

Study of direct iron smelting processes in the laboratory furnace

Author: Gaal, Sean

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Study of Direct Iron Smelting Processes in the Laboratory Furnace

Sean Gaal

A thesis submitted in partial fulfilment

of the requirements for the degree of

Doctor of Philosophy

Materials Science and Engineering

University of New South Wales

September, 2000.

Certificate of Originality

I hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, nor material which to a substantial extent has been accepted for the award of any other degree or diploma at UNSW or any other education institution, except where due acknowledgment is made in the thesis. Any contribution made to the research by others, with whom I have worked at UNSW or elsewhere, is explicitly acknowledged in the thesis.

I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.

Sean Gaal

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Publications

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S. Gaal, O. Ostrovski, 'Sulphur Slag-Metal-Gas Partitioning in the Laboratory Smelting Reduction Furnace', *Proceedings 60th Ironmaking Conference*, Pittsburgh, 2000 pp. 365-376.

S. Gaal, O. Ostrovski, 'Slag-Metal-Gas Reactions in the Iron Smelting Reduction Furnace', *MINPREX 2000*, AIMM, Melbourne Australia, 2000, pp. 597-604.

Abstract

The aim of this project was to investigate the direct iron smelting process, particularly, behaviour of Australian coals with different volatile matter, reduction of iron ore under different operational conditions and partitioning of sulphur between metal, slag and gas phases.

Direct iron smelting reduction was examined using a modified 50 kg induction furnace. The furnace was equipped with continuous raw material feeding, a top oxygen lance, argon bottom bubbling, and sensors for measurement of gas and bath temperatures, gas composition and other parameters. In the base case, iron ore was charged at the rate of 1.5 kg/h, coke flow rate was adjusted to maintain the char fraction in the slag at 30 wt%, the oxygen flow rate was 100 Nl/min and the post combustion ratio (PCR) was 60%. The PCR was varied from 45 to 75 % by changing the lance height relative to the bath surface.

Smelting reduction of Whaleback iron ore was investigated at different post combustion ratios and iron ore feed rates using coke and coals with different volatile matter. An increase in the post combustion ratio increased the concentration of iron oxide in the slag. This was attributed to re-oxidation of metallic droplets ejected into the gas phase and carbon depletion in the bath. The main mechanisms for iron oxide reduction was by char particles in the slag and carbon dissolved in iron droplets. The rate of iron oxide reduction increased with increasing iron oxide concentration in the slag, with a slight deviation from a linear function, which was related to the increase in the mass-transfer coefficient in the slag and slag foaming with increasing carbon monoxide evolution at elevated iron oxide concentrations. A maximum iron oxide content in the slag of 10 wt% is recommended to avoid excessive slag foaming.

Carbonaceous materials examined in this project included blast furnace coke, low volatile (17.2% & 19.5% VM), medium volatile (23.9% & 25.5% VM) and high volatile (44.6% VM) coals. The char to slag ratio was a key factor in the operation of the smelting reduction furnace; it was essential for iron oxide reduction, combustion and

slag foam stability. A char to slag ratio of 30 wt % was found to be optimum for the operation of the smelting reduction furnace.

Coal de-volatilisation upon charging into the smelting reduction furnace was much higher than expected from the proximate analysis. As the volatile matter of the coal increased, the quantity of char was reduced. During de-volatilisation of a high volatile coal (44.6% VM), the coal size was drastically reduced due to fracture, increasing the quantity of dust formed, which was then carried away by the large volume of gas generated. This high volatile yield made the coal unsuitable for the formation of char in the smelting reduction furnace, and for furnace operation.

High fixed carbon and low volatile matter were found to be the most important qualities of the coal for the direct iron smelting reduction process.

Sulfur metal / slag / gas partitioning was examined in the laboratory smelting reduction furnace for different carbonaceous materials, iron ore feeding rates and post-combustion ratios. Coal consumption, the sulphur content of the coal and the post combustion ratio were found to be the major factors affecting the hot metal sulphur content. Significant quantities of sulphur, up to 95%, were removed to the gas phase (in the base case 72%). Sulphur concentration in the gas phase increased with increasing sulphur content in the slag and the post combustion ratio.

Sulphur in the gas phase was found to be primarily sulphur dioxide. The rate of sulphur oxidation by the furnace gas was controlled by the chemical reaction step. The proportion of hydrogen sulphide measured in the off-gas increased dramatically when coke was replaced with coal, which was attributed to the de-volatilisation of the coal.

Oxygen potential at the slag / metal interface assessed from the sulfur partitioning was found to be in the range 5.8×10^{-13} to 1.1×10^{-15} atmospheres, which was below the oxygen partial pressure estimated from Fe / FeO or Mn / MnO ratios, above that estimated at the char/slag interface, and relatively close to the oxygen partial pressure assessed from the phosphorous slag / metal partitioning. Slag / metal equilibrium in the smelting reduction furnace was not achieved.

Heat losses to the water-cooling system in the laboratory smelting furnace were disproportionably large due to the small furnace capacity; because of this the heat transfer efficiency of the laboratory furnace was low and the gas temperature at the furnace exit was always less than the bath temperature.

An increase in the post combustion ratio and specific energy of the fuel improved furnace performance. The rate of coal consumption increased with the volatile matter of the coal.

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1 Introduction

Iron is the least expensive and most widely used metal in the world. In 1999, 521 million tons of iron and 754 million tons of steel were produced globally (Fenton, 2000).

The blast furnace dominates the world production of iron, but there are significant challenges to be overcome in order to maintain its reign. The pressure on the blast furnace route is highlighted by the steady decline in market share from 96 % in 1992 to 93 % in 1999 (ISS, 2000).

Blast furnaces are only economical for large-scale production of pig iron, which requires high capital expenditure. To operate a blast furnace it is necessary to produce coke and agglomerated ore (pellets or sinter), which also require large capital investments and produce substantial particulate and gaseous pollutants (Astier, 1990, Fine *et al.*, 1989, Neuschitz and Hoster, 1989, Steffen, 1989, Hatano *et al.*, 1986).

Environmental concerns are becoming more prominent within society and to conform to new regulations it is becoming more expensive, especially for integrated steel plants (Hoffman, 1991). It is estimated that 15 % of the capital cost in building a new steel plant is ascribed to environmental control equipment and the disposal cost of waste (by-product) streams is approximately \$20/ton of steel produced by the integrated plants (Smith and Corbett, 1988, Szekely and Trapaga, 1994).

Another incentive to the promotion of alternative ironmaking is the recent emergence of mini-mills, which have grown from less than 1 % of the total steel production in 1960 to 34 % in 1999. Mini-mills are limited by the available feed materials, resulting in relatively low quality steels due to the shortage of high quality scrap steel. To reduce the dependence of mini-mills on the scrap market, the use of directly reduced iron has been adopted as a scrap substitute. These plants would also benefit from the introduction of small direct smelting reduction plants that could produce sufficient virgin iron units to allow the mini-mills to compete with the integrated steel plants by producing a high quality steel (Eketorp, 1988, Smith and Corbett, 1988).

At present, the blast furnace is being altered to meet some of these challenges. For instance, the implementation of pulverised coal injection and even waste plastic injection through blast furnace tuyeres has reduced the reliance on coke. Clearly there are also opportunities for new technologies, which has lead to the concurrent development of several alternate ironmaking processes.

For an alternative process to be competitive with the conventional blast furnace process, the following are prerequisite (Itaya *et al.*, 1988, Aukrust, 1988, Lu *et al.*, 1986, Gou *et al.*, 1992);

- 1. Simple process flow and low investment cost
- 2. Efficient utilisation of cheaper energy sources
- 3. Utilisation of fine ores without agglomeration
- 4. Less environmental pollution
- 5. Flexible production rate

There are various new methods to produce iron currently being developed, which can be broadly categorised as direct reduction and direct smelting reduction. Ideally, the new processes attempt to address these issues by developing small, efficient and flexible plants, which can utilise raw materials directly. These new processes endeavour to meet the above criteria, all to varying degrees of success.

COREX is the only smelting reduction process currently operating commercially. It is a two stage operation in which direct reduced iron (DRI) from a shaft furnace is charged directly into a smelter – gasifier. COREX does not have a simple flowsheet, requiring the control of two inter-dependent processes, it consumes substantially more fuel than the blast furnace, only utilising 45% of the energy from the coal required, cannot operate with fine iron ore (although this is now being investigated) and is unable to vary the production rate. Yet, Eichberger and Schiffer, 1990, calculated that the cost of liquid iron is approximately 20% less than from a blast furnace.

A number of direct smelting reduction processes are under development. Among them are Russian ROMELT and Australian AusIron processes, which combine both the smelting and reduction within the one vessel, with post combustion above the bath to increase the fuel efficiency. This increases the energy utilisation within the process, but still generates off-gas with a high energy value.

To utilise the chemical energy of the off-gas, smelting reduction processes such as DIOS and HIsmelt, use the off-gas to partially reduce the iron ore, normally only to wustite. The integration of post combustion of the bath gases, direct utilisation of raw materials, including fine iron ore and high volatile matter coals, and partial pre-reduction of the iron ore increases the fuel efficiency, reduces the pollution generated and enhances the economics of operation. These benefits make the potential operating costs more appealing than COREX, but there are still operating problems to be addressed before they become a proven technology.

Integrated iron and steelmaking, heavily dependent on blast furnaces, will be important contributors to world steel production for at least the next 20 years. However, without significant improvements, the blast furnace cannot remain viable in the long term and it is essential that the development of so many promising and viable alternatives continue.

There are several challenges facing direct smelting reduction processes. They must:

- utilise low cost fuel in an energy efficient manner, which requires high post combustion ratios and heat transfer efficiency
- control refractory wear rates, which are challenged by the high temperatures and aggressive slag
- produce high quality metal, low in sulphur and phosphorus
- maintain high productivity

This thesis will investigate the performance of the laboratory smelting reduction furnace under different operating conditions, including the use of different carbonaceous materials, varying post combustion ratio and iron ore feed rate.

2 Literature Review – Alternative Ironmaking Processes

New processes that have been proposed and developed to replace the blast furnace can all broadly be placed into two categories, direct reduction and direct smelting reduction. Direct reduction produces a solid iron product, while direct smelting reduction yields liquid iron. The main purpose of this investigation is to evaluate the performance of Australian minerals in the direct smelting reduction process with a thick slag layer. Following is a brief outline of some of the processes, with emphasis on direct iron smelting.

2.1 Direct Reduction

Iron produced in direct reduction processes is referred to as either Directly Reduced Iron (DRI) or Hot Briquetted Iron (HBI). Direct reduction uses either natural gas or coal (Dey *et al.*, 1993, Smith, 1988) to reduce the iron ore to sponge iron, which contains at least 90 % iron. The majority of DRI is consumed in adjacent electric arc furnaces (Quintero and Dominguez, 1992), as there are transportation problems. HBI is increasingly considered as a competitive source of high grade iron for steelmaking, particularly in scrap short areas of the world (Dancy, 1990, Esdaile and Motlagh, 1991, Ohmi *et al.*, 1983). Although direct reduction produces a high grade of virgin iron, it is really only suitable as a scrap alternative, and for this reason can not directly replace the blast furnace in an integrated steel plant.

2.2 Direct Iron Smelting Processes

Direct smelting reduction produces hot iron in a molten state, which is suitable for direct use in the steelmaking Basic Oxygen Furnace (BOF). There are several direct iron smelting processes, which are at various stages of development. The most representative of them are COREX, DIOS, AISI, HIsmelt, Romelt and AusIron, which will be briefly presented below.

2.2.1 COREX

The COREX process is a 2 stage operation using a DRI shaft furnace to pre-reduce iron ore, directly coupled to a melter gasifier which is charged with coal and limestone (Figure 2-1) (Kepplinger *et al.*, 1990). Oxygen is injected into the bottom of the melter gasifier to generate heat, using a bottom tuyere arrangement. The hot gases from the melter gasifier are fed into a reduction shaft furnace after dust removal, to pre-reduce the iron ore (Delport, 1990, 1992).



Figure 2-1 Schematic representation of the COREX process (Feinman, 1999).

COREX has a high degree of pre-reduction (up to 90%), no post combustion and uses steaming coal and lump or agglomerated iron ore pellets to operate (Hauk, 1990, Rhee *et al.*, 1992).

The current capacity of the Corex process in South Korea is 700 000 t/a. It consumes slightly above one tonne of coal per tonne of hot metal, but 55 % of the total energy input is exported as fuel gas. The utilisation of the fuel gas produced is essential to the operation of COREX. If there is a market for this excess energy, then the cost of liquid iron is approximately 20 % less from COREX than from a blast furnace (Eichberger and Schiffer, 1990).

Dippenaar *et al.*, 1990, found that the impact of the COREX process on the environment is considerably less harmful than that of the integrated ironmaking facilities used at present.

2.2.2 HIsmelt

HIsmelt is a smelting reduction process that operates with post combustion of 50 - 75%, high heat transfer efficiency and partial pre-reduction. The raw materials for the process are fine ores and coal, with a pre-heated air blast for post combustion (Figure 2-2).

The original concept of a horizontal vessel has been replaced by a vertical cylinder, to control the rate of refractory wear (Fonner, 1999). The process differs from the AISI and DIOS processes in several ways, as the coal and pre-reduced ore are injected directly into the metal phase, where rapid dissolution and smelting occur. Off-gassing generates an intense mixing zone between the metal and slag phases. Heat transfer from post combustion to the bath is high, due to the large volume of slag and metal ejected into the gas phase (Gudenau *et al.*, 1993). Re-oxidation of the metal droplets is minimised by the use of air, although dust generation and heat losses are increased due to the high off-gas volume (Cusack *et al.*, 1992, Wright, 1992). The air is pre-heated in stoves, as in the blast furnace, using the off-gases from the fluidised pre-reduction furnace, and is able to be enriched by oxygen.



Figure 2-2 Schematic diagram of the HIsmelt process (Feinman, 1999).

2.2.3 Deep Slag Smelting Processes

Deep slag smelting reduction processes are comprised of two vessels, a pre-reduction furnace and a smelting reduction furnace. Two deep slag smelting process, AISI (Figure 2-3) and DIOS (Figure 2-4) are very similar, except that AISI operates with iron ore pellets and DIOS utilises iron ore directly. The pre-reduction furnace is charged with iron ore at the top, which is reduced in a fluidised bed using the off-gases from the smelting reduction furnace. Only minimal pre-reduction of iron ore is carried out (typically only to wustite), which reduces sticking problems within the fluidised bed and increases productivity (Katayama *et al.*, 1993b, Neuschutz, 1991).



Figure 2-3 Schematic diagram of the AISI process (Feinman, 1999).

The smelting reduction furnace consists of a vertical cylinder, similar to a BOF, with a deep slag layer above an iron bath (Hayashi *et al.*, 1986). Coal and pre-reduced iron ore are added directly onto the slag layer within the furnace, where they are entrained. An oxygen lance inserted through the top of the furnace provides bath turbulence and post-combustion of the carbon monoxide and hydrogen, improving the fuel efficiency of the process (Oeters and Saatci, 1986). Bottom bubbling into the iron bath provides additional mixing within the furnace, and increases the heat transfer efficiency (Katayama *et al.*, 1993a). To maintain a continuous process the slag and metal are tapped periodically. The deep slag layer is required for the following reasons:

- 1. to reduce re-oxidation of the molten iron
- 2. for increased heat transfer and post combustion
- 3. to reduce dust generation
- 4. increased reduction of iron oxide (Sheikhshab Bafghi et al., 1992).

Re-oxidation of the molten iron occurs when the oxygen jet penetrates through the slag layer and into the iron bath (Tokuda *et al.*, 1988), resulting in decreased productivity

and increased iron dust generation (Katayama *et al.*, 1993a). Heat is transferred to the iron bath from the post combustion reactions both above and within the slag layer. Heat transfer within the slag layer is mainly due to the circulation of metallic droplets (Ibaraki, 1994) and coal particles (Katayama, 1992), which also suppress the slag foaming (Iso *et al.*, 1988).



Figure 2-4 Schematic diagram of the DIOS process (Feinman, 1999).

2.2.4 ROMELT

The ROMELT process was developed in the Soviet Union in the 1980's (Figure 2-5). A major feature of this process is that there is no pre-reduction, simplifying the operation of the process. A mixture of air and oxygen is injected into the smelter through 2 rows of tuyeres, which allows post combustion ratios of up to 90%. The extremely high temperatures generated in the gas phase and the aggressive slag is contained by water cooled panels in the smelters walls and roof. Coal and ore are gravity fed through the

top. ROMELT has high energy consumption due to the lack of pre-reduction and extensive water cooling (Feinman, 1999).



Figure 2-5 Romelt process (Feinman, 1999).

2.2.5 AusIron

A similar process is also under development in Australia called AusIron (Figure 2-6). It is a bath process, and operates with submerged Sirosmelt lances and no pre-reduction (Floyd *et al.*, 1992).



Figure 2-6 AusIron process (Floyd et al., 1992).

2.3 **Operating Parameters**

There are many factors that affect the performance and operating characteristics of the smelting reduction furnace. It is important to have an understanding of the individual factors, and how the interaction between them can be optimised to give the best possible furnace performance, that is, a high iron ore reduction rate, low coal consumption and low dust losses.

2.3.1 Post Combustion Ratio

Direct iron smelting processes can be competitive with blast furnace ironmaking only on the basis of efficient utilisation of energy, which involves optimisation of the post combustion reactions. Post combustion reactions involve the combustion of carbon monoxide and hydrogen released from the slag bath:

$$CO + \frac{1}{2}O_2 = CO_2$$
 (2-1)

$$H_2 + \frac{1}{2}O_2 = H_2O$$
 (2-2)

The post combustion ratio is defined as:

$$PCR = \left(\frac{\%CO_2 + \%H_2O}{\%CO_2 + \%CO + \%H_2O + \%H_2}\right) \times 100 \,(\%)$$
(2-3)

With a post combustion ratio of only 50 % it is possible to supply 60 % of the energy requirements for the process. The remaining carbon monoxide and hydrogen are then available for pre-reduction of the iron ore (Takahashi *et al.*, 1992).

Katayama, 1992, found that to decrease coal consumption, high post combustion and heat transfer efficiency are required. As the post combustion ratio increases, the coal consumption is reduced until a critical value is reached which depends on the type of carbonaceous material used (Figure 2-7). When the post combustion ratio is increased beyond the critical value, the heat transfer efficiency is reduced and the coal consumption is increased.



Figure 2-7 Relation between post combustion and fuel consumption for various types of carbonaceous materials (Katayama, 1992).

2.3.2 Heat Transfer Efficiency

Although it is possible to produce a large amount of energy by post combustion, it is also necessary to transfer this heat to the slag bath where it is required. Otherwise, the heat from post combustion is lost with the off-gases and the fuel requirements increase, as represented in Figure 2-7.

By definition, heat transfer efficiency is 100 % when the temperature of the exhaust gas is the same as that of the metal bath. The heat transfer efficiency (HTE) is defined as:

$$HTE = \left(1 - \frac{\text{superheat of exhaust gas}}{\text{heat generated by post combustion}}\right)$$
(2-4)

Hirata *et al.*, 1992, define superheat of exhaust gas as the sum of the heat lost in the exhaust gas, which is superheated to over the metal bath temperature. Heat losses from the vessel, other than in the exhaust gas, are not included as they are unavoidable (Katayama *et al.*, 1993b).

Ibaraki, 1994, considered heat transfer to the slag bath from the gas phase, where heat is generated by post combustion reactions. It was suggested that 20 % of the heat is transferred by radiation from the hot gases to the slag and 20% by radiation from the post combustion flame to the cavity formed by the oxygen jet. The heat is then transferred from the surface of the slag to the bulk by the circulation of the slag and suspended char and iron particles. It is suggested that the remaining energy is supplied by direct combustion of the char circulating within the slag, but this is not a consideration when determining the heat transfer from the post combustion reactions. Convective heat transfer to the bath and the effect of slag and metal droplets ejected from the bath is not considered.

Zhang and Oeters, 1991a, 1991b, concentrated on the role of slag and metal droplets in heat transfer to the slag bath. They suggested that as the droplets leave the melt, they are superheated above the bath temperature by radiation and convective heat transfer from the hot gases generated during post combustion. The droplets then fall back into the melt and transfer their heat to the slag phase. This is supported by Katayama *et al.*, 1993, who found that large amounts of material is splashed into the freeboard.

The transfer of heat to the iron melt occurs by the circulation of char within the slag phase. For this to be efficient, it is necessary to maintain a large char to slag ratio and adequate bottom bubbling, so that the slag phase is well mixed (Ogawa *et al.*, 1992).

Heat transfer to the slag bath is a complicated phenomenon, and the role of each mechanism changes depending on the operation and characteristics of the smelter investigated. The dominant mechanisms are radiation from the post combustion flame, radiation and convection from the furnace gases, and radiation and convection to the droplets ejected from the bath into the freeboard. The relative importance of each mechanism has not been clearly determined.

2.3.3 Iron Ore Reduction

In the smelting reduction furnace, iron oxide dissolved in the slag is reduced by char particles, carbon dissolved in metallic droplets in the slag phase and at the slag/metal interface by carbon dissolved in the metal bath. The main mechanism is the reduction reactions 2-5 and 2-6 with char and carbon dissolved in metallic droplets.

$$(FeO) + C (char) = CO + Fe$$
 (2-5)

$$(FeO) + \underline{C} = CO + Fe \tag{2-6}$$

Selected literature data on the rate constant for the reduction of iron oxide by both char and carbon dissolved in iron are presented in Tables 2-1 and 2-2, respectively.

Investigator	Rate Constant	Temp
Philbrook and Kirkbridge, 1956	$1.2 \times 10^{-4} (\text{gFeO/cm}^2/\text{min}/(\%\text{FeO})^2)$	1703 K
Tarby and Philbrook, 1967	$7.7 \times 10^{-4} (gFeO/cm^2/min/(%FeO))$	1773 K
Sheikhshab Bafgi et al., 1992b	$3.3 \times 10^{-3} (\text{cm/s})$	1573 K
Sarma et al., 1996	$4.5 \times 10^{-7} \text{ (molFeO/cm2/s)}$	1723 K
Lee et al., 1997 [#]	8.88 x 10 ⁻⁵ (mol-O/cm ² /s)	1773 K
Seo and Kim, 1998	$3.19 \times 10^{-5} \text{ (molFeO/ cm}^2/\text{s/(%FeO)}^{0.96}\text{)}$	1773 K
Story et al., 1998	$5.0 \ge 10^{-5}$ @ 3.0% FeO (mol/cm ² /s)	1773 K
Min <i>et al.</i> , 1999	$1.67 \times 10^{-7} (molFeO/ cm^2/s/(%FeO)^{1.26})$	1723 K

Table 2-1 Rate constant for reduction of iron oxide by solid graphite.

[#] High concentration FeO.

Rate Constant	Temp
5.8 x 10 ⁻⁴ (gFeO/cm ² /min/(%FeO) ²)	1703 K
3.6 x 10 ⁻⁴ (gFeO/cm ² /min/(%FeO))	1773 K
5.8×10^{-5} (molFeO/cm ² /min/atm)	1653 K
$7.0 \ge 10^{-5}$ (molFeO/cm ² /min/atm)	1683 K
$7.7 \times 10^{-4} (\text{gFeO/cm}^2/\text{min}/(\%\text{FeO})^2)$	1793 K
$2.5 \times 10^{-7} (molFeO/cm^{2}/s/(%FeO))$	1673 K
7.34 x 10 ⁻⁴ (m/s)	1723 K
$3.1 \times 10^{-6} \text{ (molFeO/cm}^2/\text{s/(%FeO))}$	1473 K
6.1×10^{-7} @ 3.0 % FeO (mol/cm ² /s)	1723 K
$8.25 \times 10^{-5} \text{ (mol/cm2/s)}$	1773 K
$3.19 \times 10^{-5} \text{ (molFeO/ cm}^2/\text{s/(%FeO)}^{0.96})$	1773 K
8.7×10^{-3} @ 3.0 % FeO (molCO/m ² /s)	1673 K
	Rate Constant $5.8 \ge 10^{-4}$ (gFeO/cm²/min/(%FeO)²) $3.6 \ge 10^{-4}$ (gFeO/cm²/min/(%FeO)) $5.8 \ge 10^{-5}$ (molFeO/cm²/min/atm) $7.0 \ge 10^{-5}$ (molFeO/cm²/min/atm) $7.7 \ge 10^{-5}$ (molFeO/cm²/min/(%FeO)²) $2.5 \ge 10^{-7}$ (molFeO/cm²/s/(%FeO)) $7.34 \ge 10^{-4}$ (m/s) $3.1 \ge 10^{-6}$ (molFeO/cm²/s/(%FeO)) $6.1 \ge 10^{-7}$ @ 3.0 % FeO (mol/cm²/s) $8.25 \ge 10^{-5}$ (molFeO/cm²/s) $8.7 \ge 10^{-5}$ (molFeO/cm²/s/(%FeO))^{0.96}) $8.7 \ge 10^{-3}$ @ 3.0 % FeO (molCO/m²/s)

Table 2-2 Rate constant for reduction of iron oxide by carbon dissolved in iron (saturated solution).

^{*} High concentration FeO.

Ibaraki, 1994, found that the proportion of iron oxide reduction from molten slag by carbon dissolved in metal droplets is higher than that of char in a smelting reduction furnace, but this is accredited to the higher reduction rate of the metal droplets.

