REGRESSION ANALYSIS OF END-POINT DATA FROM DYNAMIC BASIC OXYGEN FURNACE MODEL

by

René Guindon

Submitted to the Department of Electrical Engineering, The University of Ottawa, Ottawa, in partial fulfillment of the requirements for the degree Master of Science.

Department of Electrical Engineering,
Faculty of Pure and Applied Science,
The University of Ottawa,
Ottawa 2, Canada.

1969

Approved for the Department
of Electrical Engineering

Supervisor

Chairman of the Examination
Committee

Chairman of the Department

CONTENTS

PAGE

PAGE

ACKNOWLEDGEMENTS

I wish to express my appreciation to Dr. J. Kruus of the University of Ottawa and to Dr. C. M. Woodside of the National Research Council for suggesting and supervising this joint project between the University and the Council. I would also like to thank them for their inspiring discussion and guidance throughout this work. Parts of the PCF model are results of Dr. C. M. Woodside research work; activity of iron oxide and formulation for the deoxidation of silicon and manganese are examples.

I am thankful to Mr. J. Rowlands of the "Statistical Research Service Canada, Department of Agriculture" for permission to use his Regression Analysis computer program.

This work was supported by the National Research Council of Canada through grants No. A-2580 and No. A-4157.

LIST OF SYMBOLS

a_{FeO} = Activity of iron oxide.

A_1, A_2 = Constants fitted to determine O'_{Mn}

b_1, b_2, b_3 = Factors which include the net effect of diffusion layer area, the thickness and diffusion rate constant.

a_i = Raoultian activity of component i in the metal or slag phase.

BOF = Basic Oxygen Furnace.

C = Carbon

CaO = Calcium Oxide (Lime)

CO = Carbon monoxide.

CO_2 = Carbon dioxide.

C_X = Effective specific heat of the elements X in dilute solution, including the temperature coefficient of the heat of solution.

ΔF^o = Free energy change of reaction in calories (i.e. total free energy of the products diminished by the total free energy of the reactants).

Fe = Iron

FeO = Iron Oxide.

f_i = Henrian activity coefficient.

γ_i = Raoultian activity coefficient.

h_i = Henrian activity of component i in the metal or slag phase.

h_d = Heat deficit.

H_{Fe} = Heat required to raise one lb of Fe from 25°C to 1300°C.

ΔH = Heat content (enthalpy) of the bath.

$\Delta H_{1527,X}$ = Enthalpy of one lb of liquid X in solution in iron at 1527°C, including heats of fusion and solution.

K_i = Equilibrium constant of the component i

lb = Pound

Min = Minimum

Mn=Manganese

MnO = Manganese oxide

M.W. = Molecular weight

O = Oxygen

O_B = Wt % oxygen in the bulk iron

O_{CO} = Wt % oxygen in equilibrium with the CO in the gas bubbles

O_{FeO} = Wt % oxygen in equilibrium with the slag FeO, determined by the slag concentration.

O_S = Wt % oxygen in iron in equilibrium with pure gaseous oxygen, or with pure FeO K_{FeO}

P_{CO} = Pressure within a carbon monoxide bubble.

R_C = Conduction resistance

R_r = Radiation resistance

R_1, R_2, R_3, R_4, R_5, R_6, R_7 = Diffusion rate of oxygen

Si = Silicon

SiO_2 = Silicon dioxide

t = time

T_b = Temperature of the metal bath in °C

TI = Initial temperature of the metal bath

Wt% i = Weight percent of component i in the metal bath

XH = Time interval

X_1 = Parameter representing the initial temperature.
X_2 = Parameter representing initial Si
X_3 = Parameter representing initial C
X_4 = Parameter representing initial scrap
X_5 = Parameter representing initial Mn
TI = Initial temperature
Y_1 = Time of blow
Y_2 = Final temperature
Y_3 = FeO formed

[ ] = Component in liquid metal phase
( ) = Component in liquid slag phase
$\langle\rangle$ = Component in solid phase
$\{\}$ = Component in gas phase
α = Parameter used in determining the ratio of Wt% Si and Wt% Mn
α_1, α_2 = Constant in temperature dependence function O'_{Mn}
α_3 = The Si-Mn rate parameter
$\beta_1, \beta_2, \beta'_1, \beta'_2$ = Proportionality constants used in determining the rates R_5 and R_7
δ = Heat transfer parameter.

ABSTRACT

The dynamic model described in this thesis for the Basic Oxygen Furnace (BOF) is an approximate one with the general characteristics of an oxygen steel furnace expressed through the thermodynamic relationships. It describes the behaviour of a system with oxygen, iron, carbon, lime, silicon dioxide and manganese oxide in a simplified way. Also the effect of small amounts of silicon and manganese added to the bath are described. Simulation using this model reproduces most of the important aspects of data in the literature (except for the phenomenon of "slopping" and associated erratic behaviour.)

From the model, end-point data was then generated for different initial conditions and a least squares equation was fitted to this data in terms of linear and non-linear variables. The characteristics of the end-points that are of interest, that is, the time of blow, the final temperature and the amount of FeO formed, can then be predicted if the initial conditions are specified.

CHAPTER 1

INTRODUCTION:

The manufacture of molten steel can be represented as a two-stage process beginning with the blast furnace.

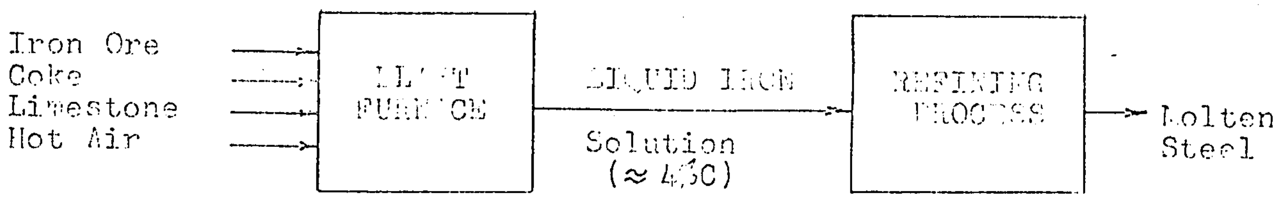


Fig. 1 BLOCK DIAGRAM OF MANUFACTURE OF MOLTEN STEEL

The 4% Carbon liquid iron solution is usually called pig iron which has to be refined in order to get steel. Of the refining processes the most popular ones are:

a. Open Hearth Furnace

b. Electric Arc Furnace

c. Basic Oxygen Furnace (BOF)

For the purpose of this thesis we will consider only the BOF process. Oxygen was first used for the refining of pig iron some 30 years ago. Its use did not become general, however, because its application was dependent upon special local conditions of molten metal analysis and scrap availability. But since 1952 the rate of development has been enormous.

Since the BOF process has no external thermal sources, it is important to choose correct input weights of hot metal, scrap, and auxiliary raw materials in order to achieve a certain target temperature at the end of blowing the heat. For this purpose, a mathematical model of the thermal balance has to be established. This operation requires the solution of thermal-balance equation, containing so many components that some kind of computer is necessary, not only to perform the calculations quickly, but also to avoid mistakes in the results. It is quite evident that computer manufacturers discovered in the BOF process a very welcome field of application for computer techniques and an increasing stream of literature is being devoted to this subject. (1) However, much of this literature is rather disappointing, for in most cases no detailed information about the basic mathematical expressions has been given.

In the thesis, basic mathematical expressions are given to describe a model for the Basic Oxygen Furnace. The model may appear artificial, as for example in the "heat deficit", or in treating reaction rates very simply, but for our purpose the simplest model that accounts for the gross feature of real furnace operation was desirable.

The purpose of the thesis was to finish the development of the model started by the National Research Council; that is to describe a method for determining the rates of oxidation of Silicon and Manganese and to determine the oxygen level when both occurs together in the metal bath; to consider a "heat deficit" function which would represent a feature of the real furnace; to simulate the model on the digital computer and also do an analysis of the end-point data in order to find some of the non-linearities in the model which could be used at a later date on real furnace data.

Hence the thesis consist of two parts:

1. The description of a dynamic model for the BOF process and

2. A least squares fitting analysis of the end-point data.

The appendices are devoted to the computational aspects of some of the functions which arose in the description of the model.

1.1 DESCRIPTION OF THE BOF PROCESS

The BOF process involves blowing almost pure oxygen at supersonic speed into the metal bath through a water-cooled copper lance lowered vertically through the vessel mouth to within a certain distance above the metal surface. The vessel used is cylindrical, closed at one end, with a concentric or eccentric section terminating in the open mouth of the vessel at the other end. The open end has a diameter considerably smaller than the maximum of the vessels centre section.

The high velocity of the oxygen jet causes it to penetrate slag and metal and performs a dual function:

a. It oxidizes iron in the bath; the iron oxide thus produced reacts in turn with the other alloying elements,

b. The momentum of the jet provides a very high degree of agitation, hence promoting the rates of the transport controlled chemical reactions. This arrangement allows mass transfer rates that are some 20 to 50 times faster than those encountered in open hearth steelmaking. (2)

The operation of the process consist in charging the scrap, followed by the hot metal from the blast furnace. The lance is then lowered and oxygen injection commences. After a few seconds, ignition takes place and some or all of the required lime is then added.

If ore is used as a coolant to replace some, or all of the scrap, the charge ore is added at the same time as the first lime.

Since the reactions occuring in the process are exothermic(i.e. heat is evolved from the reaction) the temperature increases quite drastically. Thus, in order for the process to end at the specified or required temperature scrap, ore, or both are added to the system and act as a coolant for the reactions.

CHAPTER 2

PHYSICAL ASPECTS OF THE MODEL

The object of steelmaking is to reduce to acceptable values the concentration of the impurity elements in the iron solution while obtaining specified final temperatures.

2.1. BASIC ASSUMPTIONS

In the derivation of the model we have assumed that:

a. The oxygen concentration throughout the iron is uniform. This assumption is not unreasonable since the bath is a big turbulent mass of material. Samples taken at various depths in the bath during the boil of an open-hearth furnace showed negligible concentration gradients within the metal and slag layers.(3) There is no reason to suspect these results to be different for the BOF process.

b. Surface zone reactions are those in which the reaction occurs at the surfaces between phases.(4) The concentration at the reaction site for surface zone reactions is determined by an equilibrium condition for the reaction. This assumption seems to be valid at steelmaking temperatures (1300°C to 1600°C) since the reaction itself, at the reaction site, proceeds very fast and maintains the local equilibrium, so that the reaction rate is limited by the transport (diffusion) of raw materials and products to and from the site. All reactions considered, except the formation of SiO_2, are assumed to be surface zone reactions. The formation of SiO_2 is assumed to be a volume zone reaction (5) which occurs throughout the body of the molten iron solution.

2.2 PHYSICAL MECHANISMS

The basic physical mechanisms can be separated by their region of occurence. Gaseous oxygen is blown into the bath from the lance and dissolves in the molten iron. The dissolved oxygen reacts in the bulk metal with silicon to form silicon dioxide, which subsequently dissolves into the slag. The basis of the slag is the lime which is added as a part of the charge.

At the slag-metal interface, manganese and iron oxidation reactions are at equilibrium, their rate limited by diffusion of reacting materials to the site. Carbon monoxide is formed at a gas-metal interface and leaves the bath. Some of the carbon monoxide burns at the top of the vessel to form carbon dioxide. Scrap, ore, or both added to the furnace will melt and dissolve in the bath during the first part of the heat.

Figure 2. summarizes the reactions, which are discussed in more detail in the following subsections.

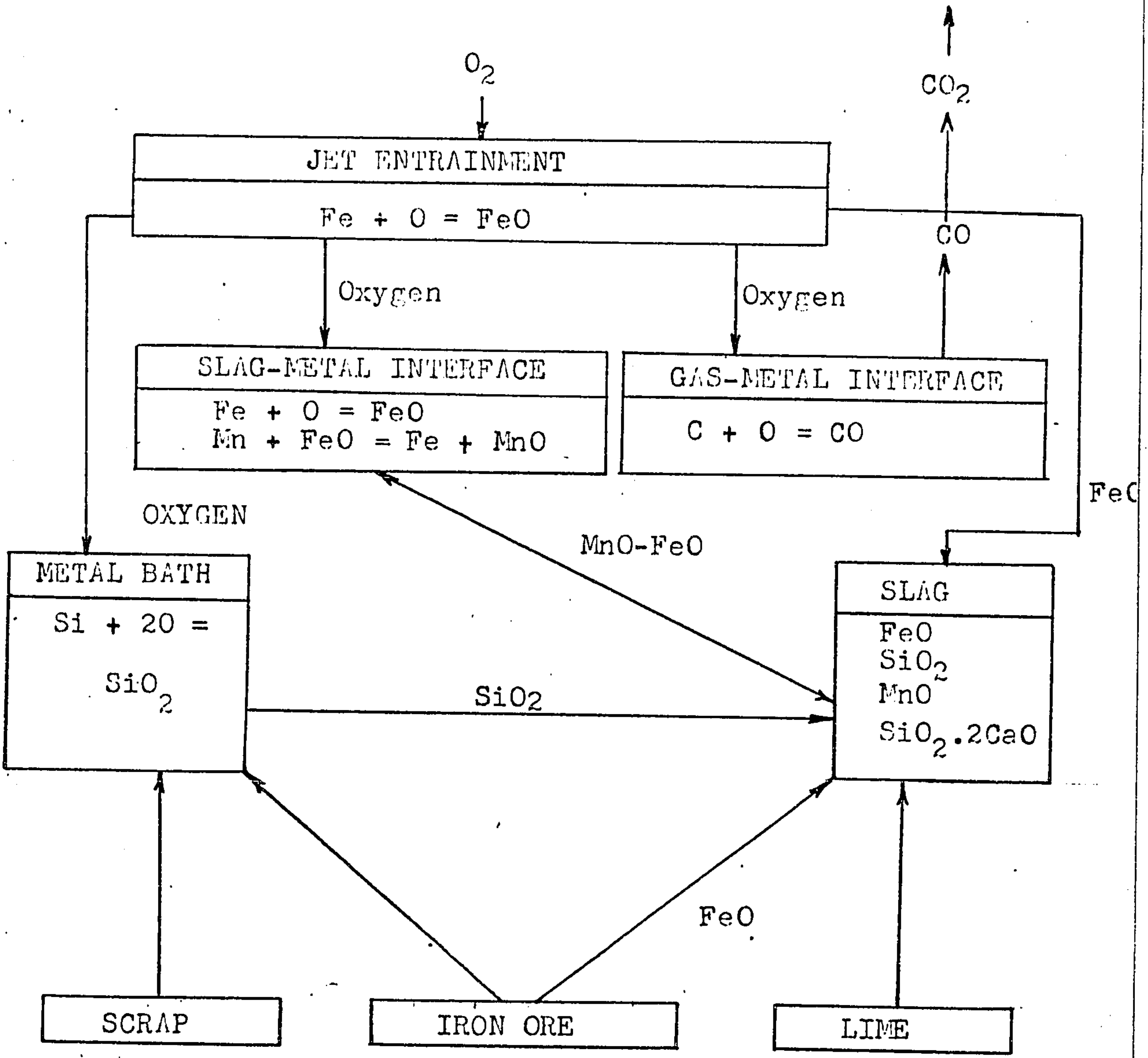


Fig. 2 SCHEMATIC DIAGRAM OF THE REACTIONS (6)

2.2.1 SOURCE OXYGEN

Oxygen from the oxygen lance must dissolve into the liquid blast furnace iron where then the dissolved oxygen is available for chemical combination with carbon, iron, manganese and silicon. Oxides of iron, manganese and silicon join the dissolved lime to form a complex liquid solution called the steelmaking slag. Oxide of carbon, CO (gas formation) bubbles up through the iron and leaves the process as a waste gas.

Since oxygen is blown into the bath it exists throughout the body of the iron as bubbles. A boundary layer then exists between the oxygen bubble and the bulk metal. (7)

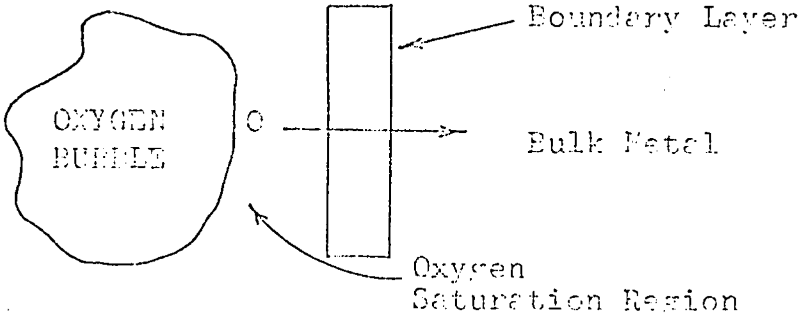


Fig.3 OXYGEN SUPPLY TO BULK METAL

From the above figure, the metal adjacent to the boundary layer reacts with the oxygen bubble to form a ferrous oxide phase.

