KINETICS OF THE ZINC SLAG FUMING PROCESS

by

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(Department of Metallurgical Engineering)

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
January 1983

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ABSTRACT

A study involving in-plant measurements, laboratory analysis and mathematical modelling was conducted to elucidate the kinetics of the zinc slag fuming process. The traditional assumption has been that the process operates at thermodynamic equilibrium. The results of industrial measurements at five different companies has demonstrated that this approach is not correct.

Chemical assays of the slag show carbon levels in the range of 0.1 - 1.0% and char particles have been extracted from slag samples. Tuyere back-pressure measurements revealed that the predominant mode of gas injection behavior is bubbling. This evidence indicates that a portion of the coal injected into the furnace is entrained in the slag.

A model of the direct coal particle-slag reaction was developed and incorporated into an overall model of the slag bath. This model included the behavior of the water-jacketed wall, a treatment of coal combustion in the tuyere gas stream, and a model of the entrained coal residence time.

Fitting of the data to eleven industrial fuming cycles showed that the fraction of coal entering the bath was consistently about 35%. About 50% of the coal is combusted in the tuyere gas stream and 10% passes through the bath unconsumed.
Calculated oxygen utilization ranged from 70-95%, dependent on slag depth.

The slag fuming process is therefore kinetically controlled. There are essentially two critical parameters: the fraction of coal entrained in the slag, and the rate of ferrous iron oxidation. The rate of ferric reduction balances ferric inputs to the bath by displacing previously reduced zinc from the entrained coal-slag reaction bubbles.

Process efficiency can be increased therefore by increasing entrainment of coal in the bath, perhaps by the use of high pressure injection, and by reducing ferrous iron oxidation. The latter objective may be achieved by more complete combustion of tuyere coal or pre-combustion. A significant control advantage might be gained by separating these two functions to different sets of tuyeres.

In continuous fuming operations the model would suggest that improved efficiencies could be obtained by using a more coarsely ground coal, higher fixed carbon coals, and operating at intermediate temperatures.
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<td>$A_x$</td>
<td>Surface area of $x$</td>
<td>$m^2$</td>
</tr>
<tr>
<td>$A_o$</td>
<td>Boudouard Reaction Rate</td>
<td>kPa$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$a_j$</td>
<td>Activity of species $j$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$B$</td>
<td>Boudouard Reaction rate</td>
<td>kg s$^{-1}$</td>
</tr>
<tr>
<td>$C$</td>
<td>Furnace coal rate</td>
<td></td>
</tr>
<tr>
<td>$C_p^j$</td>
<td>Concentration of species $j$ in phase $p$</td>
<td>kg·mole m$^{-3}$</td>
</tr>
<tr>
<td>$c_j$</td>
<td>Wt. fr. of $j$ in coal where $j$ is:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$fc$: fixed carbon</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$vol$: volatiles</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$ash$: ash</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$moist$: moisture</td>
<td></td>
</tr>
<tr>
<td>$D$</td>
<td>Ratio of ferrous to ferric diffusivity</td>
<td></td>
</tr>
<tr>
<td>$D_j$</td>
<td>Self-diffusivity of species $j$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$D_j^p$</td>
<td>Inter-diffusivity of species $j$ in phase $p$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$d_x$</td>
<td>Diameter of $x$, thickness of $x$</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>where $x$ is: $p$: particle</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b$: bubble</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$st$: water-jacket steel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$sl$: frozen wall slag</td>
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<tr>
<td>$E$</td>
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<td>m$^3$ s$^{-1}$</td>
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<td>$E_a$</td>
<td>Boudouard Activation Energy</td>
<td>kJ kg·mole$^{-1}$</td>
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<td>Fraction of coal entrained in slag</td>
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<td>$F_j^p$</td>
<td>Wt. fr. of species $j$ in phase $p$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$f$</td>
<td>Tuyere bubble frequency</td>
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<tr>
<td>$G$</td>
<td>Molar quantity of carbon in char particle</td>
<td>kg·mole</td>
</tr>
<tr>
<td>$g_p$</td>
<td>Thermal conductivity of phase $p$</td>
<td>J m$^{-1}$ s$^{-1}$ k$^{-1}$</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravitational acceleration</td>
<td>ms$^{-2}$</td>
</tr>
<tr>
<td>$H$</td>
<td>Equilibrium constant</td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>( h )</td>
<td>Slag bath height</td>
<td></td>
</tr>
<tr>
<td>( h_t )</td>
<td>Heat transfer coefficient slag-wall</td>
<td></td>
</tr>
<tr>
<td>( K_x )</td>
<td>Equilibrium constant of reaction ( x )</td>
<td></td>
</tr>
<tr>
<td>( k_j )</td>
<td>Mass-transfer coefficient of species ( j )</td>
<td></td>
</tr>
<tr>
<td>( L )</td>
<td>Furnace length</td>
<td></td>
</tr>
<tr>
<td>( M )</td>
<td>Mass of slag bath</td>
<td></td>
</tr>
<tr>
<td>( M_p )</td>
<td>Mass of phase ( p )</td>
<td></td>
</tr>
<tr>
<td>( N_j )</td>
<td>Mole fraction of species ( j )</td>
<td></td>
</tr>
<tr>
<td>( n_j )</td>
<td>Molar quantity of species ( j )</td>
<td></td>
</tr>
<tr>
<td>( \dot{n}_j )</td>
<td>Molar mass-transfer rate of species ( j )</td>
<td></td>
</tr>
<tr>
<td>( P_j )</td>
<td>Partial pressure of species ( j )</td>
<td></td>
</tr>
<tr>
<td>( p )</td>
<td>Secondary bubble path length</td>
<td></td>
</tr>
<tr>
<td>( q )</td>
<td>Heat transfer rate</td>
<td></td>
</tr>
<tr>
<td>( R )</td>
<td>Gas constant</td>
<td></td>
</tr>
<tr>
<td>( \dot{r} )</td>
<td>Rate of reaction</td>
<td></td>
</tr>
<tr>
<td>( r_x )</td>
<td>Radius of ( x )</td>
<td></td>
</tr>
<tr>
<td>( S )</td>
<td>Molar lime-to-silica ratio</td>
<td></td>
</tr>
<tr>
<td>( s_l )</td>
<td>((C+ash)/C) wt ratio in char particle</td>
<td></td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>( t )</td>
<td>Time</td>
<td></td>
</tr>
<tr>
<td>( U )</td>
<td>Number of furnace tuyeres</td>
<td></td>
</tr>
<tr>
<td>( V_x )</td>
<td>Volume of ( x ), where ( x ) is:</td>
<td></td>
</tr>
<tr>
<td>( v_x )</td>
<td>Velocity of ( x )</td>
<td></td>
</tr>
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<td>( v_j )</td>
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<td>( W_j )</td>
<td>Wt. fr. of ( j ) in slag wall</td>
<td></td>
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Greek Symbols

\[ \gamma_j \] Activity coefficient of species \( j \)

\( \sigma \) Surface tension \[ N \, m^{-1} \]

\( \theta \) Wetting angle \( \text{(degrees)} \)

\( \rho_p \) Density of phase \( p \) \[ kg/m^3 \]

\( \rho_{p,m} \) Molar density of phase \( p \) \[ kg\cdotmole/m^3 \]

\( \Delta \rho \) Density difference, \( \rho_1 - \rho_g \) \[ kg \, m^{-3} \]

\( \mu \) Viscosity of slag \[ kg \, m^{-1} \, s^{-1} \]

\( \lambda \) X-ray wave length \[ m \]

\( \varepsilon_t \) Tuyere gas column porosity

\( \varepsilon_{sl} \) Slag porosity

\( \tau \) Dimensionless diffusion time

Other Symbols

\( \Delta H_w \) Heat of water \((20^\circ C - gas, 100^\circ C)\) \[ J \, kg\cdotmole^{-1} \]

\( \Delta H_{s,ZnO} \) Heat of solution of ZnO in slag \[ J \, kg\cdotmole^{-1} \]

\( \Delta H_x \) Heat of reaction \( x \) (See Table 6.3) \[ J \, kg\cdotmole^{-1} \]

\( Re \) Reynolds Number

\( Pe \) Peclet Number

\( Sh \) Sherwood Number

\( Eo \) Eotvos Number
### Phases (subscripts and superscripts)

<table>
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<tr>
<th>sl</th>
<th>Slag</th>
<th>tb</th>
<th>Tuyere bubble</th>
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<tr>
<td>b</td>
<td>Bubble</td>
<td>bl</td>
<td>Blast</td>
</tr>
<tr>
<td>i</td>
<td>Interface</td>
<td>w</td>
<td>Water</td>
</tr>
<tr>
<td>p</td>
<td>Char particle</td>
<td>st</td>
<td>Steel</td>
</tr>
<tr>
<td>g</td>
<td>Gas</td>
<td>f</td>
<td>Final</td>
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### Rate Phenomena (superscripts and subscripts)

<table>
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<tr>
<th>r</th>
<th>Reduction</th>
<th>cons</th>
<th>Consumption</th>
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<tr>
<td>m</td>
<td>Melting</td>
<td>gen</td>
<td>Generation</td>
</tr>
<tr>
<td>o</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>Combustion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>Input</td>
<td></td>
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I would like to extend my sincerest thanks to Dr. Keith Brimacombe for his untiring enthusiasm and guidance throughout this project. Sincere thanks is also extended to Dr. Gerry Toop for his invaluable assistance and continuous support, without which this work would not have been possible. A personal note of thanks is due to my wife for her particular patience and many efforts in helping me to complete this thesis.

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CHAPTER I

INTRODUCTION: SLAGS AND SLAG PROCESSING

Slags are ubiquitous actors in pyrometallurgical processes, where they often play vital albeit mysterious roles. In general the slag is involved in both the physical and chemical processing of the metal by fulfilling several functions. These may include: refining of the melt by the absorption of unwanted liquid or solid components, thermal insulation of the melt, protection of the melt from the surrounding atmosphere and control of the supply of refining materials to the melt. To satisfy these demands the slag must have a particular set of properties which are controlled by its composition and temperature. Of necessity the slag must have a lower melting point than the melt, it must have a lower specific gravity and finally must be immiscible with the melt. These requirements ensure that the slag forms a relatively fluid and distinctly separate phase on the surface of the melt. In addition the slag must have a chemical composition such that it can react with the melt in the desired way to remove impurities. This requirement must be met within the limits imposed by the above constraints which usually means that some compromise be reached between the physical and chemical properties of the slag. For example, to dephosphorize and desulphurize steel it would be desirable to use a very high lime slag but such a material would be solid at steel making temperatures and consequently of little practical use.
Finally it must be appreciated that within the context of industrial processes, slags arise from three sources. The first contribution to the slag is gangue material introduced with the concentrate or ore. Second are fluxes deliberately added during the smelting operation, and thirdly the slag may be built up in part by oxidation of the melt, be it metal or matte. If to these considerations are added questions of availability of materials, economics, and natural variation in the gangue composition the whole problem becomes quite complex. As a result the efficiency with which slag performs any one of its functions is limited. Thus, for example, heat is lost from the melt through the slag and the refining of the melt is not as complete as it possibly could be. These types of problems can be dealt within a particular process for example by increasing the thickness of the slag layer on the melt or increasing the mass of slag to compensate for the inefficient refining.

There exists however a series of problems associated with the presence of a slag that cannot be so easily resolved. One of the most important of these and that which forms the raison d'etre for this thesis, is the fact that metal values are unavoidably lost to the slag during processing. The losses can be of two forms. First are chemical or solution losses in which a metal dissolves in the slag due to the prevailing chemical potential. Second are physical losses such as the entrainment of copper droplets in converter slag. Together or separately these losses can amount to a significant fraction of the metal input to a process and therefore justify their removal.
This operation is appropriately termed slag cleaning. Other problems of this group include refractory attack and erosion, disposal of slag, and the thermal burden imposed on smelting processes by the presence of the slag. These will not be discussed further as they are beyond the scope of this thesis.

Before proceeding, and in view of the above statements, it is worth mentioning the general philosophy that has guided the use of slags in industrial practice: tradition. For reasons that will become apparent below, slags are very complex phases and are difficult to understand in theoretical terms. (Part of this problem is the fact that they are solutions not dominated by any particular species.) Also due to the paucity of experimental data, little is known of their physical and chemical properties on a comprehensive scale. These two factors combine to ensure that slags are used in a largely empirical and unimaginative fashion based upon traditional practices. Until a better understanding of slags is achieved the analysis of slag-related problems and the development of slag processes is destined to be slow. To summarize what is known and thereby provide some background for the discussions to follow, a short review of slag chemistry will be made before slag cleaning and slag fuming are introduced.

1.1 Slag Chemistry

'Slag' is a generic term used to describe a mixture of molten oxides which may also contain sulphides and halides in
smaller proportion. In practice slags are usually based on silicates and aluminates of metal oxides such as lime (CaO), magnesia (MgO), and ferrous oxide (FeO). Sulphides only appear as impurities and halides (most often CaF$_2$) are added only in specialized applications. Because of the predominantly ionic character of the alkali and transition metal oxides and the more covalent type bonding of silica and alumina, molten mixtures of these compounds become quite complex.

When ionic compounds melt they simply form ionic melts as in the case of CaO:

\[
\text{CaO}_\text{(s)} \rightarrow \text{Ca}^{2+}_\text{(l)} + \text{O}^{2-}_\text{(l)} \quad \cdots \text{(1.1)}
\]

When silica melts the process is more complicated. Within the lattice of SiO$_2$ each Si atom is surrounded by four oxygen atoms each shared with a different Si atom. The structure can be envisaged as a three dimensional network of these tetrahedra. As silica is heated the network starts to break down to form large "ions" such as (Si$_9$O$_{21}$)$^{6-}$ and a small number of Si$_{4+}$ ions. Further heating acts to reduce the average size of these ions say to (Si$_3$O$_8$)$^{8-}$. Eventually at a very high temperature the melt would consist of (SiO$_4$)$^{4-}$ tetrahedra and an equal number of Si$_{4+}$ ions ($1723^\circ$C).

When a mixture of an ionic oxide and silica is melted together the dissociation of the metal oxide generates O$^{2-}$ ions which act to break up the silica network:
As a result a substantial reduction in the melting point is achieved (1436°C at 36% CaO; 74% SiO₂). The addition of other oxides can lead to further reductions in the melting point and viscosity.

The most elementary understanding of slag systems is based upon the simple chemistry of the acid-base model. Following the Bronstead's theory for aqueous solutions a basic oxide has been defined as one which contributes O²⁻ ions to the melt, eg. CaO in Equation 1.1. An acid oxide is one which accepts O²⁻ ions, eg. SiO₂ in the presence of CaO:

\[ \text{SiO}_2 + 2\text{O}^{2-} \Leftrightarrow (\text{SiO}_4)^{4-} \]  \hspace{1cm} (1.3)

Finally an oxide may behave as a base in the presence of a stronger acid, eg. Al₂O₃ in the presence of SiO₂:

\[ \text{Al}_2\text{O}_3 + 3\text{O}^{2-} \Leftrightarrow 2\text{Al}^{3+} + 3\text{O}^{2-} \]  \hspace{1cm} (1.4)

or

\[ \text{Al}_2\text{O}_3 + \text{SiO}_2 \Leftrightarrow (\text{SiO}_4)^{4-} + 2\text{Al}^{3+} + \text{O}^{2-} \]  \hspace{1cm} (1.5)

and an acid in the presence of a stronger base (Al₂O₃ in CaO):

\[ \text{Al}_2\text{O}_3 + \text{O}^{2-} \Leftrightarrow (\text{Al}_2\text{O}_4)^{2-} \]  \hspace{1cm} (1.6)

In these terms a reasonable qualitative understanding of the behavior of slags can be developed. For example viscosity can often be related roughly to a ratio such as the Index of Basicity.

\[ \text{Index of Basicity} = \frac{\text{wt}\% \text{ basic oxides}}{\text{wt}\% \text{ acid oxides}} \]
There have been several attempts to formulate theoretical models from elementary thermodynamic and physical chemical principles as reviewed by Gaskell. These have been only partially successful and generally deal with only binary systems (e.g. MO - SiO₂) over a restricted composition range. In addition, they usually make use of one or more empirical parameters which are not readily subject to measurement. It suffices to say that modelling of slag systems is only in its early stages of development and it will be some time before a comprehensive understanding of slag chemistry is arrived at. In the meantime, our analysis of slag systems must, in large part, be drawn from extrapolations or interpolations of experimental data.

In summary, in spite of our lack of knowledge, it is generally agreed that slags are ionic liquids consisting of metal cations (e.g. Ca²⁺, Fe²⁺, Zn²⁺, Mg²⁺, etc.) oxygen anions (O²⁻) and complex anions such as (SiO₄)⁴⁻, (Si₂O₇)⁶⁻ and (Al₂O₄)²⁻. Due to this structure, diffusivities in polyanionic slags tend to be roughly an order of magnitude lower in slags than in liquid metals. Thermal conductivity also tends to be quite low. In addition, melting points are usually not well defined because viscosity is a strong function of temperature. The ionic nature of the melt also ensures that there are strong interactions between various species, resulting in non-ideal thermodynamic behavior, i.e. large and variable activity coefficients.
1.2 Slag Cleaning

The term 'slag cleaning' refers to a metallurgical process whereby metal values are recovered from the slag phase. There are basically three different approaches to this problem. The most predominant are pyrometallurgical reductive processes in which molten slag is treated with a reducing agent such as coal or pyrites to reduce dissolved metals to a metallic or sulphide form. For example, one process for the recovery of copper and nickel from slags derived from the smelting of copper - nickel ores is reduction by coke in an electric furnace to produce a liquid copper - nickel alloy. The second cleaning process is 'settling' by which contained metals or metal sulphides rise or sink to form a distinct layer from which the slag can be separated. Settling may follow a reductive process or simply be used on its own. In general if settling is an important aspect of the slag cleaning process an electric arc furnace is used to ensure that relatively quiescent slag conditions are achieved. The third approach is slag milling and flotation. This involves grinding the cooled slag and separating metallic and sulphide particles by a standard rougher-cleaner type circuit. This method has the advantage of more efficient recoveries (5-10% better than the electric furnace route for copper and nickel) and roughly half of the energy consumption. The disadvantages include a capital cost of about twice the pyrometallurgical route and the inability to recover less noble metals such as lead, zinc, and tin.
As the name implies, 'slag cleaning' is usually a secondary operation which lies outside the main flow of the smelting process. This situation has arisen due to a lack of understanding of slag systems and has been perpetuated by the absence of the development of slag processing technology. Instead of attempting to use slag as active vehicles of metallurgical extraction, the attempt has been to minimize all 'losses' to the slag and correct for failures in this area by slag cleaning. This is not necessarily the most efficient solution to the problem. For example, it might be better to effect the separation of two metals by operating under conditions which promote the transfer of one to the slag phase from which it will be subsequently recovered.

This discussion will not be pursued here, except to note that it has only been in recent years that the problem of slag treatment of slag processing has been seriously addressed. Current understanding of slag systems and their treatment is comprehensively reviewed by Floyd and Mackay\(^3\). As their paper reveals, our knowledge is sketchy and only beginning to provide a proper perspective from which slag processing can be viewed. See also the review by Snelgrove and Taylor\(^4\).

The whole question is neatly illustrated by the process of zinc slag fuming. The origin, the history and the development of this process presents a vivid picture of the problems, pitfalls and philosophy of slag processing. The kinetics of zinc slag fuming, the focus of this thesis, will be dealt with after this background has been discussed.
1.3 Zinc Slag Fuming

Zinc slag fuming is the reductive treatment of molten slag to recover dissolved zinc. The process is carried out in a rectangular water-jacketed furnace on a batch basis. A schematic drawing of a cross section of the furnace is shown in Fig. 1.1. A charge consisting of approximately 50 tonnes of molten or molten and solid slag is charged to the furnace at the beginning of the cycle. A reducing mixture of a reductant, usually pulverized coal, and air is blown into the bath through sets of tuyeres which are set along the bottom of the long dimension on both sides of the furnace. The coal, normally of the bituminous or sub-bituminous class, is ground to 80% -200 mesh (B.S.S.) and applied to the slag at a rate of 50-75 kg/min. It is carried by what is termed the "primary air" which has a volume flow rate of about 30 m$^3$/min. The main blast or "secondary air" enters the tuyere behind the coal stream with a volume flow rate of 300-400 m$^3$/min. In some operations this blast is preheated up to 700°C.

Within the furnace the reducing mixture reduces the zinc from a dissolved oxide to metallic zinc, a gas at operating temperatures which lie between 1150 and 1325°C. The overall reactions are then:

$$\text{ZnO}_{(\text{slag})} + \text{C}_{(\text{coal})} \rightarrow \text{Zn}_{(g)} + \text{CO}_{(g)} \quad \ldots(1.7)$$

$$K_{1200^\circ C} = 395, \quad \Delta H = 364000 \text{ J}$$
Figure 1.1 Schematic of Fuming Furnace Cross-Section
and

$$\text{ZnO}_{\text{slag}} + \text{CO}_{(g)} \not\rightarrow \text{Zn}_{(g)} + \text{CO}_2(g) \quad \ldots (1.8)$$

$$K_{1200^\circ C} = 0.129, \quad \Delta H = 192500 \text{ J}$$

The zinc vapour and tuyere gases pass out of the bath into the freeboard space of the furnace where the zinc is oxidized to a zinc oxide fume which is subsequently captured in a baghouse. Oxidation is accomplished by the tuyere gas stream and air which leaks into the furnace above the bath, sometimes referred to as 'tertiary air'. For this reason the gas stream is very hot and to recoup some of this heat the gases are usually passed through a steam boiler before entering the baghouse.

Slag fuming is normally applied to the recovery of zinc and lead from lead blast furnace slag. At two operations however, it is used to treat copper reverberatory slag. In the former case the slag initially contains 13-18% zinc, and in the latter case about 8%. Fuming usually is carried out until the slag contains 1.5-2.5% zinc at which point the furnace is tapped and the slag is granulated and stockpiled. The overall cycle takes about 3 hours including 30 minutes for charging and tapping. The remaining time, about 150 minutes, is termed the "fuming period" during which the majority of the zinc extraction takes place. The fuming period is often subdivided into an initial heating period followed by proper fuming. The heating period involves operating at a reduced coal rate in order to ensure more complete combustion of the coal and thereby heat the bath to a desirable
operating temperature. This is often necessary because many plants hold the blast furnace slag in ladles for up to several hours before charging to the slag-fuming furnace.