The rate constant of iron oxide reduction was found by Seo and Kim, 1998 and Sommerville *et al.*, 1980, to be the same for both carbon dissolved in metal droplets and char, while Philbrook and Kirkbridge, 1956, Tarby and Philbrook, 1967, Sarma *et al.*, 1996, Lee *et al.*, 1997, all report very similar values. Indeed, the rate of reduction appears to be highly dependant on the experimental procedure, rather than the use of either char or carbon dissolved in metal as the reductant.

Reduction reactions 2-5 and 2-6 proceed through the gas phase and may be presented as a sum of the following reactions.

$$(FeO) + CO = CO_2 + Fe \tag{2-7}$$

 $CO_2 + C \text{ (char) or } \underline{C} = 2 CO$ (2-8)

Philbrook and Kirkbridge, 1956, suggested that the reaction of iron oxide reduction is second order with respect to the iron oxide concentration in the slag, but were unable to deduce a reaction mechanism. Tarby and Philbrook, 1967, concluded that the rate of reduction is controlled by mass transfer in the slag phase, and that the reduction reaction is of the first order. Sommerville, Greiveson and Taylor, 1980, found that the rate of reduction was chemical reaction controlled at either the gas / metal interface or the gas / slag interface, depending on experimental conditions.

Bafgi *et al.*, 1992, derived that the rate limiting stage of iron oxide is mass transfer in the slag phase. Story *et al.*, 1998, came to the conclusion that the iron oxide reduction may be mix controlled or controlled by the chemical reaction depending on sulphur content, reductant, and other parameters.

Foaming of the slag makes the situation even more complex. In accordance with Murthy, Hasham and Pal, 1994, the rate of reduction of iron oxide is not affected by slag foaming.

While Bafgi *et al.*, 1992, concluded that slag foaming has a profound effect on the rate of iron oxide reduction, and that the rate of reduction decreases with increasing iron oxide concentration. In accordance with Bafgi *et al.*, 1992, the rate of iron oxide reduction from the foaming slag can be presented as:

$$-\frac{d(\%FeO)}{dt} = k_a A / V_s (\%FeO)$$
(2-9)

Where k_a is an apparent rate constant, A is the reaction area and V_s is the slag volume.

The slag is foamed by the evolving carbon monoxide bubbles, which stir the bath. Generation of carbon monoxide bubbles from the reaction of iron oxide reduction increases the mass transfer coefficient, apparent rate constant and slag volume. The first two factors favour the reduction rate, while the last one decreased the rate of iron oxide reduction in accordance with Equation 2-9. The net effect of increasing iron oxide concentration in the slag, and the corresponding increase in the carbon monoxide bubbles generated seems to slightly decrease in the value of k_aA/V_s .

Ibaraki, 1994, reported that in a smelting reduction process with a similar char to slag ratio, 40% of the iron oxide reduction occurs at the slag-char interface, and 60% of iron oxide is reduced by iron droplets suspended in the slag.

There is little consensus about the rate of iron oxide reduction or the importance of the factors that affect it. This reflects the difficulties in characterising the specific conditions and highlights the need for a deeper understanding of the reactions and mechanisms within the smelting reduction furnace.

2.3.4 Slag Foaming

The smelting reduction furnace is strongly affected by the slag foaming ratio (SFR), which can be determined by the calculated slag and iron volume and the measured level of the top surface of the slag.

$$SFR = \frac{\text{slag volume + gas volume}}{\text{slag volume}}$$
(2-10)

The production rate within the vessel is limited by the volume occupied by the foamed slag, as when foaming is not controlled there is a risk of slag overflowing from the converter (Iso *et al.*, 1988). To overcome this it is possible to reduce the foaming by the introduction of carbonaceous materials, reduction of slag viscosity (through slag chemistry or increased temperature), low iron oxide content in the slag or through the increase of iron ore pre-reduction (Ito and Fruehan, 1989, Hara, 1990). Although Kitamura and Okohira, 1992, found that the slag foaming ratio increased with lower viscosity slags.

An increase in the quantity of slag decreases dust generation of iron and coal, and also tends to reduce the carbon content in the metal bath (Katayama *et al.*, 1993a). When there is a thick slag layer it is possible to effectively separate the iron oxide in the bottom of the slag layer from the oxygen jet, which increases the post combustion ratio and decreases iron dust generation.

The slag foaming phenomenon is caused by a vast quantity of fine CO gas bubbles generated at the slag-metal interface by the iron oxide reduction reaction (Hara and Ogino, 1992, Kitamura and Okohira, 1992). Surface active components such as SiO_2 , P_2O_5 and CaF_2 stabilise foam, by decreasing slag surface tension. The volume of gas produced within the furnace can be controlled by increasing the pre-reduction degree of the iron ore, pressurising the furnace or using minimal bottom injection of both gas and coal (Katayama *et al.*, 1993a).

High temperatures and low slag basicity are favourable to suppress the slag foaming, as both of these factors reduce the viscosity of the slag (Gudenau *et al.*, 1992). Large quantities of char in the slag layer is essential for controlling the foaming of slag and operating the furnace efficiently (Ogawa *et al.*, 1992, Hayashi *et al.*, 1986). The overflow of slag from the vessel is considered to be one of the major limitations to productivity increases, and for this reason it is important to understand how to suppress slag foaming (Gou *et al.*, 1993b).

2.3.5 Coal Consumption and Usage

The elimination of coke as a reductant and the direct utilisation of cheap coal are common aims for the new smelting reduction processes. The rate of coal consumption within the smelting reduction furnace is one of the most critical economic indicators for the viability of the process.

The coal consumption rate is dependent on the type of coal, post combustion ratio and the heat transfer efficiency of the process. The post combustion ratio is a measure of the proportion of the energy released within the furnace, while the heat transfer efficiency dictates the utilisation of that energy.

The volatile matter is the critical operating parameter when optimising fuel consumption, as shown in Figure 2-7. Katayama *et al.*, 1992, found that the fuel requirements increased with the volatile matter content of the coal and that the optimum post combustion ratio also increased with the volatile matter content. The minimum fuel requirements found by Katayama *et al.*, 1993, for different types of coal in a 5 ton vessel are shown in Table 2-3. The fuel rates for a larger vessel would be lower due to reduced heat losses.

Coal Type	Minimum Coal Consumption, kg/t-HM	Critical Post Combustion Ratio, %
High Volatile Coal, 36.8% VM	1500	40
Medium Volatile Coal, 25.8% VM	1200	50
Coke	900	65

Table 2-3 Fuel requirements in a 5 ton smelting reduction furnace.

Katayama, 1992, suggests that when coal with a high volatile matter content is used in the smelting reduction furnace, the operating efficiency deteriorates due to the increase in oxygen requirements by the dispersion of coal fragmentation, which increases the fixed carbon consumption. It is suggested that some pre-treatment of coal may be beneficial to the operation.

Another factor is the gas generated by coal de-volatilisation, which consumes energy that is only partially recovered by the post combustion reactions. This increases the fuel requirements, resulting in higher gas volumes and shorter gas residence time, limiting the post combustion ratio.

The literature concurs that for deep slag smelting processes that the furnace operation is optimal when low volatile coals are utilised.

Coal in the smelting reduction furnace;

- 1. reduces the iron ore
- 2. supplies the necessary heat for the reduction reactions and smelting of raw materials
- 3. controls slag foaming
- 4. enhances heat transfer within the slag

To efficiently operate the smelting reduction furnace, it is necessary to minimise the coal consumption. The energy requirements of the process should be met as much as

possible by the post combustion reactions, and the char used for reduction of the iron ore, not direct combustion.

To make full use of the coal it is necessary to maintain a high post combustion ratio and heat transfer efficiency, while minimising carbon losses in the off-gases. The volatile matter within the coal is liberated when the coal undergoes rapid heating as it enters the furnace. Katayama *et al.*, 1993b, found that when the volatile matter in coal is increased, and all other experimental conditions are kept constant, then the post combustion ratio decreases.

Coal dust generation is increased when using high volatile coals, due to the fragmentation of coal when rapidly heated. With high heating rates the volatiles within the coal are quickly released, causing the coal to fragment and produce undersized particles that are entrained within the off-gases. To decrease the rate of de-volatilisation and reduce fragmentation it was found that preheating the coal to 850 °C was sufficient to remove the volatiles with minimal fines production (Katayama *et al.*, 1993b). This results in an increased post combustion ratio, but also in the loss of the coal volatiles as a source of heat (Fruehan *et al.*, 1988). The post combustion of volatiles can provide large quantities of heat to the furnace (Takahashi *et al.*, 1992).

The overall reaction of iron ore reduction to metallic iron in a molten bath at 1500 °C theoretically requires 4.6 GJ/t Fe.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \tag{2-11}$$

This is supplied by burning coal. The combustion products formed under the prevailing conditions are carbon monoxide and hydrogen, due to the Boudouard and water gas shift reactions, given below:

$$CO_2 + C \rightarrow 2 CO \tag{2-12}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2-13}$$

When partially reduced iron ore is used, then the following reaction occurs, which produces 33 % less CO, effectively reducing slag foaming and increasing furnace productivity:
$$FeO + C \rightarrow Fe + CO$$
 (2-14)

The heat of combustion of carbon to carbon monoxide is approximately 9.4 GJ/t-carbon and for carbon monoxide to carbon dioxide is approximately 23.5 GJ/t-carbon. For a typical high volatile coal, the combustion of hydrogen to water produced 11.8 GJ/t-coal (8.8 GJ/t-fixed carbon) (Takahashi *et al.*, 1992). From these values it can be seen that when a high degree of post combustion is used, the fuel efficiency of the process increases substantially.

2.3.6 Particle Size of Raw Materials and Feeding Methods

In order to produce iron with easily obtained and cheap raw materials, it is necessary to reduce the pre-treatment steps as much as practically possible. To accomplish this, the process should be developed so that both iron ore and coal can be fed into the furnace with a large size distribution, or at least with a proportion of fines. Katayama *et al.*, 1993b, investigated the effects of particle size and feeding methods on the smelting reduction process. It was found that;

- 1. The amount of carry-over was negligible for fine ore, but about ten times as high for fine coal. The poor wettability of coal in slag seems to be the cause of this problem.
- 2. The carry-over of coal can be reduced by increasing the amount of slag, protecting the coal from ascending gas currents and decreasing the velocity of the gas current by pressurising the vessel.
- 3. When a stream of raw materials is poured into the furnace, the entrainment of particles in the off-gas is negligible if the surface area of the stream is kept to a minimum.
- 4. Excessive bottom bubbling required for the injection of fine ores into the metal bath caused a decrease in the post combustion ratio and increased iron dust generation, therefore the intensity of the bottom bubbling should be limited.

2.3.7 Bottom Bubbling

Bottom bubbling has been found to be essential within the smelting reduction furnace for effective heat and mass transfer (Katayama, 1992, Katayama *et al.*, 1993b). Nitrogen is the most common gas bubbled through the furnace bottom.

Hirata *et al.*, 1992, found that by increasing the stirring intensity of the metal and slag using bottom injection of nitrogen, the heat transfer efficiency and the iron reduction rate were increased.

When injecting fine coal through the bottom of the furnace, the operation of the process is improved, but only to a certain level, after which the increased gas injection becomes detrimental to the post combustion ratio due to the increase in metal droplets and increases the iron dust generation (Katayama *et al.*, 1993b).

When oxygen is injected through the base of the furnace, it is necessary to shroud the jet with natural gas, which cracks and absorbs the heat of the reaction between the oxygen and dissolved carbon. This is done to protect the refractories from excessive wear at the base of the furnace.

2.3.8 Oxygen Lance

The oxygen lance height has a significant effect on the post combustion ratio. There have been several investigations to improve the post combustion ratio by adjusting the oxygen lance, with the following general recommendations (Gou *et al.*, 1993a, Koria, 1988, Conochie *et al.*, 1984, Floyd and Lightfoot, 1984, Takahashi *et al.*, 1992);

- 1. special soft blowing practices
- 2. increased lance height to improve oxygen coverage of slag
- 3. special lances with secondary oxygen ports
- 4. separate injection ports from the side or bottom of the furnace

2.3.9 Refractory Limitations

A major practical problem with smelting reduction processes is refractory selection. There are extremely high temperatures at the top of the furnace, in the post combustion region and off-gas ducting. Temperatures in excess of 2000 °C have been reported for the off-gas temperature (Katayama, 1992).

If a low degree of pre-reduction is achieved in the fluidised bed, due to a high post combustion ratio, then there will be an iron oxide rich slag, which is extremely corrosive to the refractory lining (Katayama *et al.*, 1993a) and promotes slag foaming.

The refractories used in the DIOS process were a dolomite brick (Ogawa *et al.*, 1992) or a magnesia/chromite brick for the walls and magnesia for the base (Takahashi *et al.*, 1992).

2.4 Sulphur Partitioning Between the Gas and Slag

Sulphur slag / gas partitioning was mainly investigated in laboratory experiments with well controlled gas compositions and temperatures. The mechanism of sulphur transfer between the gas and slag is dependent upon the form of sulphur within the slag, either sulphide or sulphate, and the gas composition.

Conditions in the smelting reduction furnace are quite different from those in the experiments on slag/gas reactions. Therefore, experimental data available in the literature should be applied with care.

The de-volatilisation of coal will release the organic component of the sulphur directly into the gas, depending on the size of the coal, the heating rate and the residence time in the gas before entrainment within the slag. Sulphur released by de-volatilisation may be dissolved into the slag.

The combustion of char in the slag may also liberate sulphur directly. Katayama *et al.*, 1993c, and Ibaraki, 1994, have shown that the char within the slag is mainly floating on the surface. So, any sulphur released from char with the volatiles on the slag surface would be likely to escape directly to the gas phase.

Sulphur metal/slag/gas partitioning depends on the chemistry of these phases, temperature and oxygen potential. In the smelting reduction furnace, temperature and oxygen potential are non-uniform in the slag and gas phases.

The temperature of the slag at the slag / gas interface has been found to be at least 50 - 100 K higher than the bulk slag temperature (Hirata *et al.*, 1992). The gas temperature in the smelting reduction furnace has been calculated by Panjkovic, 1998, to be at least 400 K higher than the slag temperature, depending on the furnace conditions. The reaction temperature between the slag and gas is difficult to measure, but it is significantly higher than the metal bath temperature.

The gas phase has a significant variation in composition across the surface of the bath. At the centre of the bath, where the oxygen jet hits the bath surface, the oxygen partial pressure is high; it decreases with increasing distance from the centre across the bath surface (Panjkovic, 1998). The oxygen potential is low in the slag, and is relatively high in the gas phase at the slag surface.

The slag bath contains a large quantity of char, which will keep the oxygen potential within the bulk of the slag low. Even for the slag saturated with FeO, the oxygen potential would be below 10^{-8} atmospheres. Typically, the smelting reduction furnace slag contains below 10 wt% FeO, and the bulk oxygen potential within the slag is less than 10^{-9} atmospheres. At such oxygen partial pressures, the principal form of sulphur in the slag is sulphide (S²⁻).

Research in the behaviour of sulphur in the smelting reduction furnace has been quite limited. The mechanism for the removal of sulphur from the slag in a smelting reduction furnace has not been adequately addressed in the literature. The proportions of sulphur released from the slag and directly from the coal are generally unknown. Usachev *et al.*, 1991, studied the partitioning of sulphur between the gas/dust – slag – metal phases in the ROMELT process. The ratio for sulphur partitioning for the Romelt process and a blast furnace is shown below in Table 2-4.

Sulphur bearing phase	Mass % of sulphur	
	Blast Furnace	Romelt Process
Gas and Dust	10	91
Slag Bath	86	6
* Metal Bath	4	3

They derived expressions for the equilibrium distribution of sulphur in the metal/slag and slag / gas-dust phases. No reaction mechanisms were suggested.

2.4.1 Thermodynamic Consideration

Insight into the mechanisms of sulphur transfer from the slag to the gas was mainly developed on the basis of laboratory studies of the slag/gas reactions (Turkdogan and Pearce, 1963, Pelton *et al.*, 1974, Stoehr and Pezze, 1975, Mori *et al.*, 1980, Agrawal *et*

al., 1983). It was established that sulphur is removed from the slag to the gas phase by the oxidation of sulphide ions. In ironmaking and steelmaking slags, sulfur is predominantly combined with calcium in the form of calcium sulphide. In this case, the de-sulphurisation reaction is:

$$(CaS) + 3/2 O_{2(g)} = SO_{2(g)} + (CaO)$$
 (2-15)

In an ionic form, the de-sulphurisation reaction can be presented as:

$$(S^{2-}) + 3/2 O_{2(g)} = SO_{2(g)} + (O^{2-})$$
 (2-16)

Sulphur exists in the slag predominantly as sulphide at oxygen potentials below 10^{-5} atmospheres. When the oxygen potential in the slag is above 10^{-4} atmospheres, then the sulfate phase prevails, and the de-sulphurisation reaction is:

$$(CaSO_4) = SO_{2(g)} + 1/2 O_{2(g)} + (CaO)$$
(2-17)

or in the ionic form:

$$(SO_4^{2-}) = SO_{2(g)} + 1/2 O_{2(g)} + (O^{2-})$$
(2-18)

Oxidation of sulphide to sulphate was observed by Mori *et al.*, 1980, who studied desulphurisation of slags using oxygen – argon gas mixtures, with oxygen partial pressures from 0.001 to 1 atmospheres. They found that the rate of slag desulphurisation was in accord with reactions presented above. Reaction rates for sulphide slags were high for high oxygen partial pressures, while the de-sulphurisation rate for sulphate slags was highest in argon atmospheres.

Stoehr and Pezze, 1975, and Ozturk *et al.*, 1994, also suggested that sulphide in a slag exposed to a high oxygen potential is oxidised to sulphate, which retards the formation of sulphur dioxide. However, the formation of sulphate ions is slow (Mori *et al.*, 1980, Pelton *et al.*, 1974). Thus, under highly oxidising conditions sulphate can be formed on the surface of the slag, however, in a circulating slag bath, the surface is continuously renewed, and sulphate will be transformed to sulphide in the bulk of the slag bath, where the oxygen potential is low. Therefore, in the smelting reduction furnace, sulphide in the slag reacts with the oxidising gas atmosphere.

Predominantly, sulphur dioxide is detected in the gas phase from slag de-sulphurisation. However, in the reaction of slag with water, hydrogen sulphide is formed (Pelton *et al.*, 1974, Stoehr and Pezze, 1975):

$$(S_2^{2-}) + H_2O_{(g)} = H_2S_{(g)} + (O_2^{2-})$$
 (2-19)

Ozturk *et al.*, 1994, suggested that the slag in the smelting reduction furnace is desulphurised by the following reactions:

$$FeS_2 + H_2 = FeS + H_2S$$
 (2-20)

$$FeS + H_2O = FeO + H_2S$$
(2-21)

More often, hydrogen sulphide in the gas phase is formed as a result of the reaction of sulphur dioxide, evolved by slag de-sulphurisation when hydrogen is present in the gas phase (Agrawal *et al.*, 1983):

$$SO_{2(g)} + H_{2(g)} = H_2S + O_2$$
 (2-22)

However, in the smelting reduction furnace, water is consumed by water gas shift reaction:

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$
(2-23)

Carbon monoxide is regenerated by the Boudouard reaction:

$$\operatorname{CO}_2(g) + \operatorname{C}(s) \to 2 \operatorname{CO}(g)$$
 (2-24)

Under the given conditions, gas phase thermodynamics favours sulphur dioxide above hydrogen sulphide, which was observed experimentally.

2.4.2 Kinetic Considerations

The transfer of sulphur from the slag to the gas phase includes the following steps:

- 1. Mass transfer of sulphur in the slag phase
- 2. Chemical reaction at the gas/slag interface
- 3. Mass transfer in the gas phase

Agrawal *et al.*, 1983, showed that the rate of sulphur removal from the slag was controlled by mass transfer in the gas phase when the gas velocity was below 0.04 m/s. The concentration profile of sulphur in the partially reacted slag bath was measured as a function of the slag depth using a micro-probe. The concentration was uniform and agreed well with the bulk sulphur concentration, which confirmed that sulphur mass transfer in the slag was not the rate limiting step. It was concluded that interfacial chemical reactions controlled the process of de-sulphurisation at higher gas velocities. The possible mechanisms of de-sulphurisation reactions, suggested by Agrawal *et al.*, 1983, are shown in Table 2-5. Slag de-sulphurisation is represented by the following reactions:

$$(S2-) + 2CO_{2 (g)} = SO_{2 (g)} + 2CO (g)$$
(2-25)

$$(S^{2-}) + H_2O_{(g)} = H_2S_{(g)} + \frac{1}{2}O_{2(g)}$$
 (2-26)

Turkdogan and Pearce, 1963, studied sulphurisation and de-sulphurisation of slags at low oxygen potentials, using CO/CO₂ gas mixtures. They found that the rate of desulphurisation increased with the oxygen partial pressure. The rate of sulphur transfer was mass transfer controlled when the melt was 10-15 mm deep, but at shallower depths it was mix-controlled by mass transfer and chemical reaction at the slag / gas interface.

Rate Controlling Step		Rate Expression (dNs/dt)
1	H ₂ O Adsorption: H ₂ O _(g) + \Box = H ₂ O(ad)	$-k_1'P_{H_2O}$
2	H ₂ O Dissociation: H ₂ O(ad) + 2 \square = 2H(ad) + O(ad)	$-k_2'P_{H_2O}$
3	Dissociative Adsorption: $H_2O_{(g)} + 3\Box = O(ad) + H_2(ad)$	$-k_{3}'P_{H_{2}O}$
4	Dissociative Adsorption: $H_2O_{(g)} + \Box = O(ad) + H_{2(g)}$	$-k_4'P_{H_2O}$
5	H ₂ Desorption: $2H(ad) = H_{2(g)} + 2\Box$	$-k_{5}'P_{H_{2}O}$
6	CO_2 Adsorption: $CO_{2(g)} + \Box = CO_2(ad)$	$-k_6'P_{CO_2}$
7	CO_2 Dissociation: $CO_2(ad) + \Box = CO(ad) + O(ad)$	$-k_{7}'P_{CO_{2}}$
8	Dissociative Adsorption: $CO_2(g) + 2\Box = CO(ad) + O(ad)$	$-k_{8}'P_{CO_{2}}$
9	Dissociative Adsorption: $CO_2(g) + 1\Box = CO(g) + O(ad)$	$-k_9'P_{CO_2}$
10	CO_2 Desorption: $CO_2(ad) = CO_{2(g)} + \Box$	$-k_{10}P_{CO_2}$
11	Charge Transfer: $[S^{2-}] + O(ad) = S(ad) + [O^{2-}]$	$-k_{11}\Gamma_{S^2} - P_{H_2O}^{\frac{1}{3}}$
12	O-S(ad) Formation: $S(ad) + O(ad) = O-S(ad) + \Box$	$-k_{12}\Gamma_{S^2} - P_{H_2O}$
13	SO ₂ (ad) Formation: O-S(ad) + O(ad) = SO ₂ (ad) + \Box	$-k_{13}\Gamma_{S^2} - P_{H_2O}$
14	SO ₂ (ad) Desorption: SO ₂ (ad) = SO _{2(g)} + \Box	$-k_{14}\Gamma_{S^2} - P_{H_2O}$
15	H-S(ad) Formation: S(ad) + H(ad) = H-S(ad) + \Box	$-k_{15}^{'}\Gamma_{S^{2}}-P_{H_{2}O}^{2/3}$
16	$H_2S(ad)$ Formation: $H-S(ad) + H(ad) = H_2S(ad) + \Box$	$-k_{16}\Gamma_{S^2} - P_{H_2O}$
17	$H_2S(ad)$ Desorption: $H_2S(ad) = H_2S_{(g)} + \Box$	$-k_{17}\Gamma_{S^2} - P_{H_2O}$
18	$S_2(ad)$ Formation: $2S(ad) = S_2(ad) + \Box$	$-k_{18}\Gamma_{S^2}^2 - P_{H_2O}^{2/3}$
19	$S_2(ad)$ Desorption: $S_2(ad) = S_{2(g)} + \Box$	$-k_{19}\Gamma_{S^2} - P_{H_2O}^{2/3}$

Table 2-5 Rate expressions for slag de-sulphurisation, Agrawal et al., 1983.

k = rate constant, $\Gamma = surface concentration$, P = partial pressure.

Pelton *et al.*, 1974, performed a series of experiments using a sulphur containing slag, which was exposed to a gas of known oxygen content. The principal method of sulphur removal to the gas phase was the oxidation of sulphide ions (Reaction 2-15); no

appreciable amount of sulphate ions was detected within the bulk of the slag. They found that the slag evolved sulphur dioxide at a rapid rate when the oxygen partial pressure was in the range 0.003 to 0.1 atmospheres. When $pO_2 > 0.1$ atmospheres, a transition in the rate occurred early in the process, with the fast initial rate followed by a slower rate. They concluded that this transition resulted from the "poisoning" of the surface at higher values of pO_2 by absorbed oxygen or oxy-sulphide species.

Pelton *et al.*, 1974, showed that when the oxygen partial pressure was lower than 0.1 atmospheres the rate was controlled by transport in the gas phase. In more oxidising atmospheres, the rate was found to be controlled by chemical reaction at the slag / gas interface. Mori *et al.*, 1980, also concluded that the de-sulphurisation rate was controlled by the slag / gas interfacial chemical reaction. However, intrinsic kinetic control was suggested for oxygen partial pressures below 0.33 atmospheres.

Diffusion of sulphur in the slag was found to be rate limiting for foamed slags, as reported by Ozturk *et al.*, 1994. The rate of sulphur removal was a function of circulation rate of a highly foamed slag.

