# Scale Formation in a Walking-Beam Steel Reheat Furnace

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#### Abstract

In hot strip mills, in the steel industry, reheat furnaces are utilized to reheat slabs, billets, blooms, etc., to uniform 10lling temperatures prior to hot working.

During this reheating operation, hot steel surfaces react with the in-furnace oxidizing atmosphere resulting in the formation of an iron oxides layer (scale). The yield loss due to this phenomenon depends on furnace operating conditions, i.e. steel temperature, excess combustion air, steel residence time in the furnace, etc., and ranges between 1.5 to 3% of reheated steel.

In this research, the oxidation of a mild steel during reheating cycles as a function of furnace atmosphere, steel residence time in the furnace and steel temperature was investigated.

It has been found that scale formation was most sensitive to oxygen levels in the furnace, steel residence time and temperature. A saving of up to 35% of steel lost to scale was achieved by reducing the excess air in the furnace from 70% to 20%. Also, longer residence time and higher temperatures of the steel in the furnace resulted in the formation of excessive amounts of scale.

#### **K**ésumé

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En sidérurgie, des fournaises sont utilisées pour réchauffer des brames, des lingots et des billettes, avant le laminage à chaud, afin de porter l'acier à la température de travail à chaud.

Au cours de l'opération de chauffage, les surfaces chaudes de l'acier réagissent avec l'atmosphère de la fournaise pour former une couche d'oxyde de fer (calamine). Les pertes de production dues à ce phénomène dépendent des conditions d'opération de la fournaise (i.e. la température de l'acier, l'excès d'air de combustion, le temps de résidence dans la fournaise, etc.) et varies entre 1.5 et 3% de l'acier réchauffé.

Dans la présente étude, l'oxydation d'acier doux durent des cycles de chauffage a été étudié en fonction de l'atmosphère de la fournaise, du temps de résidence de l'acier dans la fournaise et de la température de l'acier.

Il a été démontré que la formation de calamine était particulièrement sensible au niveau d'oxygène dans la fournaise, au temps de résidence et à la température de l'acier. Les pertes d'aciers dues à la calamine ont pu être réduites jusqu'à 35% en diminuant l'excès d'air de combustion dans la fournaise de 70 à 20%. De plus, les temps de résidence plus long ainsi que des températures plus élevées ont résulté en des formations importantes de calamine.

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# CHAPTER ONE

# INTRODUCTION

Reheat furnaces and soaking pits, in steel plants, are used to heat slabs, blooms, billets and ingots to a uniform rolling temperature prior to hot working. Nowadays, soaking pits, which are batch units, are being constantly replaced by reheat furnaces, especially in steel plants with high production rates. Reheat furnaces can be classified as batch type or continuous type. Continuous type include pusher, rotary-hearth, walking-beam and roller-hearth type furnaces. In all of these, walking-beam reheat furnaces are considered "state of the art". These furnaces are direct-fired with the fuel being either natural gas, coke oven gas, synthetic gas ( a mixture of methane gas, air and coke oven gas), blast furnace gas or fuel oil.

The walking-beam reheat furnace under investigation, described in detail in Chapter Three, is used to reheat slabs of different sizes. The steel slabs can be charged at different temperatures, i.e., warm (directly from the continuous caster), ambient temperature (from the slab yard) or/and mixed. The thickness of the slabs in most cases is constant. A wide variety of steel

**1** IN **FRODUCTION** 

grades is also common.

As the slabs are walked through the furnace, their temperatures rise. However, the rate of temperature increase depends on the firing rates in the individual zones of the furnace. In the early stages of reheating, the slabs are exposed to low heating rates to avoid the development of thermal stresses. The slabs are then exposed to intense heating up to the soak zone, where soaking temperatures are maintained to achieve a uniform slab temperature for subsequent rolling.

As the steel surface temperature rises, it reacts with the furnace oxidizing atmosphere ( $O_2$ ,  $CO_2$ ,  $H_2O$ , etc.) producing an oxide layer (scale layer). The thickness of the scale layer depends on slab residence time in the furnace, its surface temperature, the aggressiveness of the oxidizing atmosphere, etc.. The loss of steel due to scaling typically ranges between 1 and 3% of approximately 27 cm thick slabs being reheated, depending on the above parameters.

There are a number of advantages and disadvantages to scale formation on slabs. The advantages are: (1) scale eliminates surface defects such as impurities of mould powder embedded in the surface from the continuous caster, oxides and surface cracks, and hence results in smooth and clean steel surface, (2) the heat given-off to the steel during the oxidation process (exothermic reactions), which accounts for about 2 to 3% of total heat input and (3) the scale layer reduces the heat flux from the slab to the environment (due to its lower thermal conductivity) when the slabs are transported to the rolling mill. The disadvantages of scale formation include: (1) steel loss representing a mass loss between 1 to 3% of the slab depending of furnace operating conditions and slab thickness, (2) scale pile-ups inside the furnace and slab transport path which requires a furnace shut-down period for cleaning and (3) hindered heat transfer from the furnace environment into the steel, necessitating longer heating cycles.

It is important then to minimize scale formation during reheating to a level to which it is advantageous. This of course requires a full investigation of all relevant parameters in the operation of the furnace. However, because of the complexity of the process, i.e., industrial I. INTRODUCTION

conditions, and time constraints, a thorough investigation of all parameters was not possible in the present work. Consequently, in this thesis, the work was limited to the following, (1) air/fuel ratio and its effect on scale formation and (2) slab residence time in the furnace at different furnace locations. The work also involved a number of pre-trials in order to develop a procedure for the full trials.

In summary, the objective of this research was to investigate scale formation of a particular steel grade in an industrial steel reheat furnace. The aim was to gain knowledge on the important parameters affecting scale formation in practice and hence to control its formation to a level where it is advantageous.

In this thesis, Chapter Two presents a literature review on the oxidation of iron and some steels of interest with the aid of some general mathematical treatments for the oxidation of metals. The emphasis is put on the work that relates directly or indirectly to steel oxidation in reheat furnaces. Chapter Three presents the objectives of this work in more details, procedures and equipment for the trials. Chapter Four presents the experimental methodology and use of equipment. In Chapter Five, the analytical techniques and data processing are considered. The discussion of the results are presented in Chapter Six, followed by conclusions and suggested future work in Chapter Seven.

#### **2.1 INTRODUCTION**

There has been no shortage of research into the isothermal oxidation of iron and steel since the 1920's. The kind of work conducted can be divided into three parts, (1) the study of the properties of iron oxides, in particular wustite (FeO), (2) oxidation mechanisms under isothermal conditions and constant oxidizing atmospheres and (3) the effect of alloying elements on the oxidation of steel. However, very little work has been done on the oxidation of iron and steel in complex atmospheres and at different heating rates approximating those in a reheat furnace.

In this chapter, a literature review on the characteristics of iron oxides and their properties, the mathematical treatment of metal oxidation, especially iron, and the high temperature oxidation characteristics of iron and some steels under fixed conditions, such as temperature and oxidizing atmosphere, is presented.

Because of the wide range of studies undertaken on various steels, only work on those steels of interest was considered. The emphasis was placed on work that related, directly or indirectly, to the oxidation of steels in industrial reheat furnaces.

#### **2.2 THERMODYNAMICS AND CHARACTERISTICS OF IRON OXIDES**

When the surface of pure iron is in contact with an oxidizing atmosphere at high temperature, an oxide layer consisting of wustite, magnetite and hematite, forms. This can be best illustrated by the well known Ellingham/Richardson diagram, Figure (2.1), *Per Kofstad<sup>1</sup>*. The stable oxides of iron form, respectively with increasing temperature and oxygen partial pressure, according to the reactions:

$$3 Fe + 2 O_2 = Fe_3 O_4 \tag{2.1}$$

$$2Fe + O_2 = 2FeO \tag{2.2}$$

$$6 FeO + O_2 = 2 Fe_3O_4 \tag{2.3}$$

$$4 Fe_{2}O_{4} + O_{5} = 6 Fe_{2}O_{5}$$
(2.4)

It can be seen that iron oxidizes at very low oxygen partial pressures, e.g. at a temperature of 800 °C, equation (2.2) is at equilibrium with an oxygen partial pressure of 2 x  $10^{19}$  atm.

At temperatures higher than approximately 600 °C, the percent composition of the three oxides, wustite, magnetite and hematite are about 95, 4 and 1% respectively, Figure (2.2), *Tylecote and Mitchell<sup>2</sup>*, Sachs and Tuck<sup>3</sup>.

## 2.2.1 Wustite

Wustite is the inner most phase of the scale which forms next to the metal and is the most iron rich. Wustite, nominally represented as FeO, is a p-type conductor and is not stable below

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approximately 570 °C, *Himmel, Mehl and Birchenall*<sup>4</sup>. The density of wustite is about 5.87 g/cm<sup>3</sup>, Samsonov<sup>5</sup>.



Figure (2.1) Ellingham/Richardson diagram for some oxides of importance in the high temperature oxidation of metals and alloys, *Per Kofstad<sup>1</sup>*.

The wustite phase is highly metal deficient,  $Fe_{1,0}O$ , with its defect structure commonly interpreted in terms of doubly charged iron ion vacancies with an equivalent number of electron defects.

As a consequence, diffusion is essentially cationic via vacant cation sites, *Per Kotstad and Zeev*  $Hed^6$ , *Kubaschewski and Hopkins<sup>7</sup>*, *Birks and Meter<sup>8</sup>*. Wustite exists as a thermodynamically stable, single phase structure, over a wide range of composition. The non-stoichiometry of wustite increases with increasing temperature and does not seem to reach the stoichiometric composition FeO, Figure (2.3).



Figure (2.2) Approximate percentages of FeO, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, Sachs and Tuck<sup>3</sup>.

The non-stoichiometry as a function of temperature and oxygen partial pressure has been the subject of several investigators, and the results of various studies are in good agreement, Figure (2.4), *Per Kofstad and Zeev Hed*<sup>6</sup>.



Figure (2.3) The iron-oxygen diagram, Per Kofstad<sup>1</sup>.



Figure (2.4) Non-stoichiometry in wustite, y in  $Fe_{t,y}O$ , as a function of temperature and partial pressure of oxygen, *Per Kofstad and Zeev Hed*<sup>6</sup>.

### 2.2.2 Magnetite

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The magnetite phase,  $Fe_3O_4$ , is the intermediate phase of the scale. It is also a p-type conductor and is the main equilibrium constituent of scale below 500 °C. Its crystal structure is cubic inverse spinel,  $Hauffe^9$ . Magnetite has a density range of 5 to 5.4 g/cm<sup>3</sup>. It exists as a metal deficient oxide but at a much smaller level than wustite. It has been shown from marker and diffusion studies that both cations and anions diffuse in Fe<sub>3</sub>O<sub>4</sub>, *Hummel, mehl and Birchenell<sup>4</sup>*, *Kubachewski and Hopkins<sup>7</sup>*.

## 2.2.3 Hematite

The hematite phase,  $Fe_2O_3$ , is the outer most layer of the scale and has the highest oxygen content. Hematite is an n-type conductor and forms at temperatures above approximately

Birchenell<sup>4</sup>, Giryburg<sup>10</sup>.

800 °C. It exists in two forms,  $\alpha - Fe_2O_3$  which has a rhombohedral structure, and  $\gamma - Fe_2O_3$ , which is cubic, *Birks and Meier*<sup>9</sup>. The density of hematite is about 5.24 g/cm<sup>3</sup>. Diffusion in hematite is mainly by the migration of anions, *Kubachewski and Hopkins*<sup>7</sup>, *Himmel, Mehl and* 

# **2.3 THE OXIDATION OF METALS**

Before considering the oxidation of iron and steel, it is worthwhile presenting a general review of the mathematical developments in the oxidation of metals.

When an oxide layer forms on a metal surface, its growth, in the absence of any porosity, microchannels or cracks, continues by the inward or outward migration of anions, cations or both. This is independent of whether the controlling step of the growth is the chemical reaction at one of the reaction interfaces, i.e., metal-oxide or oxide-gas, or the rate of the diffusing species through the oxide layer. Wagner presented in 1933, what has now become a widely accepted theory on the oxidation of metals. In his theory, which is applicable to the oxidation of any metal, he assumed that oxide growth is strictly controlled by the diffusion of one ion, anion or cation, with the transport of electrons in the opposite direction to keep electoneutrality through the growing oxide layer. Before summarizing Wagner's theory, a simplified treatment is given for the diffusion controlled mechanism of oxidation.

### 2.3.1 Simplified Treatment of Diffusion Controlled Oxidation

With the assumption that transport of ions through the oxide layer is the controlling mechanism for oxidation and that chemical equilibrium is catablished at reaction interfaces, the process can be analyzed as follows, *Birks and Meier<sup>9</sup>*. The outward cationic flux,  $J_{M^{2^*}}$ , must be equal and

opposite in direction to the inward vacancy flux,  $j_{V_{\mu}}$ , Figure (2.5).





Thus

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$$J_{M^{2}} = -J_{V_{M}} = D_{V_{M}} \frac{C''_{V_{M}} - C'_{V_{M}}}{x}$$
(2.5)

Where  $D_{V_M}$ , x,  $C''_{V_k}$  and  $C'_{V_M}$  are the diffusion coefficient, oxide layer thickness and vacancy concentrations at scale-gas and scale-metal interfaces respectively.

Since thermodynamic equilibrium is assumed at the interfaces, the value  $(C''_{\nu_{\mu}} - C'_{\nu_{\mu}})$  is constant and thus

T

$$j_{V_{M}} = const. \ \frac{dx}{dt} = D_{V_{M}} \frac{(C''_{V_{M}} - C'_{V_{M}})}{x}$$
 (2.6)

Taking 
$$k' = D_{V_M} \frac{(C''_{V_M} - C'_{V_M})}{const.}, \text{ i.e.}$$

$$\frac{dx}{dt} = \frac{k'}{x} \tag{2.7}$$

Integrating the above equation from x=0 at t=0 to x=X at t=t, we get

$$X^2 = 2k't \tag{2.8}$$

Which is the common parabolic rate constant.