We have the equilibrium condition.

$$[Fe] + [O] = (FeO)$$

The iron oxide equilibrium constant K_{FeO} determines the available oxygen supply adjacent to the bubble,

$$\text{i.e.} \quad O_S = 10^{\left(2.734 - \frac{6320.0}{T_b + 273.0}\right)}$$

where O_S = Wt% of oxygen in iron in equilibrium with pure FeO (See appendix C)

The rapidity with which the reactions take place implies that they are instantaneously in a state of equilibrium.$^{(8)}$ Hence we have a state of equilibrium between the ferrous oxide phase and the oxygen content of the bubble on the bubble side of the boundary layer which forms the saturation region. Oxygen diffuses through the boundary layer into the bulk metal at the rate

$R_3 = b_3(O_S - O_B)$

where b_3 = constant

O_B = oxygen concentration, in Wt%, of bulk metal.

2.2.2 SLAG-METAL INTERFACE

At this interface two reactions must be considered. Oxygen dissolved in the bulk metal diffuses to the slag-metal interface where FeO formation takes place according to

$$[Fe] + [O] = (FeO)$$

Since the slag is not a pure iron oxide slag, the activity of FeO will be less than one. Thus

$O_{FeO} = (1/K_{FeO})\ a_{FeO}$

where a mathematical expression for this activity constant a_{FeO}, was fitted to the graph given by Bishop, Lander, Grant, and Chipman (10) which was based on the result of Taylor and Chipman (11) (See appendix D)

The FeO diffuses across the slag boundary layer and into the bulk slag at a rate given by $R_2 = b_2(O_B - O_{FeO})$

Where b_2 = constant and O_{FeO} = Wt% oxygen in equilibrium with the FeO slag.

The FeO content in the slag is also increased due to dissolved manganese in iron since Mn and Fe reacts with dissolved oxygen and forms liquid droplets of FeO and MnO. The FeO-MnO ratio in these droplets is governed by the equilibrium of the reaction.

$$[Fe] + (MnO) = (FeO) + [Mn]$$

The rate is given by R_6 which will be developed later on.

2.2.3 GAS-METAL INTERFACE

This model assumes that CO is formed at the interface between the metal bath and a CO bubble. This is consistent with the conventional view that bubbles nucleate and grow at pores in the furnace lining.$^{(12)}$

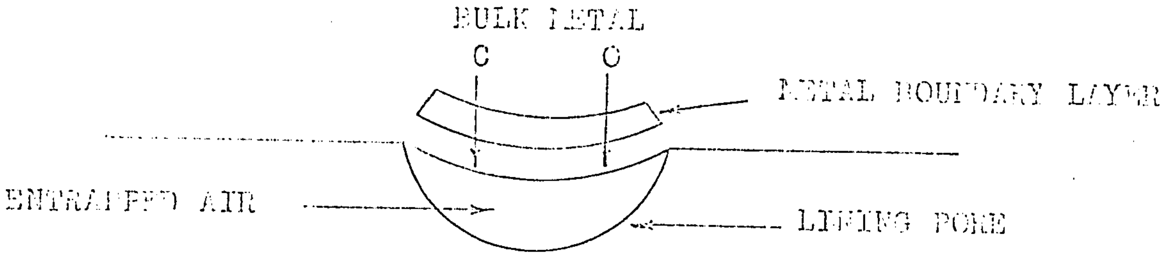


Fig. 4 CARBON MONOXIDE FORMATION SITE

When the blast furnace iron is poured, surface tension forces prevent the iron from filling completely the pores of smaller radius. Therefore a bulk metal-gas interface is formed at each pore only partially filled with metal, and it is at this interface boundary that formation of carbon monoxide occurs. Carbon monoxide bubbles continue to grow at the formation sites until they break away and rise through the body of the iron. These then serve as sites for further formation of carbon monoxide, leading to continued growth of the bubbles until they emanate from the bulk metal into the waste gas phase.

Hence, from fig. 4 carbon and oxygen atoms dissolved in the bulk metal diffuse across a metal boundary layer to the bulk metal-gas interface.$^{(13)}$ At the interface the formation of carbon monoxide occurs according to

$$[C] + [O] = \{CO\}$$

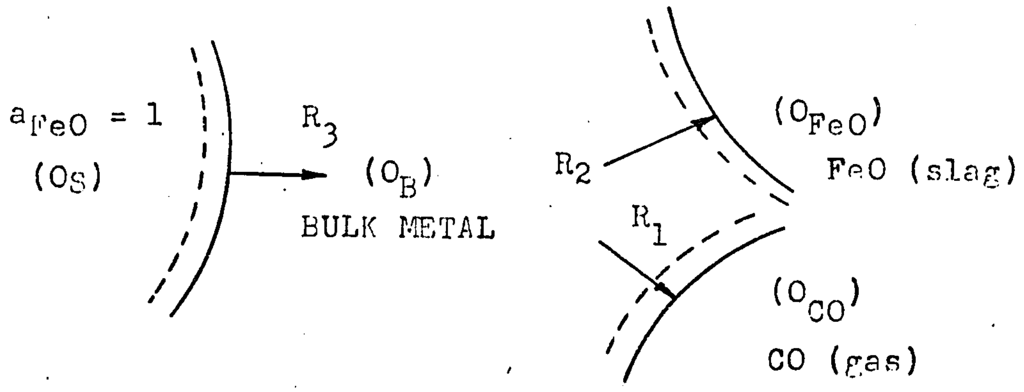
and the rate at which it is formed is given by $R_1 = h_1(C_B - C_{OC})$

Where b_1 = constant and O_{CO} = concentration of oxygen in weight % dissolved in the metal which is in equilibrium with carbon monoxide.

It should be remembered that $R_1 \geqslant 0$ since carbon monoxide leaves the process as a waste gas. Hence carbon monoxide can never decompose to carbon and oxygen.

2.2.4 CARBON BOIL IN THE BASIC OXYGEN FURNACE

Three diffusion steps have been selected as being important.$^{(14)}$



In the usual case

$$O_S > O_B > O_{FeO} \,,\, O_{CO} \tag{1}$$

Also

$$R_1 = b_1(O_B - O_{CO}) \text{ moles/hr } \geqslant 0 \tag{2}$$

$$R_2 = b_2(O_B - O_{FeO}) \quad \text{moles/hr} \tag{3}$$

$$R_3 = b_3(O_S - O_B) \text{ moles/hr} \tag{4}$$

It should be noted that b_1, b_2, b_3 are factors which include the net effects of boundary layer area and thickness and the diffusion rate constant. Since no accurate data on these factors exist, we can vary b_1, b_2 b_3 such that the net effect of FeO transport, CO transport and O_2 transport agrees with the physical furnace under consideration. It should also be noted that increasing the height of the lance results in an increase of FeO transport and a decrease of O_2 transport in the bath.

To ensure in the model that R_1 will always be $\geqslant 0$ we can consider a new variable O'_{CO} where we define

$$O'_{CO} = \mathrm{Min}(O_B, O_{CO}) \tag{5}$$

Where $\mathrm{Min}(O_B, O_{CO})$ is the minimum of the argument O_B, O_{CO}

Hence in this case $O'_{CO} \leqslant O_B$

$$R_1 \geqslant 0$$

$$\text{and} \quad R_1 = b_1(O_B - O'_{CO}) \tag{6}$$

In general if condition (1) is satisfied at some time and the bath is not altered from outside , (1) will remain true and $R_1 \geqslant 0$ will be satisfied.

Now assuming that these are the only 3 processes taking place and that there is sufficient oxygen, then $R_1 + R_2 - R_3 = 0$

$$\text{i.e.} \quad b_1(O_B - O_{CO}) + b_2(O_B - O_{FeO}) - b_3(O_S - O_B) = 0 \tag{7}$$

solving for O_B we have

$$O_B = O' = \frac{b_1 . O_{CO} + b_2 . O_{FeO} + b_3 . O_S}{b_1 + b_2 + b_3} \tag{8}$$

Hence O_B is determined by the various transport rates in and out of the bulk metal. But cases will now be considered when R_3, the rate of demand of oxygen, is limited to a maximum value and when R_1 is zero. In these cases we shall assume O_B to be the minimum of the level determined. It should be noted that some deoxidizers (notably silicon and manganese) interact and such effects must be calculated also. In the case of silico-manganese the equilibrium O_B is substantially lower than for silicon and manganese above. This case will also be considered in determining the value of O_B.

Since in the model the oxygen demand rate R_3 can increase to a value considerably higher than the possible supply of oxygen, a limited supply of oxygen has to be considered. Let us define this maximum supply rate of oxygen from the lance as B (in moles/hr)

Then $R_3 = B$ for the maximum case and (9)

$$b_1(O_B-O_{CO}) + b_2(O_B-O_{FeO})-B = 0 \tag{10}$$

Solving for O_B we have:

$$O_B = O'_B = \frac{b_1 \cdot O_{CO} + b_2 \cdot O_{FeO} + B}{b_1 + b_2} \tag{11}$$

The two cases discussed so far are taken into account by redefining O_B as

$$O_B = \text{Min}(O' , O'_B) \tag{12}$$

In order to take into consideration in the programming of the model the possibility of a demand of oxygen greater than the possible rate of supply a new variable R'_3

was considered where:

$$R'_3 = \mathrm{Min}(R_3, B) \tag{13}$$

Now another possibility can occur

i.e. when $O_{CO} > O_B$ $(\therefore R_1 = 0)$

So for completeness we consider the case

$R_3 = R_2$

$$\text{i.e.} \quad b_3(O_S - O_B) = b_2(O_B - O_{FeO}) \tag{14}$$

solving for O_B we have

$$O_B = O'' = \frac{b_2 \cdot O_{FeO} + b_3 \cdot O_S}{b_1 + b_3} \tag{15}$$

Also, limiting the rate of supply of Oxygen to B, we have

$R_3 = B = R_2$

$$O''_B = \frac{b_2 \cdot O_{FeO} + B}{b_2} \tag{16}$$

Hence all possible cases are accounted for by using

$$O_B = \mathrm{Min}(O', O'', O'_B, O''_B) \tag{17}$$

2.2.5 SILICON AND MANGANESE IN THE BOF

Silicon and Manganese together in the bath produce much lower equilibrium oxygen levels than either alone, because in the combined deoxidation product the activity of silica is lowered by the manganese. Hence the treatment of Si and Mn is very complex.

A solution was developed by approximating Fig. 6

in which 4 zones can be distinguished to the graph from R.G. Ward (15), Fig. 5 which gives a plot of equilibrium oxygen against Wt% Mn and Wt% Si together at 1600°C. If we denote the equilibrium oxygen Wt% as $O_{Si,Mn}$, it is found to be:

<u>Zone A</u>: (pure Mn)

Let $$O_{Si,Mn} = O_{Mn} = \frac{10^{\left[2.734 - \frac{6320}{T_b + 273} + 0.13(\text{Wt\% C})\right]}}{1 + (\text{Wt\% Mn}).10^{\left[\frac{6440}{T_b + 273} - 2.95\right]}} \qquad (18)$$

(see appendix C)

<u>Zone B</u>: (low Si)

$O_{Si,Mn}$ is interpolated between O_{Mn} and O'_{Mn} (see below)

<u>Zone C</u>: (intermediate Si)

Let $O_{Si,Mn} = O'_{Mn}$ (defined below)

<u>Zone D</u>: (high Si)

Let
$$O_{Si,Mn} = O_{Si} = \frac{1}{(\text{Wt\% Si})^{\frac{1}{2}}} . 10^{\left[5.5 - \frac{14575}{T_b + 273}\right]} \qquad (19)$$

(see appendix C)

The expression for O'_{Mn} was determined by fitting a line to the hyperbola-like curve in the lower left corner of Fig. 5. Fig. 7 is the line fitted to values taken from Fig. 5 which is:

$$O'_{Mn} = A_2(O'_{Mn})(Wt\%\ Mn) = A_1 \qquad (20)$$

at 1600°C

Rearranging O'_{Mn} we have

$$O'_{Mn} = \frac{A_1}{1 + A_2(Wt\%\ Mn)} \qquad (21)$$

Values taken from the graph in Ward were:(15)

Wt% Mn	O'_{Mn} (%)	(O'_{Mn})(Wt% Mn)
0.0	0.100	0.0
0.043	0.080	0.00344
0.099	0.055	0.00543
0.148	0.040	0.00592
0.210	0.027	0.00573
0.320	0.020	0.00640
0.494	0.015	0.0074
0.618	0.012	0.0077
0.765	0.010	0.0076
0.876	0.009	0.0078
0.975	0.008	0.0078
1.112	0.007	0.0078
1.321	0.006	0.0079

From which

$$O'_{Mn} = \frac{0.134}{1 + 16.0(Wt\%\ Mn)} \qquad (22)$$

If the dependence of O'_{Mn} on temperature is the same as that of O_{Mn}, the constants A_1 and A_2 can be made temperature dependent

Let
$$O'_{Mn} = \frac{\alpha_1 \cdot 10^{\left[2.734 - \frac{6320}{T_b + 273} + 0.13(\text{Wt\% C})\right]}}{1 + \alpha_2(\text{Wt\% Mn})\, 10^{\left[\frac{6440}{T_b + 273} - 2.95\right]}} \qquad (23)$$

By evaluating the numerator and the denominator at 1600°C where (22) is valid, we obtain:

$$\alpha_1 = 0.5795$$
$$\alpha_2 = 5.20 \qquad (24)$$

A suitable procedure for calculating $O_{Si,Mn}$ is then:

Zones A,B

$0 \leqslant \text{Wt\% Si} \leqslant 0.2(\text{Wt\% Mn})$

Let $\alpha = \frac{\text{Wt\% Si}}{0.2(\text{Wt\% Mn})}$

Then $O_{Si,Mn} = \alpha O'_{Mn} + (1-\alpha) O_{Mn}$

Zones C,D

$\text{Wt\% Si} \geqslant 0.2(\text{Wt\% Mn})$

$O_{Si,Mn} = \text{Min}(O'_{Mn}, O_{Si})$

Since at the beginning of the heat the Si-Mn equilibrium with oxygen is likely to control the value of O_B, we now have:

$$O_B = \text{Min}(O', O'', O_{Si,Mn}, O'_B, O''_B) \qquad (25)$$

2.2.6 Removal Mechanism of Silicon and Manganese

By taking the difference between the supply of oxygen and its absorption by diffusion-controlled reactions, a rate of supply of oxygen

$$R_4 = R'_3 - R_2 - R_1 \quad \text{moles/hr.} \qquad (26)$$

is made available for a number of other reactions.

Let $Mn + O = MnO$ use O_2 at rate R_5 moles/hr. (27)

$Fe + O = FeO$ use O_2 at rate R_6 moles/hr. (28)

$\frac{1}{2}Si + O = \frac{1}{2}SiO_2$ use O_2 at rate R_7 moles/hr. (29)

Because the ratio of MnO to FeO in the deoxidation product is fixed[(16)] (assumed to hold with silica present also) we assume that R_5/R_6 has the same ratio.

The ratio of MnO to FeO is most easily discussed by considering the manganese distribution equilibrium[(17)] equation (standard state equation):

$$(FeO) + [Mn]_{1Wt\%} = (MnO) + [Fe]$$

for which the equilibrium constant is

$$K = \frac{(a_{MnO})\,[a_{Fe}]}{(a_{FeO})\,[h_{Mn}]}$$

where K is the equilibrium constant for the reaction

$[a_{Fe}]$ is the activity (Raoultian) of component in the metal phase

$[h_{Mn}]$ is the activity (Henrian) of component in the metal phase

$(a_{MnO})(a_{FeO})$ are the activities of components in the slag phase. (See appendix C)

$$K = \frac{(g_{MnO} \cdot X_{MnO})\,[g_{Fe} \cdot X_{Fe}]}{(g_{FeO} \cdot X_{FeO})\,[f_{Mn} \cdot Wt\%\ Mn]} \qquad (30)$$

where X_i = mole fraction of i

However, the numerical values of the activity coefficients are not usually known accurately and it is convenient to transfer these all to the left-hand side of the equation, i.e.

$$K \cdot \frac{f_{FeO} \cdot f_{Mn}}{g_{MnO} \cdot f_{Fe}} = \frac{(X_{MnO})[X_{Fe}]}{(X_{FeO})[Wt\% Mn]} \qquad (31)$$

Assuming X_{Fe} = 1.0 then

$$K_m = \frac{(X_{MnO})}{(X_{FeO})[Wt\% Mn]} = 10^{\left[-2.95 + \frac{6440}{T_b + 273}\right]} \qquad (32)$$

Therefore

$$\frac{(X_{MnO})}{(X_{FeO})} = K_m(Wt\% Mn) \qquad (33)$$

Assuming that R_5/R_6 has the same ratio then:

$$\frac{R_5}{R_6} = K_m(Wt\% Mn) \qquad (34)$$

Considering the available oxygen from (26) we have:

$$R_4 = R_5 + R_6 + R_7 \qquad (35)$$

R_5 , R_6 and R_7 have been determined (see appendix E) and found to be:

$$R_5 = \frac{R_4(Wt\% Mn)}{(Wt\% Mn) + \frac{1}{K_m} + \alpha_3(Wt\% Si)} \qquad (36)$$

$$R_6 = \frac{R_5}{K_m(Wt\% Mn)} \qquad (37)$$

$$R_7 = \frac{R_4 \cdot \alpha_3 \cdot (\text{Wt\% Si})^{\frac{1}{2}}}{(\text{Wt\% Mn}) + \frac{1}{K_m} + \alpha_3 (\text{Wt\% Si})^{\frac{1}{2}}} \qquad (38)$$

In the equations for R_5 and R_7, α_3 was determined by the method of isoclines which is designed to give a graphical solution to 1st order and some 2nd order ordinary differential equations.(18) Fig. 8 is an example of such a solution for $\alpha_3 = 4$. On the graph $\dot{X}_3 = R_7$ and $\dot{X}_1 = R_5$ where the ratio is then $\frac{\dot{X}_3}{\dot{X}_1} = \alpha_3 \frac{(\text{Wt\% Si})^{\frac{1}{2}}}{(\text{Wt\% Mn})}$

The short line segments as shown at intervals along the isoclines are the slopes of R_7/R_5. A freehand sketch of the trajectory from any initial conditions may be drawn rapidly by following the changing direction of the slope field. It is now possible to choose α_3 in such a way as to obtain a Mn-Si balance in agreement with published results.