This is confronted by Agrawal *et al.*, 1983, which showed that even for a stagnant slag bath the rate is controlled by chemical reaction at the slag / gas interface when the gas velocity is above 0.04 m/s.

The mechanism for the removal of sulphur from the slag in a smelting reduction furnace has not been adequately addressed in the literature. The proportions of sulphur released from the slag and directly from the coal are generally unknown.

Slag / gas reaction experiments fail to address the non-equilibrium nature of the system in the smelting reduction furnace, particularly the oxygen potential of the slag, the consumption of oxygen within the vessel and the presence of char in the slag.

Pilot plant experiments are unable to sample the gas near the surface of the slag, allowing the gas to react in the vessel with the reducing gases and dust. The transfer of sulphur from the gas to the dust phase is a time and temperature related effect that has not been addressed in literature.

2.5 Summary and Project Objectives

It is well recognised that blast furnace ironmaking is efficient in terms of energy consumption, consistency of operation, quality of hot metal, life expectancy and productivity. However, it has inherent problems related to the strict requirements for raw materials, high capital costs and rigid operation.

It is challenged by alternate ironmaking processes, of which direct ironmaking is represented by several commercial processes, and direct iron smelting processes are under development. However, direct reduced iron has a limited use, predominantly in EAF steelmaking, while direct iron smelting processes produce hot metal suitable for direct use in the BOF, which remains the major steelmaking process.

The major advantages of direct smelting reduction are:

- low capital costs
- flexibility in feed materials
- direct use of raw materials
- less environmental pollution
- flexible production rate

The following is well established in the literature:

- direct smelting reduction is competitive with the blast furnace only under conditions of efficient utilisation of fuel through post combustion and heat transfer to the bath
- Iron reduction is controlled by carbon dissolved in iron droplets and char in the slag bath
- Slag foaming should be controlled by the use of char
- Fuel consumption is reduced at high post combustion

- Fuel consumption increases with the coal volatile matter content
- The bath is very aggressive towards the refractories

The following gaps exist in the present knowledge base:

- Rate constant for iron oxide reduction in smelting reduction processes
- Suitability of high volatile matter coals
- Partitioning of sulphur between the gas, slag and metal
- Mechanism of sulphur gasification in the smelting reduction furnace
- Behaviour of foaming slags

This project's aim was to contribute to the further understanding of direct smelting reduction by investigating the:

- Factors affecting iron reduction
- Importance of coal properties
- Partitioning of sulphur between the gas and slag phases
- Mechanism of sulphur gasification

3 Experimental Description and Development

The experimental facility was designed and manufactured to investigate the deep slag bath smelting reduction process. The main parts of the experimental facility, as presented schematically in Figure 3-1:

- Furnace to perform smelting reduction experiments, able to melt the initial metal charge, maintain the correct bath temperature and contain the metal, slag and gas
- Raw material feeding system, to maintain an accurate mass balance of carbon in the furnace and reliably deliver iron ore to the slag bath without dusting
- Gas injection system for the delivery of oxygen for post combustion and bottom stirring
- Gas analysis to control the post combustion ratio and perform an on-line mass balance
- Temperature measurement for the gas phase and control for the iron bath



Figure 3-1 Schematic of experimental smelting reduction furnace

The apparatus was developed on the basis of a 50kg induction furnace. The furnace was extended vertically and provided with a furnace lid, screw feeders, gas injection systems, extensive data logging, gas extraction and cleaning, gas sampling and analysis, and water cooling.

3.1 Furnace

The furnace was an Inductotherm 50 kg induction furnace, originally 180 mm ID by 400 mm deep, which has been increased to 450 mm deep. The extension increases the internal volume of the furnace and provides a flat interface to seal the removable extension to the top of the furnace. The furnace power supply was capable of 75 kW at approximately 1500 Hz.

3.1.1 Furnace Refractories

The furnace was originally lined using a rammable magnesia powder, Mormag Ram Fe, specifically designed for induction furnaces operating with iron. The lining was rated to 1800 °C. The magnesia was capped with Moral Mould 85P.

In the preliminary trials the furnace lining lasted for about 20 heats. As the experiments progressed, the slag bath became more aggressive towards the lining, with approximately 500g of magnesia consumed during each heat. The lining appeared to be eroded and dissolved by the slag phase, especially at the gas-slag interface.

The use of bottom bubbling gas increased the circulation of the slag and resulted in accelerated refractory wear. This excessive lining degradation was unacceptable due to the magnesia changing the slag composition during the experiment and the lining only lasting for a maximum of three experiments. The slag composition typically increased from 6% to 20% MgO during the experiment.

New dry rammable lining materials were investigated. Coral XL was eventually chosen. It was primarily a MgO.Al₂O₃ spinel, with small concentrations of other binders. The lining was rated for 1725 °C. This material typically lasts for 20 heats.

Chromium refractories are generally no longer used due to environmental concerns, and were therefore not considered.

The furnace freeboard was extended by an additional 150 mm, to give an overall working height of 600 mm. The extension was constructed from three layers of refractory. The inner ring was Moral Hycast 90T, rated at 1800 °C, with good thermal shock and slag resistance. The second layer was Moral Coolcast 155, rated at 1550 °C, which provided thermal insulation and strength, and the final layer was wet Kaowool (Kaowool with a sodium silicate binder) for added insulation.

A thermocouple was placed in the extension to measure the off-gas temperature. It was located 75 mm from the top of the furnace, protruding 20 mm into the gas stream directly below the combustion gas exit in the furnace lid.

The increased height was used for off-gas combustion and splash control. The bath level was usually maintained below 350 mm, as the extension was not designed to contain a bath of liquid slag. The extension was essential to protect the lid from slag splashing. Before the extension was constructed, the experiment was difficult to control due to constant blockages.

3.1.2 Bath Thermocouples

Mounted in the bottom of the furnace were two type B thermocouples (Platinum– Rhodium 6% / Platinum– Rhodium 30%) located opposite each other on a diameter of 140 mm (Figure 3-2). The thermocouples were embedded approximately 3 mm below the lining. The temperature recorded by the thermocouples was approximately 100 - 300 °C below the metal temperature, depending on the thickness and condition of the refractory. However, the temperature difference was constant during any single experiment. At the initial experimental stage, the thermocouples within the base of the furnace were constructed in such a manner that the metal was in contact with the alumina sheath. A small depression was made in the base of the furnace and a sheath was embedded. This gave more accurate metal temperatures, but proved to be unreliable due to breakages. Also, there was still a temperature difference due to the water cooled refractories.

A controller was used to vary the furnace power and maintain a constant temperature during the experiment. The metal temperature was measured using a graphite sheathed type B thermocouple dipped into the melt, and then compared to the furnace base temperature. It generally required at least one hour to ensure a stable differential between the refractory thermocouple temperature and the metal bath temperature. It was found that the bath temperature was controlled by the bottom thermocouples to within 25 °C of the set point.

Two thermocouples were necessary in the furnace base, as either thermocouple may break during an experiment. Without the bath thermocouples, the metal temperature may rise above the maximum refractory temperature, causing furnace failure. The effect of induction heating on the temperature measured by the thermocouples was determined by varying the power from zero to 75 kW, no effect was observed. Both thermocouple temperatures were constantly logged.



Figure 3-2 Thermocouples embedded in the base of the furnace.

3.1.3 Off-gas Temperature Measurement

It was necessary to measure the off-gas temperature to determine the heat transfer efficiency of the process. Many different methods were tested to measure the off-gas temperature.

Initially a thermocouple was inserted into the outlet gas stream, within the furnace lid (Figure 3-3). This caused blockages in the gas outlet due to particles in the off-gas adhering to the thermocouple sheath, which made the experiments unstable. Measured temperatures were normally below 1000 °C, which was considered to be incorrect.



Figure 3-3 Thermocouples in outlet gas stream

A suction pyrometer was then trialed (Figure 3-4). This was a tube 10mm in diameter with an exposed type B thermocouple suspended in the centre. A small quantity of gas was drawn through the tube and across the thermocouple. The thermocouple measured the temperature of the gas, and the gas sample was used for composition analysis within the mass spectrometer. Due to the high dust load and the sticky nature of the dust at the gas temperature the thermocouple was not reliable. The measured gas temperatures were generally below 1000 °C.

A thermocouple was then inserted 30 mm below the lid, but close to the off-gas exit tube. It was initially protected using an alumina sheath suspended from the top of the lid, to reduce the heat losses from the thermocouple to the water cooling on the lid. This was successful but the alumina sheath occasionally broke due to thermal shock and slag attack.



Figure 3-4 Suction pyrometer

Finally, a graphite sheath was attached to the alumina tube using alumina paste (Figure 3-5). This protected against slag and thermal shock. A zirconia wash was also used to reduce graphite combustion. The gas temperatures measured using this method were up to 1400 °C.



Figure 3-5 Gas thermocouple through furnace lid

The temperature of the off-gas was much lower than expected due to the water cooled refractories. It was necessary to measure the gas temperature closer to the combustion zone to calculate the heat transfer efficiency. Since the thermocouple inserted through the top of the furnace worked reliably, a longer thermocouple was constructed.

A thermocouple 550mm long, with an alumina sheath in the centre and a graphite sheath surrounding the bottom 200mm. This thermocouple was slowly extended into the flame, and the temperature and position were recorded. The thermocouple never survived above a temperature of 1500 °C, normally breaking below 1400 °C.

A thermocouple was tehn inserted 30 mm through the side of the furnace extension, 75 mm below the lid, with an alumina and graphite sheath to protect the thermocouple (Figure 3-6). This thermocouple produced results similar to the thermocouple through the lid, with temperatures measured up to 1400 °C.



Figure 3-6 Gas thermocouple through furnace extension

A two-colour pyrometer was used to determine the temperature of the luminous flame within the furnace. Temperatures in excess of 2100 °C have been measured directly. The actual temperature of the flame was at least 15 % higher due to transmission losses through the silica glass viewing port and mirror.

Temperatures could not be measured consistently, as the flame was not visible, due to the dust and fumes within the furnace.

3.1.4 Heat Losses

Water cooling of the furnace, lance and lid caused high heat losses and slag freezing to the refractories. Heat losses within the furnace account for a large proportion of all energy usage.

The furnace lining was cooled by water that passes through the induction coils, which were in intimate contact with the furnace refractories. Typically, the water temperature in the coils was between 20 and 50 °C, to stop the water from boiling and causing hot spots due to poor heat transfer to the steam. The water temperature must also be higher than ambient, to ensure that there was no condensation on the coils.

To reduce the heat flux through the furnace walls a layer of Fiberfrax 970-J paper was placed between the permanent furnace lining and the replaceable MgO.Al₂O₃ lining. This insulates the furnace and reduces the heat losses significantly. It also allowed the refractories to expand during heating.

Slag freezing on the furnace walls reduced the working volume of the furnace and damaged the lining. It was mechanically removed while hot, otherwise it could cause the furnace lining to fracture. By increasing the furnace insulation, it was possible to minimise the slag freezing to the furnace wall.

To reduce slag adhesion to the lining a graphite susceptor (150mm OD, 110mm ID, 100mm high) was trialed in the furnace to heat the slag. It was slowly consumed by the metal bath and slag. To reduce graphite consumption a zirconia refractory wash was applied to the susceptor, but it was not possible to completely protect the graphite.

If a large slag layer was frozen to the furnace after pouring the metal, it was often removed by blowing oxygen and melting the slag/metal adhering to the furnace wall. If the oxygen was not able to remove the slag from the inside of the furnace, the graphite susceptor was placed inside the furnace and the power applied to heat the ring and melt any remaining slag.

3.2 Furnace Lid

The lid was the interface through which the oxygen lance was introduced to the furnace, gas was sampled, raw material fed, off-gas removed and the gas temperature was measured. It was vital to have a reliable and functional lid.

Initially, a lid was constructed from stainless steel and various refractories. This lid was easily blocked and broken during the operation of the furnace, due mainly to slag foaming and splashing and extreme high temperatures. However, this lid was essential in the development of the final water cooled lid, although many modifications were made before the water cooled lid was designed and built. The final lid was constructed of a high temperature, furnace grade stainless steel (Sandvik 253 MA). The maximum temperature for 253MA is 1150 °C, so water-cooling was used to control the temperature. A replaceable refractory (Moral Hycast 90T, a low cement, alumina based refractory) was cast into the base of the lid to reduce heat losses from the furnace, and to prevent overheating and provide slag splash protection.



Figure 3-7 Furnace Lid

The lid centre accommodated the water cooled oxygen lance. Three general ports located in the lid were used for thermocouples, viewing, raw material feeding and sampling (Figure 3-7).

3.3 Raw Material Feeding

Raw materials were fed into the furnace using a pair of Techweigh E5 variable speed screw feeders or a cartridge feed system.

The operation of the screw feeders was initially very simple. The ore and carbonaceous materials were mixed with fluxes to achieve the required slag composition and loaded into separate hoppers. The raw materials were then fed into a common hopper, from which they fell into the furnace. The hopper was protected with argon to stop hot gases from entering the screw feeders. The screw feeders and mixing hopper were mounted on a track to easily disengage them from the furnace lid.

Several problems soon became evident, leading to major modifications to the feeding system over the duration of the project.

The screw feeder auger was 38 mm in diameter, but the required raw material size was much smaller. The largest ore particles that could be handled were 3 mm, to reduce blockages between the auger and the flight tube. The final ore feed was much smaller than 3 mm as the screw feeder tended to crush the ore while feeding, substantially increasing the proportion of fines. This was not ideal for the furnace operation due to dusting of the fine ore.

The coke/coal was easier for the screw feeder to crush, so larger initial feed material was used without the screw feeder becoming blocked. The screw feeder was found to crush the raw materials unless the size was below 1mm. For stable and consistent furnace operation, it was necessary to have large coke/coal particles (+5-16mm) to maintain a high char fraction in the slag.

The screw feeder speed was initially calibrated against the mass flowrate. The mass flowrate was measured for 1 minute intervals, for a total period of 20 minutes. At best, this was later discovered to be erratic. The flowrate was found to randomly vary by at least 20%.

The char level within the slag was a critical furnace operating parameter that must be accurately controlled. To improve the carbon mass balance calculations, a load cell was used to continuously measure the change in mass of the screw feeder. This enabled the mass of the screw feeder to be continuously recorded with an accuracy of ± 10 grams.

To reduce the iron ore dust generation, a paper cartridge of 50 grams of pre-fluxed ore was fed through an interlocked batch feeder located in the furnace lid. The ore was fed manually into the furnace at pre-determined intervals, depending on the experiment.

The paper cartridge was found to remain intact until it reached the slag. The paper was then slowly consumed and the ore was accommodated into the slag. This resulted in minimal ore dusting.

3.4 Gas Injection Systems

3.4.1 Oxygen Lance

Oxygen was injected into the furnace for coke / coal combustion and post combustion, using a water cooled copper lance. The nozzle diameter was varied from 3 to 8 mm to provide different blowing conditions, with typical oxygen flowrates of 100 -130 Nl/min. The lance was positioned approximately 100 - 150 mm from the surface of the slag bath to commence an experiment. The location of the lance was adjusted during an experiment to maintain a stable post combustion ratio.

The oxygen lance was difficult to design, as high temperatures, thermal shock and slag resistance were all essential. Initially a stainless steel tube was used, but this was consumed very quickly. An alumina tube was then used, but failed due to thermal shock. A water cooled stainless steel (253 MA) lance was then constructed. This was an improvement, but the tip started to melt. This was then discontinued due to fear of lance failure. Finally, a water cooled copper lance was constructed. This has been successful to date, although it becomes blocked periodically due to slag adhesion to the tip of the lance.

Different nozzles were used during the experimental program. The 3mm nozzle was ideal when using coke. The volatiles produced from coal required a softer blow to maintain the correct post combustion and the 8 mm nozzle performed the best.

3.4.2 Argon Injection

The bottom bubbling was required to maintain a fluid slag for initiating the experiment and maintaining slag circulation during the experiment. Argon was injected into the base of the furnace for stirring and into the lid as a purge and trace gas. The total argon flowrate was controlled by a mass flow meter. This made it possible to calculate the total gas flow leaving the furnace and to determine mass balances within the furnace during experiments.

Bottom gas injection was installed centrally in the base of the furnace. Argon was injected through a 3.175mm OD stainless steel tube at 7 Nl/min. This provided approximately 2 KW/t of stirring power. An alumina sheath was placed around the stainless steel tube to prevent refractory failure at the gas entry point. Both nitrogen and argon were trialed, but argon was used exclusively due to the possibility of air leaks interfering with the mass balance. Argon was also used intermittently to purge the gas sample line and to increase stirring from the lance at the start of an experiment.

3.4.3 LPG Injection

The use of LPG (Liquid Petroleum Gas) injection through the oxygen lance was tested, to provide heating to the slag bath before initiating an experiment. It was found that there was insufficient freeboard for adequate combustion and heat generation within the furnace. The graphite susceptor enabled a thick slag to be formed within the furnace and provided a better solution. The use of an insulating refractory paper (Fiberfrax 970-J) then replaced the graphite susceptor. LPG injection was abandoned.

3.5 Data Logging

All experimental data obtained were logged using the mass spectrometer computer, along with the gas composition. The main parameters recorded include the bath temperatures, gas temperatures, screw feeder speed and mass, furnace power, all water temperatures, water flowrate, lid temperature and off-gas duct temperature. Critical operating parameters necessary for stable operation were calculated online from the information recorded.

3.6 Gas Extraction and Cleaning

The off-gas was removed from the furnace through a stainless steel duct, where it was mixed with approximately 40 Nm³/min of air to cool the gas. Within the gas duct there was a series of water cooled copper tubes to further reduce the bulk gas temperature. The off-gas was then cleaned within the bag house and exhausted to the atmosphere. During experiments the off-gas would often flare in the gas duct, also consuming any entrained char. The ducting can reach temperatures in excess of 600 °C with a low post combustion ratio and high carbon dusting.

3.7 Gas Sampling and Analysis

A gas sample was continuously taken from the furnace through the off-gas port in the lid. The sample was rapidly cooled within an alumina tube, and then transferred through a heated tube to the mass spectrometer for analysis. The sample was filtered with a 100 μ m stainless steel mesh, followed by a special 1 μ m glass fibre Balston filter. The tubing and filters were heated to 130 °C to eliminate water condensation.

The sample was then passed across the inlet tube to the Fison's PRIMA 600 mass spectrometer. The mass spectrometer was a scanning magnetic sector instrument, with a range of 1-100 a.m.u.. It analyses the sample in approximately 5 seconds. The gases analysed were carbon dioxide, carbon monoxide, hydrogen, water, oxygen, argon, nitrogen, sulfur dioxide and hydrogen sulphide. Nitrogen and carbon monoxide were measured at 14 and 12 a.m.u., respectively. The concentration of all other gases was assumed to be low.

3.8 Water Cooling Systems

Water-cooling was used for the furnace, furnace lid, oxygen lance, off-gas ducting and furnace power generator. Although this was essential for all of these applications, it was necessary to balance the water flow to maintain minimum heat losses from the furnace. The total water consumption was approximately 140 l/min from the recirculating water supply. Water inlet temperatures were in the range of 17 - 27 °C, and outlet water temperatures were below 35 °C.

4 Operation of the Experimental Smelting Reduction Furnace

4.1 Procedure

The experiment was complicated and required a large amount of preparation. It took about 3 years to develop a detailed understanding of the process and achieve stable and consistent operation of the smelting reduction furnace.

4.1.1 Preparation

Before commencing an experiment, it was necessary to prepare the furnace, including;

- inspect furnace, lid and furnace extension, remove deposits and coat with zirconia wash
- replace refractories if required
- inspect and clean sample gas filters and tubing
- select and dry pig iron, prepare slag and coke charge for initial slag bath
- ensure sufficient raw materials were available, and correctly fluxed. Fill screw feeders with raw materials
- check all thermocouples
- check cooling water system for adequate flow
- calibrate mass spectrometer
- prepare sand mould or other receptacle for casting

4.1.2 Description of Experiments

The experimental procedure for the base case was as follows.

20 kg of pig iron was charged to the furnace and heated to 1450 °C, while 7 Nl/min of argon was continuously introduced through the furnace bottom. When the furnace had attained a constant temperature, 1.5 kg of granulated blast furnace slag was charged and blast furnace coke was introduced to provide 30 wt % char in the slag. A metal sample was then taken and the furnace was sealed.

Oxygen was blown through the top of the furnace at 100 Nl/min and the lance position was adjusted to maintain a post combustion ratio of 60 %. The post combustion ratio was determined by online mass-spectrometric gas analysis.

During the heat, char was consumed by reduction / combustion reactions. The rate of consumption was monitored by analysing the gas composition. Blast furnace coke (+5-16mm) was fed through the top of the furnace using a screw feeder, to maintain a constant 30 wt % of char in the slag. A carbon mass balance was performed using the gas composition and the coke feed rate.

After stable coke combustion was attained, BHP Mt Whaleback iron ore concentrate was introduced at 1.5 kg/h. This was found to be sufficient to separate the oxygen lance and metal, but small enough to allow accumulation during the experiment. Slag samples were taken throughout the experiment with a steel rod dipped into the bath. When the experiment was completed, the metal was sampled and the furnace was emptied.

Effects of operating variables and raw material properties on the performance of the iron smelting reduction furnace were examined relative to the base case. The key parameters varied were the ore feeding rate, post combustion ratio and the type of carbonaceous materials.

The post combustion ratio was varied from 45 to 75 % by manipulating the lance height and nozzle diameter. An 8 mm nozzle diameter was used in heats with coal, while in experiments with coke, a 3 mm nozzle was used in the lance. Two iron ores and six carbonaceous materials were investigated. The raw materials were blended with fluxes to maintain stable slag chemistry throughout the experiment. The composition of the raw materials investigated is given in Appendix 1.

4.1.3 Problems Encountered

During an experiment, several problems and irregularities could occur, each of which had a specific response and sometimes warnings. Problems included;

- blockages in the oxygen lance, off-gas tube, raw materials feed and gas sampling system
- melting or blockage of the bottom bubbling injection system
- extreme heating of the off-gas duct
- slag foaming / freezing
- loss of cooling water and water leaks
- failure of bath or gas thermocouples

Droplets ejected from the bath were often able to block or obscure parts of the furnace lid. The post combustion ratio would sometimes vary erratically due to small slag adhesions to the tip of the oxygen lane, which interfered with the oxygen jet. A rod was used to clean the nozzle when this occurred.

Obstructions in the off-gas tube and raw materials feed were corrected with a flexible spring. When the off-gas sampling system was clogged by dust the level of nitrogen measured would increase. It was cleaned by briefly isolating the system and back flushing with argon.

The flowrate of argon to the furnace bottom was maintained at 7 Nl/min, which maintained sufficient cooling to the stainless steel injection port. The port was inspected after each experiment to monitor any erosion problems.

When the post combustion ratio was low, the off-gas would flare in the gas ducting and generate significant heat. The furnace was operated to maintain a maximum gas duct temperature of 300 °C.

The slag bath would foam if the slag to char ratio was not above 10-20 %. This was monitored by the carbon mass balance.

The water cooling was constantly monitored, with pressure switches for the furnace and a mass flow meter for the furnace lid and oxygen lance. The experiment was immediately aborted if the water cooling failed.

The thermocouples in the base of the furnace were the only indication of the bath temperature. If both thermocouples failed the experiment was aborted.

4.2 Post Combustion Ratio

Post combustion in the direct iron smelting reduction process is characterised by the post combustion ratio, which is defined as:

$$PCR = \left[\frac{\% CO_2 + \% H_2 O}{\% CO + \% CO_2 + \% H_2 + \% H_2 O}\right] \times 100\%$$
(4-1)

The post-combustion ratio was determined from the off-gas analysis, monitored on-line by the mass spectrometer. A typical record of the gas composition during the experiment is presented in Figure 4-1. Data on CO_2 , H_2O , CO and H_2 concentrations used for the calculation of post combustion ratio were taken in the period of the stable operation, which was controlled for about 60 minutes in the presented heat (Figure 4-1).

The post combustion ratio is affected by the oxygen flowrate, lance nozzle diameter and lance height relative to the bath surface. In this work, the post combustion ratio was maintained by adjusting the lance height.



Figure 4-1 Typical gas composition in the laboratory smelting reduction furnace.

4.3 Effect of the Oxygen Lance Height on the Post Combustion Ratio

Oxygen introduced into the smelting reduction furnace was almost completely consumed by reactions of coal combustion and post combustion. As it is seen in Figure 4-1, the oxygen content in the off-gas during the steady state operation was below 0.5 vol %. Therefore, providing that the oxygen flowrate is constant, the less oxygen consumed for the combustion of coal, the more oxygen is available for post combustion reactions, and the higher the expected post combustion ratio.

Proportioning of oxygen between oxygen consumed by coal combustion and that which participates in the post combustion reactions depends on the delivery of the oxygen to the furnace, in particular on the lance height.

Experimental results on the post combustion ratio as a function of the lance height, (distance between the lance tip and the bath surface) are presented in Figure 4-2. It is seen from this figure that the post combustion ratio increased with the lance height. This corresponds to a trend observed by other researchers for BOF steelmaking (Gou, Irons and Lu, 1993, Takahashi *et al.*, 1992 and Aukrust, 1994).

The increase in the post combustion ratio with lance height in BOF steel-making was conventionally attributed to the increasing amount of carbon monoxide entrained into the oxygen jet, and hence available for post combustion reactions. However, Gou, Irons and Lu, 1993 showed that it is the result of the decrease in the steel decarburisation rate. The higher the lance position, the softer the oxygen blowing, the slower the steel decarburisation, and therefore, more oxygen is available for post combustion. This trend is similar to what is found in the iron smelting reduction furnace.