## 2.3.3 Wagner's Theory of Oxidation

Wagner's theory provides a mathematical treatment for the oxidation of metals. Even though it is one of the more famous theories, it is nonetheless relatively simple. The conditions for which the theory applies, Figure (2.6), Birks and Meier<sup>9</sup>, are as follows:

- (1) Oxidation proceeds only by the transport of one ion, cation or anion, with the transport of an equivalent number of electrons in the opposite direction, through the oxide layer.
- (2) Chemical equilibrium is established throughout the scale and at reaction interfaces.
- (3) The oxide phase shows negligible deviation from stoichiometry.
- (4) Oxygen solubility in the metal is negligible.
- (5) The thickness of the scale does not alter the effectiveness of space charge.
- (6) The oxide phase is compact and does not contain any porosity, microchannels or cracks.
- (7) The oxide layer is perfectly adherent.



Overall reaction:  $2M + O_2 = 2MO_1 \Delta G_{MO}^{\bullet}$ 



Since equilibrium is established at the reaction interfaces, metal ions and oxygen ions will tend to migrate across the oxide layer in opposite directions and because of the charge of ions, an electric field will be set up across the scale resulting in the migration of electrons from the metal to the atmosphere to provide neutrality in the oxide phase.

Chemical and electrical potential gradients across the scale will exist as a result of the charged ions providing the driving force for ionic migration.

The force acting upon a charged particle, i, (joules particle<sup>-1</sup> cm<sup>-1</sup>) at any location in the scale where chemical and electrical potentials are present is expressed by

$$\frac{1}{N_A} \left( \frac{\partial \mu_{\pm}}{\partial x} + Z_i F \frac{\partial \Phi}{\partial x} \right)$$
 (2.9)

where  $\frac{\partial \mu_i}{\partial x}$ ,  $\frac{\partial \phi}{\partial x}$ ,  $N_A$ ,  $Z_i$ , F are the chemical potential, electric potential, Avogadro's number, particle charge and Faraday constant respectively.

Moving through an ionic lattice under a constant force, an ion rapidly assumes a constant velocity known as the terminal drift velocity. The value of the terminal drift velocity when the ion is acted on by unit force is known as the mobility,  $B_1$ , of the species. Therefore, the flux of i (particle cm<sup>-2</sup> s<sup>-1</sup>), acted on by the force given in equation (2.9), is

$$j_{i} = \frac{c_{i}B_{i}}{N_{A}} \left(\frac{\partial \mu_{i}}{\partial x} + Z_{i}F\frac{\partial \Phi}{\partial x}\right)$$
(2.10)

where  $c_i$  is the concentration of i in particle cm<sup>-3</sup>.

The mobility and partial conductivities of particles, i, are related by

$$c_i B_i = \frac{\sigma_i}{Z_i^2 e^2}$$
(2.11)

Where  $\sigma_i$ , e are the partial electrical conductivity and electronic charge respectively.

Hence

$$j_{i} = \frac{\sigma_{i}}{Z_{i}^{2}F^{2}} \left( \frac{\partial \mu_{i}}{\partial x} + Z_{i}F\frac{\partial \phi}{\partial x} \right)$$
(2.12)

Equation (2.12) describes the flux of cations, anions, or electrons through the oxide layer. Due to their different mobilities, different species would tend to move at different rates, however, this would set up an electric field tending to oppose this independence. The rates of migration are dictated by the necessity to maintain electroneutrality throughout the scale. The predominant mobile species in oxides are cations and electrons. Taking  $Z_c$ ,  $Z_e$  and  $j_c$  as the cation charge, electron charge and cation flux respectively and knowing that for electroneutrality the condition

$$Z_{c}j_{c} + Z_{e}j_{e} = 0 (2.13)$$

must be met, the cationic flux is expressed as

$$j_{c} = -\frac{\sigma_{c}\sigma_{e}}{Z_{c}^{2}F^{2}(\sigma_{c}+\sigma_{e})}\left[\frac{\partial\mu_{c}}{\partial x} + \frac{Z_{c}}{Z_{e}}\frac{\partial\mu_{c}}{\partial x}\right]$$
(2.14)

The ionization of a metal, M, is represented by  $M = M^{Z_c} + Z_c e^{-1}$ , and hence at equilibrium

$$\mu_M = \mu_c + Z_c \mu_e \tag{2.15}$$

From equations (2.14) and (2.15)

$$j_{c} = -\frac{\sigma_{c}\sigma_{e}}{Z_{c}^{2}F^{2}(\sigma_{c} + \sigma_{e}h)}\frac{\partial\mu_{M}}{\partial x}$$
(2.16)

Equation (2.16) gives the cationic flux at any position in the scale. It is necessary to express the flux of cations in terms of scale thickness and the measurable metal chemical potential at the metal/scale,  $\mu'_{M}$ , and scale/gas,  $\mu''_{M}$ , interfaces, i.e.

$$j_{c} = -\frac{1}{Z_{c}^{2}F^{2}x}\int_{\mu'_{M}}^{\mu''_{M}}\frac{\sigma_{c}\sigma_{e}}{\sigma_{c}+\sigma_{e}}d\mu_{M}$$
(2.17)

If the concentration of metal in the oxide scale is  $C_M$  (mol cm<sup>-3</sup>) then the flux may also be expressed by

$$J_c = C_M \frac{dx}{dt}$$
(2.18)

where x is the oxide scale thickness.

From equation (2.7), the parabolic rate constant is expressed as

$$\frac{dx}{dt}=\frac{k'}{x}$$

.

comparing equations 2.17, 2.18 and 2.7, the parabolic rate constant is expressed as

$$k' = \frac{1}{Z_c^2 F^2 C_\chi} \int_{\mu''_M}^{\mu'_M} \frac{\sigma_c \sigma_e}{\sigma_c + \sigma_e} d\mu_M$$
(2.19)

The mobility,  $B_i$ , and diffusion coefficient,  $D_i$ , of a species are related by the Nernst-Einstein equation as

$$D_{i} = B_{i} k T \tag{2.20}$$

where k is Boltzmann's constant and T is absolute temperature.

From Equations 2.11, 2.20 we have

$$D_{i} = \frac{k T \sigma_{i}}{Z_{i}^{2} e^{2} c_{i}}$$
(2.21)

where  $c_i$  is the concentration in particles  $cm^{-3}$ , Thus

$$D_{i} = \frac{RT}{Z_{i}^{2}F^{2}C_{i}}$$
(2.22)

where  $C_1$  is the concentration in mols cm<sup>-3</sup>

From Equations 2.19, 2.20 and 2.21 we have

$$k' = \frac{1}{RT} \int_{\mu'_{M}}^{\mu''_{M}} D_{M} d\mu_{M}$$
(2.23)

and

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$$k' = \frac{1}{RT} \int_{\mu'_{x}}^{\mu''_{x}} D_{\chi} d\mu_{x}$$
(2.24)

for the parabolic rate constant, where  $D_M$  and  $D_X$  are the diffusion coefficients for metal, M, and non-metal, X, through the scale respectively.

Equations 2.23 and 2.24 are written in terms of variables that can be measured relatively easily, although it is assumed that the diffusion coefficient is a function of the chemical potential of the species involved. Thus, in order to be able to calculate values of the parabolic rate constant, the relative diffusion coefficients must be known as a function of the chemical potential of the mobile species. Such data are frequently not available or are incomplete. Further more, it is usually easier to measure the parabolic rate constant directly than to carry out experiments to measure the diffusion data. Thus the real value of Wagner's analysis lies in providing a complete mechanistic understanding of the process of high temperature oxidation under the conditions set out.

### **2.4 THE OXIDATION OF PURE IRON**

The oxidation of pure iron in oxygen environments will be considered first to serve as a basis for studying the oxidation behaviour of steels.

#### 2.4.1 Oxidation Mechanism

The oxidation of pure iron over a wide range of temperatures has been studied extensively. The results of that research has revealed that the controlling mechanism is by the diffusion of ions through the oxide layer and hence the parabolic behaviour, Figure (2.7), Davies, Simand and Birchenall<sup>11</sup>, Paidassi<sup>12</sup>, Schmahl, Baumann and Schenck<sup>13</sup>, Stanley, Hoene and Hutoon<sup>14</sup>, Sacks and Tuck<sup>3</sup>.

The oxidation process is controlled namely by cation transport through wustite and magnetite, *Tylecote and Mitchell*<sup>2</sup>. In the hematite phase, diffusion is mainly by anions, *Sachs and Tuck*<sup>3</sup>. However, oxygen diffusion through wustite and magnetite cannot be ruled out, in fact studies by *Engill and Wever*<sup>15</sup>, *Davies, Simand and Birchell*<sup>11</sup> seem to indicate that oxygen transport through these two phases exist. The growth rates of the three oxides, wustite, magnetite and hematite, as a function of temperature have been studied by *Paidassi*<sup>12</sup>, and the results agree well with the work of *Simand, Davies and Bircheall*<sup>11</sup>, *Kubaschewski and Hopkins*<sup>7</sup>. These rates are expressed as;

FeO: 
$$k'_{p} = 5.75 e^{\frac{-40500}{RT}}$$
 (cm<sup>2</sup>/sec.)

Fe<sub>3</sub>O<sub>4</sub>: 
$$k'_{p} = 1.05 e^{\frac{-40500}{RT}}$$
 (cm<sup>2</sup>/sec.)

Fe<sub>2</sub>O<sub>3</sub>: 
$$k'_{p} = 5.4 e^{\frac{-40500}{RT}}$$
 (cm<sup>2</sup>/sec.)

where R is 8.314 (joules/K. mole).



Figure (2.7) Metal loss of pure iron in oxygen at 1100 °C, Sachs and Tuck<sup>3</sup>.

The parabolic growth rates of the three oxides of iron are known from the measurements of *Himmel, Mehl and Birchenall<sup>4</sup>*, *Kubaschewaski and Hopkins<sup>7</sup>*, and are presented in Table (2.1).

Reaction	Temperature °C	k <sub>p</sub> (g <sup>2</sup> /cm <sup>4</sup> .sec)
Fe + $1/2 O_2 = FeO$	983 897 800	6.7 x 10 <sup>-7</sup> 2.5 x 10 <sup>-7</sup> 5.3 x 10 <sup>-8</sup>
$3FeO + 1/2 O_2 = Fe_3O_4$	1100 1050 1000	3.2 x 10 <sup>-8</sup> 1.7 x 10 <sup>-8</sup> 8.1 x 10 <sup>-9</sup>
$2Fe_3O_4 + O_2 = 3Fe_2O_3$	1 100 1 000	1.0 x 10 <sup>-8</sup> 2.3 x 10 <sup>-9</sup>

Table (2.1) Parabolic rate constants obtained experimentally for the growth of FeO, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, taken from *Kubaschewski and Hopkins*<sup>7</sup>.

On the basis of our present knowledge of the diffusional properties of iron oxides, *Birks and*  $Meier^{9}$  have proposed a simple mechanism for the oxidation of iron, Figure (2.8).

1 - The iron ionizes at the iron-wustite interface according to

$$Fe = Fe^{2^{+}} + 2e^{-}$$
 (2.25)


Figure (2.8) Oxidation mechanism of iron to form a three-layered scale of FeO, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> above 570 °C showing diffusion steps and interfacial reactions, From *Birks* and Meier<sup>9</sup>.

2 - Due to the presence of cation vacancies and electron holes in wustite, iron cations and electrons are transported to the wustite/magnetite interface. There, the magnetite is reduced to wustite according to the reaction

$$Fe^{2*} + 2e^{-} + Fe_3O_4 = 4 FeO$$
 (2.26)

Iron ions and electrons surplus to this reaction are transported through magnetite to the magnetite/hematite interface to form magnetite by the reduction of hematite according to

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$$Fe^{n+} + ne^- + 4Fe_2O_3 = 3Fe_3O_4$$
 (2.27)

The value of *n* being 2 or 3 for  $Fe^{2+}$  or  $Fe^{3+}$  ions respectively.

At the hematite/gas interface, oxygen ionizes according to

$$\frac{1}{2}O_2 + 2e^- = O^{2-} \tag{2.28}$$

Hematite is formed at the magnetite/hematite interface by ionized oxygen and metal ions in excess of equation (2.22) according to

$$2Fe^{3*} + 3O^{2-} = Fe_2O_3 \tag{2.29}$$

If iron ions are mobile in hematite, hematite will form according to

$$2Fe^{3+} + 6e^{-} + \frac{3}{2}O_2 = Fe_2O_3$$
 (2.30)

## 2.4.2 Effect of Temperature

The effect of temperature on the oxidation of pure iron is very well known. *Davies, Simand and*  $Birchenall^{U}$  investigated the effect of a wide range of temperatures on the oxidation rate of pure iron at normal oxygen pressures, Figure (2.9).

The parabolic rate constant increases exponentially with temperature according to the following Arrhenius equation

(2.27)

$$k_p = k_o e^{\frac{-Q}{RT}}$$
(2.31)

Where  $k_o$  is a constant that is a function of oxide composition and gas pressure.



Figure (2.9) Isothermal curves for the rate of increase of weight of iron oxidized in oxygen, taken from *Davies, Simand and Birchenall*<sup>11</sup>.