In addition to lead and zinc, other volatile elements present in the slag are also fumed, usually as oxides or sulphides. These include tin, cadmium, and indium. The fume also contains chlorides, fluorides, some lime, silica and iron oxides, as well as carbon. The recovery of zinc from the slag is normally 85-90% and requires 1-2 kg coal per kg zinc (3.3-6.5 kg moles C per kg mole Zn). Recovery of lead is always near 100%.

It is immediately obvious that slag fuming represents a very complex interaction of physical and chemical processes: the dynamics of gas injection into liquids, submerged combustion of coal, slag-gas reaction kinetics and slag thermodynamics. The complete description of the process is the object of this thesis and will be developed in due course.

1.3.1 History

In the nineteenth century lead was usually smelted from siliceous and carbonate ores due to the ease with which these could be treated, however, these sources of lead were rapidly exhausted and smelters were forced to use sulphide ores. Although the Scotch hearth smelting technique was available to treat these ores it could only be used effectively on relatively
pure galena (greater than 70% Pb, less than 4% iron pyrites and sphalerite). The majority of lead sulphide ores however contain a significant quantity of zinc sulphide and it therefore became necessary to develop a smelting practice that could be effectively used on them.

This, of course, was the lead blast furnace which was developed in the 1870's by the smelting companies of the western United States. The lead blast furnace treatment of ores preceded by sintering has become the mainstay of lead smelting in the twentieth century. The development of selective flotation methods for the separation of zinc and lead sulphides from iron sulphide in cryptocrystalline ores lead to even greater efficiencies. However it is virtually impossible to remove all the zinc from lead concentrates and consequently there is unavoidably zinc in the sinter charged to lead blast furnaces.

For several reasons zinc is a critical factor in the operation of lead blast furnace. Of particular importance is the fact that metallic zinc is vapour at hearth temperatures. For this reason if metallic zinc is produced in the furnace it is carried into the upper regions of the furnace where it condenses or reacts with the charge which can cause severe problems of 'bridging' of the charge and may necessitate a shutdown. Examination of an oxide Ellingham diagram, Fig. 1.2, shows that at 1200°C liquid lead can be produced from PbO at an oxygen potential of approximately 1 Pa. (10^{-5} atm). At the same temperature the reduction of ZnO requires an oxygen
This line is hypothetical and applies to stoichiometric compounds. Actual decomposition is to $\text{Fe}_2\text{O}_3$ containing $\text{Fe}_2\text{O}_4$ at lower activity.

Figure 1.2 Oxide Ellingham Diagram (from reference (8))
potential of about 1 \(10^{-7}\) Pa. \(10^{-12}\) atm). It is therefore relatively straightforward to produce lead and at the same time avoid most of the problems caused by zinc vapour. Since the zinc remains as an oxide it reports to the slag and as a result the lead smelting complexes of the world began to accumulate large slag dumps that contained up to 20% zinc.

World War I saw a sharp rise in the demand for zinc which continued into the 1920's as the physical metallurgy of zinc and its industrial potential began to be seriously investigated. This ensured a growing market for the metal thus providing a strong incentive for the development of a process that could recover the zinc from such a readily available source as a smelter slag pile. It was also realized that any technique that allowed for the recovery of substantial quantities of zinc from a lead smelting circuit could substantially reduce the degree of separation required in flotation. Finally it was appreciated that since the blast furnaces were constantly producing molten slag and that eventually this would be the major source of slag for treatment a process that could treat the slag directly, and perhaps take advantage of the contained sensible heat, would be the most desirable.

It must be appreciated that the metallurgists faced with this problem were only dimly aware what might be involved in such a process. In addition only a limited range of technology existed that might be called upon for the task. The handling of
slag had in the past been largely restricted to pouring it into pots and hauling it out to the slag dump. What was demanded was the controlled chemical and physical treatment of slag, a virtually unexplored area.

However, two fundamental facts formed the germ of their approach to the problem. The first was that zinc metal was a vapour at molten slag temperatures. The second was not as well understood, the fact that slags were essentially molten oxides; but this was sufficient to produce ideas. The earliest report on slag treatment experiments was made by G. Courtney in 1920. In this paper published in the Proceedings of the Australasian Institute of Mining and Metallurgy he describes a series of tests performed by the Sulphide Corporation of Cockle Creek, Australia. The earliest work was done in 1906 and simply involved blowing compressed air through the molten slag. Since zinc was gas at slag temperatures a 'gas purging' may have been thought to be an easy way to remove it from the slag. Although the technique did produce some fume the slag was rapidly cooled and frozen.

In the second set of experiments a coal-air mixture was used instead of air. Whether or not the coal was simply viewed as a fuel to make up the heat loss or whether it was viewed as a reductant is not clear. Either way the experiments were successful to the extent that a patent was issued to F.H. Evans and P.A. McKay in 1908. However it seems no commercial development of the idea was made at that time. Courtney goes on to
describe several other methods that were tested at Cockle Creek. These included a reverberatory furnace treatment which involved firing the slag with coke and limestone to a temperature of 1600°C. This is direct evidence that an analogy had been drawn between the reduction of solid oxides and the reduction of slag. Agitation was found to be of some assistance and recoveries of 40% were achieved. Experiments were also conducted with an electric furnace which gave recoveries of 60% without any additions of coal, coke or fluxes. A valuable lesson was learned at this point. During the first heat the slag completely dissolved the furnace lining and there after it was decided that the slag could only be effectively handled in water-jacketed furnaces. Other tests were made with a blast furnace type smelting furnace which would handle briquettes, nodules or lumps. It was only partially successful. Despite all of this work no commercial developments appear to have been made.

North America was the site of work which eventually lead to the construction of an operating furnace. In the early 1920's experiments were undertaken by the Consolidated Mining and Smelting Company at Trail, B.C. to find a means of treating the slag in an electrothermal way.10 Due to the availability of hydroelectric power at Trail, it was felt that this would be the cheapest technique. Beginning in 1925 experiments in slag cleaning were independently begun by the Anaconda Copper Mining Co., in Great Falls, Montana.11 Their initial investigations involved an electric furnace but they soon switched to studying the elimination of zinc from molten slag by the submerged
injection of pulverized coal in a copper converter. This work was done at the Tooele, Utah plant of the International Smelting Company. This was followed by the construction of experimental water-jacketed furnace and based on its success, a slag fuming plant was commissioned for the Anaconda smelter in East Helena, Montana.

This plant was built during 1927 and blown-in in December of that year.\textsuperscript{12} The furnace was 2.44 m (8 ft) by 3.66 m (12 ft) and used 22 - 10.2 cm (4 in) i.d. tuyeres. These tuyeres were borrowed from the design of burners for coal fired reverberatory furnace. These were to be improved shortly by A. Laist who designed the double-inlet tuyeres described above. These were much safer devices because they effectively prevented the coal from entering the secondary air system. The East Helena furnace treated a batch charge of 23 tonnes (25 tons) with a daily capacity of 300 tonnes. Recoveries of 85-90\% were achieved in 160 minute blowing times.

Work continued at Trail with the construction of an experimental pulverized coal furnace in 1927. Tests were also made with a combination of coal and electro-thermic reduction. In the end, it was decided that the pulverized coal method was cheaper than the electro-thermic process for the treatment of molten slag. In addition it was found that the coal-electrothermic process had problems due to the production of metallic iron. For these reasons it was decided that the pulverized coal furnace would be
developed for commercial operation. A furnace was designed in 1928, in conjunction with further pilot plant work and the assistance of the Anaconda Co. The furnace was blown-in in July, 1930.

The Trail furnace was longer, 7.9 m (20 ft), and slightly wider, 3.05 m (10 ft). In addition, it incorporated the new double-inlet tuyeres and a boiler unit to generate steam from the sensible heat of the off gases. Beyond that, it was essentially the same as the East Helena furnace. Both furnaces were regularly used to treat a mixture of solid and liquid slag in order to recover the zinc from slag dumps. Eventually, when these were consumed, the main source of slag became the blast furnaces.

Although the process gradually spread to the lead smelters of the world, it remained essentially unchanged except for particular modifications made at a few locations. (See Table 1.1 for a survey of slag fuming operations reported in the literature.) In 1951, slag fuming was applied to the recovery of zinc from copper reverberatory slag at the Flin Flon operations of Hudson Bay Mining and Smelting. However, a furnace identical to that used to treat lead blast furnace slag at Kellogg, Idaho was constructed. The second development was the introduction of a secondary blast preheat on the slag fuming furnaces of Broken Hill Associated Smelters of Port Pirie in 1967. The third development which is actually of major signi-
### TABLE 1.1

#### Slag Fuming Operations

<table>
<thead>
<tr>
<th>PLANT</th>
<th>NO. OF OPERATING FURNACES</th>
<th>START UP</th>
<th>LENGTH (m)</th>
<th>WIDTH (m)</th>
<th>NO. OF TUYERES</th>
<th>TUYERE I.D. (mm)</th>
<th>WT (kg)</th>
<th>BULK DENSITY (g/cc)</th>
<th>CHARGE TYPE</th>
<th>COAL TYPE</th>
<th>GRIND</th>
<th>PRIMARY BLAST VOLUME m³/min</th>
<th>PRIMARY BLAST PRESSURE kPa, gauge</th>
<th>SECONDARY BLAST VOLUME m³/min</th>
<th>SECONDARY BLAST TEMP. °C</th>
<th>PRIMARY + SECONDARY AIR %</th>
<th>PRIMARY + SECONDARY PRESSURE kPa, gauge</th>
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<td>ASARCO CHIHUAHUA MEXICO</td>
<td>1</td>
<td>1952</td>
<td>6.40</td>
<td>2.44</td>
<td>42</td>
<td>38.1</td>
<td>45</td>
<td>38.1</td>
<td>Sub-Bituminous</td>
<td>High Vol</td>
<td>70% -200m</td>
<td>125</td>
<td>59</td>
<td>220</td>
<td>59</td>
<td>48% of Total Air</td>
<td>52% of Total Air</td>
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<td>1927</td>
<td>6.40</td>
<td>2.44</td>
<td>40</td>
<td>38.1</td>
<td>52</td>
<td>38.1</td>
<td>High Vol Bituminous</td>
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<td>69</td>
<td>320</td>
<td>100°C</td>
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<td>2.44</td>
<td>42</td>
<td>38.1</td>
<td>45</td>
<td>38.1</td>
<td>High Vol Bituminous</td>
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<td>79</td>
<td>370</td>
<td>90°C</td>
<td>79</td>
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<td>3.66</td>
<td>2.44</td>
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<td></td>
<td>11.5%</td>
<td></td>
<td>High Vol Bituminous</td>
<td>235</td>
<td>60</td>
<td>245</td>
<td>Ambient</td>
<td>70</td>
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<td>2.44</td>
<td>28</td>
<td>44.5</td>
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<td>Sub-Bituminous</td>
<td>21</td>
<td>50</td>
<td>245</td>
<td>Ambient</td>
<td>50</td>
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<td>52</td>
<td>31.75</td>
<td>25</td>
<td>31.75</td>
<td>Bituminous</td>
<td>90% -100m</td>
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<td>Ambient</td>
<td>52</td>
<td>325</td>
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<td>30</td>
<td>56</td>
<td>46</td>
<td>56</td>
<td>Sub-Bituminous</td>
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<td>500-600°C</td>
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<td>240</td>
<td>500-600°C</td>
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<td></td>
<td></td>
<td></td>
<td>Masut, Fuel Oil</td>
<td>Total Air</td>
<td>1200-1300 m³/tonne slag</td>
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<td></td>
<td></td>
<td>Natural Gas</td>
<td>Total Air</td>
<td>1200-1300 m³/tonne slag</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 1.1 (continued)

**Slag Fuming Operations**

<table>
<thead>
<tr>
<th>PLANT</th>
<th>CYCLE TIME</th>
<th>FUMING RATE</th>
<th>NOMINAL CAPACITY</th>
<th>En RECOVERY</th>
<th>Coal Wt Ratio</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASARCO CHIHUAHUA MEXICO</td>
<td>90 min</td>
<td>575</td>
<td>85%</td>
<td></td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>ASARCO EAST HELENA MONTANA</td>
<td>90-110 min</td>
<td>635</td>
<td>85-90%</td>
<td></td>
<td></td>
<td>11,12,18</td>
</tr>
<tr>
<td>ASARCO EL PASO TEXAS ASARCO</td>
<td>30 min</td>
<td>320</td>
<td>89%</td>
<td>2.1</td>
<td></td>
<td>19,20</td>
</tr>
<tr>
<td>SELBY CALIFORNIA</td>
<td>10 min</td>
<td>86</td>
<td></td>
<td></td>
<td></td>
<td>21,22</td>
</tr>
<tr>
<td>BUNKER HILL IDAHO</td>
<td>30 min</td>
<td>68</td>
<td>90%</td>
<td></td>
<td></td>
<td>23,24,25</td>
</tr>
<tr>
<td>COMINCO TRAIL BRITISH COLUMBIA</td>
<td>42 min</td>
<td>68</td>
<td>88%</td>
<td>1.71</td>
<td></td>
<td>10,16,17,18,19</td>
</tr>
<tr>
<td>HUDSON BAY FLEM FLEM MANITOBA</td>
<td>70 min</td>
<td>68</td>
<td>88%</td>
<td>2.08</td>
<td></td>
<td>30,31,32</td>
</tr>
<tr>
<td>INTERNATIONAL SMELTING &amp; REFINING TOOLE, UTAH</td>
<td>30 min</td>
<td>120 min</td>
<td></td>
<td></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>ROLDEN KONIKAR WORKS SWEDEN</td>
<td>50 min</td>
<td>800</td>
<td>91%</td>
<td>2.8</td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>BROKEN HILL ASSOC. SMELTERS PORT PIRIE, AUSTRALIA</td>
<td>30 min</td>
<td>150 min</td>
<td>86%</td>
<td>1.02</td>
<td></td>
<td>14,34,35,36,37</td>
</tr>
<tr>
<td>D. BLAHOEV BULGARIA USSR</td>
<td>Continuous</td>
<td>48-50 T/ day-m^2</td>
<td>85%</td>
<td>1.55</td>
<td></td>
<td>15,38</td>
</tr>
</tbody>
</table>

References:
1. [17](#)
2. [11,12,18](#)
3. [19,20](#)
4. [21,22](#)
5. [23,24,25](#)
6. [10,16,17,18,19](#)
7. [30,31,32](#)
8. [18](#)
9. [33](#)
10. [14,34,35,36,37](#)
11. [15,38](#)

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*Notes:*
- Cycle time includes heating and reducing stages.
- Fuming rate is given in kg/min.
- Nominal capacity is given in T/day.
- En recovery and coal wt ratio are percentages.
ficance is the continuous fuming process developed in Bulgaria, utilizing fuel oil or 'mazut' instead of coal. Unfortunately, little is known of this process and the improvement it represents over the traditional process is therefore difficult to assess. Finally, it has only recently been learned that the Russians have developed a process for fuming by means of natural gas. Again, insufficient details are available to determine if a significant improvement in the process has been achieved.

Largely responsible for the neglect of the process has been the fact that slag fuming has been traditionally viewed as fitting only into a corner of lead or copper pyrometallurgy. In this role, it is unlikely that it would be considered to justify development by the non-ferrous industry. Development, where it has taken place, has been focused instead on the metal making operations. This, of course, reflects the philosophy that the slag phase is only a passive actor in metallurgical processing.
The chemistry and kinetics of slag fuming were only vaguely understood at the time the first furnaces were constructed. It was known that a substoichiometric mixture of coal and air gave the best fuming rates and that higher temperatures, if they could be tolerated, gave higher fuming rates. From the effect of these and other operating variables such as slag depth, hot-to-cold charge ratio, and coal type, a simple picture of what was happening in the process was developed. It was generally postulated that the coal entering the furnace burned immediately to a carbon monoxide-carbon dioxide mixture via the reactions:

\[ C + \frac{1}{2}O_2 \rightarrow CO \] ... (2.1)

\[ C + O_2 \rightarrow CO_2 \] ... (2.2)

As the gas stream then rose through the bath the carbon monoxide reacted at the gas-slag interface by the reaction:

\[ ZnO_{\text{slag}} + CO \rightarrow Zn_{\text{(g)}} + CO_2 \] ... (2.3)

to produce zinc vapour.\textsuperscript{28,23} A second school of thought, that was seemingly in the minority, considered that the reduction of the slag took place on solid particles of coal which were in contact with it\textsuperscript{39}, eg.

\[ ZnO_{\text{slag}} + C \rightarrow Zn_{\text{(g)}} + CO \] ... (2.4)
For twenty-five years these ideas represented the general understanding of the process. There were no scientific studies made until the classical work of Bell, Turner and Peters in 1954.

2.1 Thermodynamic Modelling

The first attempt to quantitatively analyse the process in terms of chemistry and kinetics was made by Bell, Turner and Peters. They assumed that the chemistry of slag fuming was as given in reactions 2.1-2.3, but in addition included the volatile components of the coal as active reductants. The volatile carbon was considered to react as fixed carbon and the volatile hydrogen reacted as follows:

\[
\begin{align*}
\text{H}_2 + \frac{1}{2}\text{O}_2 & \overset{\ddagger}{\longrightarrow} \text{H}_2\text{O} \\
\text{ZnO}^{\text{(slag)}} + \text{H}_2 & \overset{\ddagger}{\longrightarrow} \text{Zn}^{(g)} + \text{H}_2\text{O}
\end{align*}
\]

With regard to kinetics Bell et al. made the fundamental assumption that the process ran at thermodynamic equilibrium and consequently, that Reactions 2.1-2.3, 2.5 and 2.6 proceeded to equilibrium before the gas stream left the surface of the slag. This is the origin of what is frequently termed the thermodynamic model of the process.

Bell et al. developed a simple model based on mass balances on carbon, hydrogen, oxygen and nitrogen, and on the equilibrium of Equations (2.3) and (2.7):
\[ H_2O + CO \xrightarrow{\text{i.e.}} CO_2 + H_2 \] ... (2.7)

\[ K_1 = \frac{P_{\text{Zn}} P_{CO_2}}{P_{CO} a_{\text{ZnO}}} \] ... (2.8)

and

\[ K_2 = \frac{P_{CO_2} P_{H_2}}{P_{H_2O} P_{CO}} \] ... (2.9)

This is a total of six equations that can be solved for the six unknowns: \( P_{CO}, P_{CO_2}, P_{H_2}, P_{H_2O}, P_{N_2} \) and \( P_{\text{Zn}} \). The only obstacle to solving this system was that the activity of zinc oxide was not known as a function of slag composition. In order to overcome this problem the authors monitored three controlled fuming runs and measured the fuming rate as a function of zinc concentration. With the addition of a zinc balance to the above equations, a seventh unknown, the activity of zinc oxide, could be computed.

Using this data the authors analysed regular furnace operation and found that their model accounted quite well for the furnace heat balance. They then proceeded to examine the consequences of various changes in operating practise. The model showed that fuming rates could be significantly improved by increasing the hydrogen content of the fuel. The use of natural gas was calculated to bring about a 37% increase in fuming rates. They also determined that oxygen enrichment should improve fuming rates which was in agreement with earlier test
work. Preheating of the blast was also shown to be of potentially significant benefit. Finally and perhaps most interesting is the suggestion that simply by separating the heating and reducing functions of a given fuel-air mixture, fuming capacity could be increased by about 35%. This would involve heating the bath for a period at 95% of stoichiometric combustion and then switching to 55% combustion to fume. By alternating in this way or by running half the tuyeres at one level and the remainder at the other level increased efficiency could be expected. Unfortunately this idea does not appear to have been tested industrially.

As mentioned, the model was successful in predicting the effect of oxygen enrichment. It was to be later demonstrated by Broken Hill Associated Smelters that blast preheat could bring about substantial improvements as suggested by the model.14 Their model, however, was found to be at variance with the results of tests using natural gas. It was suggested in this case that due to slow reaction kinetics equilibrium was not achieved. This also appears to have been the problem with fuel oil.42

Although some discrepancies existed, the model on the whole seemed to agree relatively well with reality. This in part is to be expected since the model was initially fitted to industrial data through the activity coefficient of zinc oxide. There are a number of other weaknesses in the model which include the lack of a complete heat balance and the omission of the role of
iron oxides in the oxidation and reduction reactions. For example, magnetite and metallic iron are sometimes observed in the furnace under certain conditions. Both of these facts indicate that the simple oxidation of carbon and reduction of zinc were not the only reactions taking place. Finally the evidence for the underlying assumption of equilibrium was only indirect and there was no experimental data to support this claim.

During the summer of 1956, Kellogg conducted a 'no coal' test on No. 2 slag fuming furnace at Cominco Ltd., Trail, B.C.\(^{39}\) This simply involved shutting off the coal to the furnace for a period of five minutes and monitoring the changes which resulted. The test revealed that the ferrous iron declined and both ferric iron and bath temperature rose. A mass balance on the change for ferric iron and a heat balance based on the rise in temperature both corresponded to a 100% utilization of the oxygen in the blast. Thus it was concluded that the gas stream - slag interface was sufficiently large to allow equilibrium to be achieved. Kellogg estimated that the interfacal area is sufficient to allow fuming rates of roughly three times those normally observed. The author concluded then that the process very likely runs at equilibrium.

On the strength of the work of Bell et al.\(^ {40}\) and this experiment, Kellogg developed a comprehensive equilibrium model of slag fuming in 1967.\(^ {43}\) The model took into account the
thermodynamics of the FeO-Fe$_3$O$_4$ couple, PbO reduction as well as
the behavior of dissolved sulphur. What is critical about the
ferrous-ferric couple in the slag is that if equilibrium is
assumed then the reaction

$$\text{ZnO}_{(\text{slag})} + 3\text{FeO}_{(\text{slag})} \xrightarrow{\text{slag}} \text{Fe}_3\text{O}_4 + \text{Zn}_{(g)} \quad \cdots \quad (2.10)$$
is at equilibrium. The ferric to ferrous ratio can then be said
to control the fuming fate. Activity coefficients, where possible,
were taken from the literature. The heat balance included the
sensible heat of the input slag, the build up of a frozen slag
shell on the water jackets and the reactions above the bath. As
a result, in addition to zinc, Kellogg was able to predict the
behavior of iron, sulphur, lead and temperature with time.