2.2.7 HEAT LOSSES

The heat losses consist mostly of the radiative and conductive loss. The heat transfer is:

$$f_0(T_b) = \frac{T_b - T}{R_c} - \frac{T_b{}^4 - T^4}{R_r} \qquad (39)$$

Where T_b = temperature of the bath in °K

T = ambient temperature assumed to be 0°K

R_c = conduction resistance in °C/BTU/hr

R_r = radiation resistance in $(°C)^4$/BTU/hr

RESISTANCE

A) Conductive Loss

For our model we have considered a converter 25 Ft. high with a 12 Ft. diameter and 2 Ft. thick lining R_c was taken as a thin slab of area

$2\pi(\text{radius})(\text{height}) + \pi(\text{radius})^2$

$= (2\pi \times 6 \times 25) + (\pi \times 36)$

$= 1055.6 \text{ Ft.}^2$

Conduction resistance is given as:

$$R_c = h/A\ k \qquad (40)$$

where h = 2 Ft.

k = thermal conductivity (Value is taken to be that of magnesite brick, given by (35)

$= 0.5$ BTU/hr/Ft^2 area/Ft thick/°F

$= 0.9$ BTU/hr/Ft^2 area/Ft thick/°C

Hence R_c = 0.0021 °C/BTU/hr

b) Radiative Loss

Through some gaps in the furnace heat is radiated from the contents to the surroundings. This heat loss was considered to be approximately 5% of the final heat content.

We also have to consider:

1) the heat required to raise the scrap from 25°C to 1300°C;

2) the heat required to raise the slag to the required temperature (1300°C);

3) and the heat required to add to the lining (considered in our case to be a constant during the oxygen blow)

2.2.8 HEAT DEFICIT FUNCTION

A reasonable mechanism must be considered for the effect of adding scrap and slag at ambient temperature to the bath at 1300°C. This will be done by adding to the model a "heat deficit function." A certain fraction of the heat supplied by the exothermic reactions will be used in raising the temperature of the scrap and the slag from 25°C to 1300°C and also in supplying the heat absorbed by the lining of the vessel. The other fraction will be used in raising the temperature of the metal bath.

Initially in the model, the heat deficit at time t = 0 is:

$$h_d(0) = H_{Fe} \cdot \text{Scrap} + H_{slag}(\text{CaO} + \text{SiO}_2 + \text{Iron Ore}) + H_{lining} \qquad (41)$$

The value for the parameters H_{Fe} and H_{slag} are given by Calclough $^{(36)}$ as:

$$H_{Fe} = 300 \frac{\text{BTU}}{\text{lb}}$$

$$H_{slag} = 660 \frac{\text{BTU}}{\text{lb}}$$

where H_{Fe} = heat required to raise 1 lb of Fe from 25°C to 1300°C.

H_{slag} = heat required to raise 1 lb of slag from 25°C to 1300°C.

also H_{lining} = amount of heat supplied to the lining of the vessel.

For the model this value (H_{lining}) was experimented with and chosen to be 1024×10^4 BTU. It was seen that the heat loss can be controlled by adjusting the radiative resistance R_r. Since this radiative loss is only a certain fraction of the final heat loss in our model H_{lining} was considered as another source of heat loss. It can be ajusted to account for the observed end-point temperatures. The main control for the final temperature is the amount of scrap or ore added to the system in order to cool the process.

The rate of change of enthalpy is given by:

$$\Delta\dot{H} = -f_0(T) + \sum(\text{Heats of oxidation}). \qquad (42)$$

where the values of the heats of oxidation are given in appendix A and $f_0(T)$ is the heat transfer loss. As long as part of the charge is unmelted, the heat generated is divided between raising the bath temperature and melting the other material.

Let: $\delta\Delta\dot{H}$ = the amount of heat used to raise the temperature of the metal bath and $(1 - \delta)\Delta\dot{H}$ = the amount of heat used to raise the temperature of the scrap and the slag from 25°C to 1300°C. i.e. to diminish the heat deficit. Obviously

$$\delta = 1 \qquad \text{for } h_d(t) = 0$$

and

$$0 < \delta < 1 \quad \text{for } h_d(t) > 0$$

The rate of change of the heat deficit function is:

$$\dot{h}_d(t) = -(1 - \delta)\ \Delta\dot{H} \tag{43}$$

and by the rectangular method of integration

$$h_d(t + 1) = h_d(t) + XH \cdot \dot{h}_d\ (t) \tag{44}$$

where XH = time interval

Also the rate of change of temperature derived in appendix B is now:

$$\dot{T}_b = \frac{\delta\Delta\dot{H} - \sum_i (\Delta H_{1527,i}\ \dot{X}_i) - (T_b - 1527)\ \sum_i C_i\dot{X}_i}{\sum_i C_i X_i} \tag{45}$$

2.3 MATHEMATICAL FORMULATION OF THE BOF MODEL

The model consists of a set of simultaneous non-linear differential equations, each representing the behaviour of one of the variables in the steelmaking process. A set of state variables defines the system in a complete and self-consistent way without any redundant information.

The state variables are:

q — number of reacted moles

ΔH — heat content (enthalpy) of the bath

The state equations are:

$$\dot{q}_i(t) = r_i(\bar{Z}\ ,\ t) \qquad (46)$$

where r = boil reaction rate in moles/hr. and

$$\Delta\dot{H}(t) = -\ f_0(T_b) + \sum \text{(heat of oxidation)}\ ^{(25)} \qquad (47)$$

where

$\Delta\dot{H}(t)$ = rate of change of enthalpy

where also

$\bar{Z} = \bar{Z}(Fe,\ C,\ FeO,\ CaO,\ SiO_2,\ MnO,\ CO,\ T_b)$ quantities in lb. and in °C. (48)

We can then determine our variables

$$Fe(t) = Fe(0) - q_{Fe}(t) \times M.W.$$
$$C(t) = C(0) - q_C(t) \times M.W.$$
$$FeC(t) = FeO(0) + q_{FeO}(t) \times M.W.$$
$$SiO_2(t) = SiO_2(0) + q_{SiO_2}(t) \times M.W.$$
$$MnO(t) = MnO(0) + q_{MnO}(t) \times M.W. \qquad (49)$$
$$CaO(t) = CaO(0) \qquad \text{considered to be a constant}$$
$$Si(t) = Si(0) - q_{Si}(t) \times M.W.$$
$$T_b(t) = T_b(0) + (\text{increase in } T_b)$$

2.3.1. BASIC FLOW SHEET FOR MODEL PROGRAMMING

A. Set values for the parameters:

1. $\Delta H_{1527,i}$, C_i
2. Molecular weight of Fe, FeO, C, CO, Si, SiO_2, Mn, MnO, CaO
3. R_r, R_c, B, b_1, b_2, b_3, α_3, P_{CO}, T_b

B. Set initial conditions

$T_b(0), C(0), Mn(0), scrap(0), Fe(0), FeO(0),$

$t(0), SiO_2(0), MnO(0), h_d(0), CaO(0)$

C. Integrate the state equations

1. Determine equilibrium constants

$$K_{FeO} = 10^{\left(2.734 - \frac{6320}{(T_b + 273)}\right)}$$

$$K_{CO} = 10^{\left(-2.131 - \frac{1056}{(T_b + 273)}\right)}$$

$$K_m = 10^{\left(-2.95 + \frac{6440}{(T_b + 273)}\right)}$$

2. Calculate activity of FeO

$$a_{FeO} = 1.724 \cdot \frac{x_1}{1 + 0.240\, x_1} - 0.914$$

$$+ \left(3.89 + \frac{4.56}{1 + \left(\frac{x_1}{0.788}\right)^3} \cdot \frac{x_2}{2 + x_2}\right) \cdot$$

$$\exp\left[- \frac{x_2}{2 + x_2} \cdot \frac{1}{0.265 + 1.33 \exp\left(\frac{-x_1}{.809}\right)}\right]$$

$$+ \frac{x_2}{2 + x_2} \left(5.22\, x_1 - 3.234\right)$$

Where

$$x_1 = \frac{Z_{FeO}}{Z_{FeO} + Z_{CaO} + Z_{SiO_2}} .$$

$$x_2 = \frac{Z_{CaO}}{Z_{SiO_2}}$$

and $Z_{FeO} = FeO/(\text{Molecular Weight of } FeO)$

$Z_{CaO} = CaO/(\text{Molecular Weight of } CaO)$

$Z_{SiO_2} = SiO_2/(\text{Molecular Weight of } SiO_2)$

3. Calculate the weight % of C , Mn , Si

$$\text{Wt\% C} = \frac{100 \cdot C(lb)}{Fe(lb) + C(lb) + Mn(lb) + Si(lb)}$$

$$\text{Wt\% Si} = \frac{100 \cdot Si(lb)}{Fe(lb) + C(lb) + Mn(lb) + Si(lb)}$$

$$\text{Wt\% Mn} = \frac{100 \cdot Mn(lb)}{Fe(lb) + C(lb) + Mn(lb) + Si(lb)}$$

4. Determine the % oxygen in equilibrium

$$O_{Si} = \frac{1.0}{(\text{Wt\% Si})^{\frac{1}{2}}} \cdot 10^{\left(5.5 - \frac{14575}{T_b + 273}\right)}$$

$$O_{CO} = \frac{P_{CO}}{\text{Wt\% C}} \cdot K_{CO} \cdot 10^{(-0.09 \cdot \text{Wt\% C})}$$

$$O_{FeO} = a_{FeO} \cdot K_{FeO}$$

$$O_S = K_{FeO}$$

$$O' = \frac{b_1 \cdot O_{CO} + b_2 \cdot O_{FeO} + b_3 \cdot O_S}{b_1 + b_2 + b_3}$$

$$O'_B = \frac{b_2 \cdot O_{FeO} + b_1 \cdot O_{CO} + B}{b_1 + b_2}$$

$$O'' = \frac{b_2 \cdot O_{FeO} + b_3 \cdot O_S}{b_2 + b_3}$$

$$O''_E = \frac{b_2 \cdot O_{FeO} + B}{b_2}$$

$$O_{Mn} = \frac{10^{\left[2.734 - \frac{6320}{T_b + 273} + 0.13(\text{Wt\% C})\right]}}{1 + (\text{Wt\% Mn})\, 10^{\left[-2.95 + \frac{6440}{T_b + 273}\right]}}$$

$$O'_{Mn} = \frac{0.5795 \cdot 10^{\left[2.734 - \frac{6320}{T_b + 273} + 0.13(\text{Wt\% C})\right]}}{1 + 5.20\,(\text{Wt\% Mn})\, 10^{\left[-2.95 + \frac{6440}{T_b + 273}\right]}}$$

$$O_{Si,Mn} = \text{Min}(O'_{Mn}\ ,\ O_{Si})$$

$$O_B = \text{Min}(O'\ ,\ O''\ ,\ O_{Si,Mn}\ ,\ O'_B\ ,\ O''_E)$$

$$O'_{CO} = \text{Min}(O_B\ ,\ O_{CO})$$

5. Calculate the rate of reactions

$$R_1 = b_1(O_B - O_{CO})$$

$$R_2 = b_2(O_B - O_{FeO})$$

$$R_3 = b_3(O_S - O_B)$$

$$R'_3 = \text{Min}(R_3\ ,\ B)$$

$$R_4 = R'_3 - R_2 - R_1$$

$$R_5 = \frac{R_4(\text{Wt\% Mn})}{\text{Wt\% Mn} + \frac{1}{K_m} + \alpha_3(\text{Wt\% Si})^{\frac{1}{3}}}$$

$$R_6 = (R_5/K_m)(\text{Wt\% Mn})$$

$$R_7 = \frac{\alpha_3 . R_4 (\text{Wt\% Si})^{\frac{1}{2}}}{\text{Wt\% Mn} + \frac{1.0}{K_m} + \alpha_3 (\text{Wt\% Si})^{\frac{1}{2}}}$$

6. Calculate the heat transfer loss

$$f_o(T_b) \quad \frac{T_b}{R_c} - \frac{{T_b}^4}{R_r}$$

7. Calculate the heats of reactions.

Heats of reaction = $R_1 . 69100 - 1.8 . R_1(10080 + (0.9(T_b + 273))) + (R_2 + R_6) 114716 + 491000.R_5 + (347000 + 53600)R_7$

8. Calculate rate of change of enthalpy

$$\Delta\dot{H} = -f_0(T_b) + \sum(\text{Heats of Reaction})$$

9. Calculate derivatives of the state variables

$$\dot{T}_b(t) = \frac{\delta \Delta\dot{H} - \sum_i \Delta H_{1527,i}\dot{X}_i}{\sum_i C_i X_i} - \frac{(T_b - 1527) \sum_i C_i \dot{X}_i}{\sum_i C_i X_i}$$

$\dot{Fe}(t) = - (R_2 + R_3)$(Molecular Weight of Fe)

$\dot{C}(t) = - (R_1)$(Molecular Weight of C)

$\dot{FeO}(t) = (R_2 + R_6)$(Molecular Weight of FeO)

$\dot{SiO_2}(t) = (R_7)$(Molecular Weight of SiO_2)

$\dot{CaO}(t) = 0$

$\dot{Mn}(t) = - (R_5)$(Molecular Weight of Mn)

$\dot{Si}(t) = - (R_7)$(Molecular Weight of Si)

$\dot{MnO}(t) = (R_5)$(Molecular Weight of MnO)

$\dot{h}_d(t) = - (1 - \delta) \Delta\dot{H}$

10. Integrate the state variables

XH = time interval

$$Fe(t+1) = Fe(t) + XH(\dot{Fe}(t))$$

$$C(t+1) = C(t) + XH(\dot{C}(t))$$

$$FeO(t+1) = FeO(t) + XH(\dot{FeO}(t))$$

$$Si(t+1) = Si(t) + XH(\dot{Si}(t))$$

$$SiO_2(t+1) = SiO_2(t) + XH(\dot{SiO_2}(t))$$

$$Mn(t+1) = Mn(t) + XH(\dot{Mn}(t))$$

$$MnO(t+1) = MnO(t) + XH(\dot{MnO}(t))$$

$$CaO(t+1) = CaO(t)$$

$$T_b(t+1) = T_b(t) + XH(\dot{T}_b(t))$$

$$h_d(t+1) = h_d(t) + XH\,\dot{h}_d(t)$$

2.3.2 OXYGEN FURNACE MODEL RUN

The somewhat standard initial conditions were set to:

T_b = 1300°C

Fe = 250000 lb

C = 8000 lb

Si = 2500 lb

Mn = 1250 lb

P_{CO} = 1.25 atm.

$\alpha_3 = 4.0$

P = 3000 moles/hr

FeO = 0 lb

CaO = 12000 lb

SiO_2 = 6000 lb

MnO = 0 lb

SCRAP = 50000 lb

Rr = 50000 $°C^4$/BTU/hr

ORE = 0 lb

$b_1 = b_2 = b_3 = 40,000$

The simulation was carried out with the equations formulated so far. Again I would like to point out that SCRAP or ORE was added to the system in order to cool the process; otherwise too much heat is produced and the end temperatures go very high.

