CAO *, F6. 1,* OR AS	CAC03 *, F6.1/
. 3 6X,* M30 *,F6.1,* OR AS MGCO3 *,F6.1/6X,* SI	.02 *,F6.1/
<u>4 5X, * AL203 *, F6.1/4X, * OXYGEN WI KG *, F6.1)</u>	
WRITE(6,450)SLWT,HMWT,HMC,HMS1,HMMN,HMSU,EXH),HT	CREAT, HINEED
450 FORMAT(18HU MATERIALS OUTPUT 74X, SLAG WI KG T	
1 4X, THOI METAL WI KG TOFO. 1/7X, TUARBON PUT TO	170+2/ 3/7V
$\frac{2}{7} \times \frac{2}{7} \times \frac{2}$	577X) 55 # 510 /
3 + SULPHUK PUT + F7.37 2X3 + EXCESS HEAT NEEDED + E4	.E.3 '9E.LU+49
$\frac{4}{77} \frac{2}{77} \frac{1}{77} \frac$	LU • 47
	•
JF (10-0) 3434934	* *
514 510F	•
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	_
	Annanistan a stana sisa. A A
	· · ·
	• .
	aranana ang ang ang ang ang ang ang ang an
	•
•	

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_IRON ORE CONCENTRATE	18.1 PCT IRON AS MAGNETITE
	5.2 PCT SILICA
	<u>•5 PCT_ALUMINA</u>
	.2 PCT MNO
COAL COMPOSITION #**	82-4 PCI TOTAL CARBON
4	59-1 PCI FIXED CARBON
.	5.4 PCT HYDROGEN
	5.2 PCT OXYGEN
	1.0 PCT SULPHUR
	4.7 PCT ASH
	54.5 PCT ASH SILICA
	33-5 PCT ASH ALUMINA
SLAG COMPOSITION ***	42.0 PCT CAO
. ·	34.0 PCT SIO2
· · · · · · · · · · · · · · · · · · ·	10.0 PCT_AL203
	14.0 PCT MGO
PROCESS TEMP 1500	0 C
PREHEAT TEMP 25.1	0 C
·····	3.00 PCT CARBON .040 PCT SULPHUR
SLAG BASICITY RATIO 1. SULPHIDE CAPACITY	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03
SLAS BASICITY RATIO 1 SULPHIDE CAPACIT SULPHUR PCI _1.8	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39
SLAG BASICITY RATIO 1 SULPHIDE CAPACITY SULPHUR PCI 1.8 MNO PCI 11	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 09
SLAG BASICITY RATIO 1 SULPHIDE CAPACIT SULPHUR PCI _1.8 MNO PCI _11 ACTIV OF SIO2	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 09 068
SLAG BASICITY RATIO 1 SULPHIDE CAPACITY SULPHUR PCI 1.8 MNO PCI 11 ACTIV OF SIO2 . MATERIALS INPUT	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 09 068
SLAG BASICITY RATIO 1 SULPHIDE CAPACIT SULPHUR PCJ 1.8 MND PCI 11 ACTIV OF SID2 MATERIALS INPUT DRE WT KG 1412	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 09 068
SLAS BASICITY RATIO 1 SULPHIDE CAPACIT SULPHUR PCI 1.8 MNO PCI 1 ACTIV OF SID2 MATERIALS INPUT DRE WT KG 1412 COAL WT KG 475	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 09 068
SLAG BASICITY RATIO 1 SULPHIDE CAPACITY SULPHUR PCI 1.8 MNO PCI 11 ACTIV OF SID2 MATERIALS INPUT DRE WT KG 1412 COAL WT KG	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 09 068
SLAG BASICITY RATIO 1 SULPHIDE CAPACIT SULPHUR PCI 1.8 MND PCI 1.8 ACTIV OF SID2 1 MATERIALS INPUT DRE WT KG 1412 COAL WT KG 475 FLUX WT KG CAD 99.5 01	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 09 068 .9 .5 R_AS_CAC03_177.6
SLAG BASICITY RATIO 1. SULPHIDE CAPACIT SULPHUR PCI 1.8 MNO PCI 1.8 MO PCI 1.8 MO PCI 1.8 MAIERIALS INPUT DRE NT KG 1412 COAL NT KG 475 FLUX WI KG MGD 33.2 01	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39
SLA3 BASICITY RATIO 1 SULPHIDE CAPACIT SULPHUR PCI 1 SULPHUR PCI 1 MNO PCI 1 ACTIV OF SID2 MATERIALS INPUT JRE NT KG COAL NT KG CAD 99.5 0 MGD 33.2 0 SID2 12.4	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 09 068 .5 R AS CACO3 177.6 R AS MGC03 77.0
SLAS BASICITY RATIO 1. SULPHIDE CAPACITY SULPHUR PCI 1.8 MNO PCI 1.1 ACTIV OF SIO2 MAIFRIALS INPUI JRE NT KG LOAL NT KG GOAL NT KG MGO 33.2 01 SID2 12.4 AL203 9.1	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39