The model worked very well and required little fitting to
actual operation data. The major parameters that were adjusted
included values of the heat-transfer coefficients and activity
coefficients. In all cases apparently, the fitted values lay
within the expected limits of error. Due to the difficulty in
obtaining good industrial data, the model was verified against
a one month average performance of ASARCO's El Paso furnace.
The model was able to predict the final zinc content of the slag
and the value of the coal-to-zinc ratio for the 'average' cycle
to within 10%. Predicted temperatures and Fe$_3$O$_4$ behavior were
reasonable in terms of normal operating experience although
these were not checked against industrial measurements.
Finally the model was able to correctly account for the behavior of a slag fuming furnace during a 'no-coal' test. The model was used to demonstrate the beneficial effects of using a preheated blast. Decreasing coal moisture and coal ash were also shown to result in better fuming.

Kellogg's model represented a significant advance in the analysis of slag fuming and reinforced the idea that the process ran at equilibrium. This model conclusively established that the assumption of equilibrium in the furnace could quantitatively account for zinc elimination and at least qualitatively for the bath temperature and iron behavior.

The model was adopted and extended by a group at Broken Hill Associated Smelters, Port Pirie, Australia in the early 1970's. Grant and Barnett improved certain aspects of the model which resulted in problems when the slag depth was low. In addition, the authors extended the heat balance to include the waste heat boilers and recuperators. Improvements were also made to the flexibility of the model in handling predefined changes in input parameters such as number of weight of charges and coal rates. Grant and Barnett also carried out two extensive plant sampling campaigns in order to pinpoint more accurately the value of operating variables.

Again the agreement of the improved model with plant operation is good. Again the comparison has been made primarily to plant
averages over a large number of runs although one specific run comparison is detailed. In this case bath temperature is included and shows the model gives reasonable predictions. Unfortunately, no comparison is made with regard to the level of ferrous and ferric oxides in the slag.

It is important to mention that in order to achieve their fit, the activity coefficient of zinc oxide had to be increased 2.6 times over the value used by Kellogg, an unlikely difference considering the only weakly basic nature of ZnO. No justification is given. Considering the vital role played by this activity coefficient, it can therefore only be viewed as an adjustable parameter. This in itself is not particularly disagreeable. The ability to model an entire process with one adjustable parameter represents a considerable success. However, the whole weight of the equilibrium model now rests on this point. Significant improvement of the process can only come through an increase in this activity coefficient. The focus is then on slag chemistry and temperature. If the process is in reality kinetically controlled, fitting it with a thermodynamic parameter could be very misleading.

A further refinement of the model was made by Grant who reversed the equilibrium model to calculate the value of thermodynamic parameters required to account for observed fuming behavior. Based on the analysis of two carefully monitored fuming runs the author developed regression equations for the
activity coefficients of ZnO and PbO and for the activity coefficient ratios $3.1746 \gamma_{Fe_{0.945}O} / \gamma_{Fe_3O_4}$ and $\gamma_{CaS}/\gamma_{CaO}$. Relatively good correlations were obtained for ZnO:

$$\ln \gamma_{ZnO} = -335.18 N_{MnO} + 192.11 N_{CaO} - 36.07 N_{CaO}/N_{SiO_2} - 78.953 N_{SiO_2} + 28.417$$

and the iron oxide activity coefficient ratio. The average zinc oxide activity coefficient obtained was 3.40 (S.D. 0.50) which is 1.8 times the value originally used by Kellogg. The average iron oxide activity coefficient ratio reported is 4.19 (S.D. 1.15), 3.7 times Kellogg's value.

Despite the apparent success and implied vindication of the equilibrium model there are several problems with this paper. The first is that few fuming furnace slags contain manganese oxide to any appreciable degree immediately invalidating equations such as 2.11 in which MnO plays an obviously significant role. Second, the equation is of dubious value in any practical application due to the sensitivity to $N_{MnO}$. (A 2% change in the mole fraction MnO (e.g. 5.5 wt% Mn to 5.6 wt%) results in roughly a 25% change in $\gamma_{ZnO}$.) Considering the difficulty in obtaining an MnO assay to within 2% and the difficulty of then calculating the mole fraction, $N_{MnO}$, it becomes apparent that the equation is not readily applicable. Furthermore, given the very large coefficient for the $N_{MnO}$ term, the equation has no fundamental chemical significance.
The reported average values of these parameters are perhaps more meaningful. However considerable scatter exists in these results and they are very sensitive to the assumed level of air leakage from the tuyeres. (The calculated $\gamma_{\text{ZnO}}$ declines from 4.1 at 0% leakage to 2.9 at 10% leakage.) Although 5% leakage was assumed no measurements were made to confirm this.

In spite of the level of sophistication that the equilibrium model of slag fuming has attained it is apparent that it in many ways has remained essentially empirical. As discussed above, there is nothing wrong with this if its basic assumption is correct. Considerable evidence exists however which suggests otherwise.

2.2 Empirical Modelling

The first discussion of the idea that the zinc fuming process does not run at equilibrium is made by Quarm in 1965. Quarm cites the evidence of undocumented experiments in which the coal and air rate to a furnace were adjusted to bring about a fifty percent reduction in the calculated zinc partial pressure. In spite of this, no change in the fuming rate was observed. Quarm developed a crude model based on the observed first-order nature of the classic fuming curve, zinc in slag versus time. Quarm suggests that this first-order behavior is a result of the fuming reaction

$$\text{ZnO} + 3\text{FeO} \xrightleftharpoons{\text{Fe}_3\text{O}_4 + \text{Zn}}$$

... (2.12)
in which the concentration of ferrous oxide is maintained at a constant level by the reduction reaction

\[
\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2 \quad \ldots (2.13)
\]

The first-order nature of the fuming curve is thus due to the decline in the zinc oxide concentration. Quarm uses the empirical equation

\[
\log \left(\frac{\text{Zn}_1}{\text{Zn}_2}\right) = v(t_2 - t_1)/2.303 \quad \ldots (2.14)
\]

to model the process. \(\text{Zn}_1\) is the zinc concentration at time \(t_1\) and \(\text{Zn}_2\), the zinc concentration at time \(t_2\). '\(v\)' is the velocity coefficient of reaction 2.12. A regression analysis of the same data, only one set of which is reported, gave '\(v\)' a value of 0.06 min\(^{-1}\). This constant was then modified in linear proportion to fraction of iron in the ferrous form, e.g. if 60% of the iron was present as \(\text{Fe}^{2+}\) then the velocity coefficient would be 0.60\(v\). In order to perform a heat balance it was assumed that reaction 2.13 was at equilibrium with both magnetite and ferrous oxide present at unit activity, which is inconsistent with the basic approach to the problem.

In spite of its relatively rough assumptions the model was found to work "very well" when used to predict the behavior of the furnace from which its parameters were derived. Because the model is this specific little significance can be attributed to it beyond suggesting that the role of the iron couple \(\text{FeO-Fe}_3\text{O}_4\) is important. The gross assumptions deprive the model of any information that might lead to an understanding of the process.
In response to Kellogg's equilibrium model\textsuperscript{43}, Quarm\textsuperscript{47} introduced a new argument to counter the model. The Kellogg model assumes that both volatile and non-volatile portions of the coal burn and participate in the fuming reactions. In practise however Quarm states that coal supply is adjusted on the basis of fixed carbon content. He cites an example from the ASARCO El Paso plant operation. This is later corroborated by Yurko.\textsuperscript{26}

In 1980 Quarm\textsuperscript{48} presented a modified reaction mechanism which included zinc ferrite:

\begin{align*}
2\text{ZnO} + 2\text{FeO} & \xrightarrow{\Delta} \text{ZnOFe}_2\text{O}_3 + \text{Zn}_{(g)} \quad \cdots (2.15) \\
3\text{ZnO} \cdot \text{Fe}_2\text{O}_3 + \text{CO} & \xrightarrow{\Delta} 3\text{ZnO} + 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \quad \cdots (2.16) \\
\text{Fe}_3\text{O}_4 + \text{CO} & \xrightarrow{\Delta} 3\text{FeO} + \text{CO}_2 \quad \cdots (2.17)
\end{align*}

He also gives several sets of industrial data (zinc concentration and temperature as a function of time) and the results of model predictions which are relatively close to the measurements. In recognition of the new mechanism, velocity coefficients for both zinc oxide reduction (Equation 2.15)

\[ v = 0.03 + 0.0001 \ (T-1000) \quad \cdots (2.18) \]

and zinc ferrite reduction (Equation 2.16)

\[ v = -0.23 + 0.0018 \ (T-1000) \quad \cdots (2.19) \]

are given. 'T' is temperature in degrees Celsius. The rate of zinc fuming is then strictly dependent on temperature; and therefore by simply maintaining a certain temperature profile fuming
can be effected. This leads to interesting consequences for operating the process such as cutting the coal and air back significantly towards the end of the run when the fuming rate is low. Unfortunately the author provides no industrial verification of this concept.

In addition to the work done by Quarm, there have been two other empirical modelling exercises reported in the literature. The first is in a paper by Sundstrom describing the slag fuming plant at the Ronnskar Works of Boliden Aktiebolag in Sweden. Operating data gathered from a large number of fuming runs and the results of special tests were fitted to the regression model:

\[
Z_{n_t} = a_1 \cdot Z_{n_0} \cdot a_2 \cdot e^{(k_0 + \sum_{i} (k_i \cdot X_i))t}
\]

... (2.20)

where:

- \(Z_{n_0}\) = initial Zn concentration
- \(Z_{n_t}\) = concentration of Zn at time t
- \(X_i\) = independent variable
- \(t\) = elapsed time
- \(a_1, a_2, k_0, k_1, \ldots, k_n\) = regression coefficients

Sundstrom states that 40 independent variables are used in the equation. Unfortunately none of the variables or coefficients are given other than the following formula for 'normal' operation

\[
Z_{n_t} = 0.9 \cdot Z_{n_0} \cdot e^{(0.41 - 0.0154t)}
\]

... (2.21)

for \(40 < t \leq 250\) minutes
As a result of applying the model they have concluded that zinc extraction is primarily limited by the blast volume and that an even distribution of coal down the furnace length is necessary for maximum zinc extraction. The only other conclusion mentioned by the author is that the degree of combustion should be reduced from 80-100% of stoichiometric at the beginning of the blow to less than 50% immediately prior to tapping. No comments are advanced on the issue of kinetic versus equilibrium control.

In the second study, Ivanov et al. developed a regression model using data taken from an operating furnace over 303 batch runs. The following relationship was determined for zinc extraction

\[ Y = -41.0 - 1.3X_1 - 1.85X_2 + 83.0X_3 + 2.8X_4 + 0.47X_5 \]  \hspace{1cm} (2.22)

where:

- \( Y \) = extraction of zinc (%)
- \( X_1 \) = amount of slag in furnace, tonnes
- \( X_2 \) = ash content of coal (%)
- \( X_3 \) = consumption of coal per tonne of slag, tonnes
- \( X_4 \) = number of operating tuyeres
- \( X_5 \) = length of blow, min

The overall correlation coefficient obtained was \( r = 0.89 \).
It can be seen that increasing the amount of slag in the furnace will decrease the zinc extraction. The authors attribute this to the fact that as the weight of slag increases, the consumption of air and coal per unit of slag of course decreases. They reference however another study which concluded that higher zinc extractions could be obtained with increasing bath depth. In this case, they suggest, care might have been taken to maintain a constant blast intensity.

The negative coefficients for the coal ash term is to be expected because a higher ash content means a lower carbon content and a lower reducing power. Likewise, positive coefficients for the coal to slag ratio and blowing time are not surprising. The positive coefficient for the number of operating tuyeres is an interesting result. It implies that a full set of tuyeres provides the optimum fuming conditions, perhaps in terms of bath agitation. A reduction in the number of tuyeres would then result in a departure from ideal kinetic conditions. Perhaps it leaves quiescent zones in the slag and leads to incomplete mixing.

Although both of these models are empirical and do not directly address the question of process kinetics and thermodynamics some of the variables that have been identified as critical to the process could be interpreted as kinetic effects. The negative effect of bath weight could be explained by either a kinetic or thermodynamic argument. The same applies to the
ash content of the coal. However the effect of slag depth and
the number of operating tuyeres are clearly kinetic parameters.
The importance of blast volume or intensity, although not
absolutely conclusive, is strong evidence that the kinetic
factors of injection are vital aspects of the slag fuming
process. This conclusion is supported by Glinkov et al.\textsuperscript{50}
They present a graph of fuming furnace productivity
(kg Zn/m\textsuperscript{2}/day) as a function of blast intensity (m\textsuperscript{3}/s/m\textsuperscript{2})
which shows a direct relationship between the two.

In summary thermodynamic analysis has dominated theoretical
studies of slag fuming. Empirical modelling, in which kinetic
factors are incorporated, has been undertaken in the case of
specific furnaces and suggests that kinetics are indeed im­
portant. However, to date, there have been no attempts to
model the process from the point of view of kinetic mechanisms.

Although this section covers the literature directly relevant
to the modelling of slag fuming there are several studies on
specific aspects of the process which are valuable contributions
to our knowledge. It is important that these be reviewed and
assimilated into our final understanding of the process.

2.3 Slag Fuming Investigations

Slag fuming studies have been conducted both in the plant
and in the laboratory.
2.3.1 *Industrial Studies*

McNaughton et al. \(^{41,51}\) examined the effect of oxygen enrichment on normal fuming operation. The authors found that the addition of oxygen had beneficial results. These are summarized in Table 2.1 which represents the average of 30 tests. In the oxygen enriched tests the coal rate was slightly greater than that in the air blows. The table shows that the concentration at which the curve starts to level out is significantly lower in the oxygen enriched tests. An important factor in this effect is likely the bath temperature which is much greater in the case of oxygen enrichment. The authors make no attempt to explain their results. They suggest, however, use of oxygen enrichment may permit the development of a continuous fuming process.

It would not be productive to discuss these tests or any of the following in detail at this time. However it should be noted that a study of the Ellingham Diagram, Fig. 1.2, shows the reduction of zinc oxide with carbon becomes more favorable with increasing temperature. Oxygen enrichment also reduces the amount of tramp nitrogen introduced into the furnace and thus lowers the heat demand. In terms of the thermodynamic model, reduction of the amount of nitrogen, which serves as a diluent for the product gas of Reaction 2.3 (Zn and CO\(_2\)), would tend to reduce the rate of fuming. It is difficult to say which would be the more significant effect.
### TABLE 2.1

**Effects Of Oxygen Enrichment On Slag Fuming**

(Taken From McNaughton et al. 51)

<table>
<thead>
<tr>
<th>OXYGEN CONTENT OF BLAST (%)</th>
<th>BLOWING TIME (min)</th>
<th>INITIAL Zn (%)</th>
<th>FINAL Zn (%)</th>
<th>AVG. BATH TEMP. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.9</td>
<td>160</td>
<td>16.8</td>
<td>2.9</td>
<td>1175</td>
</tr>
<tr>
<td>23.4</td>
<td>160</td>
<td>16.9</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>24.8</td>
<td>160</td>
<td>16.4</td>
<td>0.9</td>
<td>1260</td>
</tr>
</tbody>
</table>
The use of a preheated blast has been demonstrated to produce a significant improvement in fuming rates by Blaskett at Broken Hill Associated Smelters, (BHAS) Port Pirie, Australia. Blaskett presents equilibrium model calculations done when the fuming furnace at BHAS was being designed to confirm that blast preheat would be advantageous. Furnace operation has generally confirmed the predictions of the model. Coal to zinc ratios at BHAS are 1.1 - 1.2 as compared to 1.5 - 1.6 at operations where cold blast air is used.

The use of preheated blast reduces the amount of fuel required to maintain the furnace heat balance. Essentially this allows operation at lower air-to-coal ratios and therefore more strongly reducing conditions. Improved furnace capacity and greater fuel economy would follow.

Blaskett also presents operating data which suggests that coal type has an influence on fuming efficiency. Over two periods of normal furnace operation, two different coal types were used. The results are shown in Table 2.2. Blaskett concludes that higher volatile, lower fixed-carbon coals are not as effective as bituminous coals which have a higher fixed carbon content. This is in agreement with the observations of Quarm.46,47,48

In a marked departure from traditional practise, engineers at the Non-Ferrous Metals Works 'D.Blagoev' in Plovdiv, Bulgaria developed a continuous fuming furnace based on the use of fuel
<table>
<thead>
<tr>
<th>Coal Type:</th>
<th>Ash</th>
<th>Volatiles</th>
<th>Fixed Carbon</th>
<th>PERIOD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15 %</td>
<td>18-19 %</td>
<td>A</td>
</tr>
<tr>
<td>Coal Type:</td>
<td></td>
<td>18-19 %</td>
<td>21-32 %</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>66-67 %</td>
<td>52-60 %</td>
<td></td>
</tr>
<tr>
<td>Zinc Elimination</td>
<td></td>
<td>86.1 %</td>
<td>83.9 %</td>
<td></td>
</tr>
<tr>
<td>Coal/Zinc Wt Ratio</td>
<td></td>
<td>1.10</td>
<td>1.19</td>
<td></td>
</tr>
</tbody>
</table>
oil or 'mazut'.\textsuperscript{15} The furnace which has a cross-sectional area of 5.85 m\textsuperscript{2} receives slag from a shaft smelting furnace through an intermediate electric settling furnace. The mazut is injected at a rate of 5.4 m\textsuperscript{3}/hr (35 kg/min) at 4.0 MPa (40 atm.) with sufficient air to effect 70\% of stoichiometric combustion. In his paper Abrashev emphatically states that according to their calculations the furnace operates at only 50\% of the rate predicted by an equilibrium analysis. The author states that the process is limited by diffusion kinetics. A reduction in the size of the furnace from 8.9 to 5.85 m\textsuperscript{2} cross-sectional area produced a two fold increase in furnace capacity for unchanged air and mazut flow rates. Other test results are also presented which show increased fuming efficiency as a result of increased blast intensity. Finally the author asserts that low sulphur fuels (0.5\% S) give lower zinc slags than high sulphur fuels (3.5\% S).

That the use of fuel oil is generally not efficient is confirmed by others.\textsuperscript{47} It is possible that insufficient time is available for the complete combustion of the mazut although this does not appear to be considered by Abrashev. Grant and Barnett\textsuperscript{44} contend that they have been able to predict the performance of this furnace with their equilibrium model. Unfortunately they do not give any details of how this was accomplished and do not address the evidence for the presence of kinetic factors.
The primary focus of Russian work on the industrial scale has been to develop fuming by natural gas. Initial experiments in pilot plant facilities demonstrated that it was not feasible to fume with natural gas - air mixtures due to the build up of magnetite in the slag. It was found that combustion had to be carried out prior to injection. Oxygen enrichment apparently relieved the need to carry out pre-combustion but was only successful if the blast intensity (measured in blast volume per unit volume of bath) was maintained. In this work a solid coal addition to the surface of 7 - 10% of bath weight was necessary to give suitable fuming rates. Later plant studies demonstrated that although the lump coal addition could be dispensed with, increased natural gas flow rates and oxygen enrichment to 28% were necessary to maintain furnace capacity.

Attempts were also made to develop a continuous process based on natural gas but these were only moderately successful.

2.3.2 Pilot Plant Studies

A number of pilot plant scale studies of various slag reduction techniques have been undertaken. Some of these do not deal directly with zinc slag fuming but the conclusions they draw provide valuable insights into the mechanisms by which slag cleaning takes place.
In the early 1960's, a program was initiated at BHAS, Port Pirie, Australia to study the treatment of granulated lead blast furnace slag (17.5% Zn) in a cyclone furnace. The final furnace design consisted of a 30.5 cm i.d. refractory lined cylindrical vessel into which a granulated slag-air mixture was injected at the top and a coal-air mixture near the bottom. Each mixture was injected continuously through a water cooled tuyere which was aimed tangentially to the inner wall and directed at 10° downward. A molten slag bath, approximately 12 cm in depth was maintained in the bottom. It was found that injection of the coal-air mixture directly into the slag brought about the most efficient reduction. Recoveries of approximately 70% were obtained at coal to slag ratios of about 0.3 and air preheat of 500°C.

This work was continued by Blanks and Ward with a 83.8 cm i.d. furnace capable of treating 1 tonne of slag per hour. They found that maximum efficiency was achieved when injecting the coal with 65% of the air required for stoichiometric combustion. Recoveries of about 85% were obtained at coal to slag ratios of 0.30 and slag depth of 30 cm. The authors show that equilibrium of the form described by Bell et al. was not attained. Blanks and Ward observed unburnt coal particles in the slag during tapping of the furnace which would perhaps explain this effect. Attempts to improve the situation by increasing the slag depth by 40% were not successful.
The authors were able to achieve a recovery of 94% with batch operation which compares favourably with traditional slag fuming operations. Fuel oil was tried but recoveries of only 30% were attained, confirming earlier studies.

Floyd and Conochie \textsuperscript{55,56} studies the reduction of liquid tin smelting slags in crucibles and 50 kg and 1 tonne pilot plant furnaces. Reduction was effected by the injection of a fuel; natural gas, light oil or powdered coal, and air through a top lance.

The authors found that in order to achieve acceptable fuming rates with natural gas it was necessary to entrain pulverized coal in the gas stream. During the reduction with coal it was found that only the fine coal burned in the bath and that the coarse coal was trapped in the slag. The intermediate fraction tended to be carried out of the furnace unconsumed.

Experiments performed by Floyd and Conochie in the laboratory \textsuperscript{55} demonstrated that CO was a much poorer reductant than \textsuperscript{55}H2. Considering the fact that reduction by solid coal was found to be roughly as fast as hydrogen it was concluded that reduction by solid coal must be by direct contact with the slag.

Finally a brief examination should be made of the same submerged combustion technology applied to cleaning copper slags from the converter and anode furnace. Floyd et al. \textsuperscript{57} found
that for solid reductants added directly to the surface of the slag lump coal (+6mm to -25mm) was the fastest reductant. With fine materials (-6mm) the rate of reduction decreased in order from coal, carbonized coal, coke/coal mixture, coke to partially burnt oil (slowest). This suggests that in this size range there are significant kinetic effects involved in the rate of reduction. It is interesting to note that the authors found CO gas to be an effective reductant for copper slags as compared to the tin slag mentioned above.

These papers demonstrate that kinetic considerations such as slag depth, coal entrainment in the slag and coal type appear in the study of other processes. This suggests that the claim for equilibrium, far from being the norm, is a more unusual point of view.

The remaining studies of slag fuming have been confined to laboratory experiments on the reduction of slags contained in crucibles.