Figure 4-2 The effect of lance height on the post combustion ratio.

The proportion of oxygen used for post combustion reactions can be calculated from the experimentally measured gas composition. The gas evolved from the bath in the smelting reduction furnace is due to the reactions of iron oxide reduction, coal devolatilisation and coal combustion. However, carbon dioxide and water are consumed in the Boudouard and water gas shift reactions. Therefore, gases released from the bath in a smelting reduction furnace are predominantly carbon monoxide and hydrogen, while carbon dioxide and water vapour present in the gas atmosphere are formed in the post combustion reactions. Thus, using these assumptions, oxygen consumed in the post

combustion reactions can be calculated as the sum of oxygen participating in the following reactions and from experimental data on CO_2 and H_2O concentrations.

$$CO + \frac{1}{2}O_2 = CO_2$$
 (4-2)

$$H_2 + \frac{1}{2}O_2 = H_2O$$
 (4-3)

The difference between the total amount of oxygen introduced into the smelting reduction furnace and the oxygen consumed for post-combustion reactions, gives the quantity of oxygen used for carbon combustion.

The proportion of oxygen utilised in the char combustion reaction was calculated at different lance heights (h). Results presented in Figure 4-3 show that the proportion of oxygen consumed for coal combustion decreased with increasing lance height, from about 70% at h = 160 mm to 57 % at h = 215 mm. Further lifting of the lance did not affect this proportion.



Figure 4-3 Percentage of oxygen consumed by char combustion as a function of lance height.

Correspondingly, the fraction of oxygen available for post combustion reactions increased with a decreasing proportion of oxygen consumed in the combustion reactions, resulting in a higher post-combustion ratio (Figure 4-4). The maximum stable post combustion ratio achieved in the laboratory furnace was about 80 %, which corresponds to a lance height of 215 mm and above. A post combustion ratio of 60 % in the standard operation was maintained with a lance height of 195 - 200 mm.


Figure 4-4 Post combustion ratio as a function of oxygen consumed in carbon combustion.

5 Carbonaceous Materials in the Smelting Reduction Furnace

The iron and steel industry has primarily used metallurgical coke in blast furnace operations, which is made from a high quality and high cost coal. The production of coke is capital intensive and generates dangerous pollutants.

The smelting reduction furnace is able to utilise lower grades of coal, improving the economical feasibility of ironmaking. The use of 'raw' coal minimises the capital investment and complexity of the process, reducing the environmental pollution and the associated costs.

Carbonaceous materials in the smelting reduction furnace are required to generate heat needed for smelting and reduction reactions and to reduce iron ore. Char formed from coal and entrained into the slag phase controls the slag foaming and enhances heat transfer from the gas phase to the bath.

When carbon is added to the furnace, the volatile component of the coal is quickly transferred to the gas, where it is consumed in the post combustion process. The proportion of char formed depends on the coal composition and structure.

The coal type used in the smelting reduction process also affects post combustion, heat utilisation, dust formation and hot metal chemistry, particularly the hot metal sulphur.

Different carbonaceous materials were examined, namely blast furnace coke, low volatile coal, medium volatile coal and high volatile coal. Composition of carbonaceous materials used in the work is given in Table 5-1.

	Fixed carbon (% a.d.)	Volatile matter (% a.d.)	Ash (% a.d.)	Moisture (% a.s.)
blast furnace coke	84.6	0.3	13.5	1.4
LV1 coal	72.4	17.2	9.5	0.9
LV2 coal	70.2	19.5	9.3	1.0
MV1 coal	65.5	25.5	8.0	1.0
MV2 coal	64.6	23.9	9.8	1.7
HV1 coal	49.7	44.6	5.7	19.1

Table 5-1 - Types of Carbonaceous Materials Investigated in the Smelting Reduction Furnace.

5.1 Volatile Matter and Char Formation

Coal devolatilisation occurs when the coal is heated; the particle may soften and undergo internal transformation. Moisture present in the coal will evolve early, as the temperature rises. With increasing temperature, gases and heavy tarry substance are emitted. The extent of pyrolysis can vary from a few percent up to complete gasification and can take a few milliseconds or several minutes, depending on the coal size and type, and the heating conditions. The resultant particle is refereed to as 'char'. The nature of the char is dependent on the original coal type and size, and on the conditions of pyrolysis.

In the base case, the coke used contained volatile matter below 1 wt %, which had a negligible effect on the operation of the smelting reduction furnace. However, the main driving force for the development of the direct iron smelting reduction process is the direct utilisation of coals. The effect of volatile matter on the performance of the smelting reduction furnace is a major concern in the selection of suitable coals. In this work, coals with various volatile matter contents were examined (Table 5-1).

It was observed that the use of coals instead of coke resulted in a decrease in the post combustion ratio, as more carbon monoxide and hydrogen were evolved to the furnace atmosphere as a result of coal de-volatilisation. To maintain a post combustion ratio of 60%, the lance height had to be increased from 200 mm when coke was used to 350 – 400 mm in the case of coal. The higher volatile content in the coal required a higher lance position in the smelting reduction furnace. To maintain a post combustion ratio of 60% at a more appropriate lance height of about 200 mm, the lance nozzle diameter was increased from 3 mm to 8 mm.

As it was mentioned above, an important role in the smelting reduction furnace is played by char in the slag phase, which acts as a reductant and controls slag foaming. Formation of char from coal depends strongly on the volatile matter content and devolatilisation reactions. The volatile yield is strongly affected by the heating conditions of coal, therefore, the proportion of char formed after coal de-volatilisation reactions can vary from what was determined by proximate analysis (Takahashi *et al.*, 1992).

Conditions in the smelting reduction furnace provide extremely high heating rates to a temperature of 1773 K, which result in significantly higher volatile yields than the proximate volatile matter of the coal. Indeed, for the high volatile matter coal investigated (HV1), the volatile matter yield during pyrolysis was so high that there was no char observed in the bath.

During de-volatilisation, the coal size was drastically reduced due to coal fracture, increasing the quantity of dust formed, which was then carried away by the large volume of gas generated by the coal de-volatilisation. This high volatile yield makes the coal (HV1) unsuitable for the formation of char in the smelting reduction furnace, and for furnace operation.

5.2 Carbon Consumption Rate

In the smelting reduction furnace, carbon (coke or coal) is consumed to generate energy required for heating, smelting of raw materials and for chemical reactions, to reduce iron and other oxides to the metallic phase, and for iron carburisation. Solid carbon in the smelting reduction furnace is maintained in excess relative to its requirement for these reactions, to suppress slag foaming as discussed in the previous section.

Post combustion of the furnace gas allows more efficient utilisation of coal (coke) in the smelting reduction furnace, decreasing the carbon consumption. This is illustrated by the carbon consumption in the smelting reduction processes at different post combustion ratios: COREX process with no post combustion consumes 1100 kg/t hot metal; coal consumption by emerging DIOS, HIsmelt, CCF processes with a post combustion ratio of 40 - 50 % is about 650 - 800 kg/t hot metal.

Efficiency of the post combustion reaction depends on the efficiency of transfer of the generated heat to the bath, which is defined as:

heat transfer efficiency =
$$\left[1 - \frac{\text{superheat of exhaust gas}}{\text{heat generated by post combustion}}\right] \times 100\%$$
 (5-1)

The carbon consumption in the laboratory smelting reduction furnace as a function of the post combustion ratio is plotted in Figure 5-1. The carbon consumption was calculated from data on carbon monoxide and carbon dioxide contents in the off-gas at a constant ore feeding rate and bath temperature. It does not include carbon lost in the dust, entrained in the slag or carbon dissolved in the metal. The coke consumption decreases with an increasing post combustion ratio, but the increase is relatively small. This indicates that the laboratory smelting reduction furnace has a relatively low heat transfer efficiency, as expected due to the high heat losses to the furnace walls and lance.



Figure 5-1 Carbon consumption rate as a function of post combustion ratio.

In the laboratory smelting reduction furnace, the heat loss through the furnace refractories and lance is disproportionably high, and amounts to about 50 % of the total heat produced in the experimental direct iron smelting reduction furnace, which is the main reason for the low heat transfer efficiency. For a larger scale industrial pilot plant, for example the 5-t NKK furnace, heat losses through the lance and furnace refractories were reported to be below 6 % of the total heat generated (Takahashi *et al.*, 1992).

Carbon consumption increased with increasing volatile matter content in the coal (Figure 5-2) and decreased with increasing fixed carbon content (Figure 5-3), which is in agreement with data obtained for emerging smelting reduction processes (Aukrust, 1994, Takahahsi *et al.*, 1992). This is principally due to the additional energy consumption required for coal de-volatilisation.



Figure 5-2 Carbon consumption as a function of proximate volatile matter, at a constant post combustion of 60% and ore feed rate of 1.5 kg/h.



Figure 5-3 Carbon consumption as a function of fixed carbon, at a constant post combustion of 60% and ore feed rate of 1.5 kg/h.

5.3 Summary

The post combustion ratio was strongly affected by the volatile matter content in the coal. Increasing the volatile matter content (or decreasing the fixed carbon) decreased the post combustion ratio, under otherwise the same conditions. The lower volatile coals performed better in the experimental smelting reduction furnace, as shown by the lower fuel consumption rates.

Coal de-volatilisation upon charging into the smelting reduction furnace was much higher than expected from the proximate analysis. This was attributed to the high heating rate and high temperature, compared to the conditions for the proximate volatile matter analysis. In the case of the coal with a high volatile matter content of 44.6 %, the high extent of coal de-volatilisation and its fragmentation and dusting resulted in practically no char formation. This made the high volatile matter coal inappropriate for use in the laboratory smelting reduction furnace.

6 Energy Balance

The energy to the furnace was supplied by combustion and post combustion reactions, and inductive heating. It is consumed for raw materials heating and smelting, iron ore reduction, heating the off-gases and losses to the water-cooling. An overall energy balance for each experiment is given below in Figure 6-1 and Table 6-1.



Figure 6-1 Heat Balance for the experimental smelting reduction furnace.

Exp.	Combustion	Post	Inductive	Reduction /	Water	Heating
Number	kW / %	Combustion	Heating	Heating	Cooling	Gas
		kW / %	kW / %	kW / %	kW / %	kW / %
1	9.8 / 30	16.0 / 49	9.1 / 21	5.5 / 17	21.2 / 65	5.7 / 18
2	7.0 / 26	11.8 / 43	8.3 / 31	4.2 / 16	18.2 / 67	4.7 / 17
3	8.8 / 28	15.2 / 48	6.8 / 24	5.0 / 16	21.4 / 68	5.2 / 16
4	11.0 / 30	18.5 / 50	8.5 / 20	6.0 / 17	24.2 / 66	6.3 / 17
5	9.7 / 28	15.9 / 46	9.3 / 27	5.9/17	22.7 / 65	6.2 / 18
6	9.0 / 26	14.9 / 44	10.2 / 30	5.0 / 15	24.0 / 70	5.2 / 15
7	9.1 / 32	11.5 / 40	10.6 / 29	5.2 / 18	19.1 / 66	4.6 / 16
8	9.2 / 26	17.9 / 51	6.3 / 23	5.2 / 15	23.5 / 67	6.3 / 18
9	11.9 / 33	18.6 / 51	7.7 / 16	6.3 / 17	23.9 / 66	6.1 / 17
10	10.9 / 30	18.4 / 51	7.0 / 19	5.9/16	25.2 / 69	5.1 / 14
11	9.5 / 28	16.1 / 48	7.9 / 24	6.4 / 19	22.3 / 67	4.8 / 14
12	12.3 / 34	19.4 / 53	6.5 / 14	6.5 / 18	23.3 / 63	7.0 / 19
13	11.6 / 32	18.8 / 52	6.0 / 16	7.0 / 19	23.4 / 64	5.9/16
14	13.3 / 32	21.7 / 52	6.6 / 16	7.6 / 18	26.9 / 65	7.0 / 17
15	8.6/33	10.4 / 39	10.0 / 28	4.9 / 18	17.5 / 66	4.0 / 15
16	8.3 / 25	16.5 / 50	6.9 / 25	4.8 / 15	22.5 / 69	5.5 / 17
17	11.0 / 30	17.7 / 49	7.4 / 21	5.9/16	24.6 / 68	5.6 / 16
18	14.7 / 35	23.3 / 55	4.2 / 10	7.6 / 18	25.9 / 61	8.7 / 21
19	11.1 / 33	17.5 / 52	8.5 / 15	6.1 / 18	21.5 / 64	6.0 / 18
20	5.4 / 23	8.9 / 38	8.9/38	3.4 / 15	16.7 / 72	3.0 / 13
21	6.1 / 24	9.8 / 39	6.8 / 36	3.7 / 15	17.6 / 71	3.6 / 14
22	11.0 / 30	17.7 / 48	7.9 / 21	5.9/16	25.1 / 69	5.6 / 15
23	7.2 / 28	11.9 / 47	6.4 / 25	4.4 / 17	16.6 / 65	4.5 / 18
24	5.9/27	10.0 / 45	6.1 / 28	3.8 / 17	14.7 / 67	3.5 / 16
25	6.2 / 27	11.6 / 49	5.6 / 24	4.3 / 18	14.8 / 63	4.4 / 19
26	7.8 / 28	12.8 / 46	7.4 / 26	4.5 / 16	17.9 / 64	5.6 / 20
27	12.1 / 33	18.6 / 51	5.5 / 15	6.5 / 18	21.1 / 58	8.6 / 24
28	8.3 / 29	13.0 / 46	7.2 / 25	4.8 / 17	19.0 / 66	4.8 / 17
29	6.4 / 27	10.6 / 44	6.8 / 29	3.9/16	16.0 / 67	3.9 / 16
min	5.4/23	8.9 / 38	4.2 / 10	3.4 / 15	14.7 / 58	3.0 / 13
max	14.7 / 35	23.3 / 55	10.6 / 38	7.6 / 19	26.9 / 72	8.7 / 24

Table 6-1 Energy sources and requirements, as kW / percentages.

6.1 Energy Supply

6.1.1 Combustion and Post Combustion Reactions

The principal combustion and post combustion reactions in the smelting reduction furnace are:

$$C + \frac{1}{2}O_2 = CO$$
 (6-1)

$$CO + \frac{1}{2}O_2 = CO_2$$
 (6-2)

$$H_2 + \frac{1}{2}O_2 = H_2O$$
 (6-3)

The enthalpies of reactions 6-1, 6-2 and 6-3 are 112 877, 281 885 and 247 392 J/mol, respectively.

In the operation of the laboratory smelting furnace, the post combustion ratio was maintained at a constant pre-determined value. This was achieved by adjusting the lance position as described in the chapter *Operation of the Smelting Reduction Furnace*.

The total carbon consumption was calculated from the on-line off gas analysis from the mass spectrometer. It was assumed that the coke / char combustion reaction generated carbon monoxide, while carbon dioxide and water were formed in the post combustion reactions. Argon was used as a tracer in the furnace, which allowed the flowrate of all gases to be calculated.

The total mass of carbon in the gas phase, C_t , was attributed to the carbon combustion, C_c , and iron reduction, C_r . Carbon used for reduction was known from the rate of iron ore reduction, and the carbon consumed by the combustion was calculated as:

$$C_c = C_t - C_r \tag{6-4}$$

Obviously, the heat generated by post combustion reactions increased with the post combustion ratio. This is illustrated by Figure 6-2. As the post combustion ratio increased, a smaller proportion of oxygen was utilised for combustion and the energy generated by combustion is reduced (Figure 6-3).



Figure 6-2 Energy generation by post combustion reactions, as a function of the post combustion ratio.

With an increasing post combustion ratio, the total consumption of carbon decreases (Figure 6-4). The decrease in post combustion ratio was achieved by decreasing the lance height; this made the jet 'harder'; its impact on the bath became stronger; the rate of reaction with the char / bath and rate of carbon consumption increases. Conversely, as the lance is raised, less oxygen interacts with the bath surface and more oxygen is available for post combustion. In this manner, the quantity of heat generated by both combustion and post combustion reactions were fixed for each experiment, not determined by the requirements of the process.



Figure 6-3 Energy generation by combustion reactions, as a function of the post combustion ratio.



Figure 6-4 Coke consumption, as a function of the post combustion ratio.

6.1.2 Inductive Heating

Inductive heating was used to maintain the bath temperature at a constant value of 1500 °C. The metal bath temperature was measured with a thermocouple in the base of the furnace.

The power supplied by the inductive heating was in the range of 4.2 to 10.6 kW, as determined from an energy balance, which contributed 10 to 38% of all energy supplied to the furnace.

The induction heating required to maintain the bath temperature at 1500 °C decreased with increasing post combustion ratio, as shown in Figure 6-5.



Figure 6-5 Induction heating required, as a function of the post combustion ratio.

In commercial or larger scale pilot-plant smelting reduction furnaces, external heating is not used. A stable bath temperature may be maintained by adjusting the iron ore feed rate (Katayama *et al.*, 1992)

6.2 Energy Consumption

The energy requirements for the smelting reduction furnace, as presented in Figure 8-1, were:

- 1. Losses to the water cooling
- 2. Heating gases to the exit temperature
- 3. Iron ore reduction and heating raw materials to bath temperature

6.2.1 Heat Losses to Water Cooling

The heat losses to the water cooling are the highest proportion of all energy consumed by the laboratory furnace in the iron smelting reduction process.

The following parts were water cooled with separate water circuits:

- 1. Bottom half of furnace walls
- 2. Top half of furnace walls
- 3. Oxygen lance and furnace lid

For all sections of the furnace, the water flowrate and temperature were measured. Experimental data, presented in Table 6-2, were used to calculate the heat loss to the water. The heat capacity of the water was taken to be 4.18 kJ/kg.K.



Figure 6-6 Heat losses to the water, as a function of the post combustion ratio.

Heat losses to the cooling water were examined as a function of the post combustion ratio. Calculated heat losses using the experimental data in Table 6-2, are plotted in Figures 6-6, 6-7, 6-8 and 6-9.

Refractory materials in the bottom section of the furnace were in direct contact with the iron and slag bath, which was maintained at 1500 °C. This caused a large proportion of the heat loss to the water cooling in the base of the furnace.

Heat losses to the water cooling in the bottom section of the furnace were not affect by the post combustion ratio (Figure 6-7). This was expected, as the bath temperature was kept constant in all experiments.

The rate of heat transfer is dependent mainly on the bath temperature and bath stirring, which are both essential constant for all experiments. The stirring of the bath is dominated by the bottom injection of argon, although the bath is also stirred by the induction heating and the oxygen jet.

Total heat losses increased with the post combustion ratio (Figure 6-6). This is mainly due to the increase in the heat losses with post combustion ratio in the top section of the furnace (Figure 6-8) and the oxygen lance (Figure 6-9), as a result of increasing flame and gas temperatures.

The experimental results on heat losses to the cooling water are quite scattered. The variation in experimental values may be due to different accretions and refractory wear on the furnace lining. The lining was mainly affected at the level of the slag bath and just above the slag bath, where ejected droplets had a tendency to adhere to the furnace walls.

The temperature of the water cooling to the furnace lid and oxygen lance are also presented in Table 6-2. The lid is well insulated with refractories and heat losses to the water cooling is relatively small and there would be little variation. The oxygen lance is constructed of copper with internal water cooling, which is a large heat sink for radiation from the flame and the hot furnace gases.



Figure 6-7 Heat losses from the furnace bottom, as a function of the post combustion ratio.



Figure 6-8 Heat losses from the furnace top, as a function of the post combustion ratio.



Figure 6-9 Heat losses from the furnace lid and oxygen lance, as a function of the post combustion ratio.

Experiment	Inlet water,	Top water,	Bottom	lid water,
Number	°C	°C	water, °C	°C
1	24.9	27.6	32.4	28.3
2	24.8	27.1	31.8	28.6
3	25.0	27.8	32.6	28.9
4	24.8	29.2	32.7	28.5
5	26.1	29.5	35.0	29.8
6	23.8	28.6	34.2	27.2
7	24.3	27.6	32.0	27.3
8	23.0	27.7	30.5	26.6
9	25.7	29.4	33.9	28.9
10	26.9	31.5	35.3	30.3
11	25.5	29.7	34.6	28.2
12	24.1	27.9	31.5	27.2
13	24.7	28.5	32.7	27.8
14	24.7	28.0	32.4	28.1
15	26.2	29.0	33.4	29.1
16	25.7	29.3	33.5	29.7
17	24.2	28.4	32.9	27.7
18	25.3	28.6	32.8	29.3
19	25.2	28.0	32.3	28.4
20	24.7	27.6	31.9	28.3
21	25.2	28.5	32.5	28.9
22	19.3	23.6	28.4	22.9
23	17.8	21.1	26.0	21.2
24	17.4	20.5	24.9	20.5
25	17.9	20.6	24.8	20.4
26	18.2	22.0	25.7	22.9
27	19.2	23.1	27.4	24.0
28	20.5	24.8	29.2	24.8
29	20.3	23.7	27.8	24.2
Water flowrate		23 l/min	23 l/min	42 l/min

Table 6-2 Water temperatures and flowrates.

6.2.2 Heat Loss with Exit Gas

The temperature of the exit gas was in the range 1033 to 1395 °C, depending on the post combustion ratio. The energy required to heat the gases exiting the furnace ranges from 12 to 26 % of the total energy requirements (Figure 6-1). The energy consumed to heat the off-gas to the exit temperature was found to increase with the post combustion ratio (Figure 6-10), but this is balanced by the additional energy provided by higher post combustion.

The heat losses to the furnace gases were calculated from experimental data on the gas composition, argon flowrate and heat capacity of each gas, as presented in Tables 6-3 and 6-4.

The heat losses to the off-gas were affected by the post combustion ratio and the gas flowrate. As the post combustion ratio increases the temperature of the off-gas increases (Figure 6-11) and the coke usage decreases (Figure 6-4). The reduction in coke usage reduces the gas flowrate.

The heat losses to the off-gas increase with the post combustion ratio, but this is insignificant compared to the quantity of energy generated by the increase in the post combustion ratio.

Gas	Heat Capacity (kJ/mol.K)
N ₂	1.56 + 2.39 x 10 ⁻⁴ T
O ₂	$1.98 + 6.17 \ge 10^{-5} T - 44904 / T^2$
Ar	1.19
CO ₂	$2.47 + 6.55 \times 10^{-4} \text{ T} - 46770 / \text{T}^2$
CO	1.58 + 2.87 x 10 ⁻⁴ T
H ₂	1.58 + 1.94 x 10 ⁻⁴ T
H ₂ O	$1.97 + 3.59 \ge 10^{-5} \ \text{T} - 3.28 \ge 10^{-8} \ \text{T}^2$

Table 6-3 Heat Capacity of furnace gases (Perry and Green, 1984).

Exp.	N ₂	O ₂	Ar	CO ₂	СО	H ₂	H ₂ O	Argon Flowrate
1	2.11	0.80	17.9	45.7	31.0	0.304	2.18	40
2	2.15	0.67	21.1	45.6	28.4	0.242	1.84	40
3	0.56	0.78	19.4	49.8	27.7	0.173	1.52	40
4	0.19	0.48	16.9	49.3	30.9	0.244	2.01	40
5	1.08	0.54	17.2	47.5	31.4	0.245	1.95	40
6	0.86	0.48	17.9	48.6	30.1	0.208	1.87	40
7	0.58	0.43	17.4	35.9	43.9	0.521	1.29	40
8	0.95	0.35	19.2	56.6	20.7	0.200	1.96	40
9	0.49	0.18	16.7	47.2	32.9	0.397	2.03	40
10	0.64	0.24	17.2	50.3	29.7	0.279	1.63	40
11	0.59	0.25	17.3	45.7	32.3	0.638	3.23	40
12	1.26	0.41	16.4	46.6	32.4	0.480	2.41	40
13	0.79	0.58	15.9	45.1	34.1	0.514	2.95	40
14	0.52	0.48	14.8	48.2	33.0	0.340	2.65	40
15	1.26	0.55	18.8	34.5	42.6	0.665	1.60	40
16	0.87	0.84	15.6	57.3	21.6	0.096	3.57	30
17	0.45	0.55	13.0	48.1	33.5	0.434	3.96	30
18	0.01	0.53	11.4	49.5	34.9	0.341	3.27	30
19	1.43	0.57	13.6	47.0	33.8	0.489	3.06	30
20	1.01	0.41	18.7	45.4	31.8	0.360	2.38	30
21	1.42	0.52	17.4	45.1	32.3	0.453	2.75	30
22	0.90	0.15	12.9	49.2	33.4	0.614	2.74	30
23	1.81	0.39	16.4	43.2	29.5	4.714	3.89	30
24	1.21	0.18	18.8	43.3	28.2	4.710	3.53	30
25	1.22	0.20	17.6	44.5	28.7	3.761	4.02	30
26	1.87	0.41	21.3	40.4	27.8	3.785	4.39	30
27	2.49	0.67	16.0	38.0	31.0	4.877	4.94	30
28	1.94	0.71	18.0	43.9	32.5	0.565	2.38	30
29	2.24	0.94	18.9	47.4	28.1	0.297	2.12	30

Table 6-4 Gas composition (vol%) and argon flowrate (Nl/min).



Figure 6-10 Heat losses to the furnace gases, as a function of the post combustion ratio. The off-gas temperature was strongly influenced by the operation of the furnace, especially the post combustion ratio, as shown in Figure 6-11.



Figure 6-11 Off-gas temperature as a function of the post combustion ratio.