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The dependence of the parabolic rate constant on temperature is given in Figure (2.10). The distinct break in the curve between about 560 to 600 °C is obviously due to the fact that wustite is unstable below

570 °C, Kubaschewski and Hopkins<sup>7</sup>. Stanley and Hutoon<sup>7</sup> have expressed the Arrhenius equation by



Figure (2.10) Relation between rate-constant and temperature for the oxidation of high-purity iron. x Davies, Simand and Birchenall; o Schmahl, Baumann and Schenck. Taken from *Kubaschewski and Hopkins*<sup>7</sup>

$$k_p = 0.37 \ e^{\frac{-33000}{RT}}$$
 (2.32)

where R is the gas constant and T the absolute temperature.

## 2.4.3 Effect of Oxidizing Atmosphere

The effects of oxygen, steam and carbon dioxide on the oxidation of pure iron has been studied by *Rahmel and Engell<sup>16</sup>*, *Smeltzer<sup>17</sup>*, *Sachs and Tuck<sup>3</sup>*.

## 2.4.3.1 Effect of Oxygen

Rahmell and Engell<sup>16</sup> studied the effect of oxygen levels on the rates of oxidation of iron at 700, 800 and 950 °C, respectively. The results of their work suggested that the parabolic oxidation rate

increases with increasing oxygen percentage, especially at higher temperatures. The most significant increase was found to be between 0.4 and 2% oxygen at 950 °C. The parabolic rate constants are given in Table (2.2).

## 2.4.3.2 Effect of Water Vapour and Carbon Dioxide

The effect of water vapour and carbon dioxide on the oxidation of iron has been studied by *Rahmel and Tobolski*<sup>18</sup>. They found that the scaling rate of iron is not influenced by water vapour at 750 °C, but at 850 and 950 °C, the rate increases by factors of 1.2 and 1.6 respectively. They also stated that carbon dioxide produces a smaller increase than water vapour. *Smeltzer*<sup>17</sup> has studied the effect of carbon dioxide on the scaling rate of iron in the

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temperature range 600 to 1100 °C. The results indicate that the scaling rates obeyed linear and parabolic time laws for short and long exposure times respectively.

The oxidation curves for pure iron in oxygen, steam, air and carbon dioxide at 1000 and 1100 °C are given in Figure (2.11), Sachs and Tuck<sup>3</sup>.

Temperature	Percent Oxygen	kp (g²/cm <sup>4</sup> . sec.)
700 °C	100	7.8 x 10 <sup>-9</sup>
	49.2	7.5 x 10 <sup>-9</sup>
	10.3	8.5 x 10 <sup>-9</sup>
	1.0	8.3 x 10 <sup>-9</sup>
800 °C	100	5.5 x 10 <sup>-8</sup>
	21.0	5.8 x 10 <sup>-8</sup>
	10.6	6.5 x 10 <sup>-8</sup>
	1.1	5.2 x 10 <sup>-8</sup>
950 ℃	100	5.8 x 10 <sup>-7</sup>
	37.5	5.7 x 10 <sup>-7</sup>
	15.8	5.2 x 10 <sup>-7</sup>
	4.4	5.2 x 10 <sup>-7</sup>
	2.0	4.8 x 10 <sup>-7</sup>
	0.4	

 Table (2.2) Parabolic rate constants for the oxidation of iron in oxygen

 obtained experimentally by Rahmel and Engell<sup>16</sup>.



Figure (2.11) Oxidation of pure iron, from Sachs and Tuck<sup>3</sup>.

## **2.5 OXIDATION OF STEELS**

The oxidation of steels is far more complex than that of pure iron. The complications arise from the fact that different elements with different properties are interacting simultaneously. It then becomes difficult to give the cause and effect of the behaviour of an element in the alloy. This complexity is a result of some, or all, of the following;

(1) The different affinities of alloying elements for oxygen,

- (2) The different mobilities of metal ions in the oxide phases,
- (3) The different diffusivities of different metals in the alloy
- (4) Internal oxidation of one or more alloying elements,
- (5) A solid solubility between oxides may exist,
- (6) Ternary and higher oxides may be formed,

The literature available on the oxidation of steels is tremendous and it is not practical to provide an extensive review of it. Therefore, only limited work, specific to some steels of interest, will be reviewed.

#### 2.5.1 Effect of Alloying Elements on the Oxidation Rate of Steel

As the ingredients of steels can comprise of many elements, it becomes far more complicated to determine the effect of any of these in the presence of others.

#### 2.5.1.1 Effect of Carbon

The effect of carbon on the oxidation of steel has been studied by many researchers, *Murphy*, *Wood and Jominy*<sup>19</sup>, *Cook and Rasmussen*<sup>20</sup>, *Schurmann, Beck, Rahm, Brand and Mulheim*<sup>21</sup>. In the majority of these studies, carbon has shown to decrease the scaling rate of steel. This decrease is believed to be a result of carbon oxidation to CO, which would have the tendency to retard the oxidizing action. One of the reasons for this behaviour is suggested by *Grinzburg*<sup>10</sup>. He explained that pores filled with CO develop at the scale/metal interface, and hence hinder the diffusion process of ions from the metal to the oxidizing atmosphere. Figure (2.12) shows the effect of carbon on the oxidation of different steels (refer to Table (2.3) for composition).



Figure (2.12) Effect of increasing amounts of carbon on scaling rates, *From Cook and Rasmussen*<sup>20</sup>.

## 2.5.1.2 Effect of Other Alloying Elements

Grinzburg<sup>10</sup> has considered the effect of some other alloying elements on the oxidation of steel;

Manganese does not contribute to any major effect on the oxidation of steel.

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Steel	%C	%Si	%S	%P	%Mn	%Ni	%Cr	%Mo	%Al	%Cu
1030 steel	.28-		.05	.04	.60-					
	.34				.90					
1090 steel	.85-		.05	.04	.60-					
	.98				.90					
302 steel	.15	-1	.03	.045	2	6-8	16-			
							18			
430 steel	.12	1	.03	.04	1		16-			
							18			
310 steel	.25	2	1.5	24-						
				26						
Mild steel	.065	.01	.017	.017	.29	.049			.01	.023
En 8 steel	.425	.21	.027	.021	.77	.28	.20		n.d.	n.d.
En 16 steel	.4	.24	.031	.017	.95	.14	.13	.28	n.d.	n.d.

Table (2.3) Compositions of steels considered.

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**Chromium and aluminum**, when present at residual levels in the steel, have negligible effects on its oxidation properties. At higher levels, chromium forms a protective layer of  $Cr_2O_3$  which provides oxidation resistance. Similarly, aluminum forms a hard protective layer,  $Al_2O_3$ , which reduces the oxidation rate.

Silicon reacts with oxygen diffusing into the steel below the oxide/metal interface to forms silica,  $SiO_2$ . Silica forms a separate phase, Fayalite 2FeO.SiO<sub>2</sub>, which has a melting point of 1171 °C. When this phase melts, the oxidation rate increases due to the acceleration of the diffusion process through the melten phase.

Nickel diffusion in steel is low and hence it is concentrated at the steel /oxide interface which lowers the oxidation rate. The resulting nickel alloy has the tendency to increase scale adhesion to the substrate. The problem becomes more severe when nickel is present at high concentrations.

Copper, like nickel, is concentrated at the metal/oxide interface but does not cause scale stickiness as in the case of nickel.

#### **2.6 SCALE FORMATION IN REHEAT FURNACES**

Scaling of steel in the presence of gaseous products of combustion add to the complexity of the oxidation process. Limited studies have been reported by some authors such as Cook and Rasmussen<sup>22</sup>, Hemsath and Vereecke<sup>22</sup>, Sachs and Tuck<sup>23</sup>, Selenz and Oeters<sup>24</sup>, Minaev, Ol'Shanskii and Shurova<sup>25</sup>, on various aspects of scaling in complex environments.

A major element in the complexity of scale formation in reheat furnaces is its inconsistency, which again, is a result of interacting parameters in the furnace,  $Blazevic^{26}$ .



Only some of those elements contributing to the inconsistency of scale formation have been considered by researchers.

## 2.6.1 Reactions and Heating in a Reheating Process

Reheat furnaces are direct fired type furnaces with the fuel being, depending on burner design and fuel type availability, natural gas, coke oven gas, blast furnace gas, fuel oil, etc.. Many reactions can take place during reheating; however the main reactions that provide heat to the system are as follows:

Methane, CH<sub>4</sub>, which is the main constituent of natural gas burns, according to the reaction

$$CH_4 + 2O_2 = CO_2 + 2H_2O_{(s)}$$
(2.33)

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Hydrogen, H<sub>2</sub>, which is the main constituent of coke oven gas burns according to

$$H_2 + 1/2O_2 = H_2O_{(g)}$$
(2.34)

Sulphur, S, from fuel oil, at higher temperatures burns according to

$$S + O_2 = SO_2 \tag{2.35}$$

Carbon monoxide, CO, burns according to

$$CO + 1/2O_2 = CO_2$$
 (2.36)

The levels of combustion products depend on the percent combustion air used Incomplete combustion gives rise to combustibles in the combustion products. *Cook and Rasmussen*<sup>20</sup> studied the equilibrium products of the combustion of natural gas related to percentage theoretical combustion air and these are shown in Figure (2.13).

Note that as the percent combustion air decreases, the oxidants  $H_2O$  and  $CO_2$  decrease, while those of reducers, CO and  $H_2$ , increase.

The air/gas ratio also has a big impact on the adiabatic flame temperature. Figures (2.14, 2.15) give the theoretical adiabatic flame temperature as a function of percent combustion air and combustion air temperature. It can also be seen that high combustion air temperatures result in dramatic increases in flame temperatures.

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Figure (2.13) Equilibrium products of combustion of natural gas related to percentage theoretical combustion air, From *Cook and Rasmussen*<sup>20</sup>.



Figure (2.14) Theoretical adiabatic flame temperature with air/gas ratio, From *Cook and Rasmussen*<sup>20</sup>.



Figure (2.15) Adiabatic flame temperature for combustion of natural gas in preheated air, From *Hemsathe and Vereecke<sup>22</sup>*.

## 2.6.2 Oxidation of Steel in Combustion Products

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Iron and other alloying elements in steel react with various gases in the furnace resulting in complex products. Some of the important reactions of iron in addition to those in equations (2.1), (2.2), (2.3) and (2.4) are;

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The oxidizing reactions

$$Fe + H_2O = FeO + H_2 \tag{2.37}$$

$$Fe + CO_2 = FeO + CO \tag{2.38}$$

The reducing reactions

$$FeO + CO = Fe + CO, \tag{2.39}$$

$$FeO + H_2 = Fe + H_2O \tag{2.40}$$

Cook and Rasmussen<sup>20</sup> have presented the work of Jominy, Murphy and Marshall to provide the equilibrium temperature at which iron and iron oxide are stable at different  $CO_2/CO$  and  $H_2O/H_2$  ratios, as shown in Figure (2.16). Thus for any oxidation temperature, if both ratios are held to the left of the curves, the entire work-atmosphere relationship will remain on the reducing side.



Figure (2.16) Equilibrium temperature at which various gas ratios of CO<sub>2</sub>/CO and H<sub>2</sub>O/H<sub>2</sub> are neutral to iron, From *Cook and Rasmussen*<sup>20</sup>

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*Minaev, Ol'Shanskii*<sup>25</sup>, *et al* have studied the oxidation of steels 35, 45, 60, 80 and U8A, in combustion products from natural gas at different temperatures with varying air consumption coefficients. The results of their work are given in Figure (2.17).



Figure (2.17) Influence of air combustion coefficient on amount of scale formed at specimen temperature, °C, of: a 1200, b 1100, c 1000, d 900, figures on curves give grade of steel, from *Minaev, Ol'Shanskii, Volkova and Shurova*<sup>25</sup>.

With all the investigated steels, a change in the air consumption coefficient from 1.1 to 0.9 at high temperatures results in a marked drop in the oxidation rate, while a further decrease in this

coefficient from 0.9 to 0.7 has very little effect on it. Their work also included the oxidation of steel 35 in gaseous fuels natural gas, coke oven gas and blast furnace gas combustion products, Figure (2.18). It can be seen that the oxidizing potential of natural gas differs only slightly from that of blast furnace gas.



Figure (2.18) Influence of different gaseous fuels on amount of scale formed at: a T=1250 °C, b T=1200 °C, c T=1100 °C, d T=1000 °C.

Cook and Rasmussen<sup>20</sup> have studied the oxidation of AISI 1030 carbon steel at different temperatures as a function of percent combustion air, Figure (2.19). It indicates that all higher temperatures require deficiencies in the air-gas ratio approaching 50 percent to heat steel in a scale-free manner.

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Sachs and  $Tuck^{23}$  have studied the oxidation of iron, mild steel, En 8 steel and En 16 steel, (refer to Table (2.3) for compositions), in single and synthetic atmospheres at constant temperature and two heating rates.

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Figure (2.19) Quantitative effect of air/gas ratio on the scaling rates of AISI 1030 carbon steel, at constant temperatures, from Cook and Rasmussen<sup>20</sup>.

The compositions of the atmospheres used in their work are given in Table (2.4). From their work it was observed that an increase in steam at higher oxygen levels had no effect on the scaling rates of pure iron and mild steel but that at low oxygen, an increase of steam resulted

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in an increase of scaling rates especially above 1000 °C. An increase in oxygen content resulted in higher scaling rates than in the case of an increasing steam ratio.

No	N <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> O	Designation
1	78.30	10.8	0.90	10.1	low oxygen/low steam
2	69.60	9.60	0.80	20.0	low oxygen/high steam
3	74.7	11.7	3.6	10.0	medium oxygen/low steam
4	67.6	7.6	4.8	20.0	high oxygen/high steam
5a	74.6	8.55	5.4	7.2	high oxygen/low steam
5b	76.05	12.1	6.1	10	

Table (2.4) Composition of furnace atmosphere used in theexperimental oxidation of iron and mild, En 8, En 16steels, From Sachs and Tuck23.