2.3.3 Laboratory Studies

With rare exceptions all laboratory studies of zinc slag fuming have been conducted in the Soviet Union. The basic tenet of the Soviet approach to the process is that kinetic parameters are important. One aspect of their program, the study of injection kinetics, has been reviewed above. The majority of
their work has been conducted however, in the area of slag reduction kinetics. The first series of studies examined the coal-slag reaction. Due to the difficulty of quantitatively handling pulverized coal in laboratory experiments, slag reduction by carbon was studied by inserting graphite rods into crucibles of molten slag. 58-63

The evidence presented in these papers satisfactorily demonstrates that the reduction on graphite is indirect, that is, it takes place through an intermediate gas phase. All the studies agree that in the initial stages of reduction the rate of reduction is controlled by the Boudouard reaction on the carbon surface

\[ C + CO_2 \rightarrow 2CO \quad \ldots (2.23) \]

Several references 58,59,62 suggest that control then shifts to oxide diffusion in the slag. The other papers 61,63 conclude that control remains in the gas phase. The overall results are not conclusive but indicate under ordinary conditions the rate of reduction lies in a region of transitory control between oxide diffusion and carbon gasification. Several papers examining the carbon reduction of iron oxide containing slags 64-66 support these conclusions.

The Russian work has also concentrated on the role played by iron and iron oxides in the reduction process. Several papers 67,68 examine the reduction of molten slags on iron rods.
Unfortunately the papers are inconsistent, contradictory and incomplete. A series of papers attempt to unify the carbon and iron reduction of zinc slags in a single model. The basic experiments performed in these studies were graphite rod reductions of zinc and iron containing slags in small crucibles. Models were developed by performing a differential mass balance on each species, taking into account diffusion and assuming first-order reaction kinetics. Experiments were then performed and the data fitted into the model to determine the various reaction parameters. Correlations often showed that the rate constants fitted at different temperatures obeyed an Arrhenius relationship.

One problem with the results is that rate constants show enormous variation from one experiment to another and appear to be strongly dependent on slag composition. Secondly, the models incorporate two active forms of metallic iron in the slag, Fe* which lies at the gas-slag interface and is accessible to the gas, and Fe° which is 'dissolved' in the melt. No experimental evidence is presented for either of the species. In addition, their models use a parameter which is the 'surface area' of the Fe* phase, a rather bold extrapolation of a hypothetical concept. Finally, the diffusion coefficients obtained from their work are significantly higher than would normally be expected for slag systems. All of this suggests that although the work is interesting, it is far from conclusive. It is of little help in analysing the slag fuming process.
as a whole, because no coherent attempt is made to study the
effect of process parameters.

Two investigations 78,79 studied the effect of surface-active
agents on the rate of reduction of zinc from slag melts.
Vanyukov et al.78 determined that the addition of a few percent
of FeS or Na2O to fuming slag greatly accelerated the reduction
of slag drops on a graphite surface. These substances are also
shown to bring about a significant drop in the surface tension
of the slag which the authors suggest would improve the capture
of coal particles by the slag and hence increase the rate of
reduction.

Mazurchuk et al.79 examined the effect of P2O5, Na2O,
CaF2 and FeS on the gaseous reduction of iron containing slags
and found that each additive except P2O5 increased the rate of
reduction. P2O5 reduced the rate. Experiments were also con­
ducted on the effect of these additions on the pulverized coal
reduction of zinc slags. Two types of trials were made. In the
first the coal was impregnated with Ca(OH)2 and Na2O. In the
second dry FeS and Na2O powder was added to the coal. Again
the presence of the surface active agent was beneficial and found
to bring up to a 350% increase in reduction rate. The authors
suggest that in the case of a soda addition, the improvement was
due to increased wettability of the coal, catalysis of the
Boudouard reaction, and increased oxide diffusivities in the
slag immediately surrounding the entrained coal particle.
Suzuki et al. studied the gaseous reduction of copper converter and lead blast furnace slags. Nitrogen gas as well as mixtures of CO, CO\(_2\), H\(_2\) and CH\(_4\) were blown through 300 gram batches of slag contained in alumina crucibles.

The experiments with N\(_2\) were particularly interesting. The authors found that the copper converter slags showed virtually no volatilization of zinc when agitated by bubbling N\(_2\) through them. Blast furnace slags of comparable zinc content showed significant fuming rates when agitated in this manner. The significant difference between the two slags is their carbon content. The blast furnace slag contained 0.2-0.3% carbon whereas the copper smelting slags contained none. The agitation by N\(_2\) apparently stirs the carbon into reaction with the slag allowing zinc oxide reduction to take place. This interpretation is supported by the fact that the fuming rate with N\(_2\) was several orders of magnitude higher than that predicted by equilibrium. The traditional explanation for this effect has been that fuming occurs via the reaction

\[
\text{ZnO} + 3\text{FeO} \xrightarrow{\Delta} \text{Zn(g)} + \text{Fe}_3\text{O}_4 \quad \ldots (2.24)
\]

Fuming with reducing gas mixtures (CO-CO\(_2\)) demonstrated that again carbon in the slag was an important component in the process, especially at higher temperatures. Experiments with lime additions to the blast furnace slag showed that at lower temperatures (1220\(^\circ\)C), the addition of lime had no significant effect on the rate of fuming. At 1280\(^\circ\)C, increasing the lime
reduced the rate of fuming, perhaps due to a resultant increase in slag viscosity.

2.4 Industrial Observations

Finally there are a number of industrial observations reported in the literature which perhaps provide some additional clues to process operation.

Murray indicates that the fuming rate increases with temperature although in another reference it is stated that if too high a temperature is reached fuming performance will suffer. The fact that fuming rates improve with temperature was confirmed by operating personnel at Cominco Ltd., Trail, B.C.

McNaughton observed that the efficiency of bituminous and subbituminous coals were equal provided that the ash content was the same. Volatile matter was not found to participate in the reduction reactions as suggested by Bell et al.

Yurko and McNaughton state that the presence of sulphur in the slag has a deleterious effect on zinc elimination. This was observed when dry lead dross was added to the slag. No discussion of the importance of sulphur in the coal or sulphur in blast furnace slag is made.
Feddersen et al. 23, in tests on the slag fuming furnace at Bunker Hill, observed that slag depth was an important factor in zinc elimination. Unfortunately no data is presented except for the implication that increasing bath depths increased the fuming rate.

Mast and Kent 30 note that for furnace operation at Hudson Bay Mining and Smelting, Flin Flon, Manitoba, a minimum total air flow of 270 m$^3$/min (9500 cfm), independent of coal rate, is required otherwise zinc elimination suffers.

2.5 Summary

It is apparent that a review of the literature concerning slag fuming leads to no satisfactory conclusion. On one hand there exists a complete model of the process which denies the influence of kinetic factors. On the other, a haphazard collection of experiments which suggest that kinetic factors are important. In the middle are several empirical models of the process which incorporate kinetic effects. The two extremes cannot be reconciled and the empirical models are too weak to support either side. No clear picture emerges.

The assumption that equilibrium is achieved in the furnace has been used to develop a model of the complete process. The model can be successfully fitted to industrial data to give a satisfactory simulation of the process. This fact has
essentially been used to justify the initial assumption.

The only other attempts to model the entire process have been empirical. Unfortunately, these are poorly documented and although they tend to support a kinetic interpretation of the process the evidence is not conclusive. It is difficult to attach a particular interpretation to a variable with certainty due to the possibility that it may represent several factors.

A significant amount of evidence does exist however which implies that slag fuming is a kinetically controlled process. Industrial tests have shown that fuming with either fuel oil or natural gas does not take place at equilibrium. In these cases fuming can be enhanced if steps are taken to improve kinetics, such as pre-combustion. Industrial evidence also exists which indicates fuming rates are dependent on blast intensity and slag depth. Fairly convincing data is available which suggests that the process must be run to the fixed carbon content of the coal and that volatile matter does not appear to play a significant role which is directly contrary to the equilibrium model. Pilot plant and laboratory experiments suggest that coal-slag interaction may be a major reaction system. Other experiments reveal that in this case oxide diffusion control might be important.
The question of what role equilibrium and kinetics play in the process therefore remains. It is critical to the development of slag processing that this issue be resolved. It may open up new vistas or simply quiet nagging doubts. Either way, it will provide a firm foundation from which further explorations may be made.
CHAPTER III

OBJECTIVES

It is anticipated from an analysis of the literature that kinetic factors are critical to the operation of zinc slag fuming. The fact that kinetic considerations have been treated empirically or ignored in the past has stifled possible development of the process. Only a theoretical understanding of kinetics will allow a proper assessment of the potential of slag fuming.

The objective of this thesis then is to determine and study the kinetics of zinc slag fuming and assess the implications of these results for process improvement. It should be noted that even if it is demonstrated that equilibrium is achieved, it is not necessarily the most desirable operating condition. It is possible that maximum fuming efficiency is achieved before equilibrium is reached or under conditions that are different than those which are traditionally considered to exist.

It is immediately obvious that an analysis of slag fuming kinetics is a complex task. The number and variety of kinetic processes taking place is at least as great as any other pyrometallurgical process. The injection of the air-coal mixture involves a two-phase flow through a pipe and the interaction of this flow with the liquid slag. The problem is complicated by the fact that conditions are not isothermal and heat transfer from the slag to the injected mixture will take place. Further-
more not only will the coal react with the slag but also with the gas stream. The combustion of coal is itself only partially understood for well defined systems. The evolution of the gas stream as it rises through the bath is a matter of speculation. The reaction of coal with slag has never been studied in detail. The field of gas-slag reactions has received little attention. The physical and chemical properties of the slag, such as viscosity, surface tension, and oxide activity coefficients and diffusivities, which are likely to be important to kinetic processes, are poorly known. The melting and freezing behavior of slag on water-jacket surfaces has never been studied. And so on.

These, however, are only general observations. Before an attempt can be made to apply what knowledge is available and define those areas to explore further it is necessary to address a series of fundamental questions. The mode of injection behavior, be it bubbling or jetting, must be determined before an intelligent discussion of bath motion or the fate of the coal can be undertaken. The mechanism of slag reduction, whether it be gas-slag reactions or coal-slag reactions must be elucidated. The behavior of the slag on the water jackets during heating and cooling of the furnace must be investigated. It is difficult to develop more specific objectives than this because so little is known of the process. Furthermore in what directions the investigations will lead will largely be determined as it is conducted.
One definite conclusion can be drawn however. The study must be primarily conducted on industrial furnaces. It is only on an industrial scale that there would be any hope of identifying process dynamics. Laboratory studies would be premature because the system as a whole is too imprecisely defined.

The major thrust of this thesis has therefore been the acquisition and analysis of industrial data.
CHAPTER IV

EXPERIMENTAL TECHNIQUES

As discussed, it was of primary importance to obtain as much information as possible from operating slag fuming furnaces. The following sections describe the experimental techniques applied to the acquisition of industrial data and the laboratory methods involved in analysis of slag samples obtained from industrial sampling.

4.1 Industrial Tests

As with most industrial furnaces, observations of process operation must be indirect. Because slag fuming is a batch process, the most important data to obtain is a record of the manner in which the slag changes with time as a function of operating variables. Since the process is concerned with the elimination of zinc from the slag, the basic information required is the zinc content of the slag as a function of coal and air flow rates.

4.1.1 Slag Sampling During The Fuming Cycle

The objective of this procedure is to obtain a comprehensive set of data on a slag fuming cycle. It is important therefore that the slag samples accurately reflect the state of the bath
at temperature, particularly the zinc, ferrous and ferric levels. To accomplish this a water quench was incorporated into the sampling procedure. The following procedure was developed:

1) A sample and an estimate of the amount of slag left in the furnace from the previous run is obtained. The sample may either be taken from the last slag flowing out of the furnace at the end of the tap or from a bar sample after the tap hole has been closed.

2) A sample of each charge to the furnace, hot and cold, is taken and an estimate of the weight of each addition made. If this is impossible a composite would suffice.

3) Once the run has started the task is to obtain a series of quenched samples (of several hundred gram size) through the furnace charge port using an iron bar. A 5 m length of 6 mm (1/4 in) steel pipe (the size and length used for lancing the blast furnace) serves this purpose well. In addition a 3-4 m length of 100 mm (4 in) channel or angle iron placed to form a trough is required to prevent contamination of the sample once it is taken from the furnace. Also available should be a hose or bucket of water. The procedure is then to:

a) run the length of pipe into the furnace through the charge port until it touches the bottom of the furnace. (Because the pipe is not very rigid it bends in an arc toward the bottom 1-2 m from the end of the furnace.) See Fig. 4.1.
Figure 4.1  Schematic of Charge Port Sampling
b) let it sit for roughly 5-10 seconds (or until ~ 3 mm of slag has frozen onto it) and then withdraw it.

c) place the length of pipe with slag into the trough and quench with water from the bucket or hose.

d) then break the slag from the pipe and place it in a sample bag. Wash out the trough.

4) One sample is taken immediately after the last hot pot has been charged, and then one every 10 minutes thereafter into the tapping period.

5) Finally, as at the beginning, a sample of the heel left in the furnace is taken again, either by sampling the last slag in the tap or by a bar sample following the above procedure.

A record of operating parameters is, of course, vital to an analysis of a fuming cycle. The following time-dependent variables were monitored and recorded:

a) temperature
b) primary blast volume and pressure
c) secondary blast volume and pressure
d) coal rate
e) coal type and composition.

Within an industrial installation it is not always possible to carry out a predefined procedure. It must be recognized that compromises may be necessary. In particular the following
modifications to the above procedure were made in specific cases:

1) In some operations slag sampling through the charge port is not feasible and quenched tuyere samples must be taken instead. The procedure was basically the same as for charge port samples except that a 2 m bar was used through a tuyere.

2) It is not always possible to obtain charge samples and in these cases at least information on the total charge weight and make up (hot slag and cold slag) should be obtained.

3) Third, temperature and blast volume measurements are not necessarily made continuously. In these situations at least some 'average' value should be obtained.

4.1.2 Tuyere Back-Pressure Measurements

The objective of this procedure is to measure and record the pressure fluctuations generated by the injection of the coal-air mixture into the liquid slag. It has been established by Hoefele and Brimacombe that tuyere back-pressure directly reflects tuyere tip pressure. A study of the dynamics of injection can therefore be carried out by attaching a high frequency pressure transducer to the back of a tuyere.

A low voltage solid state pressure transducer (National Semiconductor LX1704D) was obtained and calibrated. The transducer is referenced to the atmosphere and contains a pressure sensitive area on a silicon chip. A power supply and
amplifier operating on 110 line AC voltage is required to use the transducer. An oscilloscope with a screen storage facility (Tektronix Type 564, Vertical Type 3A3, Time Base Type 564) was used to observe and store the pressure traces. An oscilloscope camera mount and polaroid camera (Tektronix Camera C-12) were used to photograph stored pressure signals.

In order to attach the pressure transducer to the tuyere, a 38.1 mm (1.5 in)-to-6.35 mm (0.25 in) pipe reducing fitting was attached to the back of the tuyere. A 6.35 mm (0.25 in) pipe-to-tubing adaptor was fitted to the reducer and 6.35 mm (0.25 in) plastic tubing used to attach the transducer to the adaptor (See Fig. 4.2).

4.1.3 Tuyere Photography

The objective of this procedure is to obtain a visual record of injection phenomena.

A plexiglas window was placed across the end of a 10 cm length of 38.1 mm (1.5 in) pipe. This was fitted to the back of the tuyere and the valve opened (See Fig. 4.2) permitting a view down the length of the tuyere into the furnace. In order to obtain a clear view it was necessary to turn off the coal to the tuyere.
Figure 4.2  Schematic of Tuyere Back-Pressure Measurement Technique
A 16 mm Bolex movie camera with a 16 to 100 Vario Switar lens was used at 64 frames per second to photograph injection phenomena. Both colour and black and white film were used and it was determined that colour film gave the finest detail. Grain effects were clearly visible with 400 ASA film. 100 ASA film at a lens setting of \( f = 4 \), with a shutter speed of \( 1/64 \) second revealed the most detail. Attempts to observe the slag surface were not successful.

A 35 mm single lens reflex camera with a 200 mm lens was used on one occasion to take black and white stills of tuyere tip accretions.

In both cases a tripod was used to stabilize the camera. Exposure settings were determined in repeated trials.

4.1.4 Tuyere Accretion Sampling

The objective of this procedure is to obtain samples of accretions which build up at the tuyere tip.

A 9.53 mm (0.375 in) hole was drilled in the tuyere window described above. A probe was assembled by placing a 1.3 m length of 6.35 mm (0.25 in) rod inside a 1 m length of 6.35 (0.25 in) pipe. 15 mm of the end of the rod was bent at a right angle to form a hook.
With the probe inserted through the hole in the window it was possible to observe the hook and manipulate it to measure the size and shape of the accretion and take samples.

4.2 Laboratory Methods

In order to extract the maximum amount of information from the slag samples obtained during fuming cycle sampling, a number of laboratory methods were used. It was assumed that the quenched bar samples were faithful records of the state of the slag at bath temperature. By applying this assumption the slag samples become valuable clues to the operation of the process.

4.2.1 Chemical Analysis of Slag Samples

Chemical analysis of the slag samples was performed by the assay labs of Cominco Ltd., Trail, B.C. They routinely perform slag analysis for the metals and oxides of interest to this study.

Assays for all metals (Zn, Pb, Fe, Cu), oxides (CaO, SiO₂, MgO, Al₂O₃) and non-metal (S) were done by X-ray emission spectrography. Carbon assays were performed using a LECO analyser. Analysis for ferrous iron was carried out by a wet chemical oxidative technique using potassium dichromate. The procedure is summarized in Appendix I. Ferric iron reported in the thesis is the difference between total iron determined by
X-ray analysis and ferrous iron obtained by wet chemistry. Uncertainty in these results will be discussed in Section 4.3.

4.2.2 Slag Dissolution and Particle Extraction

This procedure was developed to determine whether or not coal or coke particles are present in the slag. The following methods were finally adopted:

1) Approximately one gram of finely ground slag (-100 mesh B.S.S.) is accurately weighed and placed in the bottom of a cleaned 125 ml polypropylene bottle.

2) Several drops of water are added to the slag to wet it. The bottle is then clamped in a stand and placed in a water bath resting on a hot plate. The bottle is submerged roughly one-quarter of its length and angled away from the experimenter at about 20°. The whole assembly is set up at the back of a fume hood.

3) The water bath temperature is brought to 80°C and 10 ml of concentrated hydrofluoric acid is added slowly to the slag.

4) The digestion is allowed to continue for 30 to 45 minutes over which time the water bath temperature is increased to 100°C. The bottle should be gently rocked occasionally during this period. This is best accomplished by slightly tipping the whole stand.
5) Following digestion in HF 10 ml of a 2:1 mixture of HCl-HF is added slowly to the slag.

6) This stage of the digestion is carried out for 90 minutes in a boiling water bath. Again occasional stirring of the mixture is undertaken by gentle rocking.

7) At the end of this period 80 ml of 4% boric acid is added to the bottle.

8) The bottle remains in the bath for another 60 minutes, again with occasional stirring.

9) After this stage is complete, the hot solution is quickly filtered through a millipore filter into a flask under vacuum. A Millipore filtration apparatus was used with a 0.50 \( \mu \)m Schleicher and Schuell Teflon filter. The bottle is rinsed as necessary with distilled water or ethanol.

10) Following filtration, the filter with residue is removed and stored in a petri glass.

The above procedure was derived from a study of several references. 82-85

4.2.3 Slag Density and Porosity Measurements

Measurement of the true density of the slag was undertaken by the procedure outlined in the ASTM Standard Method of Test for True Specific Gravity of Refractory Materials.
(ASTM Designation: C135-66). The method essentially measures the amount of water displaced by a known weight of ground sample. The method used in this study followed the ASTM Standard except that 25 ml pycnometer bottles were used instead of 50 ml bottles. The bottles containing sample and partially filled with water were boiled under reduced pressure rather than at atmospheric pressure.

The bulk density of bar-quenched slag samples was measured using a water displacement technique. Due to the relatively high porosity of the slag (approximately 30%) and the fact that both open and closed pores occupied a significant volume it was necessary to develop a method of coating the surface. It was important to find a way of effectively enclosing the open or surface pore volume. This problem was critical because the bubbles of a millimeter or so in diameter lay broken open on the surface. The most satisfactory technique found was to wrap the slag samples in wax. Wax film of a thickness of 0.127 mm (0.005 in) was used. Often a thinner film, obtained by stretching the standard film, was used. The following procedure was developed:

1) A large piece of bar quenched slag was selected and accurately weighed ($W_1$). Due to the friable nature of the highly porous slag the largest pieces available were roughly 15 mm x 10 mm x 2.5 mm. These pieces weighed roughly 0.2 g.

2) The piece was then wrapped in the thin layer of wax film.
The minimum amount of wax was used, usually sufficient to cover the surface in one layer only. Care was taken to stretch the wax tightly across surface pores.

3) The wrapped sample was weighed ($W_2$).

4) The weight of the sample immersed in water was then measured ($W_3$). This was done by simply suspending a wire weighing basket in a beaker of distilled water by a thin wire from the balance arm. This system was calibrated with aluminum weights (0.1 and 0.2 gm) to correct for the displacement caused by the immersion of the extra length of suspension wire when a sample is in the basket. The correction was expressed as 'k', the displaced weight per unit of measured weight, (gm/gm).

5) The bulk density was then calculated with the formula:

$$\rho_{\text{slag, bulk}} = \frac{W_1}{\frac{W_3 (1 + k)}{\rho_{\text{water}}} - \frac{W_2 - W_1}{\rho_{\text{wax}}}}$$

... (4.1)

where:

$W_1, W_2, W_3, k$ are defined above

$\rho_x = \text{density of } x$

Due to the uncertainty in the measurements and the likely inhomogeneity of small slag pieces, at least four different pieces were measured in each case. Slag porosity was then calculated from the above measurements.
4.2.4  X-Ray Diffraction Analysis

In order to analyse the slag for crystalline components X-ray diffraction was used.

X-ray diffraction was carried out with a Philips machine (diffractometer type PW 101220, power supply type PW 1011/80). An iron tube (Philips, type PW 2107/00) was used, normally at a setting of 36 kV and 26 mA. The time constant in the counting circuit was set at 2 seconds.

4.2.5  Reflected Light Microscopy

Reflected light microscopy was used to study the physical and crystalline structure of the slag samples. The slag and contained crystalline phases were too opaque to examine by thin section.