Experiment	Gas Flowrate Gas Ten	
Number	Nl/min	°C
1	223	1226
2	190	1358
3	206	1258
4	237	1234
5	233	1363
6	224	1238
7	229	1133
8	208	1395
9	240	1163
10	232	1047
11	231	1033
12	244	1244
13	251	1069
14	270	1157
15	213	1086
16	192	1321
17	232	1125
18	263	1322
19	220	1197
20	161	1143
21	172	1240
22	232	1135
23	183	1233
24	160	1176
25	170	1260
26	211	1366
27	281	1389
28	200	1220
29	159	1301
minimum	159	1033
maximum	281	1395

Table 6-5 Gas temperatures and flowrates.

6.2.3 Energy Required for Iron Ore Reduction and Heating Raw Materials

Raw materials – coke or coal and iron ore, were charged to the smelting reduction furnace at room temperature and heated to the bath temperature of 1500 °C.

Energy required to heat coke to the bath temperature was taken as 3.6 MJ/kg (Perry and Green, 1984).

The energy required for the reduction of iron oxide (Rao, 1985):

$$Fe_2O_3$$
 (solid) + 3 C (solid) = 2 Fe (liquid) + 3 CO (gas) (6-5)

is 4.95 MJ/kg (iron oxide and carbon are at room temperature and the iron and carbon monoxide is at 1500 °C).

The energy required to heat the raw materials to the bath temperature and reduce the iron ore is only 15% to 21% of the total energy requirements (Figure 6-1).

The high heat losses required a large quantity of coal for combustion, but the slag bath is only able to reduce a relatively small quantity of iron ore. This led to a small proportion of the energy being required for melting iron ore and iron ore reduction, compared to the energy required for heating the large proportion of coal used in the furnace (Figure 6-12).



Figure 6-12 Energy required to heat coke and reduce the iron ore.

6.3 Overall Energy Balance

It is not feasible to perform a critical heat balance with the experimental smelting reduction furnace, due to the relatively small size and the high heat losses associated with water cooling. Heat losses to the water cooling in the laboratory furnace are high in comparison with a larger furnace.

The primary energy sources were the combustion of char, post combustion of furnace gases and additional induction heating to maintain the bath temperature.

The induction heating provided 12% to 38% of the energy requirements, which is significant, but provided a small degree of balance against the unavoidable heat losses which accounted for 58% to 73% of the total energy losses.

As the post combustion ratio was increased from 45% to 75%, the energy released inside the furnace increased from 23 to 37 kW, which corresponded to 62% to 88% of the energy requirements for the operation of the furnace.

Iron reduction only accounted for 4.2% to 7.5% of the total energy requirements, which was less than the sensible heat required to heat the gases before they left the furnace.

The gas temperature at the furnace exit was always less than the bath temperature, due to the water cooling. This made the calculation of heat transfer efficiency above 100%, which is meaningless.

7 Iron Ore Reduction

The productivity of the smelting reduction furnace is determined by the rate of iron oxide reduction, which is dependent on the composition of the slag, char to slag ratio, char reactivity, bath temperature, slag circulation rate, and other operational parameters (Katayama *et al.*, 1992, Ibaraki, 1994).

This work examined the effects of iron ore feeding rate and post combustion ratio on the reduction of iron oxide. The experimental conditions in the laboratory smelting reduction furnace are presented in Table 7-1

Parameter	Range
Bath surface area	0.0254 m^2
Quantity of slag	1.5 – 3.0 kg
Quantity of metal	≈ 20 kg
Oxygen flowrate	100 Nl / min
Bottom bubbling rate	7 Nl / min
Quantity of char in the slag	30 wt % of the slag
Size of char fed into furnace	+ 5 – 16 mm
Mean size of char in slag	< 8 mm (by observation, nominal size 3 mm)
Surface area of char (base case)	$0.6 - 1.6 \text{ m}^2 (1.1 \text{ m}^2)$
Concentration of FeO, (base case)	1.3 – 6.4 wt % (3.0 wt %)
Post combustion ratio (base case)	45 – 75 % (60 %)
Induction power (stirring / heating)	0 – 15 kW
Bath temperature	1500 °C

Table 7-1 Experimental conditions

7.1 Effect of Ore Feed Rate on Iron Oxide Concentration in the Slag

Furnace productivity is measured as the quantity of iron generated over a fixed period. By understanding the effect of iron ore flowrate it is possible to maximise the furnace productivity.

For continuous operation, where slag is tapped from the furnace during the heat, high levels of iron oxide in the slag lead to reduced utilisation of raw materials. This is dependent on the quantity of slag produced. Therefore, optimisation of the iron ore flowrate must also consider the carry-over of iron oxide.

The iron oxide concentration as a function of the iron ore feed rate was investigated at a constant post combustion ratio of 60%. The results are plotted in Figure 7-1.

As the iron ore feed rate increased, the concentration of iron oxide in the slag also increased. Similar results were obtained by Katayama *et al.*, 1992 for 100-t smelting furnace at NSC. An increase in the iron oxide content of the slag above 10 wt% caused an increase in the slag foaming, which became abnormally intensive, disrupting furnace operation. Because of this, the iron ore feed rate was limited to an iron oxide concentration in the slag of approximately 10 wt%.



Figure 7-1 Iron oxide concentration in the slag as a function of iron ore feed rate, at a constant post combustion ratio of 60%.

7.2 Effect of Post Combustion on the Iron Oxide Concentration

The post combustion ratio was varied from 45 to 75 % at a constant iron ore feed rate of 1.5 kg/h. The iron oxide content in the slag is plotted *vs* post combustion ratio in Figure 7-2. Although there is scatter in the results, the trend for the iron oxide in the slag to increase with the post combustion ratio is obvious.



Figure 7-2 Iron oxide concentration in the slag as a function of post combustion ratio, at a constant iron ore feed rate of 1.5 kg/h.
The gas atmosphere is oxidising with respect to the metallic iron. The oxygen partial pressure calculated from the CO/CO₂ ratio at 1600 - 1700 °C is in the range of $10^{-5} - 10^{-7}$ atmospheres, depending on the actual post combustion ratio and temperature, which is well above the oxygen partial pressure for the Fe-FeO equilibrium. Metallic droplets ejected to the gas atmosphere are partially re-oxidised. Firstly, carbon dissolved in droplets is oxidised. When the surface of the droplet is depleted of carbon, iron begins to oxidise. Iron re-oxidation increases with an increasing post combustion ratio. This is confirmed by mathematical modelling which shows significant re-oxidation rates of metallic droplets at high post combustion ratios (Zhang and Oeters, 1991, Panjkovic *et al.*, 1999).

Oxidation of iron in the metallic bath, exposed to the oxidising gas atmosphere as a result of intensive stirring by the evolving gas and bottom gas injection, is protected from oxidation by the high carbon content. However, an increase in the post combustion ratio may result in the partial bath decarburisation, which would slow the iron oxide reduction process. An increase in the droplet re-oxidation and bath decarburisation may explain the increase in the iron oxide concentration in the slag.

7.3 Iron Reduction Kinetics

Reduction of iron ore in the smelting reduction furnace is discussed in the literature review. Iron oxide dissolved in the slag is reduced by either the char suspended in the slag or carbon dissolved in iron droplets.

An analysis of the proportion of iron oxide reduced by each mechanism is discussed by Ibaraki, 1994, who reported that in a smelting reduction process with a similar char to slag ratio, 40% of the iron oxide reduction occurs at the slag-char interface, and 60% of iron oxide is reduced by iron droplets suspended in the slag.

Assuming that iron oxide in the laboratory smelting reduction furnace is reduced by char and metallic droplets in the same proportion as found by Ibaraki, 1994, the reduction rate can be assessed using the following data:

- the average char particle is of 3 mm diameter
- char density is 1100 kg/m³
- the char to slag ratio is 30 wt%
- iron droplets are 2 mm diameter
- iron density is 6800 kg/m³
- iron to slag weight ratio is 0.5.

Using the rate constants of 7.7×10^{-4} and 3.6×10^{-4} gFeO/cm²/min/(%FeO) for char and iron droplet reduction, respectively, (Tarby and Philbrook, 1967) the iron oxide reduction rate for the experimental base case is 1.9 kg/h, which compares well with the actual reduction rate of 1.4 kg/h. This implies that the main mechanism of iron ore reduction in the laboratory smelting reduction furnace is also reduction by char and metallic droplets in the slag phase.

7.4 Effect of Ore Feed Rate on Carbon Consumption

The rate of carbon consumption was studied at a variable iron ore feed rate, while the post combustion ratio was maintained constant at 60%. Carbon consumption is defined in this section as the amount of carbon consumed by the reaction of iron oxide reduction, and carbon burnt by oxygen. The rate of carbon consumption was determined through an on-line mass balance, and the results are shown in Figure 7-3. Carbon consumption increases with increasing iron ore flowrate, at a rate of 0.46 kg C / kg iron oxide.



Figure 7-3 Carbon consumption as a function of iron ore feed rate.

The overall reaction or iron oxide reduction can be represented by the following reaction:

$$Fe_2O_3 + 3C = 2Fe + 3CO$$
 (7-1)

Stoichiometrically, Reaction 7-1 requires 3 moles of carbon per mole of haematite, which corresponds to 229 grams of carbon for every kilogram of iron oxide.

The energy requirement for iron oxide reduction is approximately 4.42 MJ/kg iron oxide. To generate this energy at 60 % post combustion, an additional 52 grams of carbon is required. Additional energy is also required for heating any moisture in the feed material and melting fluxes and gangue, which requires 21 grams. Thus, the total carbon requirement for 1 kg of iron ore is 302 grams. From experimental data presented in Figure 7-3, the carbon consumption is 460 g C / kg iron oxide.

The heat losses in the experimental smelting reduction furnace are high, due to the small size and extensive use of water cooling in a furnace of this type. Therefore, the total heat requirements are not representative of a larger scale furnace. Although the change in the energy requirements due to an increase in the iron ore flowrate are higher than theoretical calculations, the comparison is reasonable.

7.5 Summary – Iron Ore Reduction

The rate of iron ore reduction was investigated in the laboratory smelting reduction furnace for different iron ore feed rates and post combustion ratios.

An increase in the iron ore feed rate caused a corresponding increase in the carbon consumption. It was found that the carbon consumption rate increased by 0.5 kg / kg Fe₂O₃, at a post combustion ratio of 60%.

Concentration of iron oxide was found to increase with the feed rate of iron ore. The rate of iron oxide reduction in the slag exhibited a non-linear increase with FeO concentration, which was related to the increase in the mass-transfer coefficient in the slag and slag foaming with increasing carbon monoxide evolution at elevated FeO concentrations.

The post combustion ratio was varied in the range of 45 to 75 % by adjusting the lance height. It was demonstrated that an increase in the post combustion ratio increased the concentration of iron oxide in the slag, decreasing the iron ore reduction rate. This was attributed to re-oxidation of metallic droplets ejected into the gas phase and carbon depletion in the bath.

The main mechanisms for iron oxide reduction was by the char particles in the slag and carbon dissolved in iron droplets.

8 Gas / Slag / Metal Interactions in the Direct Smelting Furnace

The quality of steel is affected strongly by sulphur and phosphorus, which enter the steel with the hot metal, and are removed from the steel by treatment in a ladle or BOF. The cost of steel treatment can depend on the amount of sulphur and phosphorus in the steel. To minimise the cost of steel production, the ironmaking process is optimised to reduce the hot metal sulphur and phosphorus concentrations.

In the direct iron smelting process, sulphur is partitioned between the metal, slag and gas phases, while phosphorus is distributed between the metal and slag. Slag / metal partitioning depends on the oxygen partial pressure. It is therefore vital to examine the oxygen partial pressure to determine the hot metal sulphur and phosphorus.

8.1 Oxygen Partial Pressure

The oxygen partial pressure is defined here as the partial pressure of oxygen in the gas phase in equilibrium with metal and slag phases. For a system at equilibrium, the oxygen partial pressure is the same in the gas, slag and metal and the oxygen partial pressure of a system can be determined by measuring the oxygen partial pressure in any single phase. However, phases in the smelting reduction furnace are not at equilibrium.

The smelting reduction furnace combines reducing conditions for iron oxide reduction and relatively oxidising conditions of the post combustion reactions.

Reduction of iron ore occurs mainly in the slag phase, where the oxygen partial pressure is typically 10⁻¹⁵ to 10⁻¹³ atmospheres. The oxygen partial pressure in the slag is maintained at this low level by suspended char particles and iron droplets with dissolved carbon. It depends on the slag and metal chemistry, temperature and iron ore feed rate into the furnace.

Some char, which tends to float on the surface of the slag bath, is also oxidised (Ibaraki, 1994). The composition of the gas phase is dependent on the gas temperature, oxygen flowrate, lance height and geometry. The oxygen partial pressure in the furnace atmosphere is assessed to be 10^{-8} to 10^{-4} atmospheres.

This illustrates that metal, slag and gas phases in the iron smelting reduction furnace are not at equilibrium. Iron oxide dissolved in the slag is continuously reduced by carbon dissolved in metal droplets, char and by carbon dissolved in the metal bath at the slag / metal interface. The bulk of the iron oxide is reduced by metallic droplets and char in the slag phase. Ibaraki, 1994, estimated that in the 100-t NSC smelting reduction furnace, about 60 % of iron oxide was reduced by carbon in metallic droplets and 40 % by char in the slag.

In this work, char in the slag phase was maintained at 30 wt %, which is similar to the char fraction in the slag (20 - 40 wt %) for the NSC furnace. So, the mechanism of iron ore reduction suggested by Ibaraki, 1994, is applicable to conditions employed in this project.

The metal bath is intimately mixed with the slag by the bottom gas bubbling, induction stirring and the oxygen jet. This gives a basis to consider slag and metal phases at steady state to be at 'quasi-equilibrium' for the purpose of oxygen partial pressure calculations at the slag / metal interface.

Under steady state conditions, when the chemistry of metallic and slag phases is constant, the oxygen partial pressure of the bath can be assessed from the partitioning of elements between the metal and slag phases, in particular from the Fe / FeO and Mn / MnO reactions.

Partitioning of elements between slag and metal phases and, therefore, the bath oxygen partial pressure, are affected by experimental parameters such as; temperature, char fraction in the slag, slag chemistry, post combustion ratio and ore feed rate.

Manganese content in Whaleback iron ore and coke is negligible (Appendix 1). It enters the furnace with the pig iron, which contains 0.35 to 0.75 wt % Mn (average 0.55 wt%). Manganese is partially oxidised and distributed between the metal and slag.

As a result of iron ore reduction, the mass of metal and slag phases increase slowly. However, the manganese partitioning coefficient (Mn) / [Mn] is about constant under steady state conditions of constant temperature and post combustion ratio.

8.2 Iron Metal / Slag Partitioning

Iron metal / slag partitioning can be represented by the reaction:

$$Fe_{(l)} + \frac{1}{2}O_{2(g)} = (FeO)_{(l)}$$
 (8-1)

There are several relationships for the standard Gibbs free energy for Reaction 8-1 reported in literature. Turkdogan, 1993, recommended the following equation for the standard Gibbs free energy of Reaction 8-1, derived from an analysis of published data.

$$\Delta G^{\circ} = -225 \ 460 + 41.26 \ T \ (J/mol) \tag{8-2}$$

The equilibrium constant (K_{Fe}) for Reaction 8-1 is:

$$K_{Fe} = \frac{a_{FeO}}{a_{Fe}P_{O_2}^{\frac{1}{2}}} = \frac{x_{FeO}\gamma_{FeO}}{a_{Fe}P_{O_2}^{\frac{1}{2}}}$$
(8-3)

Where;

T = temperature of the slag / metal interface (K) a_{FeO} = activity of FeO in the slag γ_{FeO} = activity coefficient of FeO in the slag x_{FeO} = mole fraction of FeO in the slag a_{Fe} = activity of iron in the bath P_{O_2} = partial pressure of oxygen in the gas phase corresponding to the equilibrium

Then, the partial pressure of oxygen can be presented as:

between the slag and metal phases

$$P_{O_2} = \left(\frac{x_{FeO}\gamma_{FeO}}{a_{Fe}K_{Fe}}\right)^2 \tag{8-4}$$

In the present work, the mole fraction of FeO in the slag was determined by chemical analysis. The total iron concentration present in the slag was measured by XRF. The

oxidation state of the iron was determined by titration, using a standard method (BHP, 1992, 1994).

Experimental data on the iron oxide concentration in the slag and the iron concentration in the metal are presented in Table 8-1. Activity of iron oxide in the slag was taken from the diagram in Figure 8-1, obtained by Björkvall *et al.*, 1999.



Figure 8-1 Iso activity lines of 'FeO' in the system CaO-'FeO'-MnO-SiO₂ with a constant mole fraction of MnO ($x_{MnO} = 0.05$). The standard state is pure liquid 'FeO'. (Björkvall *et al.*, 1999)

The activity of iron in the metal bath was taken from El-Kaddah and Robertson, 1977, Figure 8-2.



Figure 8-2 Activity of iron in the Fe – C solution at 1550 °C (El-Kaddah and Robertson, 1977).

The partial pressure of oxygen calculated using the iron / iron oxide equilibrium was from 1.2×10^{-12} to 3.7×10^{-11} atmospheres.

The iron oxide content of the slag, and hence the oxygen partial pressure, is a strong function of several experimental variables, such as; temperature, char fraction in the slag, bottom gas injection rate, slag chemistry, post combustion ratio and ore feed rate.

All experiments were performed over a small temperature range of 1450 - 1500 °C, the char fraction in the slag was maintained at 30 wt % and argon was injected for stirring at 7 Nl/min.

The composition of the slag was varied in some experiments. The main difference was magnesia content in the slag. In the base case the magnesia concentration was 6 wt %. In some experiments it was 20 wt %. However, the effect of magnesia on the iron oxide concentration in the slag was slight.

Exp.	%FeO	% Fe	P O ₂
1	2.62	94.80	1.10E-11
2	3.45	95.02	7.12E-12
3	2.38	94.87	6.65E-12
4	3.19	96.25	1.02E-11
5	5.27	94.62	3.64E-11
6	4.05	94.23	2.43E-11
7	1.94	94.96	5.38E-12
8	4.02	94.28	3.37E-11
9	3.28	94.86	1.18E-11
10	1.97	94.89	3.96E-12
11	6.32	94.73	3.67E-11
12	2.31	94.70	3.36E-12
13	5.81	95.71	1.76E-11
14	6.36	93.89	2.57E-11
15	2.77	94.67	4.73E-12
16	5.01	93.97	1.81E-11
17	1.87	93.62	2.36E-12
18	4.07	94.20	6.47E-12
19	2.73	94.31	4.87E-12
20	3.44	94.55	5.31E-12
21	2.70	94.80	7.12E-12
22	1.39	94.04	1.61E-12
23	1.32	93.87	1.87E-12
24	3.74	95.24	8.21E-12
25	3.59	95.99	8.25E-12
26	2.68	95.16	2.76E-12
27	2.52	95.71	3.09E-12
28	1.44	94.14	1.18E-12
29	4.03	95.82	7.29E-12

Table 8-1 Oxygen partial pressure calculated from the iron slag / metal partitioning.

8.3 Manganese Slag / Metal Partitioning

In the smelting reduction furnace with stable operation, constant temperature and post combustion ratio, the manganese partitioning coefficient (Mn) / [Mn], was about constant.

Manganese partitioning between metal and slag phases is described by the following reaction.

$$[Mn]_{(l)} + \frac{1}{2} O_{2(g)} = (MnO)_{(l)}$$
(8-5)

The standard Gibbs free energy of this reaction (Henrian standard state is used for [Mn], and pure MnO for (MnO)) can be calculated by Equation 8-6 (Turkdogan, 1993, Sigworth and Elliot, 1974).

$$\Delta G^{\circ} = -368 \ 130 + 107.8 \ T \ (J/mol) \tag{8-6}$$

The equilibrium constant (K_{Mn}) for Reaction 8-5 is:

$$K_{Mn} = \frac{a_{MnO}}{a_{Mn}P_{O_2}^{\frac{1}{2}}} = \frac{x_{MnO}\gamma_{MnO}}{[\% Mn]f_{Mn}P_{O_2}^{\frac{1}{2}}}$$
(8-7)

Where;

 a_{MnO} = activity of MnO in the slag

 γ_{MnO} = activity coefficient of MnO in the slag

 x_{MnO} = mole fraction of MnO in the slag

 a_{Mn} = Henrian activity of manganese in metal

 f_{Mn} = activity coefficient of manganese in metal

 P_{O_2} = partial pressure of oxygen in the gas phase corresponding to the equilibrium between the slag and metal phases

Rearranging Equation 8-7, the partial pressure of oxygen can be calculated as:

$$P_{O_2} = \left(\frac{x_{MnO}\gamma_{MnO}}{[\% Mn]f_{Mn}K_{Mn}}\right)^2$$
(8-8)

Concentration of MnO in the slag was measured using XRF. The activity coefficient of MnO in the slag was calculated using Equation 8-9, obtained by Ohta and Suito, 1998, and the results of XRF analysis of the slag presented in Appendix 3.

$$\log \gamma_{MnO} = 0.19 \,(\% CaO) + 0.023 \,(\% MgO) - 0.023 \,(\% SiO_2) + 0.129$$
(8-9)

The activity coefficient of manganese in the metal was calculated using interaction parameters (Equation 8-10) (Steelmaking Data SourceBook, 1988), and results of the spark emission and Leco analysis of the metal (Appendix 3).

$$\log f_{Mn} = -0.0538 \,(\%C) - 0.0327 \,(\%Si) + 0.0046 \,(\%Mo) - 0.0072 \,(\%Ni) - 0.06 \\ (\%P) - 0.048 \,(\%S) - 0.05 \,(\%Ti) + 0.0039 \,(\%Cr)$$
(8-10)

The partial pressure of oxygen calculated using the manganese / manganese oxide equilibrium was 2.0×10^{-11} to 2.7×10^{-9} atmospheres.

Exp.	% MnO	γ MnO	% Mn	f Mn	P O ₂
1	2.22	3.0971	0.3490	0.56	2.70E-09
2	1.58	1.4270	0.2260	0.55	6.94E-10
3	2.70	2.5930	0.3930	0.55	1.83E-09
4	2.77	2.4243	0.7650	0.58	3.93E-10
5	1.72	2.9604	0.3960	0.55	8.58E-10
6	1.46	3.9206	0.5220	0.53	7.19E-10
7	1.96	3.4785	0.2930	0.56	2.67E-09
8	0.89	4.8443	0.4840	0.53	4.09E-10
9	1.35	2.3024	0.3230	0.55	5.23E-10
10	1.16	2.3227	0.1830	0.55	1.32E-09
11	2.51	2.4960	0.2820	0.55	2.71E-09
12	2.94	1.2370	0.3270	0.55	8.95E-10
13	3.30	1.3526	0.4150	0.56	7.93E-10
14	2.67	1.5060	0.2770	0.56	1.38E-09
15	1.83	1.1224	0.5430	0.56	9.76E-11
16	1.15	1.4156	0.5420	0.53	6.65E-11
17	0.71	1.1710	0.5010	0.50	2.52E-11
18	0.67	1.4298	0.6540	0.55	2.03E-11
19	1.63	0.8192	0.5090	0.54	4.70E-11
20	1.61	0.6653	0.3240	0.54	8.19E-11
21	0.81	1.5442	0.5570	0.57	3.05E-11
22	1.18	1.2215	0.4080	0.51	1.01E-10
23	1.11	1.3186	0.5820	0.51	4.81E-11
24	2.74	1.0983	0.3540	0.58	4.63E-10
25	1.31	1.2298	0.3840	0.55	1.25E-10
26	2.53	0.7157	0.4050	0.59	1.31E-10
27	4.51	0.7781	0.5740	0.61	2.12E-10
28	1.44	1.0279	0.4170	0.52	1.06E-10
29	2.89	0.9770	0.3820	0.61	3.32E-10

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Table 8-2 Data for the calculation of the partial pressure of oxygen from the Mn - MnO equilibrium.

8.4 Correlation of Fe / FeO and Mn / MnO Partitioning

A comparison of the oxygen partial pressure calculated from both the iron and manganese metal / slag partitioning for all experimental data is shown in Figure 8-3. This figure outlines the differences between the oxygen partial pressure calculated from the Fe / FeO and Mn / MnO equilibrium.



Figure 8-3 Oxygen partial pressure calculated using the Mn / MnO equilibrium versus the oxygen partial pressure from the Fe / FeO equilibrium.

The oxygen partial pressure calculated from the Fe-FeO equilibrium is generally lower than the oxygen partial pressure found from the Mn-MnO equilibrium.

The equilibrium between the iron, manganese, iron oxide and manganese oxide can be represented by Reaction 8-11.

$$(FeO)+[Mn] = (MnO) + Fe_{(l)}$$
 (8-11)

The standard Gibbs free energy of this reaction can be derived from Equations 8-2 and 8-6.

$$\Delta G^{\circ} = -142\ 670 + 66.54\ T\ (J/mol) \tag{8-12}$$

The equilibrium constant (K) for reaction 8-11 is:

$$K = \frac{a_{MnO}a_{Fe}}{a_{Mn}a_{FeO}} = \frac{x_{MnO}\gamma_{MnO}a_{Fe}}{[\%Mn]f_{Mn}x_{FeO}\gamma_{FeO}}$$
(8-13)

Concentration of (FeO) in the slag can be calculated from the Mn / MnO partitioning (Table 8-2) as:

$$x_{FeO} = \frac{x_{MnO} \gamma_{MnO} a_{Fe}}{[\% Mn] f_{Mn} \gamma_{FeO} K}$$
(8-14)

A comparison of the calculated and measured concentrations of FeO in the slag is shown in Table 8-3. Calculated FeO concentrations are between 4.5 and 57 % of the measured values.