#### 2.6.3 Scale Free Heating

Cook and Rasmussen<sup>20</sup> have developed a strategy for scale-free heating, Figure (2.20). During the initial heating period, steel is heated at stoichiometric air/gas ratios utilizing preheated combustion air until the surface temperature of the steel reaches about 1400 °F (760 °C). Percent combustion air is then reduced to 50% of stoichiometry from 1400 to 1900 °F (760 to 1040 °C) surface temperature. The steel is then heated to 2300 °F (1260 °C) while maintaining 50% combustion air at this temperature.



Figure (2.20) Heating stages to produce a scale-free heating of steel, From *Cook and Rasmussen*<sup>20</sup>.

# chapter THREE

# OBJECTIVES, EQUIPMENT AND EXPERIMENTAL PROCEDURE

## **3.1 INTRODUCTION**

To investigate a certain phenomenon taking place in large industrial units such as steel reheat furnaces, it is often the case that laboratory experiments are set up to simulate some aspect of the process taking place in the industrial unit. Although this approach is necessary to provide scientific findings under controllable conditions, difficulties are usually encountered in applying these laboratory findings to industrial units. Moreover, a lack of understanding of the exact operation and of the different parameters in an industrial unit causes some of these difficulties. Thus, it is important to conduct as many industrial experiments as possible in order to identify these parameters and thus develop a strategic procedure for investigating them in the iaboratory.

The aim of this work was to study the phenomenon of scale formation of steel taking place in a 350 ton/hour direct fired steel reheat furnace. The large number of parameters affecting this process necessitates a tremendous amount of preparatory work in order to come up with the most practical procedure.

The parameters directly influencing scale formation are slab temperature, in-furnace atmosphere

 $(O_2, CO_2, H_2O, CO)$ , steel grade and steel residence time in the furnace. However, to monitor these parameters, furnace controls and measurement points must be known.

### **3.2 OBJECTIVES**

The objectives of the scale work were to:

- 1 Develop an experimental procedure to allow for scale sampling during passage of slabs through the industrial reheat furnace.
- 2 Assess scale losses associated with existing furnace operation.
- 3 Identify parameters influencing scale formation in the furnace.
- 4 Alter such parameters, whenever possible, to minimise scale formation in the furnace.
- 5 Investigate scale adhesion to the substrate, surface quality and quality of descaled slab, if deemed problematic.

In order to give an overview of the experimental set up adopted for this work, the equipment lay out together with a description are first considered in the following sections

#### **3.3 FURNACE DESCRIPTION**

The walking-beam steel reheat furnace under investigation can be divided into twelve zones, (see Figure (3.1)). The design is that of a double row, top and bottom fired walking beam furnace. It consists of twelve zones of combustion control arrangement. A total of 121 burners are installed in all the zones except in the unfired zone. These include longitudinal or side burners in all the zones with the exception of the top soak zone where radiant roof burners are used. The preheat and charge zones (top and bottom) burners are fired either with coke oven gas, mixed gas, or with No 6 fuel oil. All other zones are fired with coke oven gas or mixed gas and air.

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The combustion system is of the recuperative type, with air preheated to about 500 °C. The products of combustion in the furnace, depending on fuel type, are CO<sub>2</sub>, H<sub>2</sub>O (steam), N<sub>2</sub>, O<sub>2</sub> (in the case of excess air), sulphur oxides, NO<sub>x</sub> and traces of combustibles (in the case of incomplete combustion). The furnace combustion control was by means of a microprocessor type instrumentation system. A programmable controller directs movements of the walking beams for moving slabs through the furnace at pre-designated rates.

The walking mechanism is split at the mid of the furnace length to allow for independent charging and discharging speeds. Thus, slabs walk through the furnace by means of stationary and moving beams. The moving beams lift up the slabs, advance them a certain distance, lower the slabs in the new position and return to their initial position. This cycle is repeated for each walk.

In the furnace, steel slabs of different grades are charged at different initial temperatures for varying residence times. The furnace operation depends on many factors such as initial slab temperature, mill delays, slab dimensions, gaps between slabs, production rates, etc.. Therefore, a considerable amount of time was spent in controlling the furnace so as to allow for

the variability of the influencing parameters. Since taking scale samples from actual slabs in the furnace was not possible, small steel samples of identical sizes were used to monitor scale formation. Much work went into the sample

of identical sizes were used to monitor scale formation. Much work went into the sample preparation and insulation to obtain scale formation which is representative of scale formation on actual slabs. The other challenging aspect is extracting scale samples from different positions along the furnace and hence to allow for time-scaling curves. Fortunately, the furnace was equipped with side ports which were used to retrieve the steel sample. All of these details will be discussed in later sections.

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## **3.4 EXPERIMENTAL SET-UP**

During the experiments, a large number of furnace operating data was monitored on-line. This data included fuel and air flow rates for individual zones, fuel composition ( $H_2$ ,  $CH_4$ , CO,  $CO_2$ ,  $O_2$ ), slab data (slab temperature and slab walking rates through the furnace) and furnace atmosphere (oxygen, carbon dioxide and carbon monoxide). The hardware for data collection can be categorized into two parts, the furnace equipment (Honeywell and Vax), and the McGill data acquisition system equipment. The Honeywell TDC-3000 is used as the Level I furnace control computer, while the Level II (Vax System) provides calculated slab temperatures. The McGill equipment was limited, since most of the data that was required from the furnace can be accessed from the two furnace control systems. The McGill data acquisition system, manufactured by Schlumberger, is based on a number of Isolated Measurement Pods (IMPs), distributed across the plant and linked to an IBM AT compatible computer located in the furnace control pulpit via a twisted pair cable.

A schematic illustration of the arrangement of the individual units used in the collection of data from the reheat furnace, is given in Figure (3.2). These units include data acquisition equipment and furnace control equipment and are described below:

#### Water Cooled Sampling Probes, [2], [3]

Water cooled probes were used to aspirate in-furnace gases for on-line analysis. The probes were assembled from internal and external stainless steel tubes. Water flows through the inner tube and exits from the outer one. This cooling water was needed to quench the hot gases aspirated so as to prevent possible reactions among them and also to protect the probe from over-heating. The water flow rate required depended on zone temperature, probe location, and depth of insertion into the furnace. The flow rate was adjusted by monitoring the exit water temperature.



Figure (3.1) Schematic illustration of five zone walking-beam steel reheat furnace (not to scale).



Figure (3.2) Schematic illustration of experimental set-up.

- [1] Reheat Furnace
- [2] [3] Water Cooled Sampling Probes[4] Nova 370 (Portable Combustion Analyzer)
- [5] ANARAD Model AR-205 (Combustion Efficiency Monitor)
- [6] Nova Model 7500P5 (Fuel Gas Analyzer)
- [7] Anarad Model AR-411 ( CH<sub>4</sub> Analyzer)
- [8] [9] [10] [11] Model 160T DC Volts/Process Current Transmitters [12] 3595 Series Isolated Measurement Pods (IMPs)
- [13] IB." Compatible with IMP Adapter Card
- [14] Honeywell Control System
- [15] Vax system
- [16] Data Processing

## NOVA 370 (Portable Combustion Analyzer). [4]

A Nova 370 was used to measure the levels of  $O_2$ ,  $CO_2$  and CO in the soak zone. It has a built in sample pump which draws in flue gases through a stainless steel probe. The oxygen and CO sensors are of the electrochemical "fuel cell" type producing small electrical signals proportional to the gas being detected. A thermal conductivity sensor was used to measure the rate at which the sample gas conducts heat from a heated thermistor, by reference to a similar thermistor surrounded by air.

#### ANARAD Model AR-205 (Combustion Efficiency Monitor), [5]

The Anarad analyzer was used to measure  $CO_2$ , CO and  $O_2$  in the combustion products. This particular instrument was used in the intermediate zone. This is a non-dispersive infrared (NDIR) gas analyzer. It measures the concentration of a selected gas species in a multi-component gas mixture by measuring the infrared adsorption of the selected component in the gas mixture.

#### NOVA Model 7500P5 (Fuel Gas Analyzer), [6]

This analyzer was used to measure fuel composition. The ranges of fuel components,  $O_2$ ,  $H_2$ , CO, CO<sub>2</sub> and CH<sub>1</sub> are, 0-2%, 0-100%, 0-10%, 0-5% and 0-30%, respectively.

Oxygen is detected by a customer replaceable electrochemical sensor, hydrogen by a thermal conductivity sensor (compensated for temperature,  $CO_2$  and  $CH_4$  effects), CO,  $CO_2$  and  $CH_4$  by an infra-red detector.

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#### ANARAD Model AR-411 (CH<sub>4</sub> Analyzer), [7]

Because of a limit in the range over which methane can be measured by the Nova Model 7500P5, (0-40%) this additional analyzer was required. This instrument is capable of measuring  $CH_4$  in the fuel in the range of 0 to 100%. It is a non-dispersive infrared, single channel, single cell analyzer.

### Model 160T DC Volts/Current Transmitters, [8], [9], [10], [11]

This model type accepts a DC voltage, either unipolar or bipolar, from 100 mV to 100 V spans, or current input signal and converts it to a 4 to 20 mA or 10 to 50 mA process current output. The input impedance is 5 megohms minimum.

## 3595 Series Isolated Measurement Pods (IMPs), [12]

The 3595 series of Isolated Measurement Pods (IMPs) are multi-channel data collecting stations, designed to be operated remotely by a host computer or data logger. The host is linked to the IMPs by one simple 2-wire cable, up to 1 km long. This link, called S-Net, is used to power the IMPs, as well as for bi-directional data to and from the host.

## IBM Compatible, [13]

An IBM Compatible AT personal computer was used to collect the data sent by the IMPs. It was equipped with an IMP adapter card.

## 3.5 SAMPLE AND SLAB TEMPERATURE MEASUREMENTS

The temperature of one sample and a test slab was measured for comparison utilizing a Thermophil-Stor instrument. This instrument is ideal for monitoring temperatures in high temperature environments.

### 3.5.1 Thermphil-Stor Type 4468

The Thermophil-Stor type 4468 rode with the test slab through the furnace. It was powered with an integrated set of Ni-Cd cells, ensuring 10 hours of service in the case of continuous operation. The electric parts, consisting of a measuring circuit, an amplifier, an A/D transducer and a measuring value storage are built into Dewar vessels which in turn are surrounded by high temperature-insulating material. Resistance thermometers (Pt 100 DIN) of insulated jacket thermocouples were used as temperature probes.

#### **3.6 PLANIMETER**

The irregular surface area of the scale pieces was measured using a Planimeter. This instrument was extremely accurate, Figure (3.3), consistently yielding good results with ordinary, careful treatment.

Scale pieces to be measured were drawn on a piece of paper using a sharp pointed pencil tracing the irregular edge of the scale piece. In measuring an area, the instrument is placed on the area in such a way that with the tracer point in the middle of the area, the pole arm is approximately at right angles to the tracer arm. The area is circumscribed, after taking a reading of the wheel at the starting point, in a clockwise direction by means of the tracer point, and the measuring wheel is read. The second reading is then subtracted from the first and the surface area deduced.

### **3.7 SCANNING ELECTRON MICROSCOPE (SEM)**

The scanning electron microscope was used for scale composition analysis. The back-scatter technique was employed to provide good contrast between the various iron oxide phases on the basis of differences of their densities. The SEM consists basically of four main systems;



## Figure (3.3) The Allbrit Planimeter instrument used to measure the irregular scale surface area.

- The illuminating/imaging system which produces the electron beam and directs it onto the sample. It comprises an electron gun and several magnetic lenses that serve to produce a collimated, coherent beam of electrons which can be focused onto the specimen.
- 2 The information system which includes the data released by the sample during electron bombardment and detectors which discriminate among, and analyze, these information signals.

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- 3 The **display system** which consists of one or two cathode-ray tubes for observing and photographing the surface of interest.
- 4 The vacuum system which removes gases from the microscope columns which would otherwise interfere with high-resolution imaging.

#### **3.8 EXPERIMENTAL PROCEDURE**

For each experiment the following steps were taken;

- 1 A test slab to carry the samples through the furnace was inserted in the heating line-up.
- 2 The water cooling system for the sampling probes was started and the sampling probes were inserted in the furnace through the side wall, both in the soak and intermediate zones.Figure (3.4) shows a water cooled probe inserted in the furnace to measure in-furnace atmosphere.
- 3 The gas analyzers were turned on and connected to the sampling probes, while starting the McGill data acquisition s<sub>3</sub> tem, Vax system, for data collection.
- 4 Six samples were placed on top of the test slab, on the side closest to the furnace side wall, as shown in Figure (3.5).
- 5 The test slab and samples were charged into the furnace and the charge time was recorded.
- 6 The slab's movement through the furnace was continuously monitored from the furnace monitoring screens in the control pulpit.
- 7 When the test slab arrived at a given side window, a sample was retrieved using the sample

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retriever shown in Figure (4.1) and the time was recorded. A walkie-talkie was used for communication with the furnace operator.

- 8 Immediately after a sample was retrieved, it was placed in an air-tight box that was continuously flushed by a flow of nitrogen.
- 9 Steps six to eight were repeated for the remainder of the scale samples riding through the furnace.
- 10 Once the test slab had been discharged from the furnace, the data acquisition system was stopped.
- 11 The sampling probes were removed from the furnace and the water cooling system was disconnected.
- 12 All required data from the Honeywell and the Vax Systems were down-loaded to the PC for further analysis.



Figure (3.4) A water cooled sampling probe inserted through the furnace side wall.

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Figure (3.5) Six insulated steel samples placed on top of a test slab just before charging into the furnace.