Slag pieces were mounted in epoxy. A cycle alternating between vacuum and atmospheric pressure was applied to force epoxy into the open pores. The mounted slag was ground from 80 grit to 600 grit and then polished, first with 5 μm diamond paste and then with a 1 μm diamond paste on silk. The slags were polished for 2-5 minutes on each cloth making slow circuits counter to the rotation of the wheel. The surface was then washed in soap and water and dried with ethanol before viewing. No etching was done.
Photomicrographs were taken with a reflected light camera microscope (Zeiss ULTRAPHOT).

4.3 Accuracy of Chemical Analysis

In order to properly assess the results of any quantitative calculation it is necessary to know the uncertainty in the data. In some cases this is relatively straightforward, in others, very difficult.

4.3.1 Effect of Sulphide on the Ferrous Iron Assay

It has been suggested that sulphur dissolved in slags as sulphide will interfere with the determination of ferrous iron by reducing ferric to ferrous iron during acid digestion. 39 This would occur through the reaction:

\[ 2\text{Fe}^{3+} + S^{2-} \overset{\text{aq}}{+} 2\text{Fe}^{2+} + S^0 \quad \ldots \text{(4.2)} \]

\[ E^0 = +1.278 \text{ v} \] (reduction potential)

Assuming that the oxygen potential in the slag is very low \((-\sim 10^{-7} \text{ Pa } (-10^{-12} \text{ atm}))\) it is virtually certain that the sulphur in fuming slag \((0 - 2.0\%)\) is present as the sulphide ion. 77 If sulphide ions are stoichiometrically reduced to elemental sulphur via Equation 4.2, the molar ratio of ferric iron reduced to sulphur oxidized is 2. This is equivalent to a weight ratio of 3.5. The effect therefore can be significant.
To assess the effect of slag sulphide on the ferrous iron assay, a laboratory test was performed. A base slag consisting of 35% SiO₂, 20% CaO and 45% mill scale was prepared, corresponding to the lime-to-silica ratio and lime and silica levels found in typical fuming slags. To this mixture was added various reducing agents and sulphides, as summarized in Table 4.1. The mixtures were prepared and fired simultaneously under slightly reducing conditions in a gas furnace at approximately 1150°C for 15 minutes. Water quenched samples were then taken and analysed for ferrous iron by the procedure outlined in Appendix I. The results are given in Table 4.1. The assay technique shows satisfactory reproducibility.

It is evident that when sulphide is added as pyrrhotite, sulphur has a definite effect on the ferrous assay, roughly equivalent to that expected from Equation 4.2 (Note that Slag 3 is an exception.) However, when sulphide is added as calcium sulphide, the ferrous assay declines slightly, roughly equivalent to a simple dilution effect.

These somewhat ambiguous results suggest that when sulphur is present in a more stable form, CaS (see Table 4.2), it has no effect on the ferrous iron assay. Apparently the residence time, at temperature, of the synthetic slag containing pyrrhotite was insufficient for the system to come to equilibrium. As observed in coal particle extraction experiments, acid digestions of fuming furnace slag left residues which contained a signifi-
TABLE 4.1
The Effect of Slag Sulphide on the Ferrous Iron Assay

Base Slag: 35% SiO₂, 20% CaO, 45% Mill Scale (Fe₀.₈₋₀.₉₀)  Temperature: 1150°C
(values in percent)

<table>
<thead>
<tr>
<th>SLAG</th>
<th>REMARKS</th>
<th>CALCULATED SLAG</th>
<th>NO S²⁻ EFFECT</th>
<th>WITH S²⁻ EFFECT *</th>
<th>ASSAYED Fe²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>base slag</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20.2</td>
</tr>
<tr>
<td>2</td>
<td>+ 'FeS'</td>
<td>1.3</td>
<td>21.8</td>
<td>26.4</td>
<td>24.8</td>
</tr>
<tr>
<td>3</td>
<td>+ 'FeS'</td>
<td>0.7</td>
<td>21.1</td>
<td>23.6</td>
<td>21.8</td>
</tr>
<tr>
<td>4</td>
<td>+ CaS</td>
<td>1.0</td>
<td>19.8</td>
<td>23.2</td>
<td>19.1</td>
</tr>
<tr>
<td>5</td>
<td>+ Fe</td>
<td>-</td>
<td>37.6**</td>
<td>-</td>
<td>24.8</td>
</tr>
<tr>
<td>6</td>
<td>+ Fe + 'FeS'</td>
<td>0.9</td>
<td>25.6</td>
<td>28.3</td>
<td>28.7</td>
</tr>
<tr>
<td>7</td>
<td>+ Fe + CaS</td>
<td>0.9</td>
<td>24.5</td>
<td>27.5</td>
<td>20.3</td>
</tr>
<tr>
<td>8</td>
<td>+ flour</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>22.6</td>
</tr>
<tr>
<td>9</td>
<td>+ flour + 'FeS'</td>
<td>1.0</td>
<td>23.7</td>
<td>27.1</td>
<td>26.5</td>
</tr>
</tbody>
</table>

* 2Fe³⁺ + S²⁻  2Fe²⁺ + S⁰ during acid digestion
** Fe + 2Fe³⁺  3Fe²⁺ during fusion
'FeS': Pyrrhotite
TABLE 4.2

Free Energy of Formation of Various Sulphides from $\frac{3}{2}S_2$ and the Metal Oxide at 1200°C

<table>
<thead>
<tr>
<th>Sulphide</th>
<th>$\Delta G^0$, 1200°C kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgS</td>
<td>175</td>
</tr>
<tr>
<td>FeS</td>
<td>96</td>
</tr>
<tr>
<td>CaS</td>
<td>88</td>
</tr>
<tr>
<td>ZnS</td>
<td>83</td>
</tr>
</tbody>
</table>

(data from Rosenqvist)
cant number of sulphide particles. This suggests that under normal fuming conditions, sulphur may simply be tied up in an insoluble form.

It has been assumed that sulphur in lead blast furnace slags has had sufficient time at temperature, to come to equilibrium and that in the fuming furnace it is in a stable form which does not affect the ferrous iron assay. The ferrous iron assays reported in the thesis therefore do not have to be corrected for sulphide sulphur.

4.3.2 Uncertainty in Assay Results

In order to determine the uncertainty in the chemical assays performed, as outlined in Section 4.2.1, a series of 16 duplicate samples were submitted for analysis. The results are presented in Table 4.3.

The absolute difference of each duplicate and the relative difference (absolute difference divided by the mean of the duplicate) were calculated. The average values for each species are summarized in Table 4.4. The approximate uncertainty in each assay is then plus or minus one half the average relative difference.

The results are acceptable for Zn, SiO₂, CaO, Fe and Fe²⁺. The uncertainty in the Fe³⁺ value is to be expected because it is obtained by the difference of two numbers which are close in value. Attempts to assay Fe³⁺ independently by a reductive
### Table 4.3
DUPLICATE ASSAY RESULTS
(Values in Percent)

<table>
<thead>
<tr>
<th></th>
<th>A1,3</th>
<th>A1,4</th>
<th>A1,5</th>
<th>A1,6</th>
<th>A1,7</th>
<th>A2A,1</th>
<th>A2B,3</th>
<th>A2B,6</th>
<th>B1,5</th>
<th>C1,4</th>
<th>C1,7</th>
<th>C2,3</th>
<th>C2,5</th>
<th>C2,10</th>
<th>C2,14</th>
<th>C2,16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>9.9</td>
<td>9.1</td>
<td>9.5(?)</td>
<td>9.4(?)</td>
<td>9.2(?)</td>
<td>4.5</td>
<td>2.5</td>
<td>0.8</td>
<td>5.1</td>
<td>5.4</td>
<td>3.4</td>
<td>10.9</td>
<td>9.9</td>
<td>5.7</td>
<td>2.9</td>
<td>2.2</td>
</tr>
<tr>
<td>Pb</td>
<td>0.12</td>
<td>0.08</td>
<td>0.07</td>
<td>0.04</td>
<td>0.04</td>
<td>0.3</td>
<td>0.14</td>
<td>0.05</td>
<td>0.07</td>
<td>0.12</td>
<td>0.13</td>
<td>0.46</td>
<td>0.5</td>
<td>0.07</td>
<td>0.11</td>
<td>0.07</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.0</td>
<td>1.4</td>
<td>1.4</td>
<td>0.3</td>
<td>0.1</td>
<td>0.03</td>
<td>0.09</td>
<td>0.03</td>
</tr>
<tr>
<td>Fe</td>
<td>24.5</td>
<td>24.5</td>
<td>24.8</td>
<td>25.2</td>
<td>25.1</td>
<td>26.4</td>
<td>24.9</td>
<td>25.2</td>
<td>28.9</td>
<td>33.0</td>
<td>34.2</td>
<td>27.8</td>
<td>28.4</td>
<td>29.8</td>
<td>30.8</td>
<td>31.1</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>22.0</td>
<td>22.4</td>
<td>22.5</td>
<td>22.9</td>
<td>22.5</td>
<td>24.5</td>
<td>24.8</td>
<td>25.2</td>
<td>25.1</td>
<td>31.5</td>
<td>32.5</td>
<td>21.5</td>
<td>20.5</td>
<td>26.5</td>
<td>27.3</td>
<td>26.4</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>2.5</td>
<td>2.1</td>
<td>2.3</td>
<td>2.3</td>
<td>2.6</td>
<td>1.9</td>
<td>0.1</td>
<td>0.0</td>
<td>3.8</td>
<td>1.5(?)</td>
<td>1.7(?)</td>
<td>6.3</td>
<td>7.9</td>
<td>3.3</td>
<td>3.5</td>
<td>4.7</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>26.5</td>
<td>26.8</td>
<td>27.1</td>
<td>27.7</td>
<td>28.2</td>
<td>27.8</td>
<td>34.7</td>
<td>36.2</td>
<td>28.3</td>
<td>26.9</td>
<td>27.7</td>
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<td>26.2</td>
<td>29.2</td>
<td>31.0</td>
<td>31.2</td>
</tr>
<tr>
<td>CaO</td>
<td>18.0</td>
<td>18.4</td>
<td>18.4</td>
<td>18.6</td>
<td>19.0</td>
<td>23.0</td>
<td>23.3</td>
<td>23.9</td>
<td>15.5</td>
<td>13.6</td>
<td>13.7</td>
<td>14.4</td>
<td>14.4</td>
<td>15.4</td>
<td>15.7</td>
<td>15.9</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>5.0</td>
<td>5.2</td>
<td>5.1</td>
<td>5.3</td>
<td>5.5</td>
<td>5.5</td>
<td>6.3</td>
<td>6.4</td>
<td>5.6</td>
<td>5.3</td>
<td>5.6</td>
<td>4.6</td>
<td>4.7</td>
<td>5.4</td>
<td>5.9</td>
<td>5.9</td>
</tr>
<tr>
<td>C</td>
<td>0.44</td>
<td>0.44</td>
<td>0.33</td>
<td>0.65</td>
<td>0.49</td>
<td>0.49</td>
<td>0.65</td>
<td>0.65</td>
<td>0.38</td>
<td>0.82</td>
<td>0.76</td>
<td>0.16</td>
<td>0.16</td>
<td>0.09</td>
<td>0.16</td>
<td>0.11</td>
</tr>
</tbody>
</table>

(?) Assay Ignored (value inconsistent with time profile)
<table>
<thead>
<tr>
<th></th>
<th>Average Absolute Difference</th>
<th>Average Relative Difference</th>
<th>Estimated Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.25%</td>
<td>7.8%</td>
<td>± 4%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3.0 %</td>
<td>10.0%</td>
<td>± 5%</td>
</tr>
<tr>
<td>CaO</td>
<td>0.74%</td>
<td>4.1%</td>
<td>± 2%</td>
</tr>
<tr>
<td>Fe</td>
<td>0.74%</td>
<td>2.6%</td>
<td>± 1.3%</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.39%</td>
<td>1.9%</td>
<td>± 1%</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.71%</td>
<td>34 %</td>
<td>± 17%</td>
</tr>
</tbody>
</table>
assay technique did not give consistent results. Because the ferric level in the slag is low (normally 0-4%) the high level of relative uncertainty represents only a moderate absolute uncertainty, e.g. at 2% Fe\(^{3+}\) the uncertainty is 2% ± 0.35% (absolute), 1.65% to 2.35% Fe\(^{3+}\). Admittedly however, the uncertainty is significant and cannot be ignored in subsequent discussions.

Carbon assays were not found to be very reproducible (See Table 4.3) and thus serve only as a qualitative indication of the presence of carbon in the slag.

4.4 Remarks

The acquisition of industrial data is always a difficult task. The problem is especially acute when measurements and sampling are conducted on a comprehensive scale during normal process operation. Often the ideals of research must be compromised and the best job done under conditions well beyond the control of the researcher. As a result the data cannot always be complete and may reflect limitations imposed by operating schedules or the plant environment. Finally it must be acknowledged that the value of operating parameters, e.g. coal rate, can often only be realistically obtained by relying on normal plant measuring devices. It is a question of trusting that the indicated levels are correct. This assumption can only be verified by self-consistent results obtained over several runs.
CHAPTER V

INDUSTRIAL RESULTS AND PRELIMINARY DISCUSSION: EQUILIBRIUM CONSIDERATIONS

In order to make a proper assessment of process kinetics it is imperative, as previously discussed, to study industrial furnaces. It is only logical that the greater the number of different furnaces and operations investigated the more comprehensive, complete and conclusive will be the results.

5.1 Results

Slag samples and operating conditions for 11 fuming cycles at five different companies were obtained. The data are presented in Figures 5.1 to 5.11 and tabulated in Appendix II. To avoid the complications introduced by using names, capital letters A through E are used to designate the different companies. The author participated directly in the sampling of the cycles reported for Company C. In the other cases, with one exception, the sampling was carried out by plant personnel at their respective locations according to the procedure outlined in Section 4.1.1. The slag samples and data were sent to the author for analysis. As mentioned earlier, chemical assays of the slags were done by Cominco Ltd., Trail, B.C. In the case of Company D the reported data was taken from the literature. 45
Figure 5.1  Cycle Al, Fuming Cycle Sampling Data
Figure 5.2  Cycle A2A, Fuming Cycle Sampling Data
Figure 5.3 Cycle A2B, Fuming Cycle Sampling Data
Figure 5.4  Cycle B1, Fuming Cycle Sampling Data
Figure 5.5  Cycle B21. Pumping Cycle Sampling Data

Elapsed Time (min)

Coal rate (kg/min)

% Fe

% Zn, Fe

% SiO₂

% CaO

% C

Coal Rate

Fe²⁺

Zn

SiO₂

CaO
Figure 5.6  Cycle B22, Fuming Cycle Sampling Data
Figure 5.7
Cycle CI, Fuming Cycle Sampling Data
Figure 5.9

From reference (45), pumping cycle, sampling data.
It should be noted that at Companies B and E it was not possible to take charge port samples. In these cases quenched bar samples were taken through the tuyeres. A study of the results will show that in several cases the data is incomplete. For example, slag bath temperature is only monitored at operations C and D. The difficulties introduced by this problem can in large part be surmounted by making reasonable assumptions and extrapolating from other operations or the literature.

Finally, it should be noted that in general the results of the slag assays from point to point through each run are self-consistent. This would tend to indicate that both the sampling and assay procedures were not subject to significant random error. Furthermore this is evidence that the results were not unduly sensitive to variations in quenching times that undoubtedly occurred.

5.2 Equilibrium Analysis

The precedent set in the literature dictates that any analysis of the data must start with an examination of the question of equilibrium. If the data supports the assumption of equilibrium, then our task will be brief. There are two areas to be addressed. First is the question of whether the slag itself is in internal equilibrium. Second is whether or not equilibrium fuming rates calculated from the data (operating parameters and slag composition) agree with observed rates.
5.2.1 Slag Carbon

A survey of the slag assays clearly reveals that carbon is found in every sample. In general, carbon is present in fuming slag in the range 0.1 to 1.0%. The presence of carbon is a non-equilibrium phenomenon.

In order to properly discuss this proposition it is necessary to briefly assess the form which carbon will take in the slag. At high temperatures, under strongly reducing conditions carbon is known to dissolve in slag as $C_2^-$ and $CN^-$ ions up to 1.3 wt%. $^{88,89}$ It also has been suggested that carbon will dissolve as a carbonate ion ($CO_3^{2-}$) under more oxidizing conditions. $^{89,90,91}$ Finally, carbon may be present as a solid either at saturation or under non-equilibrium conditions.

The studies on carbon solubility as carbide or cyanide ions were performed with CaO-Al$_2$O$_3$, CaO-SiO$_2$, and CaO-SiO-Al$_2$O$_3$ slags in the temperature range 1550 - 1725°C. $^{88-89}$ At 1600°C the solubility of carbon is significant (>0.1% C) for oxygen partial pressures less than $5(10^{-11})$ Pa ($5(10^{-16})$ atm). Carbon solubility is inversely proportional to the square root of oxygen partial pressure and also declines with temperature. Fuming furnace slag which contains a significant amount of iron is in a significantly more oxidized state. The minimum oxygen potential in this system can be calculated by assuming the slag to be saturated with metallic iron. Normally this condition is
not achieved in practice. However in this unusual case the oxygen potential would drop to $2.2(10^{-8})$ Pa ($2.2(10^{-13})$ atm) assuming $N_{FeO} = 0.4$ and $\gamma_{FeO} = 1$ and calculating via the reaction:

$$Fe + \frac{1}{2}O_2 \rightarrow FeO \quad \cdots (5.1)$$

$$K_{1200^\circ C} = 8.6(10^5) \quad (\text{from Fig. 1.2})$$

This is an oxygen potential approximately three orders of magnitude greater than that of the above iron-free slags. Carbon solubility on this basis would drop to 0.03 wt%.

Furthermore fuming furnaces are operated at considerably lower temperatures ($1200^\circ C$) which would also tend to reduce carbon solubility (by six orders of magnitude based on an extrapolation of the given data). Both of these arguments imply that carbon solubility as carbide or cyanide will be negligible in fuming furnace slag.

As previously mentioned, at higher oxygen potentials carbon may enter the slag as a carbonate ion. Ponomarenko and Kozlov conclude that in non-ferrous slags at $1550^\circ C$ in the range of oxygen potentials from $2.8(10^{-6})$ Pa ($2.8(10^{-11})$ atm) to $5.1(10^{-3})$ Pa ($5(10^{-8})$ atm) carbon solubility is approximately 0.02 wt%. Further the authors state that solubility is independent of temperature under these conditions. Pearse studied the solubility of carbon dioxide in sodium silicate melts at temperatures from $1000^\circ C$ to $1200^\circ C$. A maximum solubility of $3\%$ CO$_2$ at $1000^\circ C$ was found for the melt composition ($Na_2O$) SiO$_2$. 
at 101 kPa (1 atm) CO₂. The solubility at 1200°C was roughly one-tenth that at 1000°C. Using the free energy of formation of carbonates as a guide (Table 5.1), it could be estimated that the solubility of CO₂ in calcium-iron silicate melts should be less than in sodium silicate melts. Solubilities substantially less than 0.3% CO₂ are to be expected at 1200°C from this data. Furthermore, considering the low oxygen potential of the slag relative to 101 kPa (1 atm) CO₂, a significant reduction in the dissolved CO₂ is to be expected as well.

The above discussion suggests that for the assayed levels of carbon, the carbon present in fuming furnace slag must be at unit activity. Based on this fact, a calculation can be made of the equilibrium concentration of ZnO, FeO and Fe₃O₄ expected in the slag, using the following reactions:

\[
\text{ZnO} \text{(slag)} + \text{C (s)} \rightleftharpoons \text{Zn (g)} + \text{CO (g)} \quad \text{...(5.2)}
\]

\[
\text{FeO} \text{(slag)} + \text{C (s)} \rightleftharpoons \text{Fe (s)} + \text{CO (g)} \quad \text{...(5.3)}
\]

\[
\text{Fe}_3\text{O}_4 \text{(slag)} + \text{C (s)} \rightleftharpoons 3\text{FeO} + \text{CO (g)} \quad \text{...(5.4)}
\]

Free energy data and equilibrium constants taken from Fig. 1.2 are given in Table 5.2.

The maximum activity of ZnO in the slag will be about \(6.3 \times 10^{-4}\), assuming that gas bubbles of equal partial pressures of zinc vapour and carbon monoxide (50 kPa (0.5 atm)) are associated with the carbon. Using a zinc oxide activity
**TABLE 5.1**

Free Energy of Formation of Various Carbonates from Carbon Dioxide and the Metal Oxide at $1200^\circ$ C

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G_{1200^\circ}$ C (J/kg.mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$CO$_3$</td>
<td>-123600</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>+40800</td>
</tr>
<tr>
<td>FeCO$_3$</td>
<td>+54000</td>
</tr>
</tbody>
</table>

(Data from Rosenqvist $^{92}$)
### TABLE 5.2

Free Energies and Equilibrium Constants for the Direct Reduction of Iron Oxides and Zinc Oxide

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G_{1200^\circ C}$ (J)</th>
<th>$K_{1200^\circ C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO + C ⇌ Zn$_{(g)}$ + CO</td>
<td>-73200</td>
<td>395</td>
</tr>
<tr>
<td>FeO + C ⇌ Fe + CO</td>
<td>-73200</td>
<td>395</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ + C ⇌ 3FeO + CO</td>
<td>-115100</td>
<td>12030</td>
</tr>
</tbody>
</table>

(Data from Fig. 1.2)
coefficient of 2 from Kellogg this activity corresponds to about 0.03 wt% Zn. Repeating the calculation for Reaction 5.3, assuming the partial pressure of carbon monoxide associated with the carbon to be 101 kPa (1 atm) and the activity of iron metal formed to be unity, the equilibrium activity for FeO will be about $2.5 \times 10^{-3}$. For an activity coefficient of FeO of 2 (from Kellogg) this represents approximately 0.1 wt% Fe$^{2+}$ in slag. Finally for Reaction 5.4 making similar assumptions and using $a_{FeO} = 0.5$, the equilibrium activity of magnetite will be $1 \times 10^{-5}$. For an activity coefficient of 20 (from Kellogg) this represents 0.00009 wt% Fe$^{3+}$.

In each of the above cases the equilibrium level of dissolved species in the presence of carbon at unit activity is at least two orders of magnitude lower than that observed in practice. The slag itself is obviously not at internal equilibrium. This is, of course, a direct contradiction of the basic assumption of the equilibrium model.