This emphasises that metal and slag phases are not at equilibrium. This also implies that under given experimental conditions reduction of iron oxide at the slag / metal interface is infeasible.

Partitioning of iron and manganese between slag and metal phases occurs in different processes: iron oxide is reduced from the slag to the metal phase, while manganese is oxidised from the metal to the slag. Iron oxide is mainly reduced in the slag phase by char and metallic droplets.

Manganese is predominantly oxidised by the slag at the slag / metal interface. Higher oxygen partial pressures determined from the Mn / MnO partitioning than that found from the Fe / FeO partition implies that the oxygen partial pressure at the slag / metal interface is higher than the oxygen partial pressure in the bulk slag phase where iron reduction takes place. This may be due to partial penetration of the oxygen jet to the surface of the metal bath, increasing the local oxygen partial pressure at the slag / metal interface.

Under experimental conditions employed in this work, the char proportion in the slag was about 30 wt % and formed a char bed on the top of the slag phase. This would explain a lower oxygen partial pressure at the top of the slag in relation to the oxygen partial pressure at the slag / metal interface. Further, the oxygen jet partially penetrates the slag, and may directly oxidise the metal bath in the centre, while iron oxide is reduced by char particles in the surrounding slag.

The difference in oxygen partial pressure derived from Fe / FeO and Mn / MnO can also be attributed to different degrees of non-equilibrium for reactions of iron reduction and manganese oxidation.

Exp.	exp xFeO	calc xFeO	Exp/calc	
1	0.024	0.942	0.026	
2	0.031	0.479	0.066	
3	0.020	0.778	0.025	
4	0.026	0.365	0.072	
5	0.041	0.531	0.078	
6	0.033	0.484	0.069	
7	0.015	0.940	0.016	
8	0.030	0.365	0.083	
9	0.027	0.415	0.065	
10	0.017	0.659	0.025	
11	0.051	0.944	0.054	
12	0.021	0.542	0.039	
13	0.053	0.516	0.103	
14	0.057	0.667	0.085	
15	0.026	0.179	0.142	
16	0.045	0.147	0.306	
17	0.018	0.090	0.198	
18	0.043	0.081	0.529	
19	0.024	0.124	0.197	
20	0.032	0.164	0.196	
21	0.024	0.100	0.237	
22	0.013	0.181	0.070	
23	0.012	0.125	0.094	
24	0.035	0.392	0.088	
25	0.033	0.206	0.162	
26	0.025	0.209	0.122	
27	0.023	0.267	0.087	
28	0.014	0.186 0.074		
29	0.038	0.334	0.114	

Table 8-3 A comparison between the analysed concentration of (FeO) and the calculated concentration of (FeO) using the equilibrium relationship between Fe / Mn / FeO / MnO.

8.5 Phosphorus Slag / Metal Partitioning

Phosphorus slag / metal partitioning can be represented by the following reaction:

$$[P] + {}^{5}/{}_{2}[O] + {}^{3}/{}_{2}(O^{2-}) = (PO_{4}^{3-})$$
(8-15)

Reaction 8-15 can also be presented as:

$$\frac{1}{2} P_{2(g)} + \frac{5}{4} O_{2(g)} + \frac{3}{2} (O^{2-}) = (PO_4^{3-})$$
 (8-16)

which is the sum of Reactions 8-15, 8-17 and 8-18.

$$[O] = \frac{1}{2} O_{2 (g)}$$
(8-17)

$$[P] = \frac{1}{2} P_{2 (g)}$$
(8-18)

The equilibrium constant (K_P) for reaction 8-16 is:

$$K_{P} = \frac{a_{(PO_{4}^{3-})}}{(pP_{2})^{\frac{1}{2}} pO_{2}^{\frac{5}{4}} a_{(O^{2-})}^{\frac{3}{2}}} = \frac{f_{(PO_{4}^{3-})} (wt\%PO_{4}^{3-}) M_{P}}{k_{P} f_{[P]} [wt\%P] pO_{2}^{\frac{5}{4}} a_{(O^{2-})}^{\frac{3}{2}} M_{PO_{4}^{3-}}}$$
(8-19)

Where;

 $a_{(0^{2-})} = activity of O^{2-}$ in the slag

 $a_{(PO_4^{3-})} = activity of PO_4^{3-} in the slag$

 $f_{(PO_{i-}^{3-})}$ = activity coefficient of phosphate anion in the slag

 $f_{[P]}$ = activity coefficient of phosphorus in the metal - Equation 8-20

 k_P = equilibrium coefficient of reaction 8-18

 K_p = equilibrium coefficient of reaction 8-16

 $M_{PO_{2}^{3}}$ = molecular weight of phosphate ions

 M_P = molecular weight of phosphorus

- $pO_2 = partial pressure of oxygen in the gas phase corresponding to the equilibrium between the slag and metal phases$
- pP_2 = partial pressure of phosphorus in the gas phase corresponding to the equilibrium between the slag and metal phases

 $(wt\% PO_4^{3-}) = \text{concentration of phosphate in the slag}$ [wt% P] = concentration of phosphorus in the metal

The activity coefficient of phosphorus in the metal was calculated using interaction parameters (Equation 8-20) (Steelmaking Data SourceBook, 1988), and results of the spark emission and Leco analysis of the metal (Appendix 3).

$$\label{eq:log_f_P} \begin{split} & \text{Log } f_{\text{P}} = 0.126 \ (\%\text{C}) + 0.099 \ (\%\text{Si}) + 0.054 \ (\%\text{P}) - 0.04 \ (\%\text{Ti}) + 0.034 \ (\%\text{S}) - 0.032 \ (\%\text{Mn}) + 0.003 \ (\%\text{Ni}) + 0.001 \ (\%\text{Mo}) \end{split} \tag{8-20}$$

The ability of a slag to absorb phosphorus is described by the phosphate capacity. For reaction 8-16 the phosphate capacity is defined as:

$$C_{PO_4^{3-}} = \frac{(wt\% PO_4^{3-})}{pP_2^{\frac{1}{2}}pO_2^{\frac{5}{4}}}$$
(8-21)

The phosphate capacity of a slag can also be defined for the slag / metal partition (Reaction 8-15) as:

$$C_{PO_4^{3-}}^* = \frac{(wt\%PO_4^{3-})}{a[P] a_{[O]}^{5/2}}$$
(8-22)

Generally, phosphorus metal / slag partitioning depends upon the oxygen partial pressure and the slag composition. The use of phosphate capacity allows the characterisation of a slag only from the viewpoint of its ability to absorb phosphorus. It depends only on the slag thermodynamic properties and temperature, as it follows from Equations 8-23:

$$C_{PO_4^{3^-}} = \frac{K_P a_{(O^{2^-})}^{\frac{3}{2}}}{f_{(PO_4^{3^-})}}$$
(8-23)

Phosphorus slag / metal partitioning can be calculated as:

$$L_{P} = \frac{(wt\% PO_{4}^{3-})}{[wt\% P]} = \frac{C_{PO_{4}^{3-}} k_{P} f_{[P]} pO_{2}^{\frac{5}{4}} M_{PO_{4}^{3-}}}{M_{P}}$$
(8-24)

8-16

As it follows from Reaction 8-16 and Equation 8-23 and 8-24, phosphorus slag / metal partitioning and slag phosphate capacity increase with increasing free oxygen anion activity in the slag, $a_{(o^{2-})}$, which increases with increasing slag basicity.

The slag phosphate capacity as a function of temperature and slag composition was described using empirical relationships. For example, Sobandi *et al.*, 1998 derived the following for the phosphate capacity:

Log
$$C_{PO_4^{3-}} = 2.60\{(\%CaO) + 0.33(\%MnO) + 0.55(\%MgO) - 0.90(\%Fe_tO) - 0.77(\%PO_{2.5})\} / (\%SiO_2) + 40400 / T - 6.48$$
(8-25)

The concentration of free oxygen anions in the slag can be characterised by the socalled optical basicity. The concept of optical basicity is described in the *Partitioning of Sulphur Between the Metal, Slag and Gas.*

A number of relationships between slag phosphate capacity and optical basicity are known from the literature. However, accurate empirical relationships incorporate optical basicity and slag composition, such as suggested by Liu *et al.*, 1998:

$$\log C_{PO_{4}^{3-}} = 6.26\Lambda - 13.05 + 63617 / \text{T} - 0.63 X'_{AlO_{3}^{3-}} + 1.02 X'_{F^{-}} + 1.80 X'_{Ba_{3}^{2-}} + 0.94 X'_{Na^{+}} - 3.04 X'_{Fe^{2+}} - 2.91 X'_{Mg^{2+}} + 2.77 X'_{Mn^{2+}} \text{ (Liu et al., 1998)}$$
(8-26)

The phosphate capacity is plotted as a function of the optical basicity in Figure 8-4.



Figure 8-4 Experimental phosphate capacity of the slag plotted against optical basicity, using the oxygen partial pressure found from the Fe / FeO and Mn / MnO partitions

The phosphate capacity was calculated using experimental data on phosphorus concentration in metal and slag phases and oxygen partial pressure, estimated from the Fe / FeO and Mn / MnO partitioning.

In turn, the oxygen partial pressure for the slag / metal interface can be calculated from the (P) / [P] partitioning, as:

$$P_{O_2}^{\frac{5}{4}} = \sqrt{\frac{(\text{wt}^{0}\text{PO}_4^{3-}) M_P}{k_P f_{[P]} [\text{wt}^{0}\text{P}] M_{PO_4^{3-}} C_{PO_4^{3-}}}}$$
(8-27)

Where $C_{PO_4^{3-}}$ is the slag phosphate capacity, calculated using Equation 8-25. Oxygen partial pressure estimated from experimental data on the (P) / [P] partitioning is in the range of 3.8 x 10⁻¹⁴ to 1.7 x 10⁻¹² atmospheres. Results are given in Table 8-4.

The oxygen partial pressure calculated from the phosphorus partition is close to the values calculated from the Fe / FeO partition.

Exp.	optical	[P]	f _[P]	(PO_{4}^{3-})	$C_{po^{3-}}$	P O ₂
No.	basicity	(wt%)		(wt%)		(P)/[P]
1	0.68	0.130	3.73	0.508	4.69	1.0E-13
2	0.64	0.144	3.87	0.136	3.78	4.6E-13
3	0.67	0.091	3.85	0.223	4.41	1.4E-13
4	0.67	0.127	3.24	0.298	4.32	2.7E-13
5	0.67	0.137	3.87	0.128	4.31	1.1E-13
6	0.69	0.134	3.72	0.094	4.62	3.8E-14
7	0.66	0.127	3.64	0.115	4.28	7.8E-14
8	0.67	0.150	4.09	0.107	4.41	4.3E-14
9	0.66	0.161	3.75	0.149	4.26	1.4E-13
10	0.66	0.116	3.84	0.320	4.27	2.6E-13
11	0.67	0.124	3.88	0.163	4.11	2.8E-13
12	0.64	0.157	3.82	0.115	3.85	2.7E-13
13	0.65	0.140	3.67	0.516	3.93	1.3E-12
14	0.66	0.091	3.77	0.244	4.02	8.2E-13
15	0.64	0.111	3.62	0.187	3.74	8.2E-13
16	0.65	0.098	4.28	0.179	3.94	5.6E-13
17	0.63	0.084	4.29	0.066	3.74	3.4E-13
18	0.61	0.105	3.81	0.230	3.18	6.2E-13
19	0.63	0.116	3.95	0.162	3.54	1.2E-12
20	0.61	0.120	4.01	0.118	3.22	1.7E-12
21	0.65	0.141	3.44	0.099	4.12	1.7E-13
22	0.64	0.135	4.36	0.075	3.83	2.0E-13
23	0.65	0.142	4.37	0.112	4.07	1.6E-13
24	0.65	0.124	3.33	0.285	3.89	1.1E-12
25	0.65	0.115	3.75	0.302	3.87	9.1E-13
26	0.61	0.148	3.23	0.080	3.05	1.1E-12
27	0.63	0.138	2.90	0.070	3.43	6.5E-13
28	0.62	0.127	4.04	0.029	3.45	2.3E-13
29	0.63	0.150	2.92	0.153	3.58	1.1E-12

Table 8-4 Slag and metal phosphorus composition and the oxygen partial pressure calculated from the (P) / [P] partition.

8.6 Partitioning of Sulphur Between Metal, Slag and Gas Phases

Sulphur in the hot metal is of particular concern in the smelting reduction furnace. Organic sulphur in coal will be removed during coke making for blast furnace operations, while it is used directly in the smelting reduction furnace, increasing the total level of sulphur in the process for the identical coal. To this end, it is necessary to understand the effects of different parameters on the sulphur behaviour in the smelting reduction furnace.

The hot metal composition in the bath smelting process is dependent on the slag chemistry, gas chemistry (particularly the oxygen partial pressure) and the raw materials composition. All feed materials that enter the furnace are distributed between the metal, slag and gas phases.

Usachev *et al.*, 1991 found that with high post combustion ratios up to 91 % of the sulphur was removed to the gas and dust phases.

Partitioning of sulphur between the metal and slag is well established for slags of a similar composition to those utilised in the smelting reduction furnace. However, partitioning between the slag and gas is not so clearly defined.

8.6.1 Sulphur Distribution in the Smelting Reduction Furnace

The sulphur distribution between the metal, slag and gas is shown in Figure 8-5 for each experiment. It is obvious that a significant proportion of the sulphur can be removed to the gas phase, especially at high post combustion ratios. The sulphur in the gas phase in Figure 8-5 also includes sulphur present in the dust and fumes.



Figure 8-5 The distribution of sulphur in the gas, slag and metal phases for different experiments.

8.6.2 Sulphur Slag / Metal Partitioning

For an oxygen partial pressure below 10^{-5} atmospheres, sulphur in the slag presents in the form of sulphide, and the reaction of iron de-sulphurisation is:

$$[S] + (O2-) = (S2-) + [O]$$
(8-28)

Activity of oxygen in metal is characterised by the oxygen partial pressure, assuming that the metal is in equilibrium with the gas phase.

$$[O] = \frac{1}{2} O_{2 (g)}$$
(8-29)

In the smelting reduction furnace gas-metal equilibrium is not achieved, therefore, this is a 'virtual' gas phase, with an oxygen partial pressure that corresponds to equilibrium with metal having an activity of dissolved oxygen, $a_{[O]}$.

Similarly, the activity of sulphur in metal is characterised by the sulphur partial pressure, assuming that the metal is in equilibrium with the gas phase.

$$[S] = \frac{1}{2} S_{2(g)}$$
(8-30)

Combining Reactions 8-28, 8-29 and 8-30, the reaction of desulphurisation may be presented as:

$$\frac{1}{2} S_{2(g)} + (O^{2}) = (S^{2}) + \frac{1}{2} O_{2(g)}$$
 (8-31)

The equilibrium constant, K_s, for Reaction 8-31 is:

$$K_{S} = \frac{a_{(S^{2-})} pO_{2}^{\frac{1}{2}}}{a_{(O^{2-})} pS_{2}^{\frac{1}{2}}} = \frac{(wt\%S)f_{(s)}pO_{2}^{\frac{1}{2}}}{a_{(O^{2-})} k_{S} [wt\%S] f_{[S]}}$$
(8-32)

Where;

 $a_{(O^{2^{-}})} = \text{activity of } O^{2^{-}} \text{ in the slag}$ $a_{(S^{2^{-}})} = \text{activity of } S^{2^{-}} \text{ in the slag}$ $f_{(S)} = \text{activity coefficient of sulphur in the slag}$ $f_{[S]} = \text{activity coefficient of sulphur in the metal, Equation 8-33}$ k_S = equilibrium constant of Reaction 8-30

- pO_2 = partial pressure of oxygen in the gas phase corresponding to the equilibrium between the slag and metal phases
- pS_2 = partial pressure of sulphur in the gas phase corresponding to the equilibrium between the slag and metal phases
- $(wt\%S^{2-})$ = concentration of sulphur in the slag
- [wt%S] = concentration of sulphur in the metal

The activity coefficient of sulphur in the metal was calculated using interaction parameters:

$$f_{[S]} = + 0.111 (\%C) + 0.075 (\%Si) -0.046 (\%S) + 0.035 (\%P) - 0.026 (\%Mn) + 0.0027 (\%Mo) - 0.18 (\%Ti)$$
(8-33)

Metal composition was determined by spark emission and Leco analyses (Appendix 3).

The ability of a slag to absorb sulphur is described by the sulphide capacity. For Reaction 8-31 the sulphide capacity, C_S , is defined as:

$$C_{s^{2-}} = \frac{(wt\%S^{2-}) pO_2^{\frac{1}{2}}}{pS_2^{\frac{1}{2}}} = \frac{(wt\%S^{2-}) pO_2^{\frac{1}{2}}}{k_S [wt\%S] f_{[S]}}$$
(8-34)

Generally, sulphur metal / slag partitioning depends upon the oxygen partial pressure, temperature and the slag composition. The use of sulphide capacity allows the characterisation of a slag only from the viewpoint of its ability to absorb sulphur. It depends only on the slag thermodynamic properties and temperature, as it follows from:

$$C_{s^{2-}} = K_S \frac{a_{O^{2-}}}{f_{(S)}}$$
(8-35)

Sulphur slag / metal partitioning can be calculated as:

$$L_{s} = \frac{(wt\%S^{2-})}{[wt\%S]} = \frac{C_{s^{2-}}f_{[s]}k_{S}}{P_{O_{2}}^{\frac{1}{2}}}$$
(8-36)

As it follows from Reaction 8-31 and Equations 8-35 and 8-36, sulphur slag / metal partitioning and slag sulphide capacity increase with increasing free oxygen anion activity in the slag, $a_{(o^{2-})}$. However, single ion activities cannot be thermodynamically defined (Guggenheim, 1929). Alternatively, the concentration of free oxygen anions in the slag can be characterised by the optical basicity. The concept of optical basicity was introduced by Duffy and Ingram, 1971, and used for the calculation of sulphide capacity by Duffy *et al.*, 1978, Sommerville *et al.*, 1984, Sosinsky and Sommerville, 1986 and Young *et al.*, 1992.

The optical basicity of a slag, Λ , is the sum of the apparent optical basicity of the slag components:

$$\Lambda = X_{AO_{a/2}} \Lambda_A (AO_{a/2}) + X_{BO_{b/2}} \Lambda_B (BO_{b/2}) + \dots$$
(8-37)

Where;

 $\Lambda = \text{optical basicity}$ $\left(X_{AO_{a/2}}, X_{BO_{h/2}}, ...\right) = \text{mole fractions of the species}$ $\Lambda_{A}(AO_{a/2}), ... = \text{optical basicity values for individual oxides}$

The values of optical basicity used in this investigation are shown below.

Oxide	Optical Basicity, Λ		
Fe ₂ O ₃	0.77		
FeO	1.00		
MgO	0.78		
Al ₂ O ₃	0.60		
SiO ₂	0.46		
P ₂ O ₅	0.4		
SO ₃	0.33		
CaO	1.00		
TiO ₂	0.65		
Cr ₂ O ₃	0.70		
MnO	0.98		
SrO	1.10		
BaO	1.15		
ZnO	0.95		

Table 8-5 Optical basicity of some oxides (Young et al., 1992).

The slag sulphide capacity as a function of temperature, slag composition and optical basicity was described by empirical relationships as follows:

$$Log C_{s^{2-}} = -13.913 + 42.84\Lambda - 23.82\Lambda^{2} - (11\ 710/T) - 0.02223(wt\%SiO_{2}) - 0.02275(wt\%Al_{2}O_{3}) (\Lambda < 0.8) (Young et al., 1992)$$
(8-38)

Log
$$C_{s^{2-}} = -0.6261 + 0.4808\Lambda + 0.7197\Lambda^2 + (1697/T) - (2587\Lambda/T) + 0.0005144$$

(wt%FeO) ($\Lambda > 0.8$) (Young *et al.*, 1992) (8-39)

Log
$$C_{s^{2-}} = [(22\ 690 - 54\ 640\ \Lambda) / T] + 43.6\ \Lambda - 25.2$$

(Sosinsky and Sommerville, 1986) (8-40)

Log
$$C_{s^{2-}} = 12.0 \text{ A} - 11.9 (1773 \text{ K}) (Duffy et al., 1977) (8-41)$$

Log
$$C_{s^{2-}} = 12.6 \text{ A} - 12.3 (1773 \text{ K}) (Sommerville et al., 1984) (8-42)$$

The experimental sulphide capacity is plotted as a function of the sulphide capacity calculated using Equation 8-38 in Figure 8-6.



Figure 8-6 Experimental sulphide capacity of the slag plotted against the sulphide capacity calculated from Equation 8-38, using the oxygen partial pressure found from the Fe / FeO and Mn / MnO partitions

The experimental sulphide capacity was calculated using experimental data on sulphur concentration in metal and slag phases and oxygen partial pressure, estimated previously from the Fe / FeO and Mn / MnO partitioning.

Equation 8-38 was used to estimate sulphur slag / metal partitioning.





Calculated (S) / [S] ratios are compared with experimental values in Figure 8-7.

The use of oxygen partial pressure calculated from Fe / FeO equilibrium gives a larger degree of scatter when calculating the sulphur partition. This may be due to the use of cartridges to feed the iron ore into the furnace. The sampling of the slag may have included spikes of iron oxide, if the slag was not completely homogenous.

Disagreement between calculated and experimental (S) / [S] ratios indicates that oxygen partial pressure, which governs sulphur slag / metal partitioning, is much less than that predicted on the basis of Mn / MnO and Fe / FeO equilibrium. This reflects the fact that slag and metal phases in the smelting reduction furnace are not at equilibrium.

The oxygen partial pressure can also be calculated by the (S) / [S] partitioning. Using the relationship between sulphur partition and oxygen partial pressure (Equation 8-36) and the calculated sulphide capacity (Equation 8-38), the oxygen partial pressure can be determined:

$$P_{O_2} = \sqrt{\frac{C_{s^{2-}} k_S f_{[s]} [wt\%S]}{(wt\%S^{2-})}}$$
(8-44)

Results are given in Table 8-6. Oxygen partial pressure estimated from experimental data on the (S) / [S] partitioning is in the range of 5.8×10^{-13} to 1.1×10^{-15} atmospheres.

The oxygen partial pressure at the char / slag interface calculated from the C-CO equilibrium at 1500 °C is 2.0×10^{-16} atmospheres. The oxygen partial pressure on the slag / metal interface assessed from the sulphur slag / metal partitioning is, therefore, between the oxygen partial pressure at the char / slag interface and the value predicted from the Fe / FeO partition.

	Exp.	optical	[S]	f _[S]	(S^{2-})	Cs	P O ₂
	No.	basicity	(wt%)		(wt%)		
	1	0.68	0.045	3.14	0.473	7.60E-04	1.86E-13
	2	0.64	0.030	3.26	0.104	1.38E-04	5.95E-14
	3	0.67	0.045	3.24	0.385	3.61E-04	6.54E-14
	4	0.67	0.051	2.78	0.266	3.45E-04	1.20E-13
	5	0.67	0.028	3.26	0.313	4.15E-04	5.09E-14
	6	0.69	0.049	2.87	0.456	8.75E-04	2.59E-13
	7	0.66	0.037	3.08	0.272	3.24E-04	6.40E-14
	8	0.67	0.111	3.32	0.477	5.19E-04	5.76E-13
	9	0.66	0.036	3.16	0.515	2.94E-04	1.49E-14
	10	0.66	0.049	3.23	0.277	2.59E-04	7.80E-14
	11	0.67	0.053	3.25	0.349	3.73E-04	1.19E-13
	12	0.64	0.052	3.21	0.337	1.21E-04	1.27E-14
	13	0.65	0.059	3.08	0.268	1.99E-04	6.54E-14
	14	0.66	0.042	3.18	0.267	2.63E-04	5.99E-14
	15	0.64	0.043	3.07	0.508	9.89E-05	2.31E-15
	16	0.65	0.029	3.48	0.402	1.77E-04	6.90E-15
	17	0.63	0.039	3.15	0.490	8.70E-05	1.68E-15
	18	0.61	0.040	3.12	0.265	6.79E-05	3.66E-15
	19	0.63	0.033	3.26	0.379	6.25E-05	1.14E-15
	20	0.61	0.034	3.35	0.171	3.20E-05	1.58E-15
ſ	21	0.65	0.040	2.92	0.613	1.82E-04	4.28E-15
	22	0.64	0.052	3.51	0.641	1.13E-04	3.72E-15
	23	0.65	0.031	3.56	0.339	1.43E-04	7.98E-15
	24	0.65	0.044	2.85	0.144	1.58E-04	6.85E-14
ľ	25	0.65	0.064	3.15	0.157	1.46E-04	1.26E-13
	26	0.61	0.058	2.76	0.226	2.77E-05	1.34E-15
	27	0.63	0.061	2.52	0.156	6.51E-05	1.45E-14
	28	0.62	0.036	3.16	0.333	5.95E-05	1.44E-15
ľ	29	0.63	0.089	2.52	0.143	8.78E-05	6.70E-14
L							

Table 8-6 Sulphur concentration in the slag and metal, and the oxygen partial pressure calculated from the (S) / [S] partition.

8.6.3 Sulphur Transfer from the Slag to the Gas Phase

8.6.3.1 Experiments and Experimental Data

Three distinct series of experiments were performed to examine the sulphur slag / gas partitioning.