The blowing rate B was limited to 3000 moles/hr and it is noticeable from Fig. 9 that all the oxygen was used after 14 minutes. Without limiting B the temperature would reach an unrealistic value near the end point due to FeO formation. The constants used are given in table 2. It should be noted that high temperature data on specific heats of substances in solution (particularly from slags) is not available in an quantity over a range of 200 or 300°C a constant specific heat seems a reasonable assumption.

Fig. 9 is a plot of the REACTION RATES vs TIME. From this graph it is seen that no formation of CO occurs until all the Si(R_7) is oxidized since most of the oxygen is used for the oxidation of Si. We also note that the rate of FeO formation (R_2) goes negative after a certain time which implies that the FeO reaction is reversed and therefore accounts for a rate of CO formation greater than 3000 moles/hr. We also note that it is quite important to stop our process as soon as possible, after 19 minutes for this run, since the rate of formation of FeO increases quite drastically. This can also be seen from Fig. 10

Fig. 11 represent the temperature variation with respect to time. The non-linear part of the graph of temperature at the beginning of the blow is due to the heat used in melting the scrap and slag in the vessel. i.e.

it is the heat supplied to the "heat deficit" function.

Results of the oxidation of Si, Mn and of C are given in Fig. 12.

It is seen in this graph, carbon versus time, that oxidation of carbon is retarted for the first two to three minutes. This delay of two to three minutes was considered in the model since in the early part of the oxygen blow, while silicon still remains in the iron, the oxygen content in the bath is held at a low level; as oxygen is rapidly consumed by the oxidation of silicon, i.e.

$(O_B - O_{CO})$ across the refractory boundary layer is low.

This steady diminution of Si contents in the bulk metal, during the first few minutes of the oxygen blow was built into the model so that it would agree with the experimental results given in the literature.(19) Theoretically this may be explained by the fact that, in order to nucleate the bubble of carbon monoxide, supersaturation of the bath with oxygen must be achieved.(2) In the subsequent period an almost linear decrease of carbon with time is observed.

SUBSTANCES	M.W.	SPECIFIC HEAT C_j KWH/LB/°C AND BTU/LB/°C	ENTHALPY ($\Delta H_{1527,i}$) AT 1527°C IN KWH/LB AND BTU/LB
Fe	55.85	1.0×10^{-4} 0.3412	0.166 567.5
C	12.01	$(2.62 \times 10^{-4})3$ 2.682	(0.321)3 3295.8
Mn	54.94	1.06×10^{-4} 0.3616	0.179 369.5
Si	28.09	1.16×10^{-4} 0.3958	0.40 1364.8
FeO	71.85	1.25×10^{-4} 0.427	0.215 734.7
SiO_2	60.09	1.56×10^{-4} 0.532	0.215 734.7
CaO	56.08	1.26×10^{-4} 0.430	0.177 602.7
MnO	70.94	1.02×10^{-4} 0.3480	0.144 491.3

Table 2: Values of the parameters used in the simulation of the model.

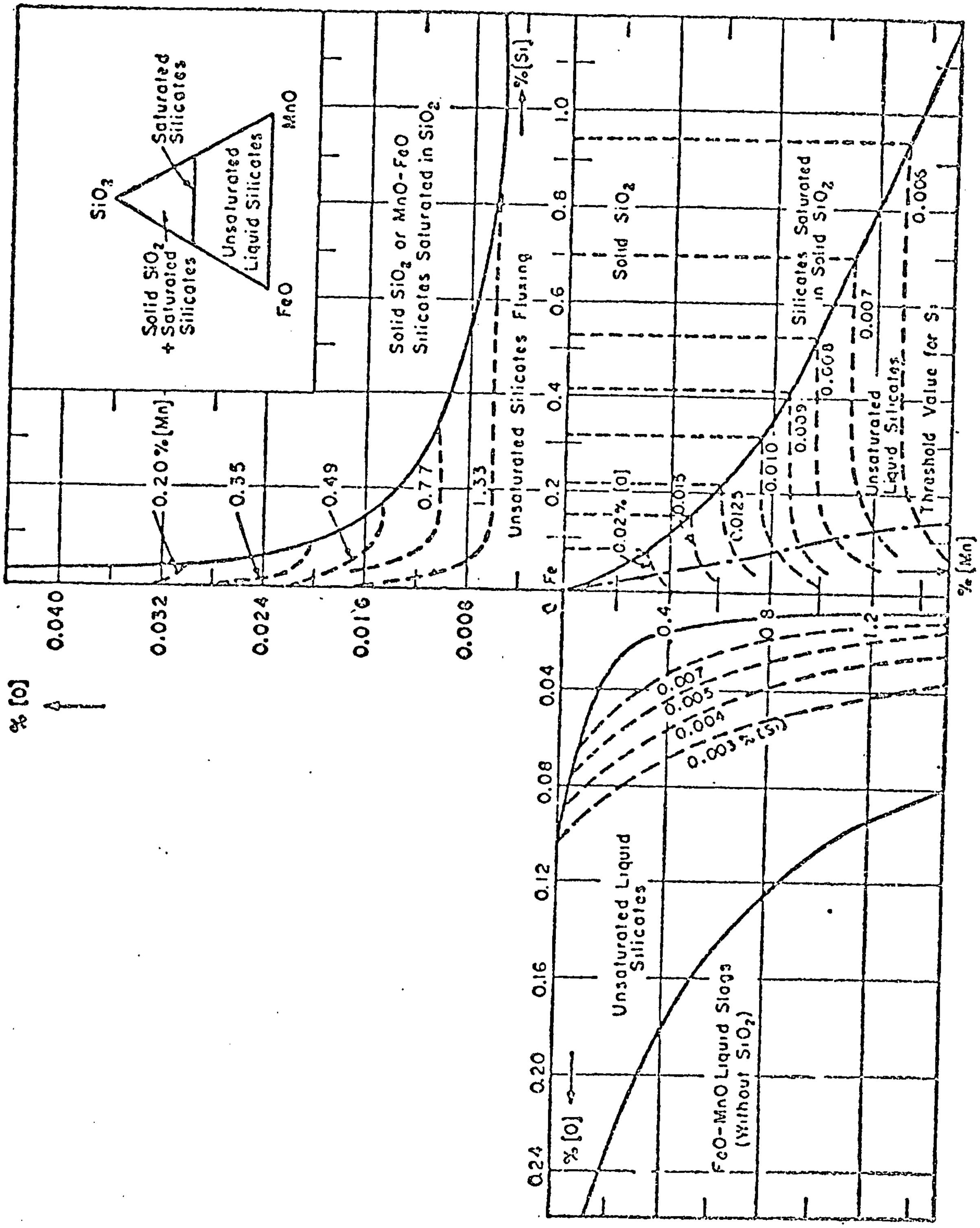


FIG 5. Diagram showing the silicon, manganese, and oxygen contents of iron in equilibrium with FeO - MnO - SiO_2 slags at 1600°C. (15)

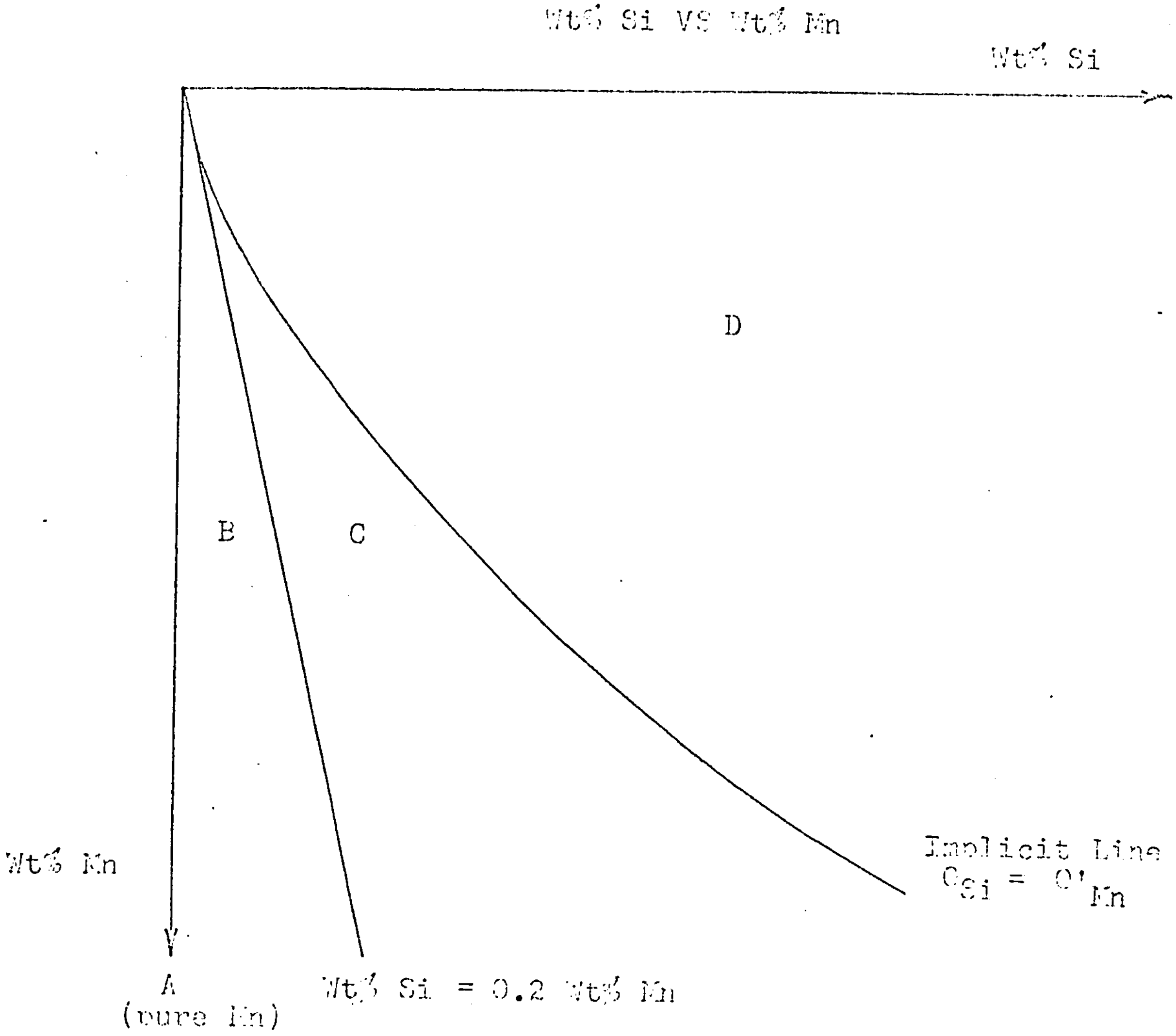


Fig. 6 Zones considered for equilibrium conditions of Silicon and Manganese.

(O'_{Mn}) VS (O'_{Mn})(Wt% Mn)

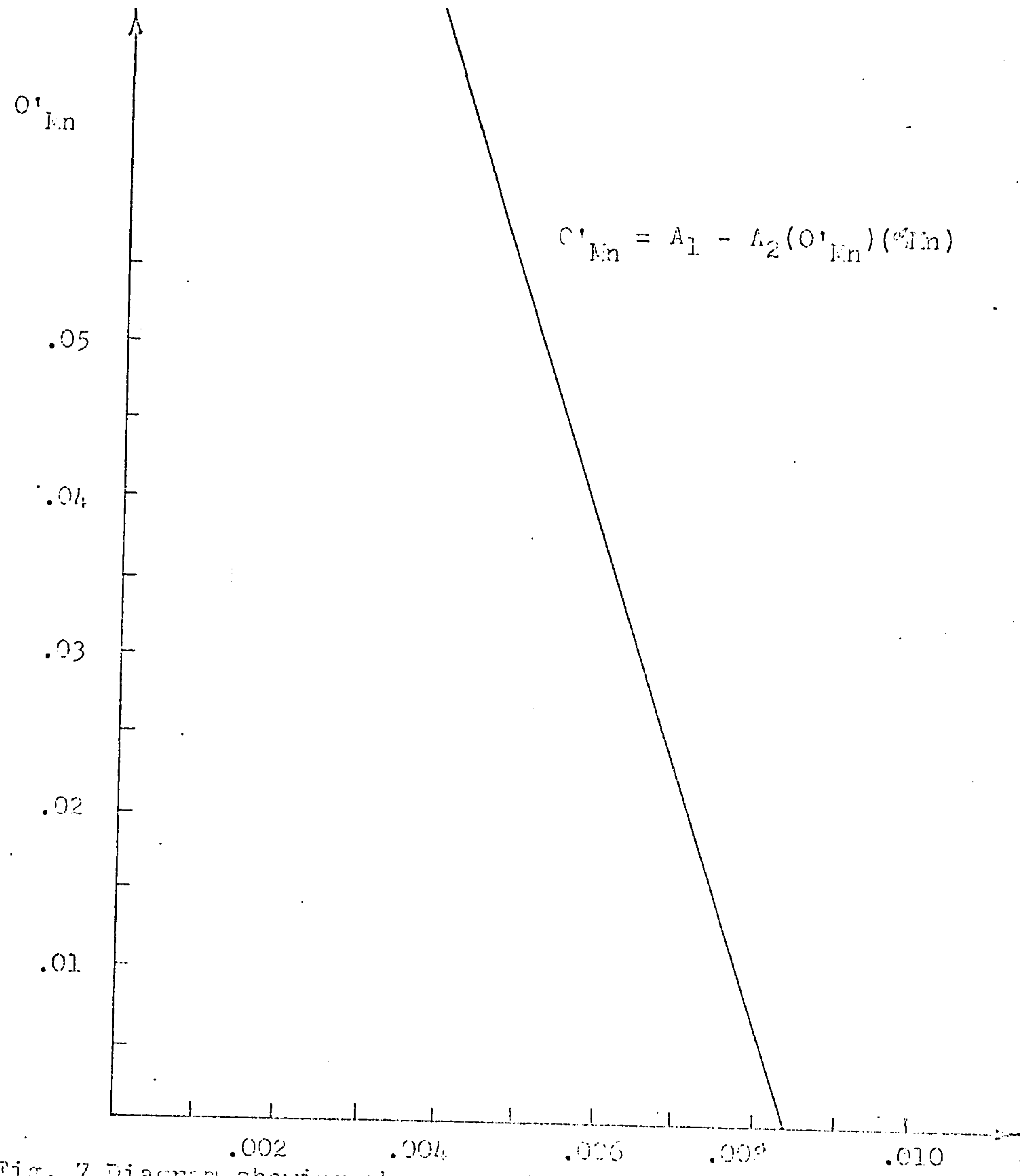


Fig. 7 Diagram showing the approximation to the hyperbola-like curve in the lower left corner of Fig. 5

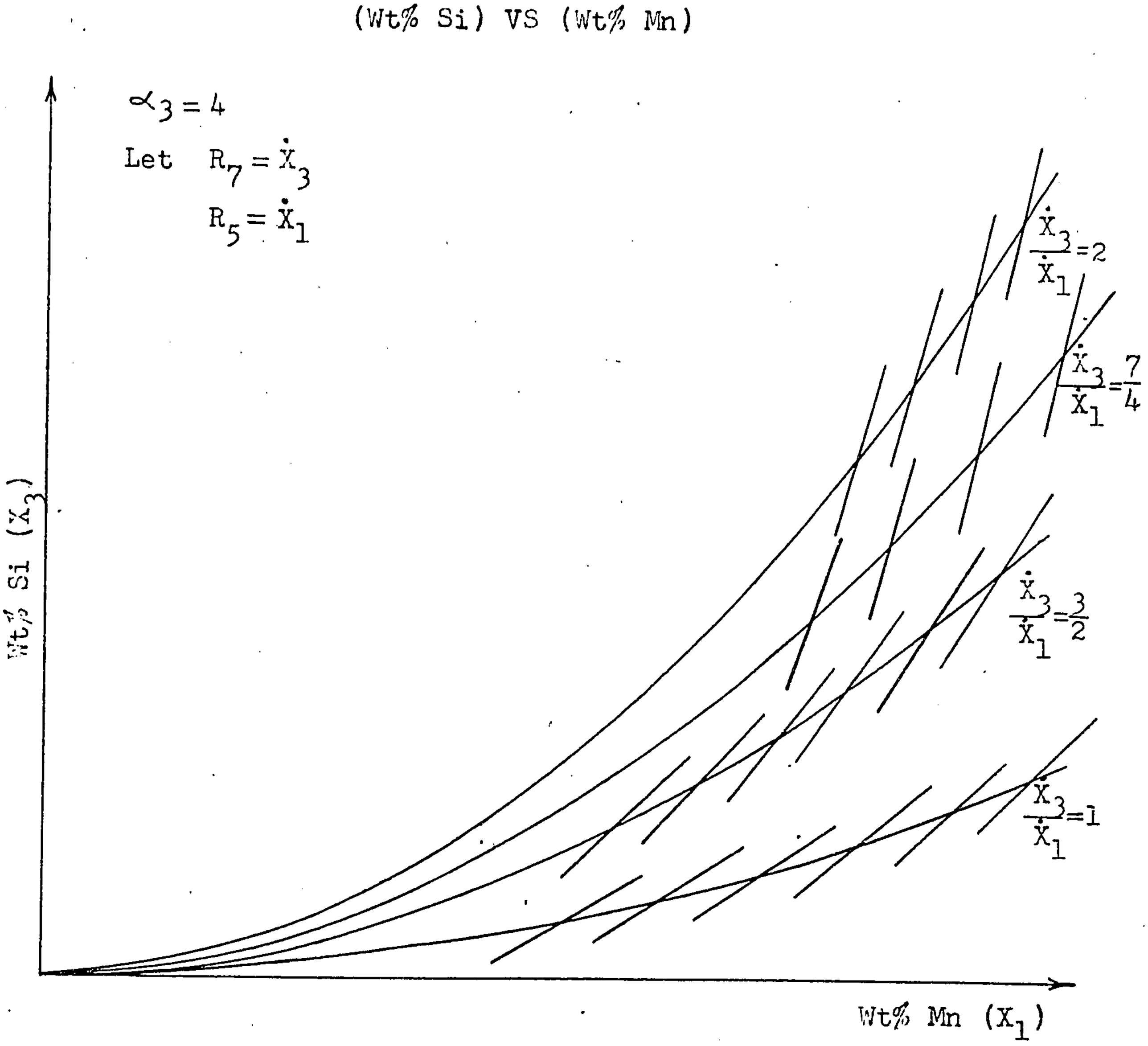


Fig. 8 Isoclines for the rate of oxidation of Si and Mn.