5.2.2 Equilibrium Fuming Rate Calculations

A second test of the thermodynamic model is to compare the equilibrium fuming rates calculated from the slag composition at each data point with the observed fuming rate at that point. A program was written, as outlined in Appendix III, to calculate the equilibrium gas composition of a coal-air mixture injected into a fuming furnace slag containing dissolved zinc oxide and
ferrous and ferric iron. From the gas composition (CO, CO₂, H₂, H₂O, Zn, N₂, O₂) the zinc fuming rate and iron oxidation on reduction can be determined. The actual fuming rate at each point was estimated by taking the slope across the point using the points on either side, correcting for changes in bath weight and intrinsic fuming rate. Owing to the fact that the assayed points are self consistent and in a majority of cases, form a smooth, almost linear curve, the slopes estimated by this method are the same as would be determined from a smoothed curve analysis. At ±4% relative uncertainty, the gross error would range from about ±50% at high zinc concentrations to about ±12% at low zinc concentrations. However the uncertainty in a smoothed curve tangent estimate will be smaller due to the information provided by other points in the smoothing process. See Appendix III.

In Figure 5.12 the observed fuming rate is graphed against the equilibrium fuming rate predicted by Kellogg data. The line on the graph has a slope of one corresponding to exact agreement. It is apparent that in most cases the model under predicts the actual fuming rate. Furthermore there is no apparent correlation at all between the two variables. Similar calculations have been performed for the data of Grant and Barnett, and Grant, shown in Figures 5.13 and 5.14 respectively. The data of Grant and Barnett in general tends to over predict the fuming rate, even accounting for possible error. Considerable scatter exists in this correlation as well.
Figure 5.12 Observed Fuming Rate versus Predicted Equilibrium Fuming Rate For Cycle Sample Points (thermodynamic data from Kellogg)
Figure 5.14: Observed pumping rate versus equilibrium pumping rate (kg mole Zn/s).
The results of the Grant model, given in Figure 5.14 are not any better. This model over predicts almost all of the points with considerable scatter, again accounting for error.

If these models are basically correct on average, the scatter should be evenly distributed around the drawn line. The results of the Grant and Barnett model come closest to approximating this. (Fig. 5.13) However, even here, there are a significant number of points spread out across the diagram to the right of which should be associated with much higher fuming rates. In all cases these points would tend to give any regression an almost horizontal slope.

In Figure 5.15 the predicted net ferric iron reduction rates of the Grant and Barnett model are graphed against the observed rates. The net reduction rate is the difference between ferric iron reduction and ferrous iron oxidation. Negative values represent net ferrous iron oxidation. Observed values are the average calculated from instantaneous changes in measured ferrous and ferric levels. It is apparent that more scatter is evident in these results than in those for the zinc fuming rate. A considerable number of points lie off this diagram, even farther away from the drawn line which indicates exact prediction. The results of the Kellogg data and the Grant data show no better correlations.
Figure 5.15

Observed Ferric Iron Reduction Rate versus Predicted Equilibrium Reduction Rate For Cycle Sample Points
(thermodynamic data from Grant and Barnett)
It should be borne in mind that these models can be fitted to the data as claimed in the literature. This fact is not in dispute. What these results imply however, is that the fitting must be done on an individual basis, cycle by cycle. As such, the concept of an equilibrium model is not interesting because it cannot be extrapolated with confidence from operation to operation and perhaps not from cycle to cycle.

This suggests that the equilibrium model is not an accurate representation of the zinc slag fuming process. One is forced to conclude that either thermodynamic conditions vary significantly from one operation to another, or kinetic factors are important. Returning to Figures 5.12 to 5.14, it is apparent that there is a maximum fuming rate which is independent of the predicted equilibrium rate. Something other than air-coal-slag equilibrium is controlling the process.

5.2.3 Slag Equilibrium

It might be argued that inspite of the evidence for non-equilibrium within the slag, given in Section 5.2.1, the zinc and iron species in the slag are in equilibrium via the reaction:

\[ 2\text{Fe}^{2+} + \text{Zn}^{2+} \leftrightarrow 2\text{Fe}^{3+} + \text{Zn}(g) \]  \ ...(5.5)

Zinc fuming would result from the escape of zinc vapour into any gas phases in contact with the slag. These might include the tuyere gas stream, the atmosphere above the bath surface and
bubbles nucleated within the slag itself. If Equation 5.5 governs the fuming rate, the following relationships hold:

\[ P_{Zn} = k \frac{a_{Fe^{2+}}^2 a_{Zn^{2+}}}{a_{Fe^{3+}}^2} \]  \ ...(5.6)

\[ P_{Zn} = k' \frac{[Fe^{2+}]^2 [Zn^{2+}]}{[Fe^{3+}]^2} \]  \ ...(5.7)

and the observed fuming rates should, in general, be proportional to the weight percent ratio term in Equation 5.7. A graph of the observed fuming rate against this term is shown in Figure 5.16.

There is no clear relationship between the two variables. Again the fuming rate is independent of equilibrium.

5.3 Summary

The results of industrial sampling in five operations have demonstrated that the equilibrium model does not readily encompass all the data. The existence of a maximum fuming rate independent of equilibrium considerations suggests that kinetic factors are critical to the process.
Figure 5.16 Observed Fuming Rate versus $[\text{Fe}^{2+}]^2[\text{Zn}]/[\text{Fe}^{3+}]^2$
For Cycle Sample Points
CHAPTER VI

LABORATORY RESULTS AND KINETIC MODEL OF THE PROCESS

It is the tenet of this thesis that the zinc slag fuming process does not run at equilibrium and consequently that a knowledge of kinetics is vital to a complete understanding of the process. To remove the assumption of equilibrium, however, is to pose many questions. The object of this chapter is to address all of these and thereby construct a complete kinetic model.

6.1 Kinetic Conception of the Process

The fundamental basis of a correct conception of the slag fuming process is the observation that carbon is present in the slag. This implies that some fraction of the coal injected into the furnace ends up in the slag. This fact has several important consequences. The first is that reduction of the slag takes place within the slag bath on solid coal particles in the absence of air. Second, if a portion of the coal is removed from the tuyere gas stream and enters the slag the oxygen to carbon ratio in the tuyere gas stream is increased. If a significant fraction of the coal is entrained in the slag, conditions in the tuyere gas stream will be too oxidizing to effect any slag reduction and the only reactions taking place will be the combustion of coal and oxidation of ferrous iron.
in the slag to ferric iron.

It is vital then that the presence of coal in the slag be confirmed in a direct way. Based on the procedure outlined in Section 4.2.2, an effort was made to extract coal particles from quenched slag samples.

6.1.1 Coal Particles in the Slag

In Fig. 6.1, 6.2 and 6.3, typical particles from two different fuming slags are shown along with their X-ray spectra. The slag samples were taken at Company C. The slag particles in Fig. 6.1 are from sample Cl,7 (Company C, Run 2, Slag Sample #7), and those in Fig. 6.2 and 6.3 from a directly water-quenched tail slag samples (C2,16). Compositions for these slags are given in Table 6.1. For purposes of comparison, a coal particle and X-ray spectrum are given in Fig. 6.4. Undigested slag from sample Cl,7 is presented in Fig. 6.5.

The particles in Fig. 6.1, 6.2 and 6.3 are roughly 15 μm in diameter which is well within the size range of the coal injected into the furnace (80% -200 mesh BSS, ≈ 75 μm). Of more significance however is the X-ray spectra of these particles which show an almost complete absence of any element with a greater molecular weight than sodium. Considering the slag assay and the elements lighter than sodium it is difficult to
Figure 6.1  Digested Slag (Cl,7) Particle
(a) Photomicrograph (x2000),
(b) X-ray Spectrum
Figure 6.2 Digested Slag (C2,16) Particle
(a) Photomicrograph (x4000),
(b) X-ray Spectrum
Figure 6.3  Digested Slag (c2,16) Particle
(a) Photomicrograph (x4000),
(b) X-ray Spectrum
TABLE 6.1

SLAG COMPOSITIONS

(Values In Percent)

<table>
<thead>
<tr>
<th></th>
<th>C1,7</th>
<th>C2,16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>3.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Pb</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td>S</td>
<td>1.4</td>
<td>0.03</td>
</tr>
<tr>
<td>C</td>
<td>0.79</td>
<td>0.11</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>32.5</td>
<td>26.4</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.4</td>
<td>4.7</td>
</tr>
<tr>
<td>CaO</td>
<td>13.7</td>
<td>15.9</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>27.7</td>
<td>31.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.6</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Figure 6.4  
Digested Kaiser Coal Particle
(a) Photomicrograph (x2000),
(b) X-ray Spectrum
Figure 6.5 Undigested Slag (C1,7) Particles
(a) Photomicrograph (x800),
(b) X-ray Spectrum
conclude that these particles are anything other than carbon. This conclusion is supported by the analysis of the coal particle, Fig. 6.4. Further evidence is the fact that many of the particles with no significant elemental analysis have surface 'blow holes' and the general appearance of coal particles which have been devolatilized. See Fig. 6.2. These results, along with the carbon assays virtually confirm the fact that coal is penetrating into the slag.

It is interesting to note that the slag carbon particles show the presence of some sulphur. This result was observed to a greater degree in particles not shown here and suggests that sulphur in the slag is present in a form which escapes acid digestion. This supports the conclusion drawn in Section 4.3.1 that the slag sulphur has no effect on the ferrous iron assay.

6.1.2 Slag Porosity

In Fig. 6.6 and 6.7, typical cross-sections of quenched slag bar samples are shown. The light grey area is slag and the dark grey areas at the edge of the pictures the epoxy matrix. The most rapidly quenched region in the samples, that next to the steel bar, is free of the small white exsolved crystals evident over most of the slag cross-section. The black shapes are pores. The pore size ranges from 20 - 500 μm with an average size of about 200 μm. Pores up to 2000 μm are regularly
Figure 6.6  Cross-Section of Quenched Slag Bar Sample (C2,3)  (x50)
Figure 6.7  Cross-Section of Quenched Slag Bar Sample (C2,3)  (x50)
observed in the slag samples. The presence of pores in the rapidly quenched region clearly indicates that small bubbles exist in the liquid slag.

If a coal particle 40 μm in diameter, consisting of pure carbon, is converted to CO gas at 1200°C, a bubble 1000 μm in diameter will be formed. Thus the bubble size found in the slag is approximately that which would be expected to result from the reaction of a coal particle with the slag. The fact that in general, only smaller bubbles are seen in Fig. 6.6 and 6.7 may simply be a function of the greater tendency larger bubbles have to rise out of the bath.

In Table 6.2 the porosity of the slag over three different fuming cycles is presented. In each operation it is evident that the slag is relatively porous in agreement with the large fraction of the cross-section in Fig. 6.6 and 6.7 occupied by bubbles.

The average bubble size expected from the break up of the tuyere gas stream can be calculated by several methods. Using the formula derived by Turkdogan \(^ {95}\) from water modelling studies

\[
\bar{d}_b = 0.053 \frac{\rho_{\text{g}}}{\sigma} \frac{1}{g t^{1/3}}
\]

the expected bubble size should be 6000 μm. (A value for surface tension of 0.33 Nm\(^{-1}\) was used, taken from Suzuki et al \(^ {80}\).) It
# Table 6.2

**Slag Porosity Through Three Fuming Cycles**  
(values in %)

<table>
<thead>
<tr>
<th>Cycle Sample No.</th>
<th>Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A1</td>
</tr>
<tr>
<td>1</td>
<td>16.0</td>
</tr>
<tr>
<td>2</td>
<td>16.7</td>
</tr>
<tr>
<td>3</td>
<td>21.1</td>
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<td>4</td>
<td>27.4</td>
</tr>
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<td>5</td>
<td>29.1</td>
</tr>
<tr>
<td>6</td>
<td>34.2</td>
</tr>
<tr>
<td>7</td>
<td>28.9</td>
</tr>
<tr>
<td>8</td>
<td>28.2</td>
</tr>
<tr>
<td>9</td>
<td>26.3</td>
</tr>
</tbody>
</table>
is obvious that this is in excess of the size observed in the slag.

The presence of coal or 'char' particles in the slag and the porosity of the slag itself both confirm that coal is penetrating into the slag. In order to gain an understanding of how this may be taking place, tuyere back-pressure measurements were made on the fuming furnace at Company C.

6.1.3 Tuyere Phenomena

In Fig. 6.8 a pressure trace sequence during the charging of a fuming furnace is shown. In each photograph the vertical scale is gauge pressure from zero at the bottom horizontal to about 83 kPa (12 psi) at the top. The time interval in each case is 2 seconds.

In the empty furnace, Fig. 6.8a, the pressure trace is constant at about 8 kPa (1.2 psi) indicating that the flow is in a jetting regime.\textsuperscript{81,96} After 19 T of liquid slag have been charged certain instabilities are found in the flow, Fig. 6.8b. This indicates a predominantly jetting regime with only a minor amount of bubbling. At 39 T charged, the flow is predominantly bubbling, Fig. 6.8c.\textsuperscript{97-100} By the time the furnace is fully charged, Fig. 6.8d, the average back-pressure is about 33 kPa (4.2 psi) and the bubbling regime is well developed. The bubbling frequency is relatively constant at 5 bubbles per second.
Figure 6.8  Tuyere Back-Pressure Measurement Sequence,
(a) Empty Furnace,  (b) 19T Charged,
(c) 39T Charged,  (d) 52T Charged.
Blast at 300 Standard m³/min
Figure 6.8  Tuyere Back-Pressure Measurement Sequence, (a) Empty Furnace, (b) 19T Charged, (c) 39T Charged, (d) 52T Charged. Blast at 300 Standard m$^3$/min
A pressure trace over a five second period is shown in Fig. 6.9. Over this more representative time the bubbling frequency is 6 bubbles per second and quite regular. In Fig. 6.10 typical pressure traces with coal to the tuyere and without coal to the tuyere are compared. In both cases the bubbling frequency is the same. However, in the case with the coal flow, the average pressure is about 4 kPa (0.6 psi) greater than in the absence of coal injection. This may simply reflect the additional pressure required to carry the two-phase mixture the length of the tuyere.

Bubbling behaviour and bubbling frequencies measured, using the pressure transducer, were confirmed by tuyere photography.

Several papers in the literature report on model studies of gas-solid injection into liquid baths. The major emphasis of these papers is the quantitative effect of the presence of particles on injection behaviour. In each case, however, penetration of the particles into the liquid was observed and is evident in the photographs presented. Unfortunately no quantitative assessment of the extent of particle entrainment was made. In general however, it was found that greater entrainment of particles occurred in those cases where the particle was wetted by the liquid. In tests made by Farias and Robertson using horizontal injection, it was found that in a bubbling regime particles tended to just
Figure 6.9
Tuyere Back-Pressure Measurement:
5 Second Interval
Figure 6.10  Tuyere Back-Pressure Measurements:
(a) with 70 kg/min coal, (b) no coal
penetrate the interface and then rise up in a column parallel to the rising bubbles. In addition, non-wetted particles tended to cluster and clump together after entering the liquid.

Thus the conclusion reached earlier that coal penetrates into the slag of the fuming furnace is consistent with the results of physical modelling. In fact, the idea that none of the coal would enter the slag is rather unreasonable. A schematic representation of the expected tuyere phenomena is shown in Fig. 6.11.

If entrained coal is to be a significant reaction site in the slag fuming process a significant fraction must penetrate the gas-slag interface. The work of O'Malley et al.\(^{105}\) and Apelian et al.\(^{106}\) allow an assessment to be made of this phenomenon.

O'Malley et al.\(^{105}\) give the following formula, based on an energy balance for the critical diameter of a particles that can penetrate through a gas-liquid interface at a 90° impact angle.

\[
\frac{d_p}{\rho_p} \geq \left| \frac{3\sigma \cos \theta}{\nu_p^2 \rho_p} \right|
\]

In order to perform the calculation, values must be found for each of the variables. The surface tension, \(\sigma\), is about 0.33 Nm\(^{-1}\) as reported by Suzuki et al.\(^{80}\) According to the available information coal particles, devolatilized coal
Figure 6.11  Schematic of Tuyere Phenomena
particles and graphite are not wetted by slag. The wetting angle, $\theta$, is essentially $180^\circ$. The density of a bituminous coal is approximately $1500 \text{ kg m}^{-3}$ although a certain variation can be expected between particles in a pulverized sample. The velocity of the coal particles in the coal-air stream injected into the furnace is difficult to estimate. Measurements made by Ghosh and Lange and Engh et al in physical models have shown solid velocities to be about half of the gas velocity. Although loadings (mass ratio of solid flow to gas flow) were of the order of that encountered in the fuming furnace, 0.1-1.0, the size of the piping is significantly smaller. In studies performed on the pneumatic transport of coal in 2.54 cm (1 in.) lines particle velocities were found to lie within 80% of the gas velocity. Using the information in Table 1.1, the gas velocity in a fuming furnace tuyere should be $100-200 \text{ ms}^{-1}$. Assuming that the velocity of coal particles that emerge from the tuyere is equal to the gas velocity and constant as the particle crosses the diameter of the tuyere bubble, the minimum particle size to penetrate the slag at $v_p = 100 \text{ ms}^{-1}$ is $d_p = 0.2 \mu\text{m}$. If a particle velocity of $50 \text{ ms}^{-1}$ is used, $d_p = 0.7 \mu\text{m}$. Since in a 80% -200 mesh (B.S.S.) virtually all of the particles will be larger than $1 \mu\text{m}$, this calculation would predict that a large fraction of the injected coal could penetrate the slag. Once in the slag, due to the high wetting angle, clustering should occur. It will be assumed that particles cluster together to form the equivalent of $80 \mu\text{m}$ particles.
This calculation assumes two things. First, that the coal particles survive their passage across the bubble without burning. Second, that their velocity is unchanged in their passage across the bubble.

The first assumption is of obvious importance. The time required for the ignition of pulverized coal-air mixture injected into a small heated enclosure was measured by Ghosh and Orning. They measured ignition time for bituminous coals as a function of furnace temperature, coal to air ratio, particle size, and coal composition. For conditions which most nearly match those in the fuming furnace tuyere bubble, an ignition time of about 30 ms was obtained. The ignition temperature of several bituminous coals was measured by Finney and Spicer as a function of particle size and coal composition. In most cases a minimum ignition temperature of 600°C was found. Assuming that a single 80 μm coal particle sits in the centre of a spherical tuyere bubble, heated exclusively by radiation, the time required to reach the ignition temperature is about 350 ms. For details see Appendix IV. The order of magnitude difference between these two figures may be due to more rapid heating of the coal particles in the actual furnace. This might result from the entrainment of hot gases into the injected coal-air stream. Since this condition is probably a more accurate representation of conditions in the fuming furnace, the lower figure will be used.
If approximately 30 ms are to pass before ignition, a coal particle moving at 50 ms\(^{-1}\) will travel 1.5 m. The maximum spherical bubble diameter at a fuming furnace tuyere will typically be \(\sim 0.6\) m (bubbling frequency of 6 per second). Considering the tendency for bubbles to rise and extend vertically during formation \(^{81,97,100}\) the actual distance across a tuyere bubble may be significantly less than 0.6 m. Since the distance the particle will travel before ignition is larger than the bubble diameter, there is a reasonable probability that the coal particle will survive its passage across the bubble.

With regard to the second assumption, it can only be suggested that the jet of coal and air entering the tuyere bubble is not significantly disrupted by the entrainment of gases from the bubble and maintains its momentum right across the bubble. This assumption is qualitatively supported by the pictures taken by Farias and Robertson \(^{100}\) and Engh et al. \(^{103}\) In these cases the incoming tuyere jet, within the bubble, clearly penetrates across the tuyere bubble.

An energy balance on coal particles which penetrate the interface indicate that their depth of penetration is less than the particle radius. Particles would therefore be subject to almost certain rejection back into the tuyere gas stream. However it must be noted that the coal particles impinging on the slag interface do not arrive discretely, but in a constant stream. As a result the particles at the interface may be pushed further
into the slag. In addition, as observed by Farias and Robertson and others, the solids stream may force a bubble cone to extend into the slag directly across from the tuyere (see Fig. 6.11). This region, containing a high fraction of coal, may be broken off from the bulk of the bubble at detachment and the coal entrained in the slag. The coal would then rise vertically in a column parallel to the tuyere gas stream.

6.1.4 Other Industrial Processes

Finally there is evidence of coal entrainment in liquid baths in two different industrial tests. Wijk and Mellberg studied (a) the carburization of molten iron by the injection of coal in argon and, (b) the decarburization of molten iron by the injection of magnetite in argon, and (c) coal gasification by injection of coal and oxygen into molten iron. In cases (a) and (b), the solid particles were found to entrain in the molten metal and react directly with the liquid. Wijk and Mellberg conclude that in a reactor, two zones are formed: the bulk of the bath and a 'jet' region consisting of a rising column of gas and accompanying liquid. The particles injected with the gas reside in this rising liquid zone and react with the bath as they rise, the rate of reaction being controlled by diffusion in the liquid phase.

Rummell describes the development and operation of a molten slag-coal gasifier. In this process, pulverized coal is
gasified by injecting it into a molten slag bath. The gasifying medium, steam or carbon dioxide, is injected into the slag through a separate tuyere. The fact that gasification proceeds indicates that the coal is entrained in the slag and is carried into the reaction directly or indirectly with the gasifying medium. Carbon was also observed in slag assays.

The inescapable conclusion of this analysis is that a significant portion of the coal injected into the furnace is entrained in the slag. Having established this fundamental concept it simply remains to construct the detailed quantitative model. In fact, the whole kinetic model follows directly from this point.

6.2 A Kinetic Model of the Process

The basic kinetic effect in the zinc slag fuming process is the partitioning of the coal between the slag bath and the tuyere gas stream. This separation establishes two distinct reaction zones: (a) a region of direct reaction between entrained coal and the slag, and (b) the tuyere gas stream.

6.2.1 The Entrained Coal - Slag Reaction Regime

Coal which penetrates into the slag bath will enter a rising column of liquid slag. This fact is evident from earlier
discussions, as well as several references in the literature. The hydrodynamics of injection in the slag fuming furnace should establish two bath circulation cells. Slag should be drawn up by the rising bubbles against the furnace wall, move across the bath surface to the centre and then descend and move out to the walls along the bottom. Coal particles which enter the slag at the tuyere level will be carried to the surface in this flow during which period they will react with the slag, enclosing themselves in a gas envelope. As these secondary, coal-formed bubbles move along the surface layer they will rise and break the surface, emptying their contents into the atmosphere above the bath. This scenario is illustrated in Fig. 6.12.