Figure (3.6) A picture showing the sample retriever through the furnace side window.

# CHAPTER FOUR

# PRE-TRIALS AND MONITORING OF EXPERIMENTAL PARAMETERS

## **4.1 INTRODUCTION**

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The industrial scale work was divided into two main parts, pre-trials and full trials. The pretrials were undertaken to provide information needed to set up a common procedure for the full trials.

Since it was not possible to retrieve scale samples from actual slabs passing through the furnace, steel samples of manageable size had to be prepared so that they can be individually extracted from the furnace side windows. The main requirement was that the scale forming on the steel samples (riding on a test slab through the furnace) was representative of scale forming on the test slab. The other requirement was that all the steel samples used for all the trials be identical.

As discussed in Chapter Two, temperature has a pronounced effect on scaling rates. This necessitates testing the effects of sample size, insulation and contact of the samples with the test
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slab, so as to achieve identical surface temperatures of the rider slab and the riding samples and, as a result, similar scaling rates.

All the samples used for this work were prepared from a signal slab and were therefore of identical composition.

The full trials were then conducted on the basis of the findings of the pre-trails, in parallel with the measurement of all parameters needed for scale data analysis. These measurements included in-furnace atmosphere, fuel composition and slab temperature profiles.

In this chapter, details of the pre-trials along with the measurement of parameters of the full trials are considered.

#### 4.2 PRE-TRIALS

The pre-trials were conducted to investigate sample retrieval from the furnace, sample size and preparation, sample insulation and sample contact with the rider slab. The duration of the pre-trials took approximately one third of the time for the total work.

#### 4.2.1 Sample Retrieval from the Furnace

Two approaches were investigated for sample retrieval. In the first, a simple long steel bar with a thinner curved end in the shape of a semi-hook was designed. The samples were then prepared with hooks welded onto them to accommodate this method. This approach was not used for subsequent work, mainly to avoid the influence of the weld on scale formation of the sample's top surface. The second approach was the design of a retriever resembling a long shovel with a hollowed arm. A rake was then passed through the hollow arm with its forked end at the flat end of the shovel. The design is shown in Figure (4.1). This approach was adopted for the subsequent trial.



Figure (4.1) Sample retriever design utilized to extract steel samples from the furnace, by D. Miller, Dofasco.

#### 4.2.2 Sample Size

One of the important sample requirements is that the scale forming on the samples is representative, qualitatively and quantitatively, of the scale forming on the actual slab. Therefore, this pre-trial focused on determining the influence of sample size on scale formation.

A set of two sample sizes were investigated (8x8x1.5 cm and 12x12x1.5 cm). The two samples were sent through the furnace and retrieved at the same time.

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It was observed that the temperature of the samples increased with decreasing sample size. Figure (4.2) gives the scaling curves of this pre-trial. The samples and the slab in this pre-trial had the same thermal history, that is, the samples were left on top of the test slab after being discharged and left to cool overnight.

From the figure, it can be seen that the small sample has about 21% more scale than the slab, while the large sample has about 6.8% more scale than the slab. The difference in scaling of different sample sizes can only be attributed to difference in their temperature-time heating profiles. The small sample will heat up at a much faster rate than the large sample, with the slab being the slowest. Because of the very similar conditions for all the samples in this pre-trial, no other parameter is suspected to cause this effect. Due to the large sample size, edge effects are not expected to alter the scaling rate.

Based on this finding, the larger sample size was chosen for the full trials.

### 4.2.3 Sample Preparation

The purpose of this set of pre-trials was to investigate the effect of sample preparation on the scaling of the steel samples. It has been divided into two parts, method of sample cutting and method of top surface grinding.

#### 4.2.3.1 Methods of Sample Cutting

Since the samples originate from actual slabs, methods of cutting these samples were investigated. A set of samples was prepared as flame-slab-cut, saw-slab-cut, transfer bar-flamecut and transfer bar-saw-cut. The flame and saw cut methods are investigated for the reason that in the case of flame cut, sample edges are exposed to very high temperatures and there exist a thermal gradient, during cutting, across the sample width. This would result in variations in the microstructure across the sample width and might alter the kinetics of the reactions.



Figure (4.2) The difference in the amount of scale formed on the actual slab and samples of different sizes.

The differently cut samples, all of the same size, were placed on a test slab and charged through the furnace and were left to cool over night on top of the test slab.

The results from this pre-trial did not indicate any major difference of scaling for the different samples. The choice was then made based on the easiest method of preparation which is transfer bar-flame-cut. Also, this method was adopted to provide samples of the same thickness as opposed to slab-cut samples.

#### 4.2.3.2 Sample Surface Grinding

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Only the scale forming on the sample top surface was considered to simulate the scale forming on the slab top surface. The amount of scale forming on the slab bottom and side surfaces was assumed to be directly proportional to that forming on the top surface. Since the top surface of the samples contains surface defects such as oxides, which may alter, in one way or another, the oxidation kinetics of the samples, a pre-trial was conducted in order to compare the scaling of normal samples and surface ground samples.

Figure (4.3) gives the scaling rates of samples with ground and normal surfaces.

It can be seen that the normal surface formed more scale than the ground surface. It is probable that the presence of an initial scale on the sample surface, results in the formation of less compact subsequent scale that contains cracks and channels through which the oxidizing atmosphere can pass to the steel surface and, therefore, the higher oxidizing rates. On the other hand, on the clean surface, the nucleation of scale is uniform and hence a smooth and compact film is produced. This will limit oxidant transport to the steel surface. In this case, it is likely that the transport of atomic oxygen inward from the gas/oxide interface to the oxide/steel interface and the counter transport of iron cations outward from the steel/oxide interface to the oxide/gas interface is the predominant transport mechanism in the oxidation process. The slower oxidation rates in this case are due to the fact that the rate of transport of anions and cations through the scale is much slower than the rate of transport of molecular gases such as oxygen, water vapour, carbon dioxide, etc., through cracks existing in the scale.



Figure (4.3) Scaling rates for samples of normal and ground surfaces.

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To insure the similarity of steel samples used for all the trials, the surfaces of all samples were ground with a hand grinder.

#### 4.2.3.3 Sample Insulation

To attain similar sample and top rider slab temperatures, sample sides insulation was considered. This is based on the idea that if a rectangular piece of the top surface of a slab (far from its edges), is considered, the predominant heat transfer taking place is from the furnace environment vertically down across this piece. Hence, by side insulating the samples, uni-directional heat transfer can be achieved.

The samples were wrapped by kaowool around the sides and held with a steel strap and then placed firmly on top of the slab to eliminate any gaps between the side insulation and the slab surface.

The results of this pre-trial are shown in Figure (4.2). It can be seen from the figure that for the large sample size, the insulated samples had 21% more scale than the uninsulated ones. For the smaller samples, the insulated had 12.5% more scale than the uninsulated ones.

The observed results contradict the theoretical expectation. This behaviour can be a result of one or both of the following reasons. First, the kaowool acts as a less insulating material than that of the scale that would have formed on the sample sides. This of coarse is a function of compactness of the material. Second, that the steel strap holding the kaowool simply opened up in the furnace and the unscaled sides allowed for greater heat transfer and hence the increase in sample temperature.

Because of the uncertainty of the insulation technique, the full trials were conducted with no sample insulation.

#### 4.2.3.5 Sample Contact With Test Slab

To improve the thermal conductivity between the samples and rider slab and hence obtain similar temperature profiles, the surface of the rider slab where samples were placed was ground. The set was then sent through the furnace.

During sample retrieval towards the end of the furnace the samples tended to stick to the slab surface and difficulties were encountered in removing them. Therefore, in the subsequent trials, samples were placed on the "as is" slab surface.

#### **4.3 FULL TRIALS**

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Based on the findings of the pre-trials, a procedure was developed in order to conduct the full trials. These trials were mainly to determine the effect of various furnace parameters, such as slab residence time in the furnace, temperature profiles, and furnace atmosphere, on the scaling rates and the characteristics of scale forming on selected steels.

#### **4.4 MONITORED EXPERIMENTAL PARAMETERS**

A number of parameters were monitored during the course of each experiment. These parameters included fuel composition (CH<sub>4</sub>, H<sub>2</sub>, CO, O<sub>2</sub>), in-furnace gaseous components (O<sub>2</sub>, CO<sub>2</sub> and CO), fuel and combustion air flow rates, and slab data such as predicted slab temperatures and slab walking rates through the furnace. The methodology of these measurements is discussed as follows;

#### 4.4.1 Fuel Composition

It was necessary to analyze fuel composition in order to be able to calculate actual/stoichiometric air ratios. The analyses were done utilizing the two fuel analyzers described in Section (3.4). The fuel delivered to the burners was homogeneous in composition. This is because the fuel was mixed in the gas mixing station located before the main fuel delivery pipe, where natural gas and coke oven gas were mixed. The point of measurement was at a pipe leading to one of the burners at the intermediate zone. Water vapour was filtered out to protect the analyzer, using a silica absorption mixture bottle located near the analyzer inlet line.

#### 4.4.2 In-Furnace Atmosphere

The gas components inside the furnace were monitored with the sampling probes and the flue gas analyzer described in Section (3.4). The two water cooled sampling probes were inserted about one meter distance through the side walls of the soak and intermediate zones. The points of measurement remained the same for all the trials. The data was acquired by the McGill data acquisition system.

The water cooled sampling probes deliver the cooled gas by suction applied by a built-in analyzer pump at a rate of about 1.5 litres per minute.

#### 4.4.3 Air and Fuel Flow Rates

Air and fuel flow rates were collected every minute by the Honeywell system and are reported in  $Nm^{3}/h$ .

#### 4.4.4 Sample and Slab Temperature

The Thermophil-Stor, Section (3.5.1), was an independent unit used to measure temperatures

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in a very high temperature environment, e.g., moving slabs in a reheat furnace. The unit was placed on the slab and passed through the furnace. Holes were drilled at selected points in the steel sample and slab, and K-type thermocouples were inserted tightly in the holes and connected to the measuring circuit of the Thermophil-Stor. After leaving the furnace, the instrument was connected to a compensation recorder and the stored information was retrieved.

## CHAPTER FIVE

## **DATA PROCESSING**

#### **5.1 INTRODUCTION**

Several calculations were applied to the raw data collected during the experiments. The collected data from the furnace such as air and fuel flow rates, fuel composition, in-furnace atmosphere and slab data were all down loaded in separate ASCI files, the largest files being the air and fuel flow rates, which were collected every minute. In order to do the calculations, e.g., air ratios, the appropriate files were imported to a Lotus work sheet.

The sample's scaling rates were evaluated by different means such as oxygen weight gain per steel surface area, percent steel loss due to scaling and steel oxidized depth. The scaling rates as a function of temperature, i.e., the parabolic rate constants, were also evaluated. Most of the graphical representations were processed using FreeLance soft ware.

In this chapter, the methods of calculations of the above mentioned parameters are provided.

#### **5.2 CALCULATIONS OF THE EFFECTIVE AIR RATIOS**

For each experiment the actual/stoichiometric air ratio was calculated for each of the individual zones of the furnace. However, the effective air fuel ratio is the ratio which samples actually meet as they travel through the furnace. Thus, as the samples are walked through the furnace, the total air ratio for all the subsequent zones of the furnace ahead of the samples (except for the preheat zone) must be averaged according to net air and gas flows.

The calculations of the effective air ratios start with the collection of the air and fuel flow rates for the individual zones. A sample of the raw data for air and fuel flow rates for one of the trials, from the Honeywell system, is given in Table(5.1).

The stoichiometric air,  $Q_{stoich,aur}$  (Nm<sup>3</sup>/h), is calculated by the equation;

$$Q_{slotch,aur} = 4.76 \ Q_{total,fuel} \frac{(2X_{CH_4} + 0.5X_{H_2} + 0.5X_{co} - X_{o_2})}{100}$$
(5.1)

Where  $Q_{total, fuel}$  and X are, respectively, the total fuel flow rate (Nm<sup>3</sup>/ hour) and the percent gas composition in fuel.

The above equation is based on stoichiometric gas reactions with combustion air, Section (2.6.1).

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TIME (minutes)	1	2	3	4	5
AIR(TOP, CHARGE ZONE)	6051 58	6033 879	6159.32	6493 83	6900 45
AIR(BOTTOM, CHARGE ZONE)	29156.16	28972 41	28759 31	28759 86	28697 62
FUEL(TOP, CHARGE ZONE)	710.26	727 81	707 72	748 55	741 65
FUEL(BOTTOM,CHARGE ZONE)	4166 56	4117 60	4072.10	4108-48	4030 16
AIR(TOP NORTH, INTERMEDIATE)	6538.59	6521 92	6458.09	6476 90	6446-58
AIR(BOTTOM NORTH, INTERMEDIATE)	4887 89	4796 19	5580 45	6458 73	7320 17
AIR(TOP SOUTH, INTERMEDIATE)	6774 13	6644 85	6573 57	6595 26	0546 78
AIR (BOTTOM SOUTH, INTERMEDIATE)	1341.92	1338 55	1461 15	1553 21	1736 43
FUEL(TOP NORTH, INTERMEDIATE)	1092 65	1076 47	1053 86	1064 72	1045 95
FUEL(BOTTOM NORTH, INTERMEDIATE)	686 95	708.65	735 45	769 10	779 04
FUEL(TOP SOUTH, INTERMEDIATE)	1115.53	1102 88	1075 36	1080 74	1061-08
FUEL(BOTTOM SOUTH, INTERMEDIATE)	219 82	219 66	217 40	278 93	249 93
AIR(TOP NORTH,SOAK)	3714 34	3670 32	3590 34	3504 54	3420 37
AIR(BOTTOM NORTH, SOAK)	2940.79	2980 90	2989 23	3007 <del>46</del>	3060-77
AIR(TOP SOUTH,SOAK)	4155 18	4120 28	4085-14	4094-11	4113 74
AIR(BOTTOM SOUTH, SOAK)	3628 44	3740 15	3820 62	3883 78	3961 93
FUEL(TOP NORTH,SOAK)	605.09	586 30	566 39	546 16	530 70
FUEL(BOTTOM NORTH,SOAK)	477 27	494 42	478 56	498-12	506-16
FUEL(TOP SOUTH,SOAK)	673.37	678 65	656 89	667 15	663 68
FUEL(BOTTOM SOUTH, SOAK)	589 26	629 08	631 04	636 83	632 68
FURNACE TOTAL AIR	69189 04	68819 47	69477 24	70827 72	72204 85
FURNACE TOTAL FUEL	10336 76	10341 52	10194 77	10398 78	10241 03

The dimensionless air ratio, R, is then computed as;

$$R = \frac{\left(\frac{Q_{actual,air}}{Q_{fuel}}\right)}{\left(\frac{Q_{storch,air}}{Q_{fuel}}\right)} = \left(\frac{Q_{actual,air}}{Q_{storch,air}}\right)$$
(5.2)

where  $Q_{fuel}$ ,  $Q_{actual,aur}$  are the fuel flow rate and actual air flow rate given to the system, respectively.