Rate VS Time

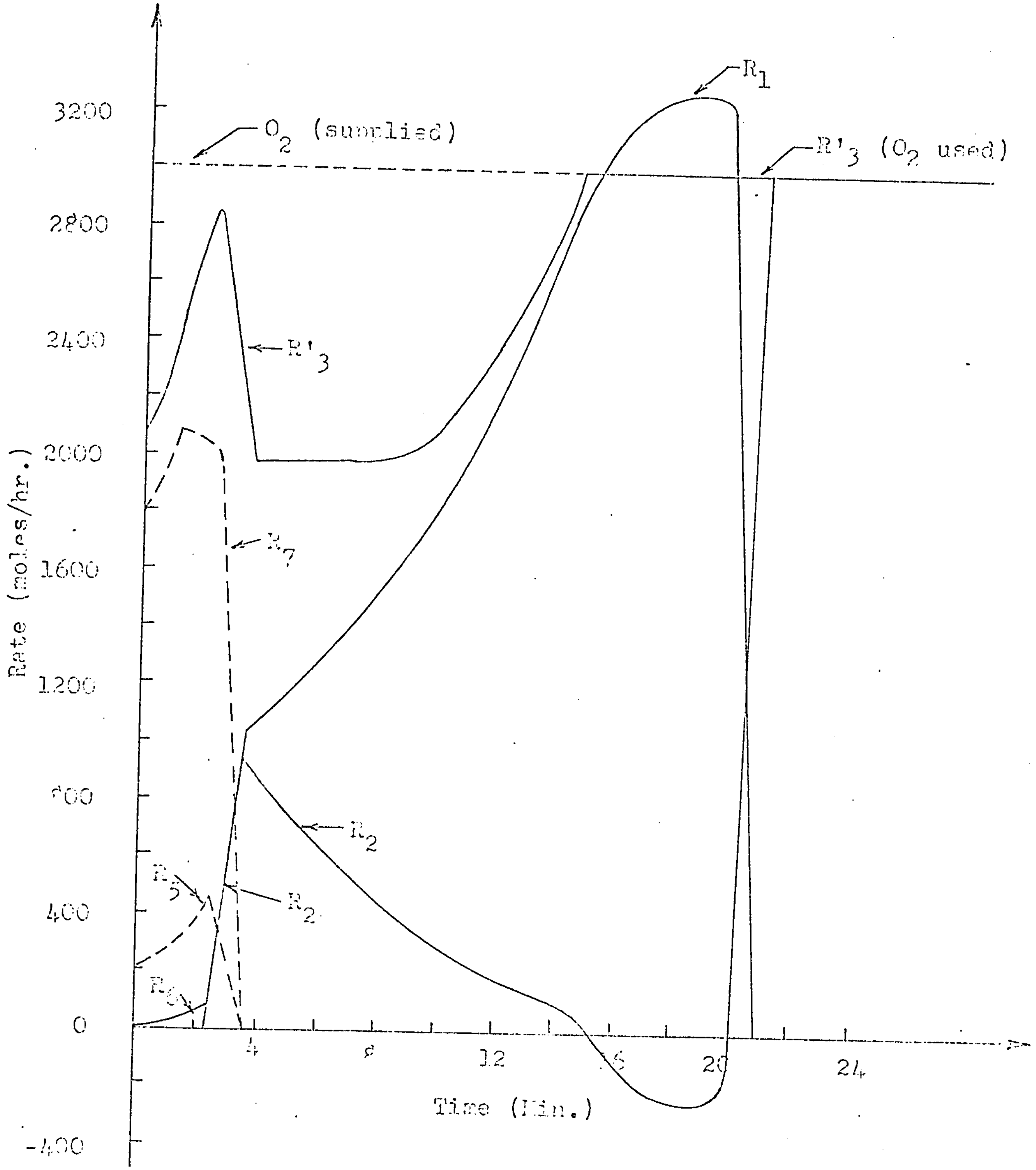


Fig. 9 Oxygen furnace model reaction rates

FeO Formed VS Time

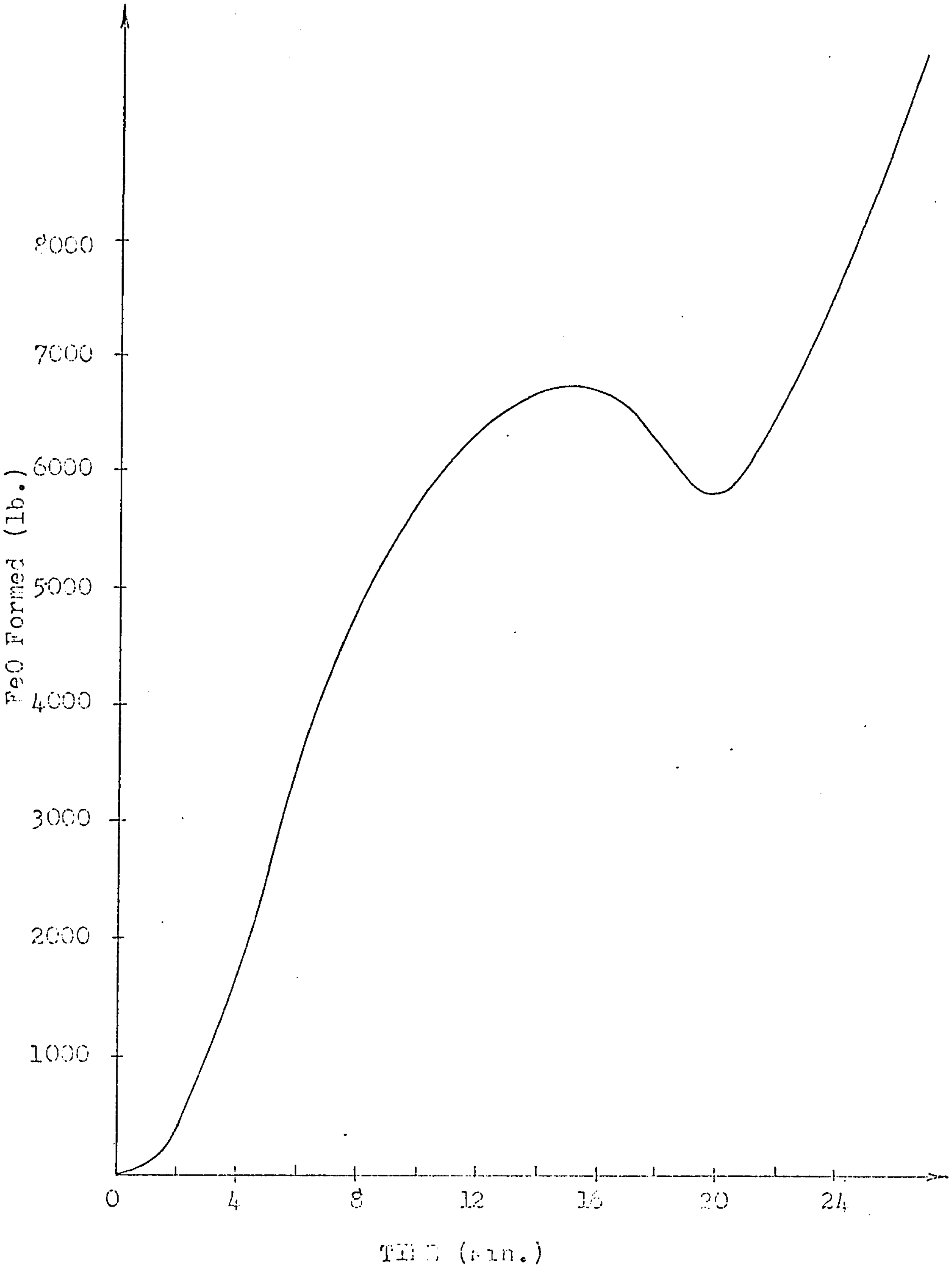


Fig. 10 Rate of formation of iron oxide

Temperature VS Time

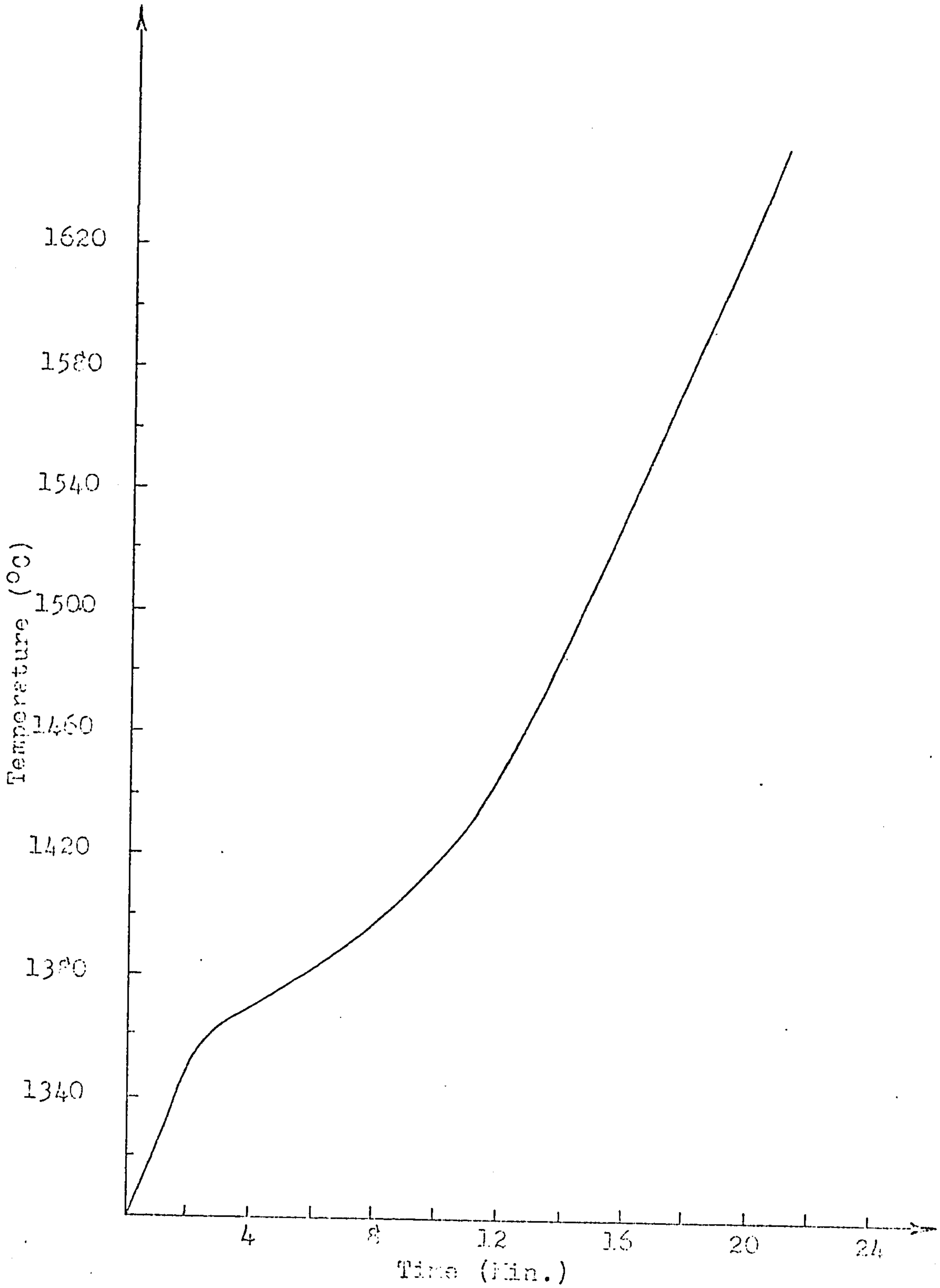


Fig. 11 Temperature for our model run.

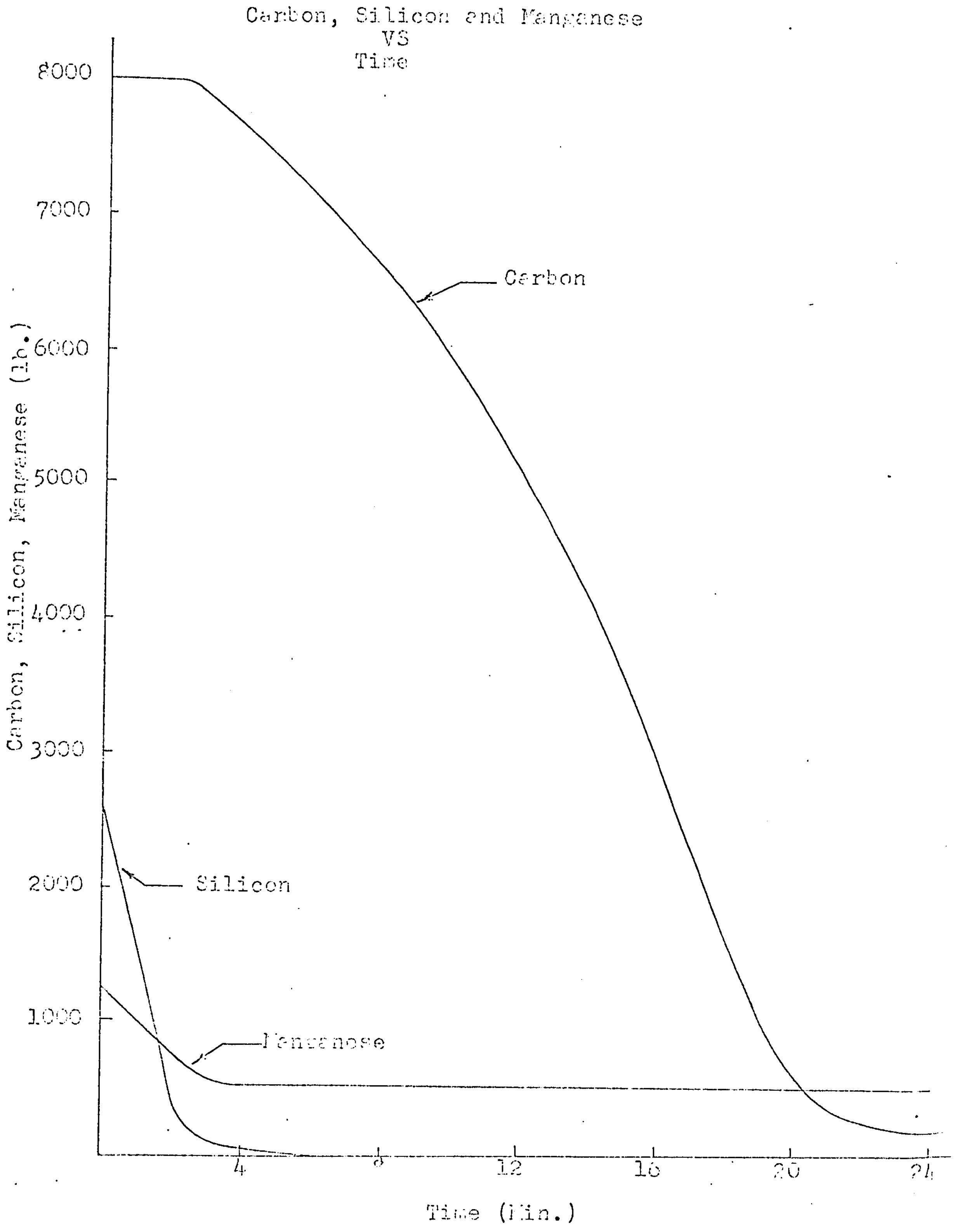


Fig. 12 Representation of the oxidation of Carbon, Silicon and Manganese for our model run.