The analysis of the fate of the entrained coal then involves modelling (a) the reaction of the coal with the slag, and (b) the residence time of coal in the bath.

6.2.1.1 The Coal Particle - Slag Reaction

Given that coal particles injected into the furnace impact the gas-slag interface at half their ignition time or less, it will be assumed that they undergo no reaction before this point. In most operations the pulverized coal is injected without drying. It will be assumed that the coal powder dries as it crosses the bubble and that this moisture becomes part of the tuyere gas stream.
Fig. 6.12 Entrained Slag Coal Reaction Sequence
At the instant the coal particle penetrates the gas-slag interface it is subject to very rapid heating due to the direct contact with the slag. This will result in virtually instantaneous pyrolysis. The behaviour of coal particles during pyrolysis is very complex. The products of pyrolysis vary from $\text{H}_2$ to organic tars, depending on coal composition, heating rate, final temperature, pressure and the residence time of volatiles around the particle. $^{93,94}$ The reaction is poorly understood. Wen and Dutta $^{94}$ suggest that for rapid heating to high temperature ($1200^\circ\text{C}$ in 1 to 10 ms) the products of pyrolysis are almost entirely gaseous with little tar production. The gas tends to contain a significant percentage of unsaturated hydrocarbons such as $\text{C}_2\text{H}_2$ (about 20%), in addition to $\text{H}_2$, $\text{CO}$, $\text{CH}_4$ and $\text{C}_2\text{H}_6$.

It would be impossible to properly account for pyrolysis in the context of the slag fuming process. It will be assumed that in pyrolysis, (a) all proximate volatile hydrogen is released as $\text{H}_2$, (b) all proximate volatile nitrogen is released as $\text{N}_2$, (c) all proximate volatile oxygen reacts with volatile carbon to form $\text{CO}$, and (d) the remaining proximate volatile carbon precipitates on the char particle.

Following pyrolysis then a devolatilized coal particle or char particle surrounded by an atmosphere of $\text{H}_2$, $\text{CO}$, and $\text{N}_2$ resides in the slag. This char particle - gas envelope system or secondary bubble then starts to react with the slag.
The reaction system which develops in schematically illustrated in Fig. 6.13. Because conditions are very reducing at the bubble interface both zinc oxide and ferric oxide will diffuse to the bubble where they will be reduced by $H_2$ or $CO$. The $CO_2$ generated by the reduction reactions

$$\text{ZnO}_{(sl)} + CO \rightleftharpoons \text{Zn}_{(g)} + CO_2 \quad \ldots(6.3)$$

$$\text{Fe}_2O_3_{(sl)} + CO \rightleftharpoons 2\text{FeO}_{(sl)} + CO_2 \quad \ldots(6.4)$$

will diffuse through the gas phase to the surface of the char particle where it will react via the Boudouard Reaction to produce CO:

$$CO_2 + C \rightleftharpoons 2CO \quad \ldots(6.5)$$

The partial pressure of Zn and $CO_2$ and $H_2O$ will therefore gradually build up in the bubble and the char particle will shrink as the bubble is swept upward by the bath.

Equation 4.6 was deliberately written in terms of $Fe_2O_3$ rather than $Fe_3O_4$. It is considered that ferric ions tend to form complexes such as $Fe_2O_4^{2-}$ or $Fe_2O_5^{4-}$ in slag. Because $Fe^{3+}$ is a smaller ion than $Fe^{2+}$ and also has a higher charge, it has a strong tendency to surround itself with oxygen ions. Thus, on a mechanistic basis the diffusion of ferric ions is not likely to be accompanied by the co-diffusion of ferrous ions.
Particle reaction model

CO, CO₂, H₂, H₂O, N₂, Zn

Zn

ZnO

Fe₃O₄

FeO

+Ve

Slag

Gas bubble

Char particle

CO

CO₂

Boudouard

Diffusion

Fig. 6.13  Slag-Char Particle Reaction System
The fact that a secondary bubble reaction system exists is supported by the evidence of electron microprobe analysis. Radial zinc and iron concentration profiles around quenched slag bubbles are shown in Fig. 6.14 and 6.15. In both cases, definite diffusion gradients are present for both species, indicating the bubbles are not at equilibrium with the slag, but are actively reacting.

It will be assumed that electron transfer through the slag via the Fe$^{3+}$/Fe$^{2+}$ couple plays no role in the reduction of Fe$^{3+}$ iron. Measurements of the electrical conductivity of FeO-CaO-SiO$_2$ melts under reducing conditions (certainly present in the vicinity of the secondary bubble) suggest that about 90% of the conduction is ionic. $^{120,95}$ Grievson $^{121}$ reviews the results of several studies of the reduction and oxidation of Fe$_x$O-Fe$_2$O$_3$ containing melts which conclude that the rate controlling process is the diffusion of iron oxide. Finally, even if electron transfer is significant, reduction must still be accompanied by the diffusion of oxygen which may then be the rate controlling step.

As discussed in the coal particle-slag reaction system described, there is also mass transfer of species within the bubble gas phase. It is important to assess whether or not this is an important rate controlling step in the reaction. In order to address this question, the structure of the secondary bubble must be established. If a rather large coal particle ($d_p=74$ μm,
Fig. 6.14  Radial Slag Concentration Profiles
From Slag Bubble Sample (C1,5)  
(x 600)
(a) Zinc   (b) Iron
Fig. 6.15  Radial Slag Concentration Profiles
From Slag Bubble Sample (B1,1)
(x 600)
(a) Zinc    (b) Iron
200 mesh B.S.S.) reacts to form a bubble consisting of \( H_2 \) and equal amounts of Zn and CO consuming all the carbon, the bubble diameter will be about 2.5 mm at 1200°C. Using a slag density of 3900 kg m\(^{-3}\) and a slag surface tension of 0.33 Nm\(^{-1}\) gives the bubble an Eotvos Number of 0.7.

\[
Eo = \frac{4g\Delta \rho r_b^2}{\sigma}
\]  

...(6.6)

The terminal rise velocity of the bubble will be about 2.8 cm/s, according to Stoke's Law:

\[
v_{\text{terminal}} = \frac{4gr_b^2\Delta \rho}{18\mu}
\]  

...(6.7)

This is assuming an average slag viscosity of 0.5 kg m\(^{-1}\)s\(^{-1}\). The bubble Reynolds Number will therefore be 0.5

\[
Re = \frac{2\rho r_b v_b}{\mu}
\]  

...(6.8)

According to Clift et al \(^{123}\) under these conditions, the secondary bubbles will behave as rigid spheres. Considering that the bubble diameter and velocity will, on average be less than the extreme values chosen above, this conclusion is sound.

For rigid spheres in creeping flow, according to Clift et al \(^{123}\), for species \( j \):

\[
Sh_j = 1 + (1 + Pe_j)^{1/3}
\]  

...(6.9)

where \( Pe \) is the Peclet Number;

\[
Pe_j = \frac{2r_b v_b}{D_j}
\]  

...(6.10)

and \( Sh \) is the Sherwood Number;

\[
Sh_j = \frac{2k_j r_b}{D_j}
\]  

...(6.11)
Equations 6.9, 6.10 and 6.11 can be solved for the mass-transfer coefficient, using a bubble velocity obtained from Equation 6.7. The Sherwood number changes from an initial value of 2 to about 50. According to Clift et al for rigid spheres in creeping flow the following criteria apply for mass transfer control for species j:

(a) if \( \frac{H (D^b_j / D^sl_j)^{1/2}}{1} \gg 1 \) ...(6.12)

there is external (slag phase) resistance control for short times,

(b) if \( \frac{H (D^b_j / D^sl_j)}{Sh_j} \gg 1 \) ...(6.13)

there is external (slag phase) resistance control for long times, where

\[ H = \frac{C^b_j}{C^sl_j} \text{ at equilibrium} \] ...(6.14)

and time is dimensionless time, defined by the equation:

\[ \tau = \frac{D^b_j}{r^2} \frac{t}{r_b^2} \] ...(6.15)

These criteria are not immediately applicable to the complex reaction system under analysis here. However, it is only in this simple form that any attempt at all can be made to answer this question. Thus, to simplify the problem, it will be assumed that Equation 6.16 defines the equilibrium

\[ \text{ZnO}_{(sl)} + C \rightarrow \text{Zn}_{(g)} + \text{CO} \] ...(6.16)

and that the 'equilibrium' gas composition at any moment is 50% zinc vapour and 50% CO, throughout the bubble. At 1200°C, a system pressure of 101.4 kPa (1 atm) and 8 wt% zinc in the
slag, \( H \) will be \( 8.5(10^{-4}) \).

The diffusivity of zinc vapour in CO can be evaluated by Chapman - Enskog theory. Using data from Turkdogan this is \( 3(10^{-4}) \text{m}^2/\text{s} \). As will be discussed later, the diffusivity of zinc in the slag phase will be about \( 2(10^{-10}) \text{m}^2/\text{s} \). For short times \((\tau < 1)\)

\[
H \left( \frac{D_{\text{Zn}}^b}{D_{\text{Zn}}^{sl}} \right)^{\frac{1}{2}} = 1.0
\]

\( t < 2\mu s \)

For long times \((\tau > 1)\)

\[
H \frac{D_{\text{Zn}}^b}{D_{\text{Zn}}^{sl}} = 1275
\]

\( t > 2\mu s \)

Thus for short times which are trivial there probably will be some form of consecutive control. For long times which comprise the entire life of the bubble, it appears that since Equation 6.13 is marginally satisfied, the reaction system will be under slag phase diffusion control.

In addition to these considerations it should be remembered that the bubble will contain several solid char particles which in all probability will not sit stationary at the centre of the bubble. The motion of these particles in the bubble will serve to enhance internal mass transport.
A simple model of this system can now be developed. In addition to the assumptions discussed above, it will be assumed that:

a) the char particle is spherical,
b) the char particle reacts only with $\text{CO}_2$, and
c) the system is isothermal at bath temperature.

There are eight unknown, time dependent quantities, $C_{\text{Zn}}^b$, $C_{\text{CO}}^b$, $C_{\text{CO}_2}^b$, $C_{\text{H}_2}^b$, $C_{\text{H}_2\text{O}}^b$, $C_{\text{N}_2}^b$, $r_p$ and $r_b$. In order to simplify the mathematics, three additional variables will be introduced. These are $W_p$, the weight of the char particle, $V_g$, the volume of the bubble gas; and $G$, the molar amount of carbon in the char particle. Eleven equations can be developed.

6.2.1.1.1 Zinc Balance

The mass transfer of zinc oxide to the bubble can be empirically characterized by the equation:

$$\dot{n}_{\text{ZnO}} = A_b \cdot k_{\text{ZnO}} \cdot (C_{\text{ZnO}}^1 - C_{\text{ZnO}}^i)$$  \hspace{1cm} \ldots (6.17)

Since zinc vapour is not consumed or generated in the bubble, this is simply equal to the rate of zinc accumulation in the bubble gas phase:

$$\dot{n}_{\text{ZnO}} = \frac{d(C_{\text{Zn}}^b V_g)}{dt} = V_g \frac{dC_{\text{Zn}}^b}{dt} + C_{\text{Zn}}^b \frac{dv}{dt}$$  \hspace{1cm} \ldots (6.18)
thus;

\[
\frac{dC_{Zn}^b}{dt} = \frac{1}{V_g} \left[ \dot{n}_{ZnO} - C_{Zn}^b \frac{dV}{dt} \right]
\] ...(6.19)

6.2.1.1.2 CO Balance

No CO enters or leaves the bubble. CO is consumed by reactions 6.3 and 6.4 and generated by the Boudouard Reaction, reaction 6.5. Thus

\[
\dot{r}_{CO,cons} = \dot{n}_{ZnO} + \dot{n}_{Fe_2O_3} \] ...(6.20)

\[
\dot{r}_{CO,gen} = 2BG \] ...(6.21)

where B is the Boudouard Reaction rate in kg mole/kg mole·s.

Equating this to the CO accumulation term gives

\[
\frac{dC_{CO}^b}{dt} = \frac{1}{V_g} \left[ 2BG - \dot{n}_{ZnO} - \dot{n}_{Fe_2O_3} - C_{CO}^b \frac{dV}{dt} \right] \] ...(6.22)

6.2.1.1.3 CO₂ Balance

Similarly to the CO balance:

\[
\dot{r}_{CO_2,cons} = BG \] ...(6.23)

\[
\dot{r}_{CO_2,gen} = \dot{n}_{ZnO} + \dot{n}_{Fe_2O_3} \] ...(6.24)

and

\[
\frac{dC_{CO_2}^b}{dt} = \frac{1}{V_g} \left[ \dot{n}_{ZnO} + \dot{n}_{Fe_2O_3} - BG - C_{CO_2}^b \frac{dV}{dt} \right] \] ...(6.25)
6.2.1.1.4  \( H_2 \) Balance

Since instantaneous internal mass transfer and internal gaseous equilibrium are assumed, the concentration of \( H_2 \) and \( H_2O \) respond instantly to changes in the concentration of \( CO \) and \( CO_2 \) by the reaction

\[
CO + H_2O \rightleftharpoons H_2 + CO_2
\]

\[
K_3 = \frac{P_{H_2}P_{CO_2}}{P_{CO}P_{H_2O}} = \frac{c^b_{H_2}c^b_{CO_2}}{c^b_{CO}c^b_{H_2O}}
\]

... (6.27)

If \( H \) is the total molar quantity of \( H_2 \) released as volatiles, then

\[
V_g c^b_{H_2} + V_g c^b_{H_2O} = H
\]

... (6.28)

and

\[
c^b_{H_2O} = \frac{H}{V_g} - c^b_{H_2}
\]

... (6.29)

Substituting Equation 6.29 into 6.27 gives

\[
\frac{c^b_{H_2}}{c^b_{CO_2}} = \left[ \frac{H}{V_g} - c^b_{H_2} \right] \frac{c^b_{CO}}{c^b_{H_2O}} K_3
\]

... (6.30)

Differentiating and solving for \( \frac{dc^b_{H_2}}{dt} \) gives:
\[
\frac{dC_{H_2}^b}{dt} = \frac{1}{c_{CO_2}^{b2} + c_{CO_2}^b c_{CO}^b K_3} \left[ c_{CO_2}^b K_3 \left( \frac{H}{V_g} - c_{H_2}^b \right) \frac{dc_{CO}^b}{dt} \right.
\]
\[\left. - \left( \frac{H}{V_g} - c_{H_2}^b \right) K_3 c_{CO}^b \frac{dc_{CO_2}^b}{dt} \right. \]
\[\left. - \frac{c_{CO_2}^b c_{CO}^b K_3^H}{V_g^2} \frac{dv_g}{dt} \right] \quad \ldots (6.31)
\]

6.2.1.1.5 \( H_2O \) Balance

As discussed above, a balance on \( H_2 \) can be performed, Equation 6.28. Differentiating this equation and solving for \( \frac{dc_{H_2O}^b}{dt} \) gives

\[
\frac{dc_{H_2O}^b}{dt} = -\frac{dc_{H_2}^b}{dt} - \left[ c_{H_2}^b + c_{H_2O}^b \right] \frac{dv_g}{dt} \quad \ldots (6.32)
\]

6.2.1.1.6 \( N_2 \) Balance

Since nitrogen does not participate in any reactions

\[
\frac{d \left[ c_{N_2}^b v_g \right]}{dt} = 0 \quad \ldots (6.33)
\]

and

\[
\frac{dc_{N_2}^b}{dt} = -c_{N_2}^b \frac{dv_g}{V_g dt} \quad \ldots (6.34)
\]
6.2.1.1.7 Bubble Radius

Based on the assumption of spherical geometry, the gas volume can be written as:

\[ V_g = \frac{4}{3} \pi r_b^3 - \frac{4}{3} \pi r_p^3 \]  

...(6.35)

Differentiating and solving for \( \frac{dr_b}{dt} \) gives

\[ \frac{dr_b}{dt} = \frac{1}{r_b^2} \left[ \frac{1}{4\pi} \frac{dv_g}{dt} + r_p^2 \frac{dr_p}{dt} \right] \]  

...(6.36)

6.2.1.1.8 Char Particle Radius

The radius of the char particle is directly related to the weight of the particle

\[ 4/3 \pi r_p^3 = \frac{W_p}{\rho_c} \]  

...(6.37)

It will be assumed that the char particle density is the same as the coal density. Differentiating yields

\[ \frac{dr_p}{dt} = \frac{1}{4\pi r_p^2} \frac{1}{\rho_c} \frac{dW_p}{dt} \]  

...(6.38)

6.2.1.1.9 Char Particle Weight

Assuming that the char particle loses weight at a rate
proportional to the rate of the Boudouard Reaction

\[
\frac{dW_p}{dt} = -BG \cdot s_1 \cdot (12.01) \quad \ldots(6.39)
\]

where \( s_1 \) is the char particle weight (carbon+ash) to weight of contained carbon after pyrolysis, and \( 12.01 \) is the molecular weight of carbon.

6.2.1.1.10 Gas Volume

The gas volume is changing as a function of the reduction reactions and the Boudouard Reaction

\[
\dot{r}_{g,\text{gen}} = 2\dot{n}_{ZnO} + 2BG \quad \ldots(6.40)
\]

\[
\dot{r}_{g,\text{cons}} = \dot{n}_{ZnO} + BG \quad \ldots(6.41)
\]

Therefore

\[
2\dot{n}_{ZnO} + 2BG - (\dot{n}_{ZnO} + BG) = \frac{d(V \rho_g)}{dt} \quad \ldots(6.42)
\]

and

\[
\frac{dV_g}{dt} = \frac{1}{\rho_g} \left[ \dot{n}_{ZnO} + BG \right] \quad \ldots(6.43)
\]

where \( \rho_g \) is the gas molar density at temperature.

6.2.1.1.11 Char Particle Carbon

The carbon of the char particle is consumed by the Boudouard Reaction, thus
6.2.1.1.12 Initial Conditions

In order to solve the above system of equations it is necessary to establish the initial conditions.

The initial gas composition and volume of the bubble is calculated, assuming equilibrium in Equations 6.26 and 6.5, and performing a mass balance on the volatile oxygen, hydrogen and nitrogen. This gives five equations in five unknowns, \( \frac{dG}{dt} = -BG \) ...

6.2.1.1.13 Thermodynamic Quantities

Thermodynamic data is required to evaluate the equilibrium constants for the various reactions involved as well as the activity coefficients of relevant slag species. The reactions and free energy data used in the thesis are given in Table 6.3.

To calculate \( \tilde{n}_{\text{ZnO}} \), it is necessary to determine the interfacial concentration, \( C^i_{\text{ZnO}} \). It is assumed that \( C^i_{\text{ZnO}} \) is the
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>$\Delta H$ (J)</th>
<th>$\Delta S_{-1}$ JK$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnO + CO $\rightarrow$ Zn + CO$_2$</td>
<td>179300</td>
<td>113.1</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>Fe$_2$O$_3$ + (3-2/x)CO $\rightarrow$ (2/x)Fe$_x$O + (3-2/x)CO$_2$</td>
<td>8870</td>
<td>.36.0</td>
<td>95,124</td>
</tr>
<tr>
<td>3</td>
<td>H$_2$O + CO $\rightarrow$ H$_2$ + CO$_2$</td>
<td>-33470</td>
<td>-29.4</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>CO$_2$ + C $\rightarrow$ 2CO</td>
<td>166570</td>
<td>171</td>
<td>95</td>
</tr>
<tr>
<td>5</td>
<td>(2/x)Fe$_x$O + (1.5-1/x)O$_2$ $\rightarrow$ Fe$_2$O$_3$</td>
<td>-291300</td>
<td>-130</td>
<td>124</td>
</tr>
<tr>
<td>6</td>
<td>(3/x)Fe$_x$O + (2-1.5/x)O$_2$ $\rightarrow$ Fe$_3$O$_4$</td>
<td>-312200</td>
<td>-125</td>
<td>124</td>
</tr>
<tr>
<td>7</td>
<td>C + O$_2$ $\rightarrow$ CO$_2$</td>
<td>-395350</td>
<td>0.544</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>C + $\frac{1}{2}$O$_2$ $\rightarrow$ CO</td>
<td>-114390</td>
<td>85.75</td>
<td>95</td>
</tr>
<tr>
<td>9</td>
<td>H$_2$ + $\frac{1}{2}$O$_2$ $\rightarrow$ H$_2$O</td>
<td>-247500</td>
<td>-55.9</td>
<td>95</td>
</tr>
<tr>
<td>10</td>
<td>Zn + $\frac{1}{2}$O$_2$ $\rightarrow$ ZnO</td>
<td>-460240</td>
<td>-198.3</td>
<td>95</td>
</tr>
</tbody>
</table>
slag concentration in equilibrium with the bubble gas composition via Equation 6.3. This essentially assumes that reaction kinetics at the interface are instantaneous. Thus

$$K_1 = \frac{P_{Zn} P_{CO_2}}{P_{CO} a_{ZnO}} \quad \ldots(6.45)$$

and

$$\gamma_{ZnO} N_{ZnO} = \frac{P_{Zn} P_{CO_2}}{P_{CO} K_1} \quad \ldots(6.46)$$

since

$$N_j = \frac{C_j}{\rho_{sl,m}} \quad \ldots(6.47)$$

then

$$C_{ZnO}^i = \frac{P_{Zn} P_{CO_2}}{P_{CO} K_1} \cdot \frac{\rho_{sl,m}}{\gamma_{ZnO}} \quad \ldots(6.48)$$

To calculate $C_{ZnO}^i$ the equilibrium constant $K_1$, as well as $\rho_{sl,m}$ and $\gamma_{ZnO}$ must be found. The equilibrium constant, $K_1$, can be obtained from Table 6.3. The slag molar density, $\rho_{sl,m}$, can be calculated from the slag density and the slag composition. The value of the activity coefficient, $\gamma_{ZnO}$, is more difficult to obtain.