Table(5.2) gives the fuel composition monitored on line and also calculations for the air ratio using equation (5.2).

Table (5.2	) Five	minute sample	calculations of	' air ratios	(flow rates are	in Nm <sup>3</sup>	'/h).
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TIME (min.)	%СН₄	%H <sub>2</sub>	%O <sub>2</sub>	Q <sub>total,fuel</sub> Table(5.1)	Q <sub>storch,aar</sub> Eqt. (5.1)	Q <sub>actual,air</sub> Table (5.1)	RATIO (R) Eqt. (5.2)
1	38.2	21.4	2.5	10336.76	41625.71	69189.04	1.66
2	38.4	20.8	2.6	10341.52	41644.88	68819.47	1.65
3	38.2	21.6	2.5	10194.77	41102.45	69477.24	1.69
4	38.3	22.0	2.5	10398.78	42122.96	70827.72	1.68
5	38.0	22.3	2.5	10241.03	41264.59	72204.85	1.75

4. DATA PROCESSING

#### **5.3 METHODS FOR THE EVALUATION OF SCALING RATES**

Scale forming on the steel samples can be recorded and characterized in at least three ways, (1) oxygen weight gain per steel surface area per time and temperature, (2) oxidised steel depth, and (3) weight of steel oxidized per weight of steel reheated (percent loss).

#### 5.3.1 Oxygen Weight Gain

As discussed in Chapter Two, the composition of the scale is about 95% FeO, 4%  $Fe_3O_4$  and  $1\%Fe_2O_3$ . Based on this assumption the scaling rate was measured. A sample calculation is given in Table (5.3).

### **5.3.2 Reaction Parabolic Rate Constant**

Based on the experiments and literature, the oxidation of iron follows the parabolic rate law.

As has been derived in Chapter Two, the parabolic behaviour can be expressed as

$$\frac{dx}{dt} = \frac{k'}{x} \tag{5.3}$$

Where  $\mathbf{k}^{\prime}$ , x and t represent the parabolic rate constant, the scale thickness, and time respectively.

Integrating the above equation;

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$$\int_{x_{i}}^{x_{f}} x dx = k' \int_{t_{i}}^{t_{f}} dt$$
(5.4)

4. DATA PROCESSING

Table (5.3) Sample Calculation of weight gain per surface area.

Note : For calculations of column number 5, it is assumed that scale composition is 95% FeO, 5% Fe<sub>3</sub>O<sub>4</sub> and that the two oxides consist of the stoichiometric value of oxygen, i.e., 22.26% atomic oxygen in FeO and 27.64% atomic oxygen in Fe<sub>3</sub>O<sub>4</sub>.

TIME	AVERAGE	THICKNESS	SCALE	OXYGEN WEIGHT	g <sub>oxygen</sub> /cm <sup>2</sup>
(	ARFA	(11111)	(9)	(9)	
	$(cm^2)$		(6)	See assumption	
	(0)				
50	3.61	0.3	0.5232	0.1179	0.03266
88	11.91	1.0	6.1536	1.3868	0.11644
110	17.26	1.6	13.0369	2.9381	0.17022
132	17.35	2.0	17.2060	3.8777	0.2235
189	17.56	3.0	24.8431	5.5989	0.3188

Where  $x_i$  and  $x_f$  are the initial and final scale thickness at  $t_i$  and  $t_f$ , the initial and final time of measurement respectively.

and hence

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$$(x_{j})^{2} - (x_{i})^{2} = k' (t_{f} - t_{i})$$
(5.5)

The above equation can be expressed in terms of weight gain per surface area  $(g^2/cm^4.s)$  as;

$$(\frac{m_f}{A})^2 - (\frac{m_i}{A})^2 = k_p (t_f - t_i)$$

Where  $k_p$ ,  $m_i$ ,  $m_f$  and A represent the parabolic rate constant used in conjunction with the weight gain, the initial and final oxygen weight in measured scale, and the oxidized steel surface area, respectively.

Equation (5.6) was used to evaluate the weight gain as a function of time. A sample calculation for the parabolic rate constant is given in Table (5.4).

#### 5.3.3 Calculations of the Arrhenius plot

From reported previous work, Section (2.4.2), the parabolic rate constant increased exponentially with temperature according to the Arrhenius equation;

$$k_p = k_o e^{\frac{-Q}{RT}}$$
(5.7)

Where  $\mathbf{k}_n$  is a constant dependent on gas composition, steel grade, etc...

Q is the activation energy of the reaction (Joules or calories)

**R** is the gas constant (8.314 joules/ K.mole or 1.987 calories/K.mole.)

T is the temperature (Kelvin).

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Taking the logarithms of both sides of the above equation gives;

$$\ln(k_p) = \ln(k_o) + (\frac{-Q}{R}) (\frac{1}{T})$$
(5.8)

(5.6)

TEMPERATURE	$(m_f/A)^2$	(m <sub>1</sub> /A) <sup>2</sup>	t <sub>r</sub>	t,	k,
(K)			(s)	(S)	$(g^{2}/cm^{4} s)$
600	0	0.00117	0	2634	4.44x10 <sup>-7</sup>
650	0.00117	0.0016	2634	2963	1.31x10 <sup>-6</sup>
750	0.0016	0.0025	2963	3292	2.74x10 <sup>-6</sup>
850	0.0025	0.0052	3292	4170	3.08x10 <sup>-6</sup>
950	0.0052	0.01	4170	4800	7.62x10 <sup>-6</sup>
1050	0.01	0.0153	4800	5268	1.13x10 <sup>-5</sup>
1150	0.0153	0.0307	5268	6584	1.17x10 <sup>-5</sup>
1200	0.0307	0.0827	6584	9878	1.58x10 <sup>-5</sup>

Table (5.4) Sample calculations of the parabolic rate constants for experiment No. 7.

Hence a plot of  $\ln(k_p)$  vs (1/T) gives a straight line with a slope equal to (-Q/R) and an intercept,  $\ln(k_o)$ , a constant.

### 5.3.4 Oxidized Steel Depth

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In determining the oxidized depth of mild steel, the following assumptions were made;

1 - The density of mild steel is similar to that for pure iron, 7.86 (g/cm<sup>3</sup>).

2 - Scale composition is 95% FeO and 5% Fe<sub>3</sub>O<sub>4</sub>.

4. DATA PROCESSING

Knowing that there is 77.4% Fe in FeO, the oxidized depth of steel,  $d_{\text{steel}}$  (mm), is determined by the equation;

$$d_{\text{steel}} = F \cdot X_{\text{scale}}$$
(5.9)

where F and  $X_{scale}$  represent a conversion factor and scale thickness (millimetres), respectively.

The conversion factor, F, is expressed as;

$$F = \frac{(D_{scale}) \dots (\%Fe_{FeO})}{(D_{steel})}$$
(5.10)

Where  $D_{scale}$  and  $D_{steel}$  are the densities of scale and steel, respectively.

The density of scale can be expressed as;

$$D_{scale} = \frac{Wt_{scale}}{A_{steel} \cdot X_{scale}}$$
(5.11)

where Wt<sub>scale</sub> is the weight of scale.

Five samples were used to determine the scale density as shown in Table (5.5). These five samples are of different thicknesses, i.e., different residence times in the furnace.

#### 5.3.5 Percent Steel Loss Due to Scaling

For industrial evaluations it is practical to report steel loss due to scaling in terms of a percent loss. This approach is specifically based on actual slab weight and dimensions which are available at the level II computer (Vax System). The weight loss of steel by scaling per unit weight of steel

reheated is determined from the equation;

	SURFACE AREA (cm <sup>2</sup> )	THICKNESS (cm)	WEIGHT (grams)	DENSITY (g/cm³)	FACTOR (F)
sample 1	12.7	0.35	19.26	4.34	0.427
sample 2	10.0	0.32	13.49	4.22	0.416
sample 3	8.3	0.22	7.21	3.9	0.384
sample 4	8.3	0.1	3.57	4.3	0.423
sample 5	3.8	0.08	1.07	3.5	0.345
AVERAGE				4.1	0.400

Table (5.5) Measurement of scale density and the conversion factor, F.

$$W = S \cdot W_g \cdot (\% Fe_{scale}) \cdot 100$$

where W = % loss (mass of steel scaled (g) / mass of steel reheated (g))

S = (surface area of steel  $(cm^{2})/mass$  of steel (g))

 $W_g$  = weight gain (mass of scale (g)/ surface area of steel (cm<sup>2</sup>)

%Fe = percent iron content in the scale.

The value S is determined from the weight and dimensions of actual long and short slabs. The value was averaged to 0.01221 ( $cm^2_{steel}/g_{steel}$ ).

In the calculations, it was assumed that

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(5.12)

4. DATA PROCESSING

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- . Steel is 100% Fe.
- . Scale consists of 95% FeO and 5%  $Fe_3O_4.$

A sample calculation of percent steel loss is given in Table (5.6).

## Table (5.6) Calculations of percent loss of steel due to scaling for a trial.

TIME (minutes)	$W_g$ $(g_{scale}/cm^2)$	$W_g$ $(g_{steel}/cm^2)$	W (%loss)
53	0.149	0.1149	0.14
85	0.318	0.2465	0.30
111	0.468	0.3610	0.44
161	0.743	0.5732	0.69
281	1.353	1.0438	1.27

# CHAPTER SIX

## DISCUSSION OF EXPERIMENTAL CONDITIONS AND RESULTS

## 6.1 INTRODUCTION

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The scale trials undertaken in this work require a consideration of the different parameters being monitored and of their behaviour. For industrial trials, unlike well controlled laboratory conditions, parameters such as oxidizing atmosphere, temperature, samples residence time in the furnace, etc., differ from one experiment to another. Moreover, some of these parameters fluctuate even within experiments. Thus, one of the major difficulties experienced in executing this work, was to attain similar experimental conditions and hence good repeatability. This was due to the complexity and many control variables in the reheating process. During a heating cycle, parameters such as mill delays, charge type, gaps between slabs in the furnace, etc.., resulted in fluctuations in furnace operating conditions. However, the most critical variable for our trials was mill delays. It is quite common for things to go wrong with the rolling mill, thereby necessitating a hold up of furnace discharging, i.e., an immediate change in furnace firing rates.

In this work, the full trials have been divided into two segments, corresponding to low and high air/fuel ratios. A set of four experiments for each was conducted. This number does not

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represent the total trials undertaken, in total, about 30 trials were undertaken. However, it was only for the last eight that our team succeeded in bringing the furnace under satisfactory control as problems were encountered along the way.

In this chapter, a discussion of trial conditions, scaling, and scale characteristics, are presented.

#### **6.2 CONDITIONS FOR TRIALS**

Because of the size of the reheat furnace and the large number of variables involved in the control system, practically every parameter in the furnace such as air and fuel flow rates, and hence furnace atmosphere were constantly changing. Trials were then conducted using the strategy of maintaining all set parameters constant so as to achieve a reasonably good repeatability. In this section, the different parameters such as air and fuel flow rates, fuel composition, furnace atmosphere and slab and sample temperature are considered.

#### 6.2.1 Air and Fuel Flow rates

Air and fuel flow rates are controlled by the furnace control system which itses the computed slab temperature in the furnace as the basis for its control algorithm. When the slab temperature, calculated by the furnace model, is lower than the set point at a particular zone in the furnace, the Level II control, Vax system, demands more heat flux from the Level I control system. The Level I control system then responds by opening the fuel and air valves to provide higher heating rates and visa versa. The temperature set point also varies with steel grade, slab size, etc. Each individual zone in the furnace operates independently and hence, when considering the total furnace operation, fluctuations arise. These fluctuations in heating rates are also a function of a number of other parameters, such as initial temperatures of charged slabs, gaps between slabs, mill delays, production rates, etc. All of these factors make it almost impossible to reproduce exactly the same conditions between the different trials.

6. DISCUSSION OF EXPERIMENTAL CONDITIONS AND RESULTS

Figures (6.1 a&b) and Figure (6.2 a&b) present typical air and fuel flow rates for the charge, intermediate, soak zones and for the entire furnace. It can be seen from these figures that the response of fuel flows to changes in air flows exhibits a time lag and also that at some periods, the air/fuel ratio approaches a minimum, while at other times it is very high. It is this mechanical behaviour of the air and fuel valves that introduce fluctuations in the oxidizing gases within the furnace. It can also be seen from these figures, that the behaviour of the individual zones is independent. Because of the heating requirements, the amount of air and fuel injected into the individual zones changes with time. It is only the soak zone that exhibits a less fluctuating behaviour. Considering the behaviour of the entire furnace, it can be seen that constant conditions are relatively short lived.