- The post combustion ratio was kept constant, as discussed in the *Operation of the Experimental Smelting Reduction Furnace* for the base case experiments. This provided experimental data for steady state experiments under different conditions.
- 2. The post combustion ratio was varied in a range of 45 to 75 % in a single experiment. The variable experiments allowed the effect of post combustion ratio on the sulphur removal from the slag to the gas to be studied under identical conditions. The post combustion ratio was varied by manipulating the lance height during the experiment.
- 3. The post combustion ratio was maintained at a constant 60 %, but the char to slag ratio was reduced over the course of the experiment from 30 wt % until the level at which the slag started to foam. During the heat, char was consumed by reduction / oxidation reactions and the rate of consumption was monitored by the analysis of the gas composition. A gradual reduction in the char to slag ratio was achieved by adding coke at a smaller rate than the char consumption. This showed the effect of the char on the rate of sulphur gasification.

Sulphur was measured in both the slag and gas phases during experiments. The concentration of sulphur in the slag and gas is shown in Table 8-7.

Sulphur in the gas phase was present in the form of sulphur dioxide and hydrogen sulphide. The hydrogen sulphide was found to be substantially less than the sulphur dioxide for all experimental conditions examined.

The concentrations of sulphur dioxide and hydrogen sulphide as a function of the post combustion ratio are shown in Figures 8-8 and 8-9. The rate of sulphur removal from
the slag phase as a function of the sulphur concentration in the slag, at a constant post combustion ratio of 60 %, is shown in Figure 8-10.

No.basicity(%)(wt%)(wol%)(vol%)1 0.68 61 0.473 0.0689 2 0.64 65 0.104 0.0303 3 0.67 65 0.385 0.0685 4 0.67 62 0.266 0.0590 5 0.67 65 0.313 0.0879 6 0.69 63 0.456 0.0510 7 0.66 46 0.272 0.0161 8 0.67 76 0.477 0.0945 9 0.66 60 0.515 0.0617 10 0.66 63 0.277 0.0940 11 0.67 60 0.349 0.0476 12 0.64 60 0.337 0.0718 13 0.65 58 0.268 0.0546 14 0.66 60 0.267 0.0569 15 0.64 45 0.508 0.0415 16 0.65 74 0.402 0.0834 17 0.63 61 0.490 0.0564 18 0.61 60 0.379 0.0615 20 0.61 60 0.613 0.0590 22 0.64 60 0.613 0.0590 23 0.65 58 0.339 0.0612 24 0.65 59 0.144 0.0557 25 0.65 60 0.157 0.0254 27 0.63 55 0.156 0.0057	Exp.	optical	PCR	(S)	SO ₂	H ₂ S
1 0.68 61 0.473 0.0689 2 0.64 65 0.104 0.0303 3 0.67 65 0.385 0.0685 4 0.67 62 0.266 0.0590 5 0.67 65 0.313 0.0879 6 0.69 63 0.456 0.0510 7 0.66 46 0.272 0.0161 8 0.67 76 0.477 0.0945 9 0.66 60 0.515 0.0617 10 0.66 63 0.277 0.0940 11 0.67 60 0.349 0.0476 12 0.64 60 0.337 0.0718 13 0.65 58 0.268 0.0546 14 0.66 60 0.267 0.0569 15 0.64 45 0.508 0.0415 16 0.65 74 0.402 0.0834 17 0.63 61 0.490 0.0564 18 0.61 60 0.379 0.0615 20 0.61 60 0.613 0.0590 22 0.64 60 0.613 0.0577 23 0.65 58 0.339 0.0612 24 0.65 59 0.144 0.0557 25 0.65 60 0.157 0.0254 27 0.63 55 0.156 0.0602 0.0216 28 0.62 58 0.333 0.0537 0.00	No.	basicity	(%)	(wt%)	(vol%)	(vol%)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1	0.68	61	0.473	0.0689	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2	0.64	65	0.104	0.0303	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3	0.67	65	0.385	0.0685	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4	0.67	62	0.266	0.0590	
6 0.69 63 0.456 0.0510 7 0.66 46 0.272 0.0161 8 0.67 76 0.477 0.0945 9 0.66 60 0.515 0.0617 10 0.66 63 0.277 0.0940 11 0.67 60 0.349 0.0476 12 0.64 60 0.337 0.0718 13 0.65 58 0.268 0.0546 14 0.66 60 0.267 0.0569 15 0.64 45 0.508 0.0415 16 0.65 74 0.402 0.0834 17 0.63 61 0.490 0.0564 18 0.61 60 0.379 0.0615 20 0.61 60 0.171 0.0633 21 0.65 60 0.613 0.0590 22 0.64 60 0.641 0.0718 23 0.65 59 0.144 0.0557 25 0.65 60 0.157 0.0254 26 0.61 59 0.226 0.0574 0.0254 27 0.63 55 0.156 0.0602 0.0216 28 0.62 58 0.333 0.0537 0.0057 29 0.63 64 0.143 0.0718 0.0055	5	0.67	65	0.313	0.0879	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	6	0.69	63	0.456	0.0510	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	7	0.66	46	0.272	0.0161	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	8	0.67	76	0.477	0.0945	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	9	0.66	60	0.515	0.0617	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	10	0.66	63	0.277	0.0940	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	11	0.67	60	0.349	0.0476	
13 0.65 58 0.268 0.0546 14 0.66 60 0.267 0.0569 15 0.64 45 0.508 0.0415 16 0.65 74 0.402 0.0834 17 0.63 61 0.490 0.0564 18 0.61 60 0.265 0.0575 19 0.63 60 0.379 0.0615 20 0.61 60 0.171 0.0633 21 0.65 60 0.613 0.0590 22 0.64 60 0.641 0.0718 23 0.65 58 0.339 0.0612 24 0.65 59 0.144 0.0557 25 0.65 60 0.157 0.0536 26 0.61 59 0.226 0.0574 0.0254 27 0.63 55 0.156 0.0602 0.0216 28 0.62 58 0.333 0.0537 0.0057	12	0.64	60	0.337	0.0718	
14 0.66 60 0.267 0.0569 15 0.64 45 0.508 0.0415 16 0.65 74 0.402 0.0834 17 0.63 61 0.490 0.0564 18 0.61 60 0.265 0.0575 19 0.63 60 0.379 0.0615 20 0.61 60 0.171 0.0633 21 0.65 60 0.613 0.0590 22 0.64 60 0.641 0.0718 23 0.65 58 0.339 0.0612 24 0.65 59 0.144 0.0557 25 0.65 60 0.157 0.0254 26 0.61 59 0.226 0.0574 0.0254 27 0.63 55 0.156 0.0602 0.0216 28 0.62 58 0.333 0.0537 0.0057 29 0.63 64 0.143 0.0718 0.0055	13	0.65	58	0.268	0.0546	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	14	0.66	60	0.267	0.0569	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	15	0.64	45	0.508	0.0415	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	16	0.65	74	0.402	0.0834	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	17	0.63	61	0.490	0.0564	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	18	0.61	60	0.265	0.0575	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	19	0.63	60	0.379	0.0615	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	20	0.61	60	0.171	0.0633	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	21	0.65	60	0.613	0.0590	
23 0.65 58 0.339 0.0612 24 0.65 59 0.144 0.0557 25 0.65 60 0.157 0.0536 26 0.61 59 0.226 0.0574 0.0254 27 0.63 55 0.156 0.0602 0.0216 28 0.62 58 0.333 0.0537 0.0057 29 0.63 64 0.143 0.0718 0.0055	22	0.64	60	0.641	0.0718	
24 0.65 59 0.144 0.0557 25 0.65 60 0.157 0.0536 26 0.61 59 0.226 0.0574 0.0254 27 0.63 55 0.156 0.0602 0.0216 28 0.62 58 0.333 0.0537 0.0057 29 0.63 64 0.143 0.0718 0.0055	23	0.65	58	0.339	0.0612	
250.65600.1570.0536260.61590.2260.05740.0254270.63550.1560.06020.0216280.62580.3330.05370.0057290.63640.1430.07180.0055	24	0.65	59	0.144	0.0557	
260.61590.2260.05740.0254270.63550.1560.06020.0216280.62580.3330.05370.0057290.63640.1430.07180.0055	25	0.65	60	0.157	0.0536	
270.63550.1560.06020.0216280.62580.3330.05370.0057290.63640.1430.07180.0055	26	0.61	59	0.226	0.0574	0.0254
28 0.62 58 0.333 0.0537 0.0057 29 0.63 64 0.143 0.0718 0.0055	27	0.63	55	0.156	0.0602	0.0216
29 0.63 64 0.143 0.0718 0.0055	28	0.62	58	0.333	0.0537	0.0057
	29	0.63	64	0.143	0.0718	0.0055

Table 8-8 Experimental results.

Note: In experiments 23 to 27 coal was used, while in all other experiments coke was used.



Figure 8-8 Sulphur dioxide in the off-gas as a function of the post combustion ratio.



Figure 8-9 Hydrogen sulphide in the off-gas as a function of the post combustion ratio, for a single experiment with varying post combustion ratio.



Figure 8-10 The rate of sulphur removal from the slag phase as a function of the sulphur concentration in the slag, at a constant post combustion ratio of 60 %.

The total sulphur in the gas increases dramatically with both the post combustion ratio and the concentration of sulphur in the slag.

Figure 8-10 shows the rate of sulphur removal as a function of the concentration of sulphur in the slag. The intercept is at 0.0015 mol/s/m^2 . This implies that sulphur is also removed from the char by the oxygen lance and the reduction of iron oxide, for a char to slag ratio of 30 wt % and a post combustion ratio of 60%.

8.6.3.2 Slag - Gas Interactions

Sulphur in the Slag

The form of sulphur in the slag affects the possible mechanisms of reaction with the gas phase. Sulphur in the slag is more stable as sulphide at a partial pressure of oxygen below $10^{-4} - 10^{-5}$ atmospheres, while above this partial pressure it is more stable as sulphate, depending on the slag composition and temperature. In the smelting reduction furnace the oxygen partial pressure is relatively low, which provides conditions for iron oxide reduction and the sulphur in the slag exists primarily as sulphide (S²⁻).

The equilibrium between sulphide and sulphate ions is represented by the following reaction:

$$(S^{2-}) + 2 O_{2(g)} = (SO_4^{2-})$$
 (8-45)

The oxygen partial pressure in the bulk of the gas phase is $10^{-8} - 10^{-4}$ atmospheres, which is controlled by the gas temperature and proportions of carbon monoxide, carbon dioxide, hydrogen and water present

Sulphur in the Gas

In these experiments, sulphur in the gas was predominantly in the form of sulphur dioxide. Although metallurgical coke was used in the majority of experiments, there was sufficient hydrogen and water in the gas (approximately 3-4 %) to form hydrogen sulphide. The proportion of hydrogen sulphide formed slowly decreased with increasing post combustion, and therefore increasing partial pressure of oxygen.

When the gas contained 3-4 vol % combined hydrogen and water, as in the base case, the ratio of sulphur dioxide to hydrogen sulphide in the off-gas was approximately 10:1, as shown in Figures 8-8 and 8-9.

When coals containing 17 - 25 % volatile matter were used, the proportion of hydrogen sulphide increased to 30 - 40 % of the total sulphur in the furnace gas. Hydrogen sulphide is formed by either; the reaction of sulphur dioxide with hydrogen in the gas

phase, as suggested by Agrawal *et al.*, 1983, (Reaction 8-46), or during de-volatilisation of the coal, when the organic sulphur is gasified in the presence of volatiles.

$$SO_{2(g)} + H_{2(g)} = H_2S + O_2$$
 (8-46)

Nevertheless, predominantly sulphur dioxide is formed, even with increasing hydrogen availability.

Sulphur dioxide is formed during either coal de-volatilisation or slag de-sulphurisation.

When coke is used, a significant proportion of the hydrogen sulphide measured in the off-gas may be formed through Reaction 8-46. This mechanism is suggested by Agrawal *et al.*, 1983, for the presence of hydrogen sulphide during slag de-sulphurisation.

Large scale studies of the behaviour of sulphur in the smelting reduction furnace have found a higher proportion of hydrogen sulphide in the gas (Aukrust, 1994, and Ratchev and Katayama, 1992). This is due to the longer gas residence time in the larger smelting reduction furnaces and the use of coal as a fuel, which produced hydrogen sulphide during de-volatilisation.

Effect of Char / Slag Ratio

It was found that the level of sulphur in the gas is independent of the quantity of char suspended in the slag. In some experiments, the char to slag ratio was slowly reduced from 30 wt % until the slag foamed, while maintaining all other variables, such as post combustion, ore flowrate and others, constant. The sulphur dioxide in the gas remained constant, as shown by Figure 8-11, until the completion of the experiment when the slag foamed.

This indicates that the main factors affecting sulphur transfer to the gas phase are the sulphur content of the slag and oxygen partial pressure of the gas phase, which is governed by the post combustion reactions.

In addition, the combustion of char on the surface of the bath does not release significant quantities of sulphur into the gas phase. Instead, the sulphur in the char is dissolved directly into the slag, as the char is consumed and the ash containing sulphur is exposed to the slag. Then, the gas reacts with the slag bath, removing the sulphur to the gas phase.

It is interesting to note from Figure 8-11 that the sulphur dioxide levels increased from 600 ppm to 2000 ppm when the slag foamed. This can be explained by:

- 1. When the slag foams, the gas hold-up in the slag, and hence the gas residence time, increases dramatically, which allows the sulphur to react to a greater extent with the gas, and increases the sulphur dioxide levels.
- 2. Combustion of char in the foaming slag and iron reduction reactions slow. This effectively reduces the gas flowrate from the furnace, while enhancing sulphur removal, so that the sulphur concentration increases.



Figure 8-11 The concentration of sulphur dioxide in the gas phase as a function of the char to slag ratio, at a constant post combustion ratio of 60 %.

8.6.3.3 Kinetics of Sulphur Removal from the Slag Phase

Removal of sulphur from the slag to the gas phase may be presented by the following reaction:

$$(S) + 2CO_{2 (g)} = SO_{2 (g)} + 2CO_{(g)}$$
(8-47)

It includes the following steps:

1. Mass transfer in the slag phase

- 2. Gasification of sulphur through a chemical reaction.
- 3. Mass transfer in the gas phase.

Diffusion of Sulphur in the Slag Phase

Transport of sulphur from the bulk to the surface of the slag has been investigated for both stagnant baths and foamed slags, but not stirred baths. It can be assumed that if transport to the surface of a stagnant bath is not a rate limiting step, then a stirred bath will only enhance the transport of sulphur to the surface, which ensures that the slag surface is always replenished by the bulk slag. Turkdogan and Pearce, 1963, Pelton *et al.*, 1974, Agrawal *et al.*, 1983, and Mori *et al.*, 1980, all found that the diffusion of sulphur in the slag was not the rate limiting step. These results were discussed in the *Literature Review*.

For a foamed slag with gas bubbles forming a boundary between the slag surface and bulk, the rate of sulphur removal was a function of circulation rate of the slag (Ozturk *et al.*, 1994). The mass transfer coefficient in the foaming slag was estimated (Ozturk *et al.*, 1994) to be $6.65 \times 10^{-7} \text{ cm}^2/\text{s}$ at 1773 K. The present study employed a vigorously stirred bath without significant foaming. The kinetic results for a foamed slag are not relevant to the present discussion.

Overall, on the basis of results obtained for a stagnant bath, it may be concluded that diffusion of sulphide to the surface of the slag is not rate limiting.

Transport of Sulphur in the Gas Phase

Agrawal *et al.*, 1983 found that the rate of sulphur removal from the slag was dependent on the flowrate of gas above the slag bath when gas velocity was below 0.04 m/s.

In this work, gas velocity was, at least, one order of magnitude higher. It is estimated that the average velocity at the surface of the slag in the experimental smelting reduction furnace was above 1 m/s. This excludes gas phase mass transfer as a rate limiting stage.

Therefore, it would be reasonable to assume that the rate of sulphur removal from slag to the gas phase is controlled by the chemical reaction step.

Kinetics of the Interfacial Slag – Gas Reaction

Under experimental conditions, sulphur is removed from the slag phase by the oxygen jet impinging on the surface of the slag. However, the composition of the gas phase at the slag / gas interface is unknown.

In the following discussion, we consider a gas phase to have a uniform composition, temperature and velocity. This is an obvious simplification of a real situation, which is often and successfully used in the mathematical modelling of the direct iron smelting process (Zhang and Oeters, 1991a, 1993a,). To be consistent using such an approach, we assume that slag desulphurisation occurs by Reaction 8-47.

The possible mechanisms for slag desulphurisation in this investigation include the following steps (Agrawal *et al.*, 1983) (see also the *Literature Review*).

	Rate Controlling Step	Rate Expression (dN _s /dt)
1	CO_2 Adsorption: $CO_{2(g)} + \Box = CO_2(ad)$	$-k_1 P_{CO_2}$
2	CO_2 Dissociation: $CO_2(ad) + \Box = CO(ad) + O(ad)$	$-k_2 P_{CO_2}$
3	Dissociative Adsorption: $CO_2(g) + 2\Box = CO(ad) + O(ad)$	$-k_3 P_{CO_2}$
4	Dissociative Adsorption: $CO_2(g) + 1\Box = CO(g) + O(ad)$	$-k_4 P_{CO_2}$
5	CO_2 Desorption: $CO_2(ad) = CO_{2(g)} + \Box$	$-k_5'P_{CO_2}$
6	Charge Transfer: $[S^{2}] + O(ad) = S(ad) + [O^{2}]$	$k_{6}'\Gamma_{S^{2}} - P_{H_{2}O}^{\frac{1}{3}}$
7	O-S(ad) Formation: S(ad) + O(ad) = O-S(ad) + \Box	$k_{7}'\Gamma_{S^{2}} - P_{H_{2}O}$
8	SO ₂ (ad) Formation: O-S(ad) + O(ad) = SO ₂ (ad) + \Box	$k_{8}'\Gamma_{S^{2}} - P_{H_{2}O}$
9	SO ₂ (ad) Desorption: SO ₂ (ad) = SO _{2(g)} + \Box	$k_{9}'\Gamma_{S^{2}} - P_{H_{2}O}$

Table 8-9 Steps of for slag desulphurisation, by Reaction 8-47.

 $k = \text{rate constant}, \Gamma = \text{surface concentration}, P = \text{partial pressure}.$

In the present investigation, slag desulphurisation occurs primarily through steps 1 to 9. Slag desulphurisation is a strong function of the post combustion ratio, which would indicate that the rate limiting steps are likely to include the adsorption / dissociation of carbon dioxide, which is indicated by steps 1 to 4. Desulphurisation is also a function of the slag sulphur content, indicating that steps 7 to 9 also influence the reaction rate.

Sulphur is a surface active component. Its surface concentration can be defined by the Gibbs absorption isotherm:

$$\Gamma_{S} = -\frac{1}{RT} \frac{d\sigma}{d\ln(\%S)}$$
(8-48)

where:

 $\Gamma_{\rm S}$ = concentration of sulphur on the surface of the slag (ions / m²)

R = universal gas constant (J/K.mol)

$$T = absolute temperature (K)$$

$$\sigma$$
 = surface tension (N/m)

Agrawal *et al.*, 1983, derived the following equation for the surface concentration of sulphur, Γ_s , by processing experimental data on the surface tension of blast furnace slag, as a function of the bulk sulphur concentration. It was determined that:

$$\Gamma_{\rm s} = 2.32 \times 10^{18} \, (\% {\rm S})^{1.64} \tag{8-49}$$

where Γ_s has units of ions / m². If Γ_s is presented in mol / m², then:

$$\Gamma_{\rm s} = 3.85 \text{ x } 10^{-6} \, (\% \text{S})^{1.64} \tag{8-50}$$

It was also shown that slag desulphurisation is a first order reaction with respect to the sulphur surface concentration, Γ_s .

The slag composition used by Agrawal *et al.*, 1983 was similar to the present investigation, so using Equation 8-49, the rate of sulphur removal as a function of the surface sulphur concentration is plotted in Figure 8-12.

The plot is approximately linear, which confirms that desulphurisation of the slag is first order with respect to the surface concentration, Γ_s . Assuming that Reaction 8-47 is irreversible, its rate, R, can be presented as:

$$\mathbf{R} = \mathbf{A} \, k_l \, \Gamma_{\rm s} \, p C O_2^{\prime\prime} \tag{8-51}$$

$$R = A K (\%S)^{1.64} pCO_2''$$
(8-52)

Where R is the rate of the reaction (mol/s/m²), A is the surface area (m²), *n* is the order of the reaction with respect to the carbon dioxide partial pressure and *K* is the overall rate constant (1/s).



Figure 8-12 The rate of sulphur removal from the slag as a function of Γ_s , (surface concentration of (S) in ions/m²) at a constant post combustion ratio of 60%.

Equation 8-52 can be presented as:

$$\log\left(\frac{R}{A \ (\%S)^{1.64}}\right) = \log(k_1) + n\log(pCO_2)$$
(8-53)

The
$$\log\left(\frac{R}{A \ (\%S)^{1.64}}\right)$$
 vs log $p(CO_2)$ is plotted in Figure 8-13.



Figure 8-13 The log (sulphur removal / $(\%S)^{1.64}$) as a function of log (pCO_2).

The rate constant, *K*, for equation 8-52 was found to be 0.05 ± 0.03 .

It also follows from Figure 8-13 that the order of the reaction of desulphurisation is 1.73 \pm 0.6 with respect to *p*CO₂.

Post combustion of carbon monoxide to carbon dioxide is the main post combustion reaction. The sum of carbon monoxide and carbon dioxide is from 75 to 85 %, with the remainder primarily argon for stirring and purging. The total hydrogen, water and sulphur bearing gases is always less than 5 % for the experiments with coke.

The oxidation of sulphur from the slag by carbon dioxide therefore explains the effect of the post combustion ratio on the rate of sulphur removal from the slag to the gas phase.

Exp.	%CO ₂	S in gas	(wt %S)	Γ_{S}	%SO ₂	%H ₂ S
		$(mol/s/m^2)$		(mol/m^2)		
1	45.7	4.47E-03	0.473	1.13E-06	0.0689	
2	45.6	3.18E-03	0.104	9.41E-08	0.0568	
3	49.8	4.10E-03	0.385	8.05E-07	0.0685	
4	49.3	4.11E-03	0.266	4.39E-07	0.0590	
5	47.5	5.83E-03	0.313	5.73E-07	0.0879	
6	48.6	3.39E-03	0.456	1.06E-06	0.0510	
7	35.9	1.33E-03	0.272	4.55E-07	0.0161	
8	56.6	5.51E-03	0.477	1.14E-06	0.0945	
9	47.2	4.32E-03	0.515	1.30E-06	0.0617	
10	50.3	6.20E-03	0.277	4.69E-07	0.0940	
11	45.7	3.30E-03	0.349	6.85E-07	0.0476	
12	46.6	5.06E-03	0.337	6.47E-07	0.0718	
13	45.1	3.34E-03	0.268	4.44E-07	0.0546	
14	48.2	3.40E-03	0.267	4.42E-07	0.0569	
15	34.4	2.01E-03	0.508	1.27E-06	0.0415	
16	57.3	4.50E-03	0.402	8.64E-07	0.0834	
17	48.1	3.85E-03	0.490	1.20E-06	0.0564	
18	49.5	4.45E-03	0.265	4.36E-07	0.0575	
19	47.0	3.96E-03	0.379	7.85E-07	0.0615	
20	45.4	2.97E-03	0.171	2.13E-07	0.0633	
21	45.1	2.98E-03	0.613	1.73E-06	0.0590	
22	49.2	4.82E-03	0.641	1.86E-06	0.0718	
23	43.2	3.27E-03	0.339	6.53E-07	0.0612	
24	43.3	2.63E-03	0.144	1.60E-07	0.0557	
25	44.5	2.71E-03	0.157	1.85E-07	0.0536	
26	40.4	3.12E-03	0.226	3.36E-07	0.0574	0.0254
27	38.0	2.13E-03	0.156	1.83E-07	0.0602	0.0216
28	43.9	2.65E-03	0.333	6.35E-07	0.0537	0.0057
29	47.4	3.29E-03	0.143	1.59E-07	0.0718	0.0055

Table 8-10 Sulphur in the gas phase.

8.7 Oxygen Partial Pressure from Char / Gas and Metallic Droplets / Gas Reactions

It is assumed that iron oxide reduction by carbon proceeds through a gas film of carbon monoxide, which adheres to the surface of the carbon.

The oxygen partial pressure at the char / gas interface can be found from the reaction of carbon monoxide formation:

$$C_{(s)} + \frac{1}{2}O_{2(g)} = CO_{(g)}$$
 (8-54)

The standard Gibbs free energy for Reaction 8-54 is (Rao, 1985):

$$\Delta G^{\circ} = -112\ 877 - 86.514\ T\ (J/mol) \tag{8-55}$$

At a temperature of 1773 K the oxygen partial pressure at the char / gas interface is 2.0 x 10^{-16} atmospheres. The partial pressure of carbon monoxide is assumed to be unity at the surface of the char particle. Any carbon monoxide formed will quickly react through the Boudouard Reaction (2-24) to form carbon monoxide.

The oxygen partial pressure at the metallic droplet / slag interface can be found from the reaction of carbon monoxide formation from the dissolved carbon in the metallic droplet.

$$\underline{C} + \frac{1}{2} O_{2(g)} = CO_{(g)}$$
(8-56)

The standard Gibbs free energy for Reaction 8-54 (for the Henrian standard state) is (Rao, 1985):

$$\Delta G^{\circ} = -90\ 293 - 123.032\ T\ (J/mol) \tag{8-57}$$

For a dissolved carbon concentration in the droplet of 4 wt % and a temperature of 1773 K, the oxygen partial pressure at the surface of a metallic iron droplet is 1.3×10^{-15} atmospheres.