CHAPTER 3

LEAST SQUARES FITTING ANALYSIS

3.1 INTRODUCTION

The least squares fitting analysis was carried out in order to predict or estimate the average value of Y (i.e. the dependent variables of interest time of blow, final temperature and FeO formed.) given the initial condition of the system. That is, we wanted a source of information about the way in which the variables Y depend on X (i.e. the initial conditions of the system) as a functional relationship.

Let us consider the linear form (20)(30)

$$Y_i = \alpha + \beta X_i \tag{50}$$

where α and β are unknown

and

$$E = \sum_{i=1}^{N} (Y_i - A - B X_i)^2 \tag{51}$$

This is known as the sum square deviation and is minimized by assuming

$$\frac{\partial E}{\partial A} = 0 \quad ; \quad \frac{\partial E}{\partial B} = 0 \tag{52}$$

$$A N + B \sum_i X_i = \sum_i Y_i \tag{53}$$

$$A \sum_i X_i + B \sum X_i^2 = \sum_i X_i Y_i \tag{54}$$

From these

$$B = \frac{N \sum_i X_i Y_i - \sum_i X_i \sum_i Y_i}{N \sum_i X_i^2 - (\sum_i X_i)^2} \qquad (55)$$

$$B = \frac{\sum_i (Y_i - \overline{Y}) (X_i - \overline{X})}{\sum_i (X_i - \overline{X})^2} \qquad (56)$$

$$A = \overline{Y} - B \overline{X} \qquad (57)$$

where

$$\overline{X} = \frac{1}{N} \sum_{i=1}^{N} X_i \qquad (58)$$

$$\overline{Y} = \frac{1}{N} \sum_{i=1}^{N} Y_i \qquad (59)$$

The multiple regression can be represented by a model of the form

$$Y = \alpha + \beta_1 X_1 + \beta_2 X_2 + \ldots\ldots\ldots\ldots + \beta_k X_k \qquad (60)$$

where each of the X_i need not be a quantity originally observed; for example, if X_1 and X_2 are actually observed variables, X_3 may be X_1^2, X_4 may be $X_1 X_2$ and so forth. We wish to minimize the expression

$$D = \sum_j (Y_j - a - b_i X_{1j} - b_2 X_{2j} - \ldots\ldots - b_k X_{kj})^2 \qquad (61$$

w.r.t. a, b_1, b_2, ..., b_k. Those values of (a, b_1, $b_2 \ldots b_k$) which do this will be called $(\alpha, \beta_1, \beta_2, \ldots \beta_k)$

Hence taking the partial derivatives with respect to a, b_1, b_2, ...,b_k and setting these equal to zero, we have:

$$\frac{\partial D}{\partial a} = 2\sum_j (Y_j - a - b_1X_{1j} - \ldots - b_kX_{kj})\ (-1) = 0 \qquad (62)$$

$$\frac{\partial D}{\partial b_1} = 2\sum_j (Y_j - a - b_1X_{1j} - \ldots - b_kX_{kj})\ (-X_{1j}) = 0$$

$$\vdots$$

$$\frac{\partial D}{\partial b_k} = 2\sum_j (Y_j - a - b_jX_{1j} - \ldots - b_kX_{kj})\ (-X_{kj}) = 0$$

Simplifying, these yield the normal equations:

$$na + b_1\sum_j X_{1j} + b_2\sum_j X_{2j} + \ldots + b_k\sum_j X_{kj} = \sum_j Y_j \qquad (63)$$

$$a\sum_j X_{1j} + b_1\sum_j X_{1j}^2 + b_2\sum_j X_{1j}X_{2j} + \ldots + b_k\sum_j X_{1j}X_{kj} = \sum_j X_{1j}Y_j$$

$$a\sum_j X_{2j} + b_1\sum_j X_{1j}X_{2j} + b_2\sum_j X_{2j}^2 + \ldots + b_k\sum_j X_{2j}X_{kj} = \sum_j X_{2j}Y_1$$

$$\vdots \qquad\qquad \vdots$$

$$a\sum_j X_{kj} + b_1\sum_j X_{1j}X_{kj} + b_2\sum_j X_{2j}X_{kj} + \ldots + b_k\sum_j X_{kj}^2 = \sum_j X_{kj}Y_j$$

The solution of the normal equations then yield estimators of α and the β_i's.

In the analysis the dependent variables are given with their multiple correlation coefficients. The multiple correlation coefficient is a measure of the linear dependence of Y upon $X_1, X_2 \ldots X_k$. It is the positive square root of the coefficient of determination denoted by R^2 which is defined as the ratio of the regression sum of squares to the total sum of squares (i.e., the fraction of the total sum of squares accounted for by the regression)

3.2 LEAST SQUARES FITTING STUDY

The characteristics of the end-points that are of interest are:

1. Time of Blow
2. Final Temperature
3. FeO Formed

These factors were developed as fitted functions of the initial factors:

X_1 = TI = initial temperature

X_2 = Si = initial silicon

X_3 = C = initial carbon

X_4 = = initial scrap

X_5 = Mn = initial manganese

and of the squares and cross-products of these variables. Scrap was varied in such a way that the nominal heat deficit "$h_d(0)$" was constant for all heats. Values of the initial condition for the run are given in table 3.

Hence if:

$$\begin{aligned} Y_1 &= \text{time of blow} \\ Y_2 &= \text{final temperature} \\ Y_3 &= \text{FeO formed} \end{aligned} \qquad (64)$$

we construct the fitted quadratic representation

$$\begin{bmatrix} Y_1 \\ Y_2 \\ Y_3 \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} \end{bmatrix} \times \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \end{bmatrix}$$

$$+ \begin{bmatrix} X_1 & X_2 & X_3 & X_4 & X_5 \\ X_1 & X_2 & X_3 & X_4 & X_5 \\ X_1 & X_2 & X_3 & X_4 & X_5 \end{bmatrix} \times$$

$$\begin{bmatrix} b_{11} & b_{12} & b_{13} & b_{14} & b_{15} \\ 0 & b_{22} & b_{23} & b_{24} & b_{25} \\ 0 & 0 & b_{33} & b_{34} & b_{35} \\ 0 & 0 & 0 & b_{44} & b_{45} \\ 0 & 0 & 0 & 0 & b_{55} \end{bmatrix} \times \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \end{bmatrix} \qquad (65)$$

3.3 RESULTS OF THE LEAST SQUARES FITTING STUDY

End-point data was generated for the analysis from the data given in table 3. The condition to end the blow was a 0.1% level of carbon. The computer program used was that of R. THOMSON and J. ROWLANDS from the "Statistical Research Service Canada, Department of Agriculture" S004 Regression.

In the technique used, the program chooses the order in which the independent variables are to be introduced into the analysis. At each step the program introduces the variable it judges the most important. The criterion used by the program in judging importance is that the introduction of a variable reduces the residual sum of squares by an amount greater than the introduction of any other variable.

At each step in the analysis the program output includes the following: (where it should be understood that regression is used to represent the least squares fitting)

1. Multiple regression equation.
2. Standard errors of the estimates of the regression coefficients.
3. An analysis of variance table showing the sums of squares for regression, broken down into the contribution of variables introduced both at the present and preceding steps.

4. The inverse matrix of the matrix of sums of squares and cross-products.
5. A table of residual variances, each item representing the residual variance that would be obtained if one of the variables not yet introduced were to be included at this step.
6. Variances, means and ranges for the dependent and independent variables, the matrix of sums of squares and cross-products, and the matrix of correlation coefficients are included in the output for each analysis.
7. A summary table is included at the end of each analysis showing the regression equation and residual variance obtained at each step.

Only 1, 2, and 3 are given in the thesis. In the thesis the standard deviation, the weighting factor and the standard error of the weighting factor also are given.

3.3.1 TIME OF FLOW

In Fig. 13 a) are tabulated the variables, linear and non-linear, in the order in which the program judges them the most important, and the standard deviation of the dependent variable "TIME OF FLOW" at each step; i.e. the standard deviation expected if one of the variables not yet introduced were to be included at this step.

Fig. 13 b) lists each of the variables together with the signed value of its weighting factor in the final fitted equation;it also lists the standard error for each of the weighting factors.

The fitted equations obtained are:

a. for the linear terms

$$\text{TIME OF BLOW} = 151.0 - 0.1110(\text{TI}) + 0.1725 \times 10^{-2} (\text{C}) + 0.9861 \times 10^{-4} (\text{Scrap}) - 0.1444 \times 10^{-2} (\text{Si}) - 0.6032 \times 10^{-3} (\text{Mn}) \qquad (66)$$

The multiple correlation coefficient is 0.975

b. for the linear and non-linear terms

$$\text{TIME OF BLOW} = a_0 + a_{31} X_1 + a_{32} X_2 + a_{33} X_3 + b_{11} X_1 X_1 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{22} X_2 X_2 + b_{24} X_2 X_4 + b_{34} X_3 X_4 + b_{44} X_4 X_4 + b_{55} X_5 X_5 \qquad (67)$$

Where

$a_0 = 1059.0$	$X_1 = \text{TI}$
$a_{31} = -1.5167$	$X_2 = \text{Si}$
$a_{32} = -0.02627$	$X_3 = \text{C}$
$a_{33} = 0.635 \times 10^{-2}$	$X_4 = \text{Scrap}$
$b_{11} = 0.5445 \times 10^{-3}$	$X_5 = \text{Mn}$
$b_{12} = 0.1890 \times 10^{-4}$	
$b_{13} = -0.3692 \times 10^{-5}$	
$b_{22} = 0.1747 \times 10^{-6}$	
$b_{24} = -0.9430 \times 10^{-8}$	

$b_{34} = 0.7009 \times 10^{-8}$
$b_{44} = 0.8656 \times 10^{-7}$
$b_{55} = -0.2039 \times 10^{-6}$

The multiple correlation coefficient is 0.995

From the fitted equations we note that;

(a) increasing the initial values of carbon and scrap makes the process take longer, and (b) increasing the initial temperature of the bath makes the process proceed faster. This agrees with what we know of the system.

The negative values of the weighting factors for Si and Mn seem to agree with the fact that since silicon and manganese oxidize very rapidly, increasing their initial values results in an increase of thermal energy. This thermal energy raises the temperature of the bath producing a faster oxidation of carbon; therefore giving rise to a shorter time of blow.

From Fig. 13 a) it is noticeable from the order of importance of the variables that the non-linear terms, in the equation for linear and non-linear terms, seems to control the fitted equation but their contribution is not felt to a very large extent for the first five variable if compared to the linear fitted equation. It therefore implies that for the considered variables the non-linearities (i.e. squares and cross-products of the variables) are not very important for the first five most important variables but the other non-linear terms contribute in reducing the standard deviation of "TIME OF BLOW" to a lower value.

3.3.2 FINAL TEMPERATURE

In fig. 14 a) are tabulated the variables, linear and non-linear, in the order in which the program judges them the most important, and the standard deviation of the dependent variable "FINAL TEMPERATURE" at each step; i.e. the standard deviation expected if one of the variables not yet introduced were to be included at this step.

Fig. 14 b) lists each of the variables together with the signed value of its weighting factor in the final fitted equation. It also lists the standard error for each of the weighting factors.

The fitted equations are:

a. for the linear terms.

$$\text{FINAL TEMPERATURE} = -357.7 + 1.265\ (\text{TI}) + 0.0265\ (\text{C}) + 0.0284\ (\text{Si}) + 0.5248 \times 10^{-3}\ (\text{Scrap}) + 0.0111\ (\text{Mn}) \qquad (68)$$

The multiple correlation coefficient is 0.985

b. for the linear and non-linear terms

$$\text{FINAL TEMPERATURE} = a_0 + a_{21} X_1 + a_{22} X_2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{22} X_2 X_2 + b_{23} X_2 X_3 + b_{24} X_2 X_4 + b_{25} X_2 X_5 + b_{45} X_4 X_5 + b_{55} X_5 X_5 \qquad (69)$$

Where:

$a_0 = -193.7$

$a_{21} = 1.1453$

$a_{22} = 0.1063$

$b_{12} = -0.6514 \times 10^{-4}$

$b_{13} = 0.2151 \times 10^{-4}$

$b_{22} = 0.2766 \times 10^{-5}$

$b_{23} = -0.1053 \times 10^{-5}$

$b_{24} = 0.2636 \times 10^{-6}$

$b_{25} = 0.1995 \times 10^{-5}$

$b_{45} = 0.1255 \times 10^{-5}$

$b_{55} = 0.1828 \times 10^{-5}$

$X_1 = TI$

$X_2 = Si$

$X_3 = C$

$X_4 = Scrap$

$X_5 = Mn$

The multiple correlation coefficient is 0.991

From the fitted equations, it is seen that initial temperature and initial weight of carbon are very important in predicting the final end-point temperature. Great care must then be taken, at the furnace, in recording these variables and the time lapse between recording the temperature and the beginning of the blow should be as short as possible.

The non-linear terms seem to control the fitted equation (linear and non-linear terms equation) but their contribution is not felt to a very large extent for the first five variables if compared to the linear fitted equation. For the next five variables the standard deviation is seen to decrease from 10.678 to 8.4360°C.

3.3.3 FeO FORMED

In Fig. 15 a) are tabulated the variables, linear and non-linear, in the order in which the program judges them the most important, and the standard deviation of the dependent variable "FeO FORMED" at each step; i.e. the standard deviation expected if one of the variables not yet introduced were to be included at this step.

Fig. 15 b) lists each of the variables together with the signed value of its weighting factor in the final fitted equation. It also lists the standard error for each of the weighting factors.

The fitted equations are:

a. for the linear terms

$$\text{FeO FORMED} = 37307.0 - 0.04508\ (\text{Scrap}) - 0.61362\ (\text{C}) - 18.3685\ (\text{TI}) - 0.2078\ (\text{Mn}) - 0.1030\ (\text{Si}) \qquad (70)$$

The multiple correlation coefficient is 0.886.

b. for the linear and non-linear terms

$$\text{FeO FORMED} = a_0 + a_{33} X_3 + a_{34} X_4 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4 + b_{15} X_1 X_5 + b_{22} X_2 X_2 + b_{24} X_2 X_4 + b_{34} X_3 X_4 + b_{44} X_4 X_4 \qquad (71)$$

Where

$a_0 = 18044.0$ $\qquad X_1 = \text{TI}$

$a_{33} = 1.7272$ $\qquad X_2 = \text{Si}$

$a_{34} = 0.4328$ $\qquad X_3 = \text{C}$

$b_{12} = -0.7527 \times 10^{-7}$ $\qquad X_4 = \text{Scrap}$

$b_{13} = -21.0042 \times 10^{-4}$ $\qquad X_5 = \text{Mn}$

$b_{14} = 1.2323 \times 10^{-4}$

$b_{15} = -0.1593 \times 10^{-3}$

$b_{22} = 0.2247$

$b_{24} = 0.9953 \times 10^{-5}$

$b_{34} = 1.5587 \times 10^{-5}$

$b_{44} = 1.2675 \times 10^{-4}$

The multiple correlation coefficient is 0.970

No data was available in order to check if the FeO FORMED at the end of the blow agreed with the actual formation in the steel industry. But the amount of FeO formed in the model can be controlled by varying the rate of oxidation of FeO.

From the least squares fitting analysis, it is seen that the "linear and non-linear terms" equation reduces the standard deviation to a greater extent even for the first five variables when comparing to the "linear terms" fitted equation. Hence it seems that for better control purposes one would have to consider the non-linear variables more closely than the linear ones. This oxidation is very non-linear. This may account for the difficulty in industry in predicting its actual formation.