For repeat trials, aimed at achieving similar conditions, specified furnace operations were practiced, by choosing clear runs with no scheduled mill delays, choosing similar steel line-ups, and setting the furnace to manual control. Further discussion of some of these elements are presented below.

#### **6.2.2 Fuel Composition**

The furnace uses a mixture of natural gas and coke oven gas and fuel oil as the combustion fuel. Fuel oil was not used in any of the trials. Further, the levels of gas components, mainly  $CH_4$  and  $H_2$ , are inversely proportional. The proportions of coke oven gas (mainly  $H_2$ ) and natural gas (mainly  $CH_4$ ), depend on their availability, and also on gas distribution within the steel plant. Figure (6.3) gives a typical on-line analysis of the fuel.

#### 6.2.3 Furnace Atmosphere

A multi-component gas exists in the reheat furnace. These components can be divided into two categories, those that are products of combustion such as  $CO_2$ ,  $H_2O$  and those



Figure (6.1) Air and fuel flow rates in Normal cubic meters per hour for (a) the charge zone, and (b) the intermediate zone.

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Figure (6.2) Air and fuel flow rates in normal cubic meters per hour for (a) the soak zone, and (b) the entire furnace.

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Figure (6.3) On line analysis of fuel mixture gas composition.

resulting from incomplete combustion such, as CO,  $O_2$  and hydrocarbons together with  $N_2$ . The levels of these gases depend on a number of factors such as fuel composition, air and fuel ratio, and infiltrated air (especially from furnace door openings). During the trials only  $O_2$ , CO<sub>2</sub> and

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6. DISCUSSION OF EXPERIMENTAL CONDITIONS AND RESULTS

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CO were monitored. Monitoring of water vapour was not possible at the time of the trials. A typical i 1-furnace gas measurement is given in Figure (6.4) from which it can be seen that the concentrations of CO<sub>2</sub> and CO are inversely proportional to the concentration of O<sub>2</sub>. The more important observation from the figure, is that the concentration levels of these gases are far from stable. More discussion of these will be given below.



Figure (6.4) In-furnace measurements of O<sub>2</sub>. CO<sub>2</sub> and CO.

## 6.3 DISCUSSION OF THE OXIDATION OF MILD STEEL FOR INDIVIDUAL TRIALS

To be able to investigate and compare the oxidation rates, it is important to discuss individual parameters such as temperature, furnace atmosphere, samples residence time in the furnace, etc. The chemical composition of the tested steel is given in Table (6.1).

Table (6.1) Chemical composition of tested steel.

	С	Mn	Р	S	Si	Cu	Ni	Cr	Sn	Ai	N <sub>2</sub>	Мо
Min.	0.025	0.15	0.000	0.000	0.000	0.00	0.00	0.00	0.000	0.020	.003	0.00
Aım	0.040	0.20								0.040		
Max	0.055	0.25	0.012	0.010	0.025	0.10	0.04	0.0 <del>6</del>	0.010	0.060	.007	0.02

#### 6.3.1 Gas Components in the Furnace

As mentioned earlier, the trials were divided into high and low air/fuel ratios A set of four for each condition, was undertaken in order to investigate the repeatability of the trials. Effective air ratios, as calculated in section (4.3) are given in Figure (6.5). There, it can be seen that the low effective air ratios ranges between 10 to 30% excess air. This ratio was the minimum that can be achieved by the furnace control system. Most of the low oxygen trials fell in this range, except for one experiment where this ratio rose to about 60% excess air for a time period of about 80 minutes. On the other hand, the high effective air/fuel ratio ranged between 40 to 90% excess air for the most part. These ratios are, of course, considered to be extremely high for such a furnace.

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As mentioned earlier, the in-furnace gas components,  $O_2$ ,  $CO_2$  and CO in the intermediate and soak zones for the low and high air/fuel ratios, were monitored. These measurements are given in Figures (6.6, 6.7, 6.8 & 6.9) respectively. From Figure (6.6), it can be seen that the oxygen levels achieved are reasonably low, for the most part. It can also be seen that the level of  $CO_2$ is inversely proportional to the  $O_2$  levels. This behaviour can be explained by considering the fact that there is just not enough excess oxygen to dilute the combustion products



Figure (6.5) Effective stoichiometric/actual air ratios for all the experiments

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Figure (6.6) In-furnace measurements of  $O_2$ ,  $CO_2$  and CO for the low air/fuel ratio experiments in the intermediate zone.



Figure (6.7) In-furnace measurements of  $O_2$ ,  $CO_2$  and CO for the low air/fuel ratio experiments in the soak zone.

This can be supported by the fact that CO is present in small concentrations and that the reaction

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$$2 CO + O_2 = 2 CO_2$$
 (6.1)

did not go to completion, hence the presence of CO. This can be seen from the graphs, such that when oxygen levels rise, carbon monoxide declines instantaneously. This observation is common for all four low air/fuel ratio trials.

In the soak zone,  $O_2$  and  $CO_2$  concentrations fluctuated quite rapidly. This behaviour corresponded to openings of the discharge door. Each time a slab was discharged, a draft of air entered the furnace and hence increased the concentration of oxygen in the soak zone, with an according decline in  $CO_2$  levels. It has been seen from the intermediate and soak zones measurements, that when the oxygen levels attain a minimum of about 0.5 %, the  $CO_2$  level reached a maximum of between 10 to 11%. Unfortunately, CO concentrations in the soak zone were not measured, owing to a damaged CO cell in the analyzer.

In the case of high air/fuel ratio trials, Figure (6.8), the intermediate zone oxygen levels averaged about 3% oxygen with concurrent levels of 6 to 7%  $CO_2$ . Again, an inverse proportionality between  $O_2$  and  $CO_2$  was observed. As a result of the high levels of oxygen, no carbon monoxide could be detected. This supports the assumption that when oxygen is not present in sufficient amounts, CO is present, and visa versa.

High air/fuel ratios resulted in extremely high  $O_2$  levels in the soak zone, Figure (6.9). This is believed to be the result of the high excess air introduced in this zone due to air infiltration through furnace discharge doors, which correspond to the high peaks in the graphs. It can also be seen from the graphs that  $CO_2$  levels were lower than  $O_2$  levels. High  $O_2$  levels were measured in all the high air/fuel ratio experiments.

In general, the two points of measurements (intermediate and soak zones), can by no means be considered as being representative of the entire furnace atmosphere. 能震



Figure (6.8) In-furnace measurements of  $O_2$ ,  $CO_2$  and CO for the high air/fuel ratio experiments in the intermediate zone.





Figure (6.9) In-furnace measurements of O<sub>2</sub>, CO<sub>2</sub> and CO for the high air/fuel ratio experiments in the soak zone.

6. DISCUSSION OF EXPERIMENTAL CONDITIONS AND RESULTS

#### **6.3.2** Temperature and Oxidation Rates

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Temperature is known to be one of the most important parameters affecting rates of oxidation. Higher temperatures accelerate the kinetics of oxidation in an exponentially increasing manner.

#### **6.3.2.1** Oxidation Temperatures

As mentioned earlier, the temperatures used in this work are those predicted by the furnace model for the top slab surface. However, from Thermophil-Stor trials, it was found that the temperatures of the samples in the early stages of oxidation exceeded those predicted for of the slab's top surface temperatures. At later stages, the temperature of the samples, and those of the top rider slab surface, were very similar. Figure (6.10) presents measured temperatures of the rider slab. From this figure, it can be seen that the maximum temperature difference between the sample and slab surface reached about 600 °C. This difference is a result of the size effect as the slab which acts as a much greater heat sink than the small sample. As a result, the slab surface experiences a much slower heating rates versus the sample. In the later stages of reheating however, the slab's top surface and the samples reach thermal equilibrium, resulting in the attainment of similar temperatures. However, during the trial, thermocouples failed, and temperatures in the later stages of reheating were not measured.

Predicted temperature profiles for the low and high oxygen experiments are given in Figures (6.11 & 6.12) respectively. From these figures, it can be seen that the temperature behaviour is quite similar. That is, the samples are exposed to low initial temperatures at the beginning of the oxidation period. A sharp increase in temperature is observed for the most part of the trial duration. Near the end of the furnace, in the soak zone, temperatures


Figure (6.10) Thermophil-Stor temperature measurements of sample and test slab going through the reheat furnace.





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Figure (6.12) Oxidation rates and temperatures for high oxygen experiments.

gradually levelled off to a constant value of about 1250 °C. This observation was common for all trials.

## **6.3.2.2 Parabolic Rate Constants and Arrhenius Plots**

The parabolic rate constants for the individual experiments are calculated in section (5.3.2) and presented in Figure (6.21). The Arrhenius plot provides an indication of the parabolic fit for the oxidation curves. It also serves as an educated guess for the classification of reaction kinetics, i.e., chemical and/or diffusion controlled reactions. Although reactions detailed information will need to be well known before a serious consideration of this method, one can nonetheless state that in general, if the activation energy of a reaction is less than about 10 kJ, the reaction is likely to be a chemically controlled reaction. On the other hand, if the activation energy of the reaction is over 50 kJ, the reaction is likely to be of mixed control. Figure (6.13 & 6.14) present the Arrhenius plots for the low and high oxygen trials. From these figures, it can be seen that the data exhibit fairly straight lines of  $\ln(k)$  vs. 1\T. However, in the case of the low oxygen trials, the activation energies for all the experiments were within the range of 40 to 60 kJ. This can be taken as a rough indication that the controlling mechanisms are likely to be of the mixed chemical and diffusion control.

# **6.3.2.3** Oxidation Rates

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The oxidation curves for all the experiments, Figures (6.11 & 6.12), can be characterized as follows: the initial state of the samples is that there was no scale on the surface prior to oxidation in the furnace. As the samples enter the furnace, scale nucleates at the clean surface. The initial rates of oxidation, up to about 60 to 70 minutes, exhibit exponential behaviour, in which a sharp increase in the rate of scaling observed. However, as the scale grows thicker, the



Figure (6.13) Arrhenius Plots for low oxygen experiments.



Figure (6.14) Arrhenius Plots for high oxygen experiments.

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oxidation rate becomes more or less linear with time. The parabolic behaviour observed during the initial oxidation was not observed owing to the fact that the increase in the sample's temperature compensates for the decrease in scaling rates owing to diffusion limitations of iron cations to the scale-gas interface or/and oxygen ions to the metal-oxide interface. The effect of these two factors seem to balance out on the basis of the present results. Owing to the presence of a complex gas environment within the furnace, the number of reactions taking place among the various gaseous species and oxidants with steel are difficult to model. In general, it appears that the initial rates of oxidation are so fast, that dissociation and adsorption of oxidant on the metal surface are rate limiting. In the case of low oxygen, where carbon monoxide is in abundance, it is reasonable to emphasise  $CO_2$  and water vapour reactions with steel. Smeltzer<sup>17</sup> has considered the mechanism of iron oxidation in  $CO_2$  to FeO. He explained these reactions as follow;

Carbon dioxide dissociates on the metal surface as

$$CO_2 \mapsto 2O_{(ads)}^{\bullet} + 2\bigoplus_{(o)}^{\bullet} + CO_{(g)}$$
 (6.2)

Where  $\bigoplus_{(o)}$  is a positive hole in the oxide-gas interface.

The oxygen adsorbed at the surface reacts with an iron cation creating an iron cation vacancy  $Fe^{++}_{\Box(o)}$  as;

$$O^{\bullet}_{(ads)} \mapsto FeO + Fe^{**}_{\Box(o)} \tag{6.3}$$

The exchange of vacancies between the oxide-gas and metal-oxide interfaces, i.e. the rate controlling step, can be expressed according to :

$$Fe^{**}_{\Box(o)} + 2\bigoplus_{(o)} \rightleftharpoons Fe^{**}_{\Box(i)} + 2\bigoplus_{(i)}$$
 (6.4)

where  $Fe^{**}_{\Box 0}$  and  $\bigoplus_{\omega}$  are the cation vacancy and the positive hole at the metal-oxide

interface respectively.

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At the metal-oxide interface, the following condition exist,

$$Fe + Fe^{**} = 0 \Rightarrow Vall$$
 (6.5)

Adsorbed oxygen at the scale-gas interface fills the positive holes to produce molecular oxygen as follows

$$O^{--}_{(ads)} + 2 \bigoplus_{(o)} \mapsto \frac{1}{2}O_2.$$
 (6.6)

Oxidation would obey a parabolic law if the concentrations of vacancies and positive holes in equations (6.2, 6.3 & 6.6) were of sufficient magnitude to cause vacancy diffusion via its gradient across the oxide scale, equation (6.4), to determine the reaction rate. Since a linear law is assumed during the initial oxidation, equations (6.2, 6.3 & 6.6) are the rate determining reactions during this initial period.

It is well known that the oxidation of most technical steels above 750 °C is, in the presence of water vapour, faster than that for steel oxidation in oxygen or dry air, Per Kofstad<sup>1</sup>. The reasons for this are poorly understood. Moreover, the presence of water vapour in the combustion products introduces different scale characteristics, such as porosity and microchannels, as will be discussed below.

The main water vapour reaction with iron that need to be considered here is as follows;

$$Fe + H_2 O \rightleftharpoons FeO + H_2 \tag{6.7}$$

There is a disagreement among researchers whether water vapour oxidizes steel faster than oxygen. In our case, oxygen certainly appears to have a more pronounced effect on the scaling

rate of this particular steel. This is based on the fact that in the low air/fuel ratios, the water vapour content was higher than in the case of high air/fuel ratio experiments. This was obtained by calculations of water vapour, using the F\*A\*C\*T system, from actual fuel composition values, Figure (6.15). The calculations were carried out for 10% and 50% excess air. One point to note in this case is that the fuel composition is not similar in the two experiments and hence some of the differences in water vapour level can be attributed to this fact.