The oxygen partial pressure at the surface of the char and iron droplets are very similar, but they are significantly lower than the oxygen partial pressure calculated from other elemental partitioning.

8.8 Summary

Oxygen partial pressure in the slag calculated on the basis of partitioning of iron, manganese, sulphur and phosphorus between the metal and slag phases, and from the char / gas equilibrium is shown in Figure 8-14.



Figure 8-14 The oxygen partial pressure calculated from: • Fe/FeO, × Mn/MnO, \blacktriangle (S)/[S], + (P)/[P] and O C/CO equilibrium.

Spanning of the oxygen partial pressure, as assessed from the partitioning of different elements, extends over seven orders of magnitude. This indicates that there is no equilibrium between the metal and slag phases, or between the char in the slag and the gas phase.

From the view point of prediction of sulphur slag / metal partitioning, the oxygen partial pressure calculated from the phosphorus slag / metal distribution gives the most reasonable results. Although, in half of the experiments the difference in the oxygen partial pressure from the (S) / [S] and (P) / [P] equilibriums is up to two orders in magnitude.

It can be concluded that the calculation of the oxygen partial pressure in the slag / metal bath in the smelting reduction furnace on the basis partitioning of elements between the slag and metal phases is unreliable.

In the smelting reduction furnace, up to 95 % of the sulphur is removed to the gas phase. In the base case investigated, the average sulphur partitioning between the metal, slag and was as follows: metal – 8wt%, slag – 20wt% and gas – 72wt%.

Sulphur in the slag was present in the form of sulphide.

Sulphur in the gas phase was primarily present as sulphur dioxide, which is formed by the oxidation of sulphide from the slag bath.

Formation of hydrogen sulphide in the gas phase was attributed to the de-volatilisation of the coal; it increased dramatically when coke was replaced with coal.

The rate of slag de-sulphurisation is controlled by the chemical reaction rate.

The sulphur content in the gas is a strong function of the post combustion ratio. It was found that a high post combustion ratio strongly enhanced the rate of sulphur gasification. The increase in the concentration of sulphur in the slag also increased the rate of sulphur removal from the slag, although its effect was not as strong as the post combustion ratio.

The rate of sulphur removal from the slag to the gas in the experimental smelting reduction furnace was described by the following equation:

$$R = A \ 0.05 \ (\%S)^{1.64} \ pCO_2^{1.73}$$
(8-58)

9 Conclusions and Recommendations

9.1 Conclusions

Blast furnace ironmaking is challenged by alternative ironmaking technologies, which can process raw materials of lower quality, are more environmentally friendly, and more responsive to changing markets.

The aim of this project was to investigate the direct iron smelting process, particularly, behaviour of Australian coals with different volatile matter, reduction of iron ore under different operational conditions and partitioning of sulphur between metal, slag and gas phases in the direct iron smelting reduction furnace.

A laboratory smelting reduction facility was constructed on the basis of a 50 kg induction furnace. It was equipped with screw feeders to deliver raw materials, oxygen lance for coke/coal combustion and post combustion, argon bottom bubbling, temperature measurement of the furnace bath and off-gas, on-line gas sampling and analysis, extensive data logging, gas extraction and cleaning systems and water cooling.

This facility was used to examine post combustion reactions, iron ore reduction, distribution of elements between metal, slag and gas phases, carbon consumption, and mass and heat balances in the direct smelting reduction furnace under different operational conditions. In the base case, iron ore was charged at the rate of 1.5 kg/h, coke flow rate was adjusted to maintain a char fraction in the slag of 30 wt%, the oxygen flow rate was 100 Nl/min and the post combustion ratio was 60%.

The post combustion ratio was varied in the range of 45-75 % by adjusting the lance height. It was demonstrated that an increase in the lance height decreases the proportion of oxygen consumed by char combustion, increasing the volume of oxygen available for post combustion reactions. The maximum stable post combustion ratio achieved in the laboratory smelting furnace was 80 %.

Carbonaceous materials examined in this project included blast furnace coke, low volatile (17.2% & 19.5% VM), medium volatile (23.9% & 25.5% VM) and high

volatile (44.6% VM) coals. The char formed by the coal de-volatilisation was entrained into the slag. The char to slag ratio was a key factor in the operation of the smelting reduction furnace; it was essential for iron oxide reduction, combustion and slag foam stability. The furnace operation was similar for a char to slag ratio in the range of approximately 20 - 40 wt %. When the quantity of char was too high, the char would float on top of the slag decreasing the post-combustion ratio. If the quantity of char in the slag decreased below about 20% the slag would abruptly foam as the iron oxide content increased. A char to slag ratio of 30 wt % was found to be optimum for the operation of the smelting reduction furnace.

Coal de-volatilisation upon charging into the smelting reduction furnace was much higher than expected from the proximate analysis. A coal, being introduced into the high temperature furnace is heated with a high rate which causes rapid de-volatilisation, fragmentation and dusting. As the volatile matter of the coal increased, the quantity of char was reduced. During de-volatilisation of a high volatile coal (44.6% VM), the coal size was drastically reduced due to fracture, increasing the quantity of dust formed, which was then carried away by the large volume of gas generated. This high volatile yield made the coal unsuitable for the formation of char in the smelting reduction furnace, and for the furnace operation.

The post combustion ratio was strongly affected by the volatile matter content in the coal. Increasing the volatile matter content decreased the post combustion ratio, under otherwise the same conditions.

High fixed carbon and low volatile matter were found to be the most important qualities of the coal for the direct iron smelting reduction process.

The main mechanisms for iron oxide reduction was by the char particles in the slag and carbon dissolved in iron droplets. The concentration of iron oxide in the slag was found to increase with the feed rate of iron ore. The rate of iron oxide reduction in the slag exhibited a non-linear increase with iron oxide concentration, which was related to the increase in the mass-transfer coefficient in the slag and slag foaming with increasing carbon monoxide evolution at elevated iron oxide concentrations. It was demonstrated that an increase in the post combustion ratio increased the concentration of iron oxide in

the slag. This was attributed to re-oxidation of metallic droplets ejected into the gas phase and carbon depletion in the bath. A maximum iron oxide content in the slag of 10 wt% is recommended to avoid excessive slag foaming.

Sulfur metal/slag/gas partitioning was examined in the laboratory smelting reduction furnace for different carbonaceous materials, iron ore feeding rates and post-combustion ratios. Coal consumption, the sulphur content of the coal and the post combustion ratio were found to be the major factors affecting the hot metal sulphur content. Significant quantities of sulphur, up to 95%, were removed to the gas phase (in the base case 72%). Sulphur concentration in the gas phase increased with increasing sulphur content in the slag and the post combustion ratio.

Sulphur in the gas phase was found to be primarily sulphur dioxide. The rate of sulphur oxidation by the furnace gas was controlled by the chemical reaction step. The proportion of hydrogen sulphide measured in the off-gas increased dramatically when coke was replaced with coal, which was attributed to the de-volatilisation of the coal.

Oxygen potential at the slag/metal interface assessed from the sulphur partitioning was found to be in the range 5.8×10^{-13} to 1.1×10^{-15} atmospheres, which is below the oxygen partial pressure estimated from Fe/FeO or Mn/MnO ratios, above that estimated at the char/slag interface, and relatively close to the oxygen partial pressure assessed from the phosphorous slag/metal partitioning. Slag/metal equilibrium in the smelting reduction furnace is not achieved.

In the laboratory smelting reduction furnace, the primary energy sources were the combustion of char, post combustion of furnace gases and additional inductive heating to maintain the bath temperature at a constant level of 1500°C. The energy was consumed for heating and melting of charge materials, iron oxide reduction and lost with the off-gas and the cooling water. Heat losses to the water-cooling system were disproportionably large due to the small furnace capacity; because of this the heat transfer efficiency of the laboratory furnace was low and the gas temperature at the furnace exit was always less than the bath temperature.

9.2 Recommendations

The developed experimental facility proved to be a valuable tool to investigate the performance of direct iron smelting reduction; particularly the post combustion ratio, iron ore reduction, behaviour of coals with different volatile matter, sulphur partitioning, and others. However, it has a significant inherent limitation with respect to examination of the heat transfer efficiency, due to high heat loss to the water-cooling. It is recommended to supplement the experimental study of the smelting reduction processes by the mathematical CFD modelling, which will take into account non-uniformity in the gas temperature, composition and velocity, heat losses, and will be able to project the results obtained in the laboratory furnace to the industrial scale smelting reduction furnace.

This project focused on the use of coals with different volatile matter. The research can be extended to study behaviour of coals having different structure, ash content and composition and other properties. Further research is recommended to examine behaviour of different iron ores, in particular titania-ferrous ores, ores with different iron oxide concentration and gangue chemistry.

Further research into slag foaming and its role in the smelting reduction process is recommended to further the understanding of iron oxide reduction from foaming slag.

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Appendix 1 Raw Material Composition

	Whaleback	N.Z. ore	BF slag	Lime	Dolomite
	Iron ore				
SiO ₂	1.4	2.17	35.3	0.84	2.25
TiO ₂	0.04	7.36	0.861	0.066	0.038
Al ₂ O ₃	0.56	3.55	14.7	0.60	1.10
T.Fe	67.8	57.1			
FeO		24.0			
Fe ₂ O ₃		33.1	0.52	0.77	5.13
MnO			0.356	0.017	0.340
Mn	0.12	0.51			
MgO	0.04	2.92	6.85	0.67	37.07
CaO	0.13	0.66	40.4	94.15	53.97
ZnO	0.003		0.004	0.007	0.031
Na ₂ O		0.1	0.18		
K ₂ O	0.010	0.04	0.506	0.007	
P ₂ O ₅	0.090	0.13	0.02	0.033	0.096
SO ₃	< 0.005	0.120	1.60		
L.O.I.	0.9		0.4	2.7	

Table A1-1 - Raw materials compositions, wt%

	BF coke	HV1	LV1*	LV2*	MV1*	MV2*
SiO ₂	45.00	28.5	57.10	60.10	58.60	64.50
TiO ₂	1.27	1.5	1.90	1.65	2.00	1.77
Al ₂ O ₃	22.80	16.1	33.20	30.90	35.70	28.90
Fe ₂ O ₃	23.00	11.86	3.50	3.50	3.30	1.47
Mn ₃ O ₄	0.11	0.09	0.03	0.04	0.04	0.02
MgO	0.61	3.7	0.40	0.50	0.60	0.43
CaO	2.27	38.0	1.10	0.70	1.40	0.20
Na ₂ O	0.46	2.2	0.40	0.50	0.40	0.54
K ₂ O	0.68	0.45	0.90	1.00	0.70	0.90
P ₂ O ₅	0.115	0.42	0.70	0.50	0.60	0.10
SO ₃	0.93		0.20	0.16	0.20	0.05
L.O.I.	1.96		0.57	0.45	0.46	1.12
Fixed C	84.6	49.7	72.4	70.2	65.5	64.6
water	1.4	19.1	0.9	1.0	1.0	1.7
V.M.	0.3	44.6	17.2	19.5	25.5	23.9
ash	13.5	5.7	9.5	9.3	8.0	9.8
sulfur	0.41	0.29	0.65	0.55	0.50	0.55

Table A1-2 – Composition of carbonaceous materials, wt%.

*Source: Queensland coals, 1986.

Appendix 2 Chemical Analysis

Exp.	SiO ₂	CaO	MgO	Al ₂ O ₃	FeO	MnO	TiO ₂	P ₂ O ₅	SO ₃	ZrO ₂
1	24.87	29.74	16.04	8.24	2.62	2.217	0.815	0.380	0.473	1.327
2	31.91	25.16	12.23	13.09	3.45	1.580	3.025	0.102	0.104	1.263
3	30.08	32.76	15.40	11.75	2.38	2.698	0.977	0.167	0.385	1.527
4	30.90	30.29	16.99	10.35	3.19	2.768	0.994	0.223	0.266	1.474
5	30.66	30.22	20.57	10.26	5.27	1.721	0.896	0.096	0.313	1.479
6	25.26	24.57	25.15	7.23	4.05	1.455	4.855	0.070	0.456	1.082
7	28.88	23.25	27.60	11.16	1.94	1.955	0.777	0.086	0.272	1.842
8	27.29	22.09	33.23	9.35	4.02	0.893	0.542	0.080	0.477	1.503
9	31.93	30.97	16.48	10.55	3.28	1.349	1.061	0.111	0.515	1.111
10	30.88	30.05	16.36	10.74	1.97	1.163	0.990	0.239	0.277	2.144
11	30.59	26.61	20.27	9.50	6.32	2.511	1.019	0.122	0.349	1.708
12	32.99	30.44	6.25	16.35	2.31	2.944	1.074	0.086	0.337	1.319
13	31.52	30.11	6.74	13.99	5.81	3.297	0.902	0.386	0.268	1.601
14	31.84	31.83	7.67	12.24	6.36	2.668	0.979	0.182	0.267	1.369
15	34.89	29.79	6.85	14.16	2.77	1.826	1.066	0.140	0.508	1.489
16	33.30	32.48	7.43	13.00	5.01	1.153	0.720	0.134	0.402	1.603
17	30.69	26.98	5.78	19.28	1.87	0.711	7.575	0.049	0.490	1.142
18	27.59	28.02	5.59	13.37	4.07	0.673	0.714	0.172	0.265	1.832
19	40.21	30.58	5.58	12.25	2.73	1.631	1.168	0.121	0.379	1.083
20	38.80	24.68	5.10	19.15	3.44	1.608	1.162	0.088	0.171	1.062
21	34.24	35.76	7.29	12.94	2.70	0.813	0.904	0.074	0.613	0.920
22	32.59	29.17	6.66	14.51	1.39	1.184	9.007	0.056	0.641	1.210
23	35.28	36.83	4.47	13.09	1.32	1.114	3.226	0.084	0.339	1.391
24	35.21	31.68	5.21	10.79	3.74	2.738	1.235	0.213	0.144	1.064
25	33.79	31.94	5.69	13.67	3.59	1.308	1.077	0.043	0.157	1.115
26	36.73	23.14	5.69	19.26	2.68	2.527	0.994	0.060	0.226	3.256
27	38.06	28.53	4.15	14.68	2.52	4.510	1.063	0.052	0.156	1.445
28	28.33	20.60	6.22	21.76	1.44	1.441	15.898	0.022	0.333	2.399
29	33.60	26.38	5.76	16.53	4.03	2.893	2.038	0.143	0.143	1.554

Table A2-1 – Slag Composition, wt%.

Exp.	С	Si	Mn	Р	S
1	4.55	0.010	0.349	0.130	0.045
2	4.65	0.010	0.226	0.144	0.030
3	4.69	0.010	0.393	0.091	0.045
4	4.17	0.010	0.765	0.127	0.051
5	4.69	0.010	0.396	0.137	0.028
6	4.62	0.072	0.522	0.134	0.049
7	4.46	0.010	0.293	0.127	0.037
8	4.70	0.248	0.484	0.150	0.111
9	4.55	0.010	0.323	0.161	0.036
10	4.62	0.010	0.183	0.116	0.049
11	4.67	0.010	0.282	0.124	0.053
12	4.62	0.010	0.327	0.157	0.052
13	4.43	0.113	0.415	0.140	0.059
14	4.59	0.010	0.277	0.091	0.042
15	4.49	0.031	0.543	0.111	0.043
16	4.68	0.543	0.542	0.098	0.029
17	4.86	0.451	0.501	0.084	0.039
18	4.58	0.587	0.654	0.105	0.040
19	4.44	0.473	0.509	0.116	0.033
20	4.69	0.159	0.324	0.120	0.034
21	4.74	0.122	0.557	0.141	0.040
22	4.58	0.072	0.408	0.135	0.052
23	4.53	0.185	0.582	0.142	0.031
24	4.67	0.010	0.354	0.124	0.044
25	4.58	0.010	0.384	0.115	0.064
26	4.51	0.069	0.405	0.148	0.058
27	4.23	0.010	0.574	0.138	0.061
28	4.80	0.153	0.417	0.127	0.036
29	4.20	0.010	0.382	0.150	0.089

Table A2-2 – Metal Composition, wt %.

Table	A2-3 -	- Gas	Composition,	vol%.
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Exp.	N ₂	O ₂	Ar	CO ₂	СО	H ₂	H ₂ O	SO ₂	H ₂ S
1	2.11	0.80	17.9	45.7	31.0	0.304	2.18	0.069	
2	2.15	0.67	21.1	45.6	28.4	0.242	1.84	0.057	
3	0.56	0.78	19.4	49.8	27.7	0.173	1.52	0.069	
4	0.19	0.48	16.9	49.3	30.9	0.244	2.01	0.059	
5	1.08	0.54	17.2	47.5	31.4	0.245	1.95	0.088	
6	0.86	0.48	17.9	48.6	30.1	0.208	1.87	0.051	
7	0.58	0.43	17.4	35.9	43.9	0.521	1.29	0.016	
8	0.95	0.35	19.2	56.6	20.7	0.200	1.96	0.094	
9	0.49	0.18	16.7	47.2	32.9	0.397	2.03	0.062	
10	0.64	0.24	17.2	50.3	29.7	0.279	1.63	0.094	
11	0.59	0.25	17.3	45.7	32.3	0.638	3.23	0.048	
12	1.26	0.41	16.4	46.6	32.4	0.480	2.41	0.072	
13	0.79	0.58	15.9	45.1	34.1	0.514	2.95	0.055	
14	0.52	0.48	14.8	48.2	33.0	0.340	2.65	0.057	
15	1.26	0.55	18.8	34.5	42.6	0.665	1.60	0.042	
16	0.87	0.84	15.6	57.3	21.6	0.096	3.57	0.083	
17	0.45	0.55	13.0	48.1	33.5	0.434	3.96	0.056	
18	0.01	0.53	11.4	49.5	34.9	0.341	3.27	0.057	
19	1.43	0.57	13.6	47.0	33.8	0.489	3.06	0.061	
20	1.01	0.41	18.7	45.4	31.8	0.360	2.38	0.063	
21	1.42	0.52	17.4	45.1	32.3	0.453	2.75	0.059	
22	0.90	0.15	12.9	49.2	33.4	0.614	2.74	0.072	
23	1.81	0.39	16.4	43.2	29.5	4.714	3.89	0.061	
24	1.21	0.18	18.8	43.3	28.2	4.710	3.53	0.056	
25	1.22	0.20	17.6	44.5	28.7	3.761	4.02	0.054	
26	1.87	0.41	21.3	40.4	27.8	3.785	4.39	0.057	0.0250
27	2.49	0.67	16.0	38.0	31.0	4.877	4.94	0.060	0.0220
28	1.94	0.71	18.0	43.9	32.5	0.565	2.38	0.054	0.0060
29	2.24	0.94	18.9	47.4	28.1	0.297	2.12	0.072	0.0060

Note: Hydrogen sulphide was only measured for the last 4 experiments

Appendix 3 Experimental Data

Experiment	Inlet water,	Top water,	Bottom water,	lid water,
Number	°C	°C	°C	°C
Water flowrate		23 l/min	23 l/min	42 l/min
1	24.9	27.6	32.4	28.3
2	24.8	27.1	31.8	28.6
3	25.0	27.8	32.6	28.9
4	24.8	29.2	32.7	28.5
5	26.1	29.5	35.0	29.8
6	23.8	28.6	34.2	27.2
7	24.3	27.6	32.0	27.3
8	23.0	27.7	30.5	26.6
9	25.7	29.4	33.9	28.9
10	26.9	31.5	35.3	30.3
11	25.5	29.7	34.6	28.2
12	24.1	27.9	31.5	27.2
13	24.7	28.5	32.7	27.8
14	24.7	28.0	32.4	28.1
15	26.2	29.0	33.4	29.1
16	25.7	29.3	33.5	29.7
17	24.2	28.4	32.9	27.7
18	25.3	28.6	32.8	29.3
19	25.2	28.0	32.3	28.4
20	24.7	27.6	31.9	28.3
21	25.2	28.5	32.5	28.9
22	19.3	23.6	28.4	22.9
23	17.8	21.1	26.0	21.2
24	17.4	20.5	24.9	20.5
25	17.9	20.6	24.8	20.4
26	18.2	22.0	25.7	22.9
27	19.2	23.1	27.4	24.0
28	20.5	24.8	29.2	24.8
29	20.3	23.7	27.8	24.2

Table A3-1 – Water temperatures for the bottom half of the furnace, top half of the furnace and the lid / lance.

Experiment	Description
Number	
1	Base case, 60% PCR, 1.5 kg iron ore/h, oxygen 100 Nl/min, coke
2	N.Z. ore, 60 % PCR, 1.5 kg iron ore/h
3	Base case, 60% PCR, 1.5 kg iron ore/h, oxygen 100 Nl/min, coke
4	Base case, 60% PCR, 1.5 kg iron ore/h, oxygen 100 Nl/min, coke
5	2 kg/hr ore, 60% PCR
6	N.Z. ore, 60% PCR
7	45 % post combustion ratio
8	75 % post combustion ratio
9	Base case, 60% PCR, 1.5 kg iron ore/h, oxygen 100 Nl/min, coke
10	Oxygen flowrate 130 Nl/min
11	2.4 kg/hr ore, 60% PCR
12	Base case, 60% PCR, 1.5 kg iron ore/h, oxygen 100 Nl/min, coke
13	2 kg/hr ore, 60% PCR
14	2 kg/hr ore, 60% PCR
15	45% post combustion ratio
16	75% post combustion ratio
17	N.Z. ore, 60% PCR
18	Oxygen flowrate 130 Nl/min
19	Base case, 60% PCR, 1.5 kg iron ore/h, oxygen 100 Nl/min, coke
20	Base case, 60% PCR, 1.5 kg iron ore/h, oxygen 100 Nl/min, coke
21	Base case, 60% PCR, 1.5 kg iron ore/h, oxygen 100 Nl/min, coke
22	N.Z. ore, 60% PCR
23	Norwich coal, 60% PCR
24	Goonyella coal, 60% PCR
25	Saraji coal, 60% PCR
26	Saraji coal, 60% PCR
27	Riverside coal, 60% PCR
28	N.Z. ore, 60% PCR
29	Post combustion ratio varied from 45% to 75%

Table A3-2 – Experimental description

Note: All experiments were performed under the same conditions as the base case, except as noted in the description for that experiment.

Experiment	gas temp,	lid temp.,	gas duct	gas C,	argon flow,
Number	°C	°C	temp.,°C	kg/h	l/min
1	1226	65.6	220	6.05	40
2	1358	81.2	225	4.77	40
3	1258	78.7	185	5.94	40
4	1234	61.0	140	6.15	40
5	1363	88.9	245	6.35	40
6	1238	81.7	210	6.14	40
7	1133	58.0	282	6.64	40
8	1395	108.9	160	5.86	40
9	1163	90.0	260	6.69	40
10	1047	87.1	273	6.53	40
11	1033	74.0	212	6.72	40
12	1244	73.8	232	6.19	40
13	1069	75.5	228	6.43	40
14	1157	88.0	217	6.68	40
15	1086	79.3	299	6.56	40
16	1321	85.7	130	5.96	30
17	1125	89.7	217	9.92	30
18	1322	109.2	268	9.31	30
19	1197	76.8	220	8.57	30
20	1143	75.4	234	5.97	30
21	1240	96.8	219	6.30	30
22	1135	86.6	77	8.55	30
23	1233	98.5	117	6.64	30
24	1176	125.5	109	6.60	30
25	1260	52.7	40	6.27	30
26	1366	112.7	159	6.81	30
27	1389	128.3	228	6.78	30
28	1220	112.0	204	6.10	30
29	1301	102.6	151	5.85	30

Table A3-3 – Temperature of the off-gas, furnace lid and gas ducting, carbon flowrate in the gas phase and argon injection rate.

Note: Gas C is the flowrate of carbon leaving the furnace calculated from the mass balance on the gas phase.

Experiment	Inlet water,	bottom water,	top water,	lid water,
Number	°C	°C	°C	°C
1	24.9	27.6	32.4	28.3
2	24.8	27.1	31.8	28.6
3	25.0	27.8	32.6	28.9
4	24.8	29.2	32.7	28.5
5	26.1	29.5	35.0	29.8
6	23.8	28.6	34.2	27.2
7	24.3	27.6	32.0	27.3
8	23.0	27.7	30.5	26.6
9	25.7	29.4	33.9	28.9
10	26.9	31.5	35.3	30.3
11	25.5	29.7	34.6	28.2
12	24.1	27.9	31.5	27.2
13	24.7	28.5	32.7	27.8
14	24.7	28.0	32.4	28.1
15	26.2	29.0	33.4	29.1
16	25.7	29.3	33.5	29.7
17	24.2	28.4	32.9	27.7
18	25.3	28.6	32.8	29.3
19	25.2	28.0	32.3	28.4
20	24.7	27.6	31.9	28.3
21	25.2	28.5	32.5	28.9
22	19.3	23.6	28.4	22.9
23	17.8	21.1	26.0	21.2
24	17.4	20.5	24.9	20.5
25	17.9	20.6	24.8	20.4
26	18.2	22.0	25.7	22.9
27	19.2	23.1	27.4	24.0
28	20.5	24.8	29.2	24.8
29	20.3	23.7	27.8	24.2

Table A3-4 – Water temperatures, common inlet, bottom and top of induction furnace, furnace lid and lance.