VARIABLES	WEIGHT IN LB. and TEMPERATURE IN °C	CORRESPONDING %
C	8000.0 10000.0 11000.0	3.5 3.8 4.15
Si	260.0 1300.0 2500.0	0.1 0.5 0.9
Mn	260.0 1250.0 2600.0	0.1 0.4 1.0
Scrap	0; then ORE 22,878.8 50,000.0; then ORE 0 25,000.0; then ORE 11515.2	
TI	1300.0 1260.0 1340.0	

Table 3. INITIAL CONDITIONS FOR THE RUN

ORDER OF IMPORTANCE	VARIABLES	STANDARD DEVIATION OF "TIME OF BLOW"	WEIGHTING FACTOR	STANDARD ERROR OF WEIGHTING FACTOR
LINEAR TERMS				
1	TI	3.4274	-0.1110494	0.00187122
2	C	2.6656	0.0017257	0.000049
3	Scrap	1.7365	0.00009861	0.299 x 10^{-5}
4	Si	1.1160	-0.0014437	0.6677 x 10^{-4}
5	Mn	0.95267	-0.0006032	0.6372 x 10^{-4}
LINEAR AND NON-LINEAR TERMS				
1	TI	3.4274	-1.5166974	0.11520571
2	C-Scrap	2.5180	0.7009 x 10^{-8}	0.5882 x 10^{-9}
3	C	1.7372	0.635 x 10^{-2}	0.10643 x 10^{-2}
4	Si	1.1171	-0.0262693	0.00145955
5	Mn^2	0.95005	-0.2039 x 10^{-6}	0.1162 x 10^{-7}
6	Si-TI	0.76003	0.1890 x 10^{-4}	0.111526 x 10^{-5}
7	TI^2	0.63893	0.5445 x 10^{-3}	0.441199 x 10^{-4}
8	$Scrap^2$	0.57814	0.8656 x 10^{-7}	0.10374 x 10^{-7}
9	Si-Scrap	0.54985	-0.9430 x 10^{-8}	0.17583 x 10^{-8}
10	C-TI	0.52910	-0.3692 x 10^{-5}	0.7184 x 10^{-6}
11	Si^2	0.51968	0.1747 x 10^{-6}	0.5671 x 10^{-7}
MEAN OF "TIME OF BLOW"		23.08 Min		

Fig. 13 a) REGRESSION ANALYSIS OF "TIME OF BLOW"

b) WEIGHTING FACTORS FOR "TIME OF BLOW"

LINEAR TERMS

ORDER OF IMPORTANCE	VARIABLES	STD DEVIATION OF "FINAL TEMPERATURE"	WEIGHTING FACTOR	STANDARD ERROR OF WEIGHTING FACTOR
1	TI	46.204	1.265	0.02113
2	C	32.150	0.0265	0.000553
3	Si	18.638	0.0284	0.000754
4	Scrap	15.221	0.5248×10^{-3}	0.3381×10^{-4}
5	Mn	10.758	0.01110	0.0007196
LINEAR AND NON-LINEAR TERMS				
1	TI	46.204	1.1453	0.03013
2	C-TI	32.145	0.2151×10^{-4}	0.59519×10^{-6}
3	Si	18.269	0.1063	0.02414
4	Mn-Scrap	11.522	0.1255×10^{-5}	0.21168×10^{-6}
5	Si-Scrap	10.678	0.2636×10^{-6}	0.21898×10^{-7}
6	Mn^2	9.0305	0.1828×10^{-5}	0.3565×10^{-6}
7	Si-TI	8.8304	-0.6514×10^{-4}	0.1810×10^{-5}
8	Si-Mn	8.6491	0.1995×10^{-5}	0.5877×10^{-6}
9	Si^2	8.5070	0.2768×10^{-5}	0.9206×10^{-6}
10	Si-C	8.4360	-0.1053×10^{-5}	0.47375×10^{-6}
MEAN OF "FINAL TEMPERATURE" 1610.476				

Fig. 14 a) REGRESSION ANALYSIS OF "FINAL TEMPERATURE"

b) WEIGHTING FACTORS FOR FINAL TEMPERATURE

LINEAR TERMS				
ORDER OF IMPORTANCE	VARIABLES	STD DEVIATION OF "FeO FORMED"	WEIGHTING FACTOR	STD ERROR OF WEIGHTING FACTOR
1	Scrap	1229.5	-0.04508	0.002262
2	C	9~~2~~61.75	-0.61362	0.037013
3	TI	750.28	-18.3695	1.41344
4	Mn	724.38	-0.2078	0.04813
5	Si	719.61	-0.1030	0.05044
LINEAR AND NON-LINEAR TERMS				
1	C-Scrap	1190.3	1.5587 x 10^{-5}	0.0958 x 10^{-5}
2	C-TI	940.28	-21.0042 x 10^{-4}	1.2038 x 10^{-4}
3	Scrap-TI	686.86	1.2323 x 10^{-4}	0.36146 x 10^{-}
4	$Scrap^2$	574.56	1.2675 x 10^{-4}	0.08279 x 10^{-}
5	Mn-TI	537.15	-0.1593 x 10^{-3}	0.01956 x 10^{-}
6	C	501.79	17.2725 x 10^{-1}	1.5952 x 10^{-1}
7	Scrap	454.28	0.4328	0.04821
8	Si-TI	444.73	-0.7527 x 10^{-7}	0.09401 x 10^{-}
9	Si-Scrap	402.94	0.9953 x 10^{-5}	0.13849 x 10^{-}
10	Si^2	380.22	0.2247	0.04124
MEAN OF "FeO FORMED" 5945.5 lb				

Fig. 15 a) REGRESSION ANALYSIS OF "FeO FORMED"

b) WEIGHTING FACTORS FOR "FeO FORMED"

CHAPTER 4

CONCLUSION

A tenth order state variable model of a BOF has been explained and described. It has been possible to achieve reasonable agreement with published results by adjusting certain model parameters; namely the diffusion parameters (b_1, b_2, b_3), the heat transfer parameter δ, the Si-Mn rate parameter α_3 and the radiative loss.

A non-linear end-point form has been found which could be used in fitting furnace end-point data if better control is to be achieved. The equation for the FeO formation (see equation (71)) is the one in which the non-linear terms are most significant. This may account for the difficulty in the industry in predicting the actual formation of FeO by using a linear model.

From the results of the analysis the process could either be controlled on the basis of the dynamic model or by use of the least squares fitted equations. If the model is used for on-line control then the initial conditions could be fed into the model and the input corrected so that the output specifications were met. The model could be used to control dynamically the lance position, but more study and work would be required.

On the other hand, if the end-point characteristics are of interest the results of the least squares fitting analysis could be used in predicting the time of blow, the final temperature and the FeO formed. A dynamic lance position control for the process would not be possible but a desirable constant position of the lance could be determined for each particular heat. This again would require more study and more work.

In order to have a better dynamic model, the following areas, in particular, need further study:

a. The diffusion control of reactions;

b. The activity function of FeO, since the equation does not completely correspond to the graph;

c. The distribution of Mn and Si, since this is only one possible representation of the oxidation process;

d. Also a better way would have to be devised for the operation of melting the scrap and representing the heat loss of the vessel from one "heat" to the other. A statistical equation based on the history of the furnaces might be found with certain constraints and used in the model.

For a more efficient use of the least squares fitting study of the model, the analysis would have to be simulated for some additional independent variables and compared to our results. The selection of the additional variables must be made on the basis of experiance in the steel process.

REFERENCES:

(1) P. Booster: "Assessment of the Limitations of Computer Control of the LD Process", Steel Times January 15, 1965, Page 82.

(2) J. Szeckely: "On Some Heat and Mass Transfer Phenomena in Steelmaking", A.I.Ch. E. - I. Chem. E. Symposium Series No. 2, 1965, London, Instn. Chem. Engrs.

(3) R.G. Ward: "The Physical Chemistry of Iron and Steel Making" Edward Arnold (Publishers) Ltd., London, 1962, Page 70.

(4) B.M. Larson: "Rates of Open Hearth Reactions", chapter in Basic Open Hearth Steelmaking, AIME, New York, 1964, Page 906.

(5) N.R. Carlson: "Mathematical Models and Control of the Oxygen Steelmaking Process" Institute in Engineering-Economic Systems, Stanford University, Report CCS-6, Dec. 1965, Page 57.

(6) A.F. Smith: "Computer Control of Basic Oxygen steelmaking Furnace", The Australasian Engineer, January 1966, Page 81-83.

(7) N.R. Carlson, Op. cit., Page 43

(8) L.S. Darken: "Kinetics of Metallurgical Reactions with Particular Reference to the Open Hearth" chapter in The Physical Chemistry of Steelmaking, Technology Press and John Wiley and Sons, Inc., New York, 1958, Page 102.

(9) R.G. Ward, op. cit., Page 171

(10) H.L. Bishop, Jr., H.N. Lander, N.J. Grant, and J. Chipman: "Equilibria of Sulphur and Oxygen between Liquid Iron and Open-Hearth - Type Slags", AIME Trans., Journal of Metals, July 1956, Page 862-868.

(11) C.R. Taylor and J. Chipman: "Equilibria of Liquid Iron and Simple Basic and Acid Slags in a Rotating Induction Furnace", AIME Trans., 1943, Vol. 154, Page 228-247.

(12) R.G. Ward, op. cit, Page 91

(13) N.R. Carlson, op. cit., Page 51

(14) C.I.M.M. Conference of Metallurgists. Queen University, Kingston. Aug. 27-30, 1967

(15) R.G. Ward, op. cit., Page 170, fig. 59

(16) R.G. Ward, op. cit., Page 162

(17) R.G. Ward, op. cit., Page 153

(18) D. Graham and D. McRuer: "Analysis of Non-Linear Control Systems" Chapter 7, John Wiley & Sons, Inc., 1961

(19) R.C. Madden: "The basic Oxygen Steelmaking Process", Chapter in Basic Open Hearth Steelmaking, AIME, New York 1964, Page 981

(20) E.J. Williams: "Regression Analysis", John Wiley & Sons, Inc., 1959

(21) A. Jackson: "Oxygen Steelmaking For Steelmakers", Adlard & Sons Ltd, Dorking, 1964 Page 22

(22) C.M. Woodside, Private communication

(23) R.G. Ward, op. cit., Page 32-33

(24) R.G. Ward, op. cit., Page 22-28

(25) R.G. Ward, op. cit., Page 29

(26) N.R. Carlson, op. cit., Page 65

(27) R.G. Ward, op. cit., Page 30, 84, 151, 167

(28) N.R. Carlson, op. cit., Page 62

(29) R.G. Ward, op. cit., Page 170

(30) N.L. Johnson, F.C. Leone: "Statistics and Experimental Design in Engineering and Physical Sciences", Volume 1, John Wiley & Sons, Inc., 1964. Pages 413-416.

APPENDIX A

HEATS OF OXIDATION (21)

It has not yet been possible to obtain the precise quantity of heat evolved by oxidation of the various elements in steel because of the difficulty and complexity of the necessary experimental work. The figures used, however, are those of A. JACKSON (21) which have been decided upon by a comprehensive study of all published information and the correlation of this with known steel-making operations; hence those shown can be accepted as being as reliable as it is possible to obtain at present.

The values used are as follows:

$Si + 2O \rightarrow SiO_2$ 112 lb of Si 28.1 lb - mole	Heat evolved 13.83×10^5 BTU 3.47×10^5 BTU/lb - mole
$C + O \rightarrow CO$ 112 lb of C 12 lb - mole	6.44×10^5 BTU 6.91×10^4 BTU/lb - mole
$C + 2O \rightarrow CO_2$ 112 lb of C 12 lb - mole	17.81×10^5 BTU 1.91×10^5 BTU/lb-mole
$Fe + O \rightarrow FeO$ 112 lb of Fe 55.85 lb - mole	2.30×10^5 BTU 1.147×10^5 BTU/lb - mole

Mn + O $\longrightarrow$ MnO 112 lb of Mn 54.95 lb - mole	2.54×10^5 BTU 4.91×10^5 BTU/lb-mole
$SiO_2 + 2CaO \longrightarrow SiO_2 \cdot 2\,CaO$ 112 lb of SiO_2 60.1 lb - mole	1.00×10^5 BTU 5.36×10^4 BTU/lb-mole

The "Heats of oxidation" was considered to be:

$$\text{HEATS OF OXIDATION} = R_1 \times 69{,}100.0 - 1.8 \times R_1\ (10080.0 + (0.9\ (T_b + 273.0))) + (R_2 + R_6)\ 114{,}716.0 + R_5 \times 491{,}000.0 + R_7 \times 347{,}000.0 + R_7 \times 53{,}600.0$$

APPENDIX B

TEMPERATURE FUNCTION (22)

The iron bath normally contains many dilute dissolved substances of which we consider the representative substance X. The presence of X reduces (usually) the melting point of the solution, its heat of fusion, and its specific heat. X also has a heat of solution which must be supplied.

The enthalpy of the solute X has the form:

$$\Delta H_X = X(\Delta H'_{1527,X} + C'_X(T_b - 1527)) \qquad (B.1)$$

where

X = mass of elements in the bath in lb.

$\Delta H'_{1527,X}$ = enthalpy of one lb. of liquid X in solution in iron at 1527 °C including heats of fusion and solution.

C'_X = effective specific heat of X in dilute solution, including the temperature coefficient of the heat of solution.

In the entire bath we can sum up $\Delta H(T)$ as:

$$\Delta H = \sum_i X_i(\Delta H'_{1527,i} + C'_i(T_b - 1527)) \qquad (B.2)$$

Where the primed quantities are the same as unprimed quantities except for dilute substances in the iron.

Then solving for T_b we have:

$$T_b = 1527 + \frac{\Delta H - \sum_i \Delta H'_{1527,i}X_i}{\sum_i C'_i X_i} \qquad (B.3)$$

Hence the rate of change of temperature is:

$$\dot{T}_b = \frac{\Delta\dot{H} - \sum_i \Delta H'_{1527,i}\dot{X}_i}{\sum_i C'_i X_i} - \frac{(\Delta H - \sum_i \Delta H'_{1527,i} X_i)\sum_i C'_i \dot{X}_i}{(\sum_i C'_i X_i)^2} \tag{E.4}$$

Since

$$\Delta H(T_b) = \sum_i \Delta H'_{1527,i} X_i - (\sum_i C'_i X_i)(T_b - 1527) \tag{E.5}$$

$$\therefore \Delta H - \sum_i \Delta H'_{1527,i} X_i = (\sum_i C'_i X_i)(T_b - 1527) \tag{E.6}$$

Hence

$$\dot{T}_b = \frac{\Delta H - \sum_i \Delta H'_{1527,i}\dot{X}_i}{\sum_i C'_i X_i} - \frac{(T_b - 1527)\sum_i C'_i \dot{X}_i}{\sum_i C'_i X_i} \tag{E.7}$$

APPENDIX C

Activities and Equilibria

1. Activities in an Ideal Solution

In an ideal solution, reaction equilibria are determined by the mole fractions of the reacting substances and the free energy change ΔF^o of the reaction. Considering the hypothetical chemical reaction

$$aA + bB = cC + dD \qquad (C.1)$$

we may write at equilibrium:

$$K = \frac{(C)^c\ (D)^d}{(A)^a\ (B)^b} = 10^{\left(-\frac{\Delta F^o}{4.575\ T}\right)} \qquad (C.2)$$

provided the products and reagents form ideal solutions.

Where K = equilibrium constant for the reaction.

(A) = mole fraction of A

ΔF^o = standard free energy of formation

T = absolute temperature in degrees Kelvin

It is not necessary that there be only one solution; for example D may form one pure liquid or solid phase, and A, B, and C form one ideal solution with some other components in it as well. Then (D) is unity, and

$$(A) = \frac{N_A}{\sum_i N_i} \qquad (C.3)$$

where N_A is the number of moles of A in the entire solution or in some part of it taken as a reference.

If one substance is a dissolved gas, then in an ideal solution its mole fraction is equal to its partial pressure in a gas in equilibrium with the solution. This is the basis of many measurements of activity which show departures from ideality. As a result, activity a_X is defined as the equilibrium partial pressure (in atmospheres). Then the reaction equilibrium is

$$K = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b} \tag{C.4}$$

Also, the equilibrium constant may be calculated at any temperature from the standard free energy. ΔF^o for the complete conversion of the reactants of the left hand side of the chemical reaction (C.1) into the products on the right hand side where each formula unit represents a gram molecule of the indicated chemical species in its standard state. The relation is: (23)

$$\Delta F^o = 4.575 \text{ T} \log K \tag{C.5}$$

where T is the absolute temperature in degrees Kelvin at which the reaction is taking place. For the purpose of our model we have

$$T = T_b + 273 \tag{C.6}$$

where T_b is the temperature of the metal bath in °C. Fortunately the standard free energy is known for the formation of most compounds and solutions of metallurgical interest, although often with less precision than we would like, so a numerical value for the equilibrium constant, K, is usually calculable.

2. Departures from Ideal Solution.

Following standard terminology (24) we shall use the symbol "a" to represent the Raoultian chemical activity of a material whose standard state is the pure material, and the symbol "h" to represent the Henrian chemical activity of a material whose standard state is a 1 Wt% solution of the material in pure liquid iron.

At steelmaking temperatures, the Henrian activity of material A dissolved in iron together with material B, C, D, etc..., is described by the following relation: (25)

$$h_A = [\text{Wt\% } A]\ f_A^{\,A} \cdot f_A^{\,B} \cdot f_A^{\,C} \cdot f_A^{\,D} \qquad (C.7)$$

The solution is considered ideal when $f_A^{\,A}$, $f_A^{\,B}$... are all unity; in the ideal case the Henrian activity of component A is equal to the weight percentage of A in the iron solution. In the non-ideal case, some or all of the "f" factors deviate from unity. The factor $f_A^{\,A}$ measures the tendency of component A, dissolved in iron by itself, to deviate from ideality. Factor $f_A^{\,X}$ measures the tendency of the presence of component X in the solution to cause component A to deviate from ideal behaviour. The activity coefficients $f_A^{\,X}$ are approximated by exponentials: (25)

$$f_A^{\,X} = 10^{e_A^{\,X}[\text{Wt\% } X]} \qquad (C.8)$$

where e_A^X are the interaction coefficients. It follows that the behavior of component A in the iron solution is ideal when all of the appropriate interaction coefficients are zero, or when components with nonzero interaction coefficients are not present.