#### 6.3.2.4 Sample Residence Time in Furnace

Sample's residence time in the furnace is extremely critical on the amount of scale formed. The sample's walking rates through the furnace for the high and low oxygen experiments are presented in Figures (6.16 & 6.17) respectively.

Some minor mill delays are observed in experiments number 3, 6, 7 and 8 which, however, did not result in any major differences on the slopes of scaling curves. In general, as seen from Figures (6.11 & 6.12), longer residence times in the furnace produced more scale, especially when the hold-up was in the high temperature zones (heating and soak zones) of the furnace.

## **6.4 COMPARISON OF OXIDATION RATES**

Having discussed the various individual parameters influencing scale formation for the different experiments, a comparison of their scaling rates is considered.

#### 6.4.1 Oxygen Weight Gain and Steel Loss

Figure (6.18) shows the scaling curves for all the experiments. It can be seen from the figure that a major difference in the oxidation curves exist between the low and high oxygen



Figure (6.15) Calculated values of  $H_2O$ ,  $O_2$  and  $CO_2$  for 10% and 50% excess air using in the calculations the actual fuel composition values for low oxygen and high oxygen experiments.



Figure (6.16) Samples walking rate through the furnace for the low oxygen experiments.



Figure (6.17) Samples walking rate through the furnace for the high oxygen experiments.

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Figure (6.18) Comparison of oxidation rates among low and high oxygen experiments. Note: dark points are for high oxygen experiments, hollow points are for low oxygen experiments.

experiments. The low oxygen experiments produced 35% less scale than those for the high oxygen experiments. Although the slopes are almost equivalent, being slightly lower for the low oxygen experiments, the main difference seems to exist during the initial time period within the furnace. That is, in the low oxygen experiments, the initial scale formed was of less thickness. This thinner scale served as a base for the growth of subsequent scale. This may indicate that the initial mechanism controlling scale formation was the rate of reaction of oxygen reaction with the clean metal surface, and because of the lower oxygen levels available for reaction, a thinner, more coherent, layer of scale was formed. The low oxygen presence in this case was supported by the fact that carbon monoxide, which is inversely proportional to oxygen, was present, as discussed earlier.

On the other hand, the h gh oxygen experiments initially formed much thicker scale, again because of the presence of higher levels of oxygen. The oxidized depths and loss of steel, as calculated in sections (3.5.4 & 5.3.5), for all the experiments are presented in Figures (6.19 & 6.20), respectively.

#### **6.5.3 Parabolic Rate Constants**

The other important parameter to be considered is the effect of temperature on the scaling rates and whether this observed difference in scaling rates was because of the temperature factor. This is considered by calculating the parabolic rate constants for all of the experiments, section (5.3.2). Figure (6.21) gives the parabolic rate constants for the low and high oxygen experiments as a function of temperature.

It can be clearly seen from the figure that the high oxygen experiments do in fact have high oxidation rates. This fact supports the argument that oxygen in the furnace is the key player in determining the oxidation rates of the tested steel.

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Figure (6.19) Oxidized steel depth for low and high oxygen experiments. Note: dark points are for high oxygen experiments, hollow points are for low oxygen experiments.

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Figure (6.20) Percent steel loss for low and high oxygen experiments. Note: dark points are for high oxygen experiments, hollow points are for low oxygen experiments.



Figure (6.21) The parabolic rate constants for all low and high oxygen experiments. Note : dark points are for high oxygen experiments, hollow

points are for low oxygen experiments.

# **6.5 SCALE STRUCTURE**

The scale samples were subjected to an examination of their microstructure. Scanning Electron Microscopy (SEM) was used to reveal the oxide phases present in the scale, using the back scatter technique. The various phases observed were identified using a microprobe.

#### 6.5.1 General Characteristics of Scale

In general, the scale consists of three solid phases, wustite (FeO), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>). The wustite phase being located adjacent to the metal substrate, was also the thickest, and contained many voids of various sizes, together with cracks and fissures, and exhibits a rough interface with the steel. The voids and cracks in this phase were concentrated closer to the metal substrate where their concentration and size was largest. Figure (6.22) shows a typical scale structure of the three oxides. It can also be seen from the figure that there are deep longer cracks, running parallel to the steel/scale interface. A hypothesis for the origins of these cracks is discussed later.

Moving through the wustite phase, away from the steel side, one encounters an increasing number of magnetite crystals dispersed in the wustite. The magnetite phase present within the wustite varies in its concentration. In the areas near the pure wustite, it is well distributed in small amounts. Further away from the wustite phase, it had formed in larger amounts which are still well spread in the magnetite phase. Some of the cracks present in these areas are surrounded by magnetite. This suggests that molecular oxygen had penetrated these cracks, oxidizing the wustite to magnetite. This is in accordance with the iron-oxygen phase diagram given in Figure (2.3). These observations are common to all scales produced in this work.

The pure magnetite phase follows the wustite-magnetite matrix at a smooth interface. Its relative thickness, which grows proportional to wustite, amounts to about 5% of the total scale in most cases. Magnetite was not seen in the very early stages of oxidation. The levels of voids and



Figure (6.22) A typical scale microstructure with its three phases, wustite (FeO), magnetite (Fe3O<sub>4</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>).

cracks are much lower in magnetite than those for wustite.

Hematite, the richest in oxygen content, was only seen in scale formed over longer periods of oxidation. It had formed at the outer surface of the scale with its relative thickness amounted to about 1 to 2% of the total scale.

Considering the scales for the low and high oxygen experiments, some differences were found. Figures (6.23 & 6.24) present the scale microstructure for the low and high oxygen experiments respectively. In the low oxygen case, the scale contained practically no hematite whereas in that formed at high oxygen levels, hematite was present. Further, for the low oxygen environments, the magnetite layer was thinner. It can also be seen that the wustite-magnetite interface is not very smooth for the low oxygen case, and that veins of wustite exist through it. The wustitemagnetite matrix for the low oxygen case is less than that for the case of high oxygen. These observations again support the belief that oxygen, in the low oxygen experiments, is not available in sufficient amounts for oxidizing reactions.

#### **6.5.1.1 Development of Scale Cracks**

A common feature of the scales is that they contains cracks of various sizes, at various locations. Crack development in no doubt caused by stress generation resulting from the growing scale. This phenomenon can be explained by considering the kinetics of oxidation. It is suggested by many researchers that scale growth takes place at various locations within the scale. One of these locations is the scale-metal interface. Oxidants penetrate the scale to the metal interface where a new oxide is formed. If the volume of the oxide is larger than the volume of metal from which it is formed (i.e., the Pilling-Bedworth Ratio, PBR), compressive stresses will develop within the scale. The PBR in the case of iron is larger than one and hence compressive stresses are expected to develop in the oxide scale. On the other hand, if supposedly the scale grows only by iron cation diffusion towards the gas interface, where the scale is seemingly stress free, stresses in the scale will still develop due to the tendency of the scale to adhere to the metal



Figure (6.23) Scale microstructure for low oxygen experiment.

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Figure (6.24) Scale microstructure for high oxygen experiment.

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surface while the metal core volume decreases owing to cation diffusion. The stresses developed can again result in the formation of cracks in the scale.

In our case, most of the cracks observed were due to stresses developed in the scale during cooling. When the metal and scale cool together, the volume of the metal contracts at a faster rate than that for the oxide, due to the higher coefficient of thermal expansion coefficient of the metal. Because of this, shear stresses develop and introduced the cracks observed in the scale. This explanation is supported by the fact that for most of these cracks, higher oxides around their edges were not observed which would have been caused the penetration of oxygen gas through them.

#### 6.5.1.2 Development of Scale Voids and Microchannels

A model for the continuous production of a porous inner layer is given by G. B. Gibbs and R. Hales<sup>43</sup>, and is presented in Figure (6.25). Metal ions diffusing outward through different paths in the scale will leave vacancies in the metal surface. These vacancies will condense at the nearest area of exposed metal, undercutting the new oxide crystals as they grow. Because of the low oxygen environment, these new crystals will grow at much slower rates than the rates of vacancies condensation, causing an undercut of these crystal. This process will be repeated after the nucleation of newer crystals.

**Kofstad**<sup>\*\*</sup> has presented the work of Buckman and Mrowec of the proposed model for the development of microchannels in growing scale, Figure (6.26). In their model, it is assumed that the scale grows by outward diffusion of metal ions and, as a result, voids eventually develop at the scale metal interface. It was assumed that metal ion diffusion along grain boundaries is much faster than lattice diffusion, and as a result of this, the grain boundary above the void opens up and gradually forms a microchannel. The channel remains open as long as the chemical

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# Figure (6.26) Schematic illustration of the model for formation of microchannels in oxide scale by preferential outward diffusion of metal ions along grain boundaries, from Kofstad<sup>1</sup>

potential of oxygen is equal at the interface of the channel to the inner part of the scale.

In this chapter, most of the work presented bas been based entirely on industrial trials and data collected during these trials. The complexity and size of the furnace investigated did not allow for any comparisons with laboratory work conducted by some researchers, which was directly or indirectly related to the oxidation of steel in reheating cycles. However, the consistency of the results collected from the 350 ton/hour steel reheat furnace, was quite acceptable.

# CHAPTER SEVEN

# CONCLUSIONS AND SUGGESTION FOR FUTURE WORK

## 7.1 INTRODUCTION

The oxidation of a metal is usually studied under extremely well controlled experimental conditions. Very sensitive equipment is used for this purpose such as Thermogravimetric Analyzers which can tect extremely small weight gains in the order of micrograms. Even under these specified conditions, some of the experimental parameters are subject to change from one experiment to another, and hence good repreducibility is quite often hard to achieve.

In the case of our work, where we were dealing with a 350 ton/hour reheat furnace, with a total of 121 burners installed in different locations and a huge number of variables that were changing minute by minute, expectations of reasonable experiment repeatability were low. However, it was expected that "ball park" information could be acquired for typical "industrial conditions".

Having these thoughts in mind, the results obtained from this work were very consistent.

Consistent oxidation trends were obtained with excellent repeatability. On the other hand, this work has raised more questions than answers regarding the mechanisms of the observed effects and the reasons behind them.

In this chapter, the conclusions to this scale work are stated, along with some recommendations regarding the reheat furnace. Also, suggestions for future work are outlined.

#### 7.2 CONCLUSIONS

1 - Limited test results are available in the literature on the oxidation of steel under conditions approximating those of the reheat furnace.

The majority of the work described in the literature is limited to the oxidation of iron and steel under well defined and constant experimental conditions. Conditions such as those that exist in typical reheat furnaces are quite difficult to achieve in the laboratory. Therein lies the difficulty of simulating reheat furnace conditions in a laboratory setting.

2 - A decreased amount of excess air for combustion, from about 70% to about 20%, resulted in 35% reduction in scale formation.

From the analysis of the furnace air and fuel flow rates and fuel composition, it was found that the furnace typically operated with an average of about 70% excess air. After many attempts, the excess air was lowered to about 20%. This adjustment in furnace control resulted in the lowering of the oxygen levels in the furnace. The experiments were carried out at these two extreme conditions and hence allowed us to attain a 35% reduction in the amount of scale formed.

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7. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

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This finding, although clearly due to the lower oxygen potential, does not indicate the way by which this reduction was achieved. It may be a result of many factors, such as the increase in CO, the lack of available oxygen to react with the metal, or/and other unknown factors. These questions require detailed experiments under well controlled conditions, simulating industrial furnace atmospheres and specific grades of steel.

3 - Longer residence times of steel in the furnace at higher temperatures resulted in the formation of excessive amounts of scale.

This finding was of no surprise. It is well known that longer exposures at higher temperatures result in the formation of more scale. Therefore, if the samples are located in the intermediate or soak zone of the furnace, scale was seen to be forming in excessive amounts. The fact that when the scale is thicker, especially in these zones, this thickness has very little effect on the rate of scale growth, and scaling was seen to proceed with little parabolic behaviour, suggesting that cracks and channels exist in the scale, through which the oxidizing gases can penetrate. On the other hand, when the steel is positioned in zones of low temperatures, such as the preheat and charge zones, longer times at these zones had very little effect on the amount of scale formed.

4 - The furnace is operating with excessive amounts of combustion air.

As discussed in (1), at the time of these tests, the furnace was operating with an excess air of about 70% average. This, of course is not desirable in many ways, such as a lower the adiabatic flame temperature plus excess oxygen and nitrogen are introduced in the furnace.

7. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

# **7.3 SUGGESTED FUTURE WORK**

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To be able to answer the many questions raised in this work regarding the effect of the different parameters on scale formation, a wide variety of laboratory work is suggested. This includes;

1 - Isothermal oxidation experiments to determine the effect of single oxidizing gases such as  $O_2$ ,  $CO_2$  and  $H_2O$  at different temperatures on the oxidation of selected steel.

2 - Isothermal oxidation experiments to determine the effect of multi-component gases, and their levels, and at different temperatures, on the oxidation of a selected steel.

3 - Experiments under time varying temperatures (i.e., heating rates) approximating those in the reheat furnace.

4 - Investigate the effect of steel chemistry (i.e., different steel grades) on oxidation rates.

5 - Investigate depth of decarburization zones vs scaling conditions.

6 - Investigate, or develop, an anti-oxidation material for steel coating as an option.

7 - Apply the laboratory findings to the industrial reheat furnace.

8 - Develop a comprehensive scale formation model, based on the laboratory experiments, to be tested with the industrial reheat furnace.

9 - Conduct a thorough investigation on scale adhesion to the substrate.

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