SLAG BASICITY RATIO 1. SULPHIDE CAPACITY SULPHUR PCI 1.8 MND PCI 1.8 MCIIV OF SID2 1.1 DRE WI KG 1412 COAL WI KG 475 FLUX WI KG GO 33.2 01 SID2 12.4 AL203 9.1 DXYGEN WI KG 772.1	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 .9 .68 .9 .5 R AS R AS MGC03 .77.0 8
SLA3 BASICITY RATIO 1 SULPHIDE CAPACIT SULPHIDE CAPACIT SULPHUR PCI 1.8 MNO PCI 1.8 MNO PCI 1.8 MNO PCI 1.1 ACTIV OF SID2 MATERIALS INPUT JRE WT KG 1412 COAL NT KG 475 FLUX WT KG MGD 33.2 OF SIJ2 12.4 AL203 9.1 JXYGEN WT KG 772.	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39
SLAG BASICITY RATIO 1. SULPHIDE CAPACITY SULPHUR PCI 1.8 MND PCI 1.8 MCIIV OF SID2 1 MAIERIALS INPUT DRE WT KG 1412 COAL NT KG 475 FLUX WT KG GO 33.2 01 SID2 12.4 AL203 9.1 DXYGEN WT KG 772.5 MATERIALS OUTPUT SLAG WT KG 236	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 09 068 .5 R_AS CACO3 177.6 R_AS MGC03 77.0 8
SLAG BASICITY RATIO 1. SULPHIDE CAPACITY SULPHUR PCI 1.8 MND PCI 1.8 MCI VOF SID2 1.8 MATERIALS INPUT DRE WT KG 475 FLUX WT KG CAD 99.5 01 MGD 33.2 01 SID2 12.4 AL203 9.1 DXYGEN WT KG 772.1 MATERIALS OUTPUT SLAG WT KG 236 HOT METAL WT KG	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 .9 05 R AS CACO3 177.6 R AS MGC03 77.0 8
SLA3 BASICITY RATIO 1. SULPHIDE CAPACIT SULPHUR PCI 1.8 MNO PCI 1.8 MATERIALS INPUT DRE NT KG 1412 COAL NT KG 475 FLUX WI KG GO 33.2 OF MGO 33.2 OF SID2 12.4 AL203 9.1 DXYGEN WT KG 772.6 MATERIALS OUTPUT SLAG WT KG 236 HOT METAL WT KG CARBON PCT 3	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 .9 09 .68 R AS MGC03 .77.0 8
SLAG BASICITY RATIO 1. SULPHIDE CAPACIT SULPHUR PCI 1.8 MNO PCI 1.8 MATERIALS INPUT DRE WT KG 1412 COAL NT KG 475 FLUX WT KG GAD 99.5 00 MGD 33.2 01 MGD 33.2 01 SID2 12.4 AL203 9.1 DXYGEN WT KG 772.5 MATERIALS OUTPUT SLAG WT KG 236 HOT METAL WT KG CARBON PCT 3 SILTCON PCT	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39
SLA3 BASICITY RATIO 1 SULPHIDE CAPACIT SULPHUR PCI _ 1.8 MNO PCI _ 1.8 MATERIALS INPUT DRE WT KG _ 1412 COAL NT KG _ 475 FLUX WT KG GAD _ 99.5 _ 01 MGD _ 33.2 01 SID2 _ 12.4 AL203 _ 9.1 DXYGEN WT KG _ 772.5 MATERIALS OUTPUT SLAG WT KG _ 236 HDT METAL WT KG CARBON PCT _ 3 SILICON PCT MANGAN PCT	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 .09 09 .68 .9 .5 R AS CAC03 177.6 R AS MGC03 77.0 8
SLAG BASICITY RATIO 1. SULPHIDE CAPACITY SULPHUR PCI 1.8 MND PCI 1.8 MATERIALS INPUT SLAC 1412 COAL NT KG 475 FLUX WT KG MGD 33.2 01 MGD 33.2 01 SID2 12.4 AL203 9.1 DXYGEN WT KG 772.1 MATERIALS OUTPUT SLAG WT KG 236 HDT METAL WT KG CARBON PCT 3 SILICON PCT MANGAN PCT SULPHUR PCT	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 .9 09 .68 .9 .5 R AS CACO3 177.6 R AS MGC03 77.0 8
SLA3 BASICITY RATIO 1. SULPHIDE CAPACIT SULPHUR PCI 1.8 MND PCI 1.8 MATERIALS INPUT DRE WT KG 1412 COAL NT KG 475 FLUX WT KG GAD 99.5 01 MGD 33.2 01 SID2 12.4 AL203 9.1 DXYGEN WT KG 772.0 MATERIALS OUTPUT SLAG WT KG 236 HDT METAL WT KG CARBON PCT 3 SILICON PCT MANGAN PCT SULPHUR PCT SULPHUR PCT EXCESS HEAT, KILO-JSUI	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39 09 068 .9 .5 R AS CACO3 177.6 R AS MGC03 77.0 8
SLAG BASICITY RATIO 1. SULPHIDE CAPACIT SULPHUR PCI 1.8 MNO PCI 1.1 ACIIV OF SID2 MATERIALS INPUT JRE WT KG 1412 COAL NT KG 475 FLUX WT KG CAD 99.5_01 MGD 33.2 01 MGD 33.2 01 SIJ2 12.4 AL203 9.1 JXYGEN WT KG 772.4 MATERIALS OUTPUT SLAG WT KG 236 HOI MEIAL WT KG CARBON PCT 3 SILICON PCI MANGAN PCT SULPHUR PCT EXCESS HEAT, KILO-JSUN HEAT NEEDED .9666E	3.00 PCT CARBON .040 PCT SULPHUR .53 Y .37E-03 39

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