Hence in a system with A, B and C in dilute solution in iron

$$h_A = [\text{Wt\% } A]\, 10^{\,e_A^A[\text{Wt\% } A] + e_A^B[\text{Wt\% } B] + e_A^C[\text{Wt\% } C]} \tag{C.9}$$

Similar expression apply to the Raoultian activity of component A in an iron solution together with components B, C, D etc...:

$$a_A = (\text{mole fraction } A)\ g_A^A \cdot g_A^B \cdot g_A^C \cdot g_A^D \tag{C.10}$$

In this case, ideal behavior of component A means that the Raoultian activity of A is equal to the mole fraction of A in solution.

Many of the interaction coefficients are given in the litterature. (27)

3. Wt% Oxygen at the Slag-Metal Interface: O_{FeO}

Around a slag globule, a distinct surface interface is assumed with slag on one side and iron on the other.

$$[Fe] + [O]_{1Wt\%} = (FeO) \tag{C.11}$$

$$\frac{a_{FeO}}{h_O \cdot a_{Fe}} = K_{FeO} = 10^{\left(-2.734 + \frac{6320}{T_b + 273}\right)} \tag{C.12}$$

Since Fe is a nearly pure liquid phase then $a_{Fe} \simeq 1$

Hence

$$\frac{a_{FeO}}{h_O} = 10^{\left(-2.734 + \frac{6320}{T_b + 273}\right)} \qquad (C.13)$$

or

$$[Wt\% \; O] = \frac{h_O}{\prod_i f_O^{\chi_i}} = a_{FeO} \frac{10^{\left(2.734 - \frac{6320}{T_b + 273}\right)}}{\prod_i f_O^{\chi_i}} \qquad (C.14)$$

The interaction may be ignored because other substances are probably oxidized and carried to slag.

Replacing [Wt% O] by O_{FeO} the final equation is:

$$O_{FeO} = a_{FeO} \cdot 10^{\left(2.734 - \frac{6320}{T_b + 273}\right)} \qquad (C.15)$$

Where a_{FeO} is given in Appendix D.

4. Wt% Oxygen in Saturated Iron:

Assuming pure iron oxide in the vicinity of the oxygen bubble the activity of FeO is assume to be one i.e. $a_{FeO} \simeq 1$ and since $a_{Fe} \simeq 1$ we have from C.14

$$[Wt\% \; O] = \frac{10^{\left(+2.734 - \frac{6320}{T_b + 273}\right)}}{\prod_i f_O^{\chi_i}} \qquad (C.16)$$

Again the interaction may be ignored and replacing [Wt% O] by C_C the final equation is:

$$O_S = 10^{\left(2.734 - \frac{6320}{T_b + 273}\right)} \qquad (C.17)$$

i.e. the weight % of oxygen in iron in equilibrium with iron oxide.

5. Oxygen in Equilibrium with Carbon Monoxide: O_{CO}

During the carbon boil there are bubbles of CO in the bath and attached to the lining. At the gas-metal surface an equilibrium condition of the reaction may be written

$$[C]_{1 Wt\%} + [C]_{1 Wt\%} = \{CO\} \qquad (C.18)$$

with an equilibrium constant:

$$K_{CO} = \frac{p_{CO}}{[h_c]\ [h_o]} = 10^{\left(+2.131 + \frac{1056}{T_b + 273}\right)} \qquad (C.19)$$

where p_{CO} is the CO bubble pressure in atmospheres, assumed constant for all bubbles.

Solving for [Wt% O] and neglecting the interaction coefficients which may be ignored we have

$$[Wt\%\ O] = \frac{p_{CO}}{Wt\%\ C} \cdot 10^{\left(-2.131 - \frac{1056}{T_b + 273} - 0.\text{[illegible]}[Wt\%\ C]\right)} \qquad (C.20)$$

Let [Wt% O] be replaced by O_{CO} the Wt% oxygen in equilibrium with the CO in the gas bubbles.

6. Silicon in the metal bath

Dissolved silicon at level [Wt% Si] in the steel bath reacts with dissolved oxygen at level [Wt% O] to produce a solid $\langle SiO_2 \rangle$ deoxidation product.

The equilibrium between silicon and oxygen in iron and silica may be represented as: (29)

$$[Si]_{1\ Wt\%} + 2\,[O]_{1\ Wt\%} = \langle SiO_2 \rangle \tag{C.21}$$

with the equilibrium constant:

$$K = \frac{\langle a_{SiO_2} \rangle}{[h_{Si}]\ [h_O]^2} \tag{C.22}$$

where

$$K = 10^{\left(11.01 - \frac{29150}{T_b + 273}\right)} \tag{C.23}$$

$$a_{SiO_2} = 1$$

$$h_O = \left[\frac{1}{h_{Si}} \cdot 10^{\,11.01 - \frac{29150}{T_b + 273}} \right]^{\frac{1}{2}} \tag{C.24}$$

From the table (27) the significant interactions are between h_O and O and Si, and between h_{Si} and O and Si. We finally obtain for the equilibrium oxygen level

$$O_{Si} = \frac{1}{[Wt\%\ Si]^{\frac{1}{2}}} \cdot 10^{\left(5.5 - \frac{14575}{T_b + 273}\right)} \tag{C.25}$$

7. Manganese in the metal bath

Dissolved manganese at level [Wt% Mn] in iron reacts with dissolved oxygen and forms liquid droplets of FeO and MnO. The presence of MnO causes the FeO to form up to a point where its activity balance the oxygen level in the bath. The FeO-MnO ratio in these droplets is governed by the equilibrium of the reaction

$$(FeO) + [Mn]_{1\ Wt\%} = (MnO) + [Fe] \qquad (C.26)$$

$$\frac{(a_{MnO})\ .\ [a_{Fe}]}{(a_{FeO})\ .\ [h_{Mn}]} = 10^{\left(-2.95 + \frac{6440}{T_b + 273}\right)} = K_m \qquad (C.27)$$

where $a_{Fe} = 1$ and $h_{Mn} = [Wt\%\ Mn]$

MnO and FeO form an ideal solution, so a_{FeO} equal the mole fraction of FeO and a_{MnO} equal the mole fraction of MnO. Also: (the mole fraction of MnO) + (mole fraction of FeO) = 1 (16) (C.28)

From C.27 and C.28 it is found that the equilibrium level of oxygen when Manganese is

$$C_{Mn} = \frac{10^{\left[2.734 - \frac{6320}{T_b + 273} + .13[Wt\%\ C]\right]}}{1 + Wt\%\ Mn\ 10^{\left(\frac{6440}{T_b + 273} - 2.95\right)}} \qquad (C.29)$$

APPENDIX D

REPRESENTATION OF a_{FeO} (IRON OXIDE ACTIVITY) in SiO_2 - CaO Slags.

Even in our simple slag with the elements Fe, O, Ca and Si in it, the tendency to formation of complex molecular associations makes the activity of FeO in slag a very nonlinear function of slag composition

$$a_{FeO} = f(\text{mole fraction of FeO, CaO, } SiO_2) \tag{D.1}$$

Figure 16, reproduced from the literature, summarizes(10) experimental data on a_{FeO}. The hump in the middle is thought to be due to the formation of 2CaO . SiO_2, which increases the concentration of FeO in the remaining CaO and SiO_2, and hence increases a_{FeO} above its mole fraction.

For the purposes of computer simulation a mathematical expression was fitted to the graph and the result of the fitted curve is traced on Figure 16.

The fitted function is

$$\begin{aligned} a_{FeO} = {} & 1.724 \cdot \frac{x_1}{1 + 0.242\, x_1} - 0.914 \\ & + \left(3.49 + \frac{4.56}{1 + \left(\frac{x_1}{0.788}\right)^3}\right) \cdot \frac{x_2}{2 + x_2} \\ & \exp\left[- \frac{x_2}{2 + x_2} \, \frac{1}{0.265 + 1.33 \exp\left(\frac{-x_1}{.809}\right)}\right] \\ & + \frac{x_2}{2 + x_2} (5.22\, x_1 - 3.234) \end{aligned} \tag{D.2}$$

Where

$$x_1 = \frac{Z_{FeO}}{Z_{FeO} + Z_{CaO} + Z_{SiO_2}} \qquad (D.3)$$

$$x_2 = \frac{Z_{CaO}}{Z_{SiO_2}} = \text{"y" ratio} \qquad (D.4)$$

and where also

$$Z_{FeO} = \frac{FeO}{71.85} \qquad (D.5)$$

$$Z_{CaO} = \frac{CaO}{56.08} \qquad (D.6)$$

$$Z_{SiO_2} = \frac{SiO_2}{60.09} \qquad (D.7)$$

FeO = mass of FeO in the slag, etc.

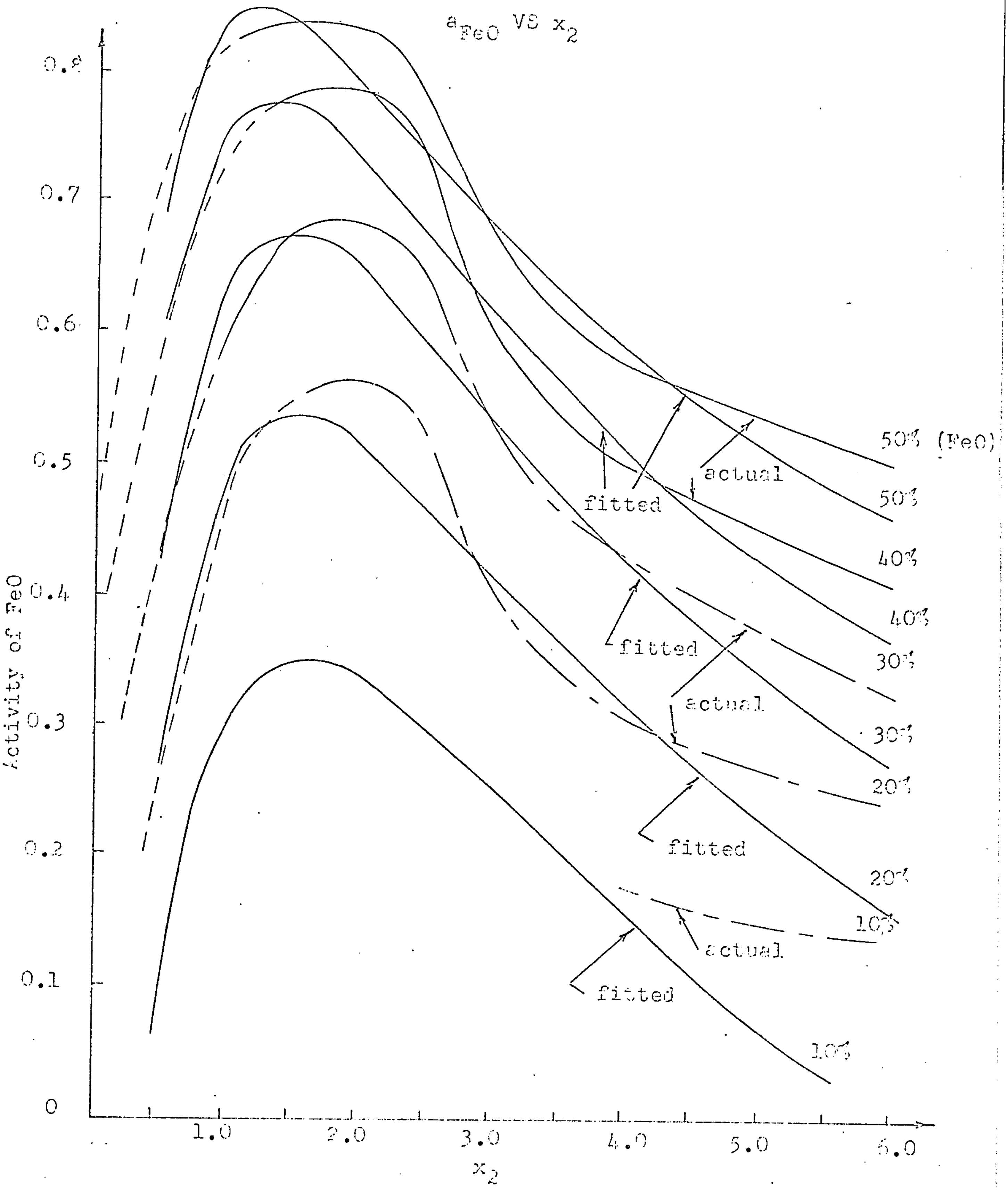


Fig. 16. Graphical representation of the Activity of FeO (10)

APPENDIX E

SOLUTION FOR R_5, R_6 AND R_7

The sharing of oxygen between the fallowing reactions

$$Mn + O = MnO \quad \text{uses } O_2 \text{ at rate } R_5 \text{ moles/hr} \tag{E.1}$$

$$Fe + O = FeO \quad \text{uses } O_2 \text{ at rate } R_6 \text{ moles/hr} \tag{E.2}$$

$$\tfrac{1}{2}Si + O = \tfrac{1}{2}SiO_2 \quad \text{uses } O_2 \text{ at rate } R_7 \text{ moles/hr} \tag{E.3}$$

must be determined on some approprite basis. A possible basis is:

$$R_5 = \beta_1(\text{Wt\% Mn})(\text{Wt\% O}) \tag{E.4}$$

$$R_6 = \frac{R_5}{Km(\text{Wt\% Mn})} \qquad \text{from equation (34)} \tag{E.5}$$

$$R_7 = \beta_2(\text{Wt\% Si})^{\frac{1}{2}}(\text{Wt\% O}) \tag{E.6}$$

where (Wt% O) is some local oxygen potential varying throughout the bath. Absorbing (Wt% O) into our constants β_1 and β_2 in the above equations since the (Wt% O) cannot be measured or calculated, we have:

$$R_5 = \beta'_1(\text{Wt\% Mn}) \tag{E.7}$$

$$R_7 = \beta'_2(\text{Wt\% Si})^{\frac{1}{2}} \tag{E.8}$$

$$\frac{R_7}{R_5} = \frac{\beta'_2(\text{Wt\% Si})^{\frac{1}{2}}}{\beta'_1(\text{Wt\% Mn})} = \alpha_3 \frac{(\text{Wt\% Si})^{\frac{1}{2}}}{(\text{Wt\% Mn})} \tag{E.9}$$

Replacing R_6 and R_7 in

$$R_4 = R_5 + R_6 + R_7 \tag{E.10}$$

in terms of R_5 we have:

$$R_4 = R_5 + \frac{R_5}{Km(\text{Wt\% Mn})} + R_5\frac{R_7}{R_5} \tag{E.11}$$

Substituting R_7/R_5 by equation (E.9) we have:

$$R_4 = R_5\left[1 + \frac{1}{K_m(\text{Wt\% Mn})} + \alpha_3 \frac{(\text{Wt\% Si})^{\frac{1}{2}}}{(\text{Wt\% Mn})}\right] \qquad \text{(E.12)}$$

Solving for R_5 we get:

$$R_5 = \frac{R_4(\text{Wt\% Mn})}{(\text{Wt\% Mn}) + \frac{1}{K_m} + \alpha_3(\text{Wt\% Si})^{\frac{1}{2}}} \qquad \text{(E.13)}$$

Considering R_5 from equation (E.9) and replacing in (E.12) we have:

$$R_4 = \frac{R_7(\text{Wt\% Mn})}{\alpha_3(\text{Wt\% Si})^{\frac{1}{2}}}\left[1 + \frac{1}{K_m(\text{Wt\% Mn})} + \alpha_3 \frac{(\text{Wt\% Si})^{\frac{1}{2}}}{(\text{Wt\% Mn})}\right] \qquad \text{(E.14)}$$

Solving for R_7 we get:

$$R_7 = \frac{R_4 \cdot \alpha_3 \cdot (\text{Wt\% Si})}{(\text{Wt\% Mn}) + \frac{1}{K_m} + \alpha_3(\text{Wt\% Si})^{\frac{1}{2}}} \qquad \text{(E.15)}$$

Hence from equations (E.13) (E.15) and (E.5) we have a method of determining the sharing of oxygen between reactions (E.1) (E.2) and (E.3).

VITA

Name: René Guindon

Born: 22 September 1944, Deschenes,
P.Q., Canada.

Educated:

Primary: Descheres, P.Q.
Secondary: Témiscaming, P.Q.
University: University of Ottawa,
Ottawa, Canada.

Course: Electrical Engineering.

Degree: B.A.Sc (Ottawa) 1966.