Grant 45 has reviewed the literature on the activity coefficient of zinc oxide. He reports values of 0.1 to 5.6 with a majority of the studies showing the value to lie in the range 0.8 to 3.0. A study of the literature has revealed only several
papers to be useful. The data of Azuma et al was in good agreement with Richards and Thorne and slightly higher than that of Filipovska and Bell. This may be due to the use of lower oxygen potentials in the work of Filipovska and Bell. Because the more oxidizing conditions in the work of Azuma et al most closely simulate the conditions in the fuming furnace, this data was selected. A regression analysis of their data gave the following equation for the activity of zinc oxide as a function of the molar lime-to-silica ratio \( S \) in the slag at 1200°C:

\[
\gamma_{\text{ZnO}} = 1.06 \, (S) + 1.88
\] \hspace{1cm} \ldots (6.49)

In order to incorporate the temperature dependence of the activity coefficient it was assumed that the temperature dependence is the same as that of FeO below an activity of 0.6, as derived from Bodsworth for the CaO-FeO-SiO\(_2\) system. Then:

\[
\ln \gamma_{\text{ZnO}} = \frac{16400(S) - 12000}{T} - 10.7(S) + 8.8 \] \hspace{1cm} \ldots (6.50)

This equation gives the activity coefficient a value of 2.4 at 1200°C at a molar lime-to-silica ratio of 0.5.

The thermodynamics of the ferric-ferrous system in the slag is significantly more complex. First, the composition of iron oxide, liquid or solid, in equilibrium with metallic iron is non-stoichiometric, i.e. \( \text{Fe}_x \text{O} \). The equilibrium oxide composition contains a certain fraction of ferric ions. For
example, in a slag containing 20 wt% CaO, 40 wt% SiO$_2$, and 40% 'iron oxide', in equilibrium with metallic iron, the 'iron oxide' portion will be 1.4 wt% Fe$_2$O$_3$, 38.6 wt% FeO or Fe$_{0.984}$O. Since the level of ferric iron found in the fuming slag is 0-4 wt% (See Fig. 5.1-5.11) it is apparent that the level of ferric iron as non-stoichiometric iron oxide may therefore be significant.

The reduction Equation 6.5 must therefore be rewritten as:

$$Fe_2O_3 + (3-2/x)CO \xrightarrow{\text{(sl)}} (2/x)FeO + (3-2/x)CO_2 \quad \ldots (6.51)$$

If $x = 1$ then this simplifies to Equation 6.5.

The reduction of ferric iron involves the transfer of ferric iron ions to the secondary bubble surface and the transfer of the ferrous ions produced back into the bulk of the slag:

$$\dot{n}_{Fe_2O_3} = -A_b \dot{k}_{Fe_2O_3} \left[ C_{Fe_2O_3}^{sl} - C_{Fe_2O_3}^i \right] \quad \ldots (6.52)$$

and

$$\dot{n}_{FeO} = -A_b \dot{k}_{FeO} \left[ C_{FeO}^{sl} - C_{FeO}^i \right] \quad \ldots (6.53)$$

As discussed earlier, what Equation 6.53 suggests is not strictly valid, i.e. that there is a co-diffusion of ferric and ferrous ions in a single compound. This however, is the best solution to a difficult problem because it accounts for
the equilibrium bath ferric-ferrous level automatically. To attempt to work with stoichiometric FeO creates problems because the standard state for thermodynamic data is defined as the non-stoichiometric compound. Furthermore the error involved in this approach is not large because the value of $x$ is close to 1. According to Bodsworth $x$ should be in the range of 0.96 to 0.99. Fuming slags generally contain $\approx 5$ wt% Al$_2$O$_3$ which will tend to associate with CaO and 'acidify' the melt. This will increase $x$ because the presence of Fe$^{3+}$ ions is stabilized by CaO which forms stable calcium ferrites. It will be assumed that $x$ is 0.99.

In order to account for the coupled diffusion of ferric and ferrous ions, Equations 6.52 and 6.53 must be combined to derive the value of $\dot{n}_{\text{Fe}_2\text{O}_3}$ required for the model. From Equation 6.51

$$\dot{n}_{\text{Fe}_x\text{O}} = \frac{2}{x} \dot{n}_{\text{Fe}_2\text{O}_3} \quad \ldots (6.54)$$

and

$$K_2 = \frac{a_{\text{FeO}} Z_{\text{Fe}_2\text{O}_3} P_{\text{CO}_2}}{a_{\text{Fe}_2\text{O}_3} P_{\text{CO}} (3-2/x)} \quad \ldots (6.55)$$

In terms of concentrations and slag molar density

$$K'_2 = K_2 \frac{\gamma_{\text{Fe}_2\text{O}_3}}{\gamma_{\text{FeO}}} \frac{(2/x-1)}{P_{\text{sl, m}}} = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} (3-2x) \frac{2}{x} \frac{1}{C_{\text{Fe}_2\text{O}_3}^{\text{Fe}_x\text{O}}} \quad \ldots (6.56)$$
Substituting Equations 6.53, 6.54 and 6.56 into 6.52 gives

\[
\frac{\dot{n}_{Fe_2O_3}}{K_2} = A_b k_{Fe_2O_3} \left[ \frac{C_{Fe_2O_3}}{C_{FeO}} \right]^{2/x} \left( \frac{P_{CO2}}{P_{CO}} \right)^{(3-2/x)} \left( \frac{2/x}{\dot{n}_{Fe_2O_3}} + \frac{s_l}{C_{FeO}} \right)^{2/x} \]. \quad (6.57)

This equation was solved iteratively using an initial estimate at \( x = 1 \).

To calculate \( K_2' \) values are required for \( \gamma_{Fe_2O_3} \) and \( \gamma_{FeO} \). The activity coefficient of \( Fe_xO \) was developed from Bodsworth\textsuperscript{119}, Richards and Thorne\textsuperscript{127} and Filipovska and Bell\textsuperscript{126}. From these sources the activity coefficient should have a value of 1.95 at 1200°C at \( S = 0.5 \).\textsuperscript{119,127} The lime-to-silica ratio dependence of the activity coefficient is 0.71.\textsuperscript{119,127}

Thus at 1200°C

\[
\gamma_{FeO} = 0.71(S) + 1.59 \quad \ldots (6.58)
\]

The temperature dependence of \( \gamma_{FeO} \) was derived from the data of Bodsworth for \( a_{FeO} \geq 0.6 \). This yields

\[
\ln \gamma_{FeO} = \frac{3300(S) + 1660}{T} - 1.89(S) - 0.64 \quad \ldots (6.59)
\]

referenced to the pure non-stoichiometric solid.
The only discussion of the activity of ferric iron in these slags is provided by Kellogg. Kellogg gives the following equation for $\gamma_{Fe_3O_4}$

$$\ln \gamma_{Fe_3O_4} = \frac{8495}{T} - 2653 \quad \ldots(6.60)$$

This can be converted to a value of $\ln \gamma_{Fe_2O_3}$, assuming that either of the theoretical iron couples in the slag $Fe_xO - Fe_2O_3$ or $Fe_xO - Fe_3O_4$ would exert the same oxygen potential. From

$$\frac{2}{x} Fe_xO + (1.5 - 1/x)O_2 \rightleftharpoons Fe_2O_3 \quad \ldots(6.61)$$

$$\frac{3}{x} Fe_xO + (2 - 1.5/x)O_2 \rightleftharpoons Fe_3O_4 \quad \ldots(6.62)$$

equating oxygen potentials gives:

$$\gamma_{Fe_2O_3} = \frac{\gamma_{FeO,1}^{NFeO,1} K_5}{N_{Fe_2O_3}^{3/x} N_{FeO,2}^{3/x} K_6} \left[ \frac{\gamma_{Fe_3O_4}^{NFe_3O_4}^{3/x} \gamma_{FeO,2}^{NFeO,2} \frac{1}{K_6}}{(1.5 - 1/x) (2 - 1.5/x)} \right] \ldots(6.63)$$

where $K_5$ is the equilibrium constant of Equation 6.61 and $K_6$ the equilibrium constant of Equation 6.62. $N_{FeO,1}$ is the mole fraction $Fe_xO$ that would be associated with the ferric compound $Fe_2O_3$ in the slag. $N_{FeO,2}$ is the mole fraction of $Fe_xO$ that would be present if the other ferric species was $Fe_3O_4$.

6.2.1.1.14 Mass-Transfer Coefficients

To calculate $\dot{\gamma}_{ZnO}$, and $\dot{\gamma}_{Fe_2O_3}$, it is necessary to calculate the mass-transfer coefficients $k_{ZnO}$, $k_{FeO}$ and $k_{Fe_2O_3}$. As
discussed above the bubble reaction system will behave as a rigid sphere and therefore the mass-transfer coefficients can be obtained from Equations 6.7 and 6.9-6.11. All terms in these equations can be evaluated as a function of model variables and values of physio-chemical properties used above. It remains then to find appropriate diffusivities.

Unfortunately there is little information on the values of diffusivity in slags in general and even less on inter-diffusivities. No studies have been conducted on lead blast furnace slags. There are several studies on the diffusivity of iron in slags, 77, 128-132 but none on zinc. The behaviour of zinc can then only be estimated by suggesting that since it has an ionic radius equal to \( Fe^{2+} \) (\( r_{Fe^{2+}} = 0.75 \ \text{Å}, \ r_{Zn^{2+}} = 0.75 \ \text{Å} \)) \(^{133}\) it will have similar diffusion properties. This is of little assistance because measurements of iron diffusivities vary over three orders of magnitude.

Mori and Suzuki 128 found values of iron inter-diffusivity of \( 5 \times 10^{-9} \ \text{m}^2\text{s}^{-1} \) to \( 4 \times 10^{-8} \ \text{m}^2\text{s}^{-1} \) in iron oxide melts at 1500°C. They suggest that in silicate melts with large anions such as \( \text{SiO}_4^{4-} \), the inter-diffusivity should be significantly lower.

Borom and Pask 129 measured the inter-diffusivity of iron in sodium disilicate glass over the range 900°C to 1100°C. They found values of about \( 2 \times 10^{-11} \ \text{m}^2\text{s}^{-1} \) for FeO at 1100°C in this system. In general inter-diffusivities for cations such as \( \text{Ca}^{2+} \) and \( \text{Fe}^{2+} \) are believed to lie in the range...
According to Richardson, as a first approximation in complex systems, inter-diffusivity may be equated to the self-diffusivity of the more rapidly diffusing species. Assuming that Fe$^{2+}$ and Zn$^{2+}$ are essentially similar and the most rapidly diffusing species in the slag then the self-diffusivity of Fe$^{2+}$ in iron calcium silicate slags will be the best estimate of the inter-diffusivity that can be made.

Agarwal and Gaskell have measured the self-diffusivity of iron in a CaFeSiO$_4$ melt over the range of 1250°C to 1540°C. This system is the closest to the lead blast furnace slag which has been investigated. They obtained the following equation for $D_{Fe}^*$ (in m$^2$s$^{-1}$)

$$\log D_{Fe}^* = \frac{5450\pm620}{T} - 1.93 \pm 0.37 - 4 \quad \text{...(6.64)}$$

The self-diffusivity at 1200°C is $2.3(10^{-10})$ m$^2$s$^{-1}$. This value lies in the middle of the expected range of inter-diffusivities. Furthermore, the activation energy in this equation is 105 kJ which is in reasonable agreement with the activation energy determined for inter-diffusivity by Borom and Pask: 125 kJ. Finally, this value is within the range of quasibinary inter-diffusivities measured by Ukyo et al. For these reasons it will be assumed that Equation 6.64 gives the inter-diffusivity of FeO and ZnO in fuming furnace slag.
The reaction of ferric iron in the slag has been written in terms of Fe$_2$O$_3$. The only reference to the inter-diffusivity of Fe$_2$O$_3$ is given by Borom and Pask. In their study they found the inter-diffusivity of Fe$_2$O$_3$ to be almost exactly one-tenth the inter-diffusivity of FeO. Having nothing else to go on, this relationship was assumed to apply in the fuming furnace slag. A value one-tenth that calculated by Equation 6.64 was used.

6.2.1.1.15 Boudouard Reaction Rate

The final term in the model to evaluate is the Boudouard Reaction rate, B. Reviews of the literature have been done by Wen and Dutta$^{94}$ and Skinner and Smoot$^{134}$. Both of these papers emphasize the almost completely empirical nature of measurements of Boudouard Reaction rates. Measured rates are sensitive to measurement techniques, particle size, system temperature and pressure, residence times and a host of other variables. Thus, although there is a wealth of information available, very little of it is directly applicable to the particle reaction model.

The most useful data is given by Skinner and Smoot$^{134}$ for bituminous coal char of a 'pulverized' size (70% through 200 mesh). The rate equation is first order in the quantity of carbon left unreacted and CO$_2$ partial pressure

$$B = A_0 \exp\left(-\frac{E_a}{RT}\right) (P_{CO_2}) \ldots (6.65)$$
where \( A_0 = 3.13 \times 10^6 \) kg·mole kg·mole\(^{-1}\) kPa\(^{-1}\) s\(^{-1}\)
\[ E_a = 196200 \text{ kJ kg·mole}^{-1} \]
for the case defined above. Unfortunately there is little to compare this to. The value of the activation energy and pre-exponential constant are reasonable in terms of other data for coals of this reactivity. Because of the paucity of information these values will be used for all bituminous and sub-bituminous coals.

6.2.1.1.16 Model Solution

The model described above is an initial value problem in a system of ordinary differential equations. This was solved using a fourth order Runge-Kutta technique with error control developed by the University of British Columbia (U.B.C.) Computing Centre. A double precision form of the routine was used.

6.2.1.2 Secondary Bubble Residence Time

The char particle-bubble system continues to react with the slag according to the model developed in Section 6.2.1.1 until it reaches the surface of the slag. By this time its velocity relative to the slag should be sufficient to carry it to the surface where its contents will be released into the atmosphere above the bath, as illustrated in Fig. 6.12. The residence time of the secondary bubble obviously will be an
important factor in determining the extent to which the char particle is consumed and the amount of zinc oxide reduced.

To make an estimate of the residence time, a slag bath geometry shown in Fig. 6.16 was considered. The tuyere gas stream is assumed to rise up the furnace wall in a column the width of which is defined by the diameter of the tuyere bubbles. The tuyere bubbles are assumed to heat to bath temperature rapidly and reach their maximum diameter at the tuyere.

The volume of the tuyere bubble is therefore

\[ V_{tb} = \frac{ET_{sl}}{UT_{bl}^f} \] ...

(6.66)

where E is the blast flow rate and U is the number of furnace tuyeres. And

\[ d_{tb} = \left[ \frac{6V_{tb}}{\pi} \right]^{1/3} \] ...

(6.67)

If the porosity of the tuyere gas column, \( \varepsilon_t \), and the porosity of the bath, \( \varepsilon_{sl} \), are known, then a volume balance on the slag in the furnace will give the expected bath height, \( h \):

\[ \frac{M}{(1-\varepsilon_{sl})\rho_{sl}} = L(W-2d_{tb})h + 2 (1-\varepsilon_t) d_{tb} h L \]

Thus

\[ h = \frac{M}{(1-\varepsilon_{sl})\rho_{sl} L (W-2\varepsilon_t d_{tb})} \] ...

(6.68)
Tuyere gas column

Slag

(a) Top view

Tuyere gas column

Liquid slag

Secondary bubble path

$\epsilon_f$

$\epsilon_{sl}$

(d) Cross section

Figure 6.16 Secondary Bubble Residence Time Geometry
Assuming that on average, the secondary bubbles leave the slag half-way through their passage across the slag bath surface (See Fig. 6.16), the secondary bubble path length, \( p \), is

\[
p_r = h + \left[ \frac{W - 2d_{tb}}{4} \right] \quad \ldots (6.69)
\]

If the velocity of the slag bath is, \( v_{sl} \), then the secondary bubble residence time is

\[
t_{res} = \frac{p}{v_{sl}} \quad \ldots (6.70)
\]

To calculate \( t_{res} \), it is necessary to evaluate \( f, \varepsilon_t, \varepsilon_{sl} \) and \( v_{sl} \). The bubbling frequency, \( f \), has been measured and as discussed in Section 6.1.3 is roughly 6 bubbles per second. The porosity of the slag itself, \( \varepsilon_{sl} \), has been measured and the results reported in Table 6.2. An average value of the porosity is roughly 0.30. The porosity of the tuyere gas column is not as readily available. It probably will be greater than 0.30. The expected radius of tuyere bubbles at slag temperature is roughly equal to the spacing between tuyeres. The tuyere bubbles therefore can be expected to overlap. In addition the bubble diameter is roughly half of the calculated bath height. This suggests that if the bubbles rise very rapidly after detachment from the tuyere, the tuyere column porosity should be about 0.5. Since the rise following detachment is not instantaneous, the porosity is perhaps greater since the bubble is resident in the zone longer. A two-dimensional array of close packed bubbles will have a porosity of 0.60. This value
falls into the expected range but is not high, and will be used in the calculations.

Finally, the bath velocity must be known. As with the porosity of the gas column, no measurements of this parameter have ever been made. From the calculations of Ashman et al.\textsuperscript{116} and others\textsuperscript{117,118} it can be safely concluded that $v_{sl}$ is of the order of 1 m/s. The probable range of bath circulation velocity is 0.5 to 2 m/s. It will be assumed that $v_{sl}$ is 1 m/s as an average of this range.

For a furnace 4.5 m long by 2.5 m wide, containing 45 T of slag at 1200°C with a blast of 300 standard m$^3$/min blowing through 30 tuyeres, this calculation gives a residence time of 2.4 seconds. This appears to be an entirely reasonable estimate.

The model of the coal-slag reaction regime is now complete. It has been assumed that all of the coal entrained in the slag at the tuyere level leaves the bath when it reaches the surface. The fact that the charge port sampling reported in the thesis reveals coal particles and secondary bubbles with slag diffusion gradients clearly indicates that a certain amount of the coal circulates through at least one complete cycle of the furnace cell. To account for this phenomenon would introduce a degree of complexity that may not be warranted and cannot be immediately justified. As stated above, it will be assumed that this
fraction of the coal is negligible.

6.2.2 Kinetics in the Tuyere Gas Stream

Coal which is not entrained in the slag but remains in the tuyere gas stream will be subject to combustion. The fact that some coal penetrates into the slag means that the oxygen to fuel ratio in the tuyere gas stream is increased. If the fraction of entrained coal is significant then there may be an excess of oxygen present. However, even if this is not the case the oxygen potential will be high. Under these conditions it is unlikely that reduction of the slag will take place. Instead there probably will be oxidation of the ferrous iron according to Equation 6.61. In addition, of course, there will also be the combustion of coal.

The combustion of coal is a very complex phenomenon and a thorough analysis of submerged combustion is well beyond the scope of this thesis. As discussed earlier the ignition time of coal in the tuyere bubbles might be expected to be of the order of 30 ms. At a bubbling frequency of 7 per second, the bubble is resident at the tuyere for about 140 ms. Combustion therefore should be well under way before the bubble detaches. Following detachment the bubble rises rapidly to the surface and during the process, breaks up into smaller bubbles. The maximum residence time for the coal-air mixture under typical conditions might be 280 ms (calculated from the analysis
in Section 6.2.1.2).

According to Essenhigh\textsuperscript{136} particles in the size range of pulverized coal have a combustion time of the order of 1 second. Hottel and Stewart\textsuperscript{137} present data showing pulverized coal combustion to complete in 500 ms. They also indicate that under certain conditions combustion may be only 90% complete in 300 ms. Other work tends to support these figures.\textsuperscript{138}

Although no definite conclusions can be drawn from this analysis it does suggest that the assumption that combustion of coal in the tuyere gas stream is complete by the time the mixture leaves the surface of the bath, is probably not correct.

This has been verified by plant sampling at Company C. In addition to oxide fume, the slag fuming process produces two minor products: boiler ash and flue 'clinker'. Together ash and clinker make up about 5 to 10% of the total output. As shown in Table 6.4, in a typical cycle all three products contain carbon. A certain amount of coal passes through the bath and a certain fraction of this escapes combustion to end up in the fume, ash and clinker. As confirmation of this, the presence of burning coal in the flue from the furnace has been observed by the author.
<table>
<thead>
<tr>
<th></th>
<th>Fume</th>
<th>Ash</th>
<th>Clinker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>46</td>
<td>38</td>
<td>48</td>
</tr>
<tr>
<td>Pb</td>
<td>29</td>
<td>29</td>
<td>21</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.6</td>
<td>2.3</td>
<td>4.4</td>
</tr>
<tr>
<td>Fe</td>
<td>0.1</td>
<td>1.3</td>
<td>4.6</td>
</tr>
<tr>
<td>Cd</td>
<td>0.7</td>
<td>1.2</td>
<td>0.2</td>
</tr>
<tr>
<td>As</td>
<td>0.5</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>C</td>
<td>1.3</td>
<td>1.48</td>
<td>0.21</td>
</tr>
</tbody>
</table>
Slag fuming furnace product samples were taken for seven different runs. Measurements of initial and final bath composition and coal rate for each of these runs allowed a mass balance to be performed around the furnace. The collected data and details of the mass balance are presented in Appendix V. Due to uncertainties in the assays and a lack of knowledge of the relative amounts of the products, the balance could not be closed precisely. However the mass balance could be solved for the range of coal carry over into the products. The results of this analysis are presented in Table 6.5. The column titled "% Coal Carry Over as Coal" represents the coal carry over required to account for the carbon balance. The "% Coal Carry Over as Coal and Coal Ash" is the coal carry over required to account for the silica-to-iron ratio in the fume relative to the slag, as well as the carbon balance.

The results suggest that about 3% of the coal passes unconsumed through the furnace directly into the products. About 10% of the coal as coal and coal ash passes through the bath to be combusted in the flues. The alternative assumption that coal ash from coal-slag reaction or submerged combustion could escape the scrubbing action of the bath is unreasonable, due to the ability of the slag to wet the ash. As the coal particle-slag reaction model (Section 6.2.1.1) can be used to show under normal circumstances the coal entrained in the bath is completely consumed before it leaves the bath surface. Therefore, the coal which passes through the bath must be
TABLE 6.5

Mass Balance Calculation of Coal Carry Over

<table>
<thead>
<tr>
<th>Cycle</th>
<th>% Coal Carry Over As Coal</th>
<th>% Coal Carry Over As Coal &amp; Coal Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min.</td>
<td>Max.</td>
</tr>
<tr>
<td>C41</td>
<td>1.9</td>
<td>2.7</td>
</tr>
<tr>
<td>C42</td>
<td>4.3</td>
<td>5.1</td>
</tr>
<tr>
<td>C43</td>
<td>2.9</td>
<td>3.3</td>
</tr>
<tr>
<td>C44</td>
<td>2.6</td>
<td>2.9</td>
</tr>
<tr>
<td>C51</td>
<td>2.8</td>
<td>3.8</td>
</tr>
<tr>
<td>C52</td>
<td>3.8</td>
<td>4.6</td>
</tr>
<tr>
<td>C53</td>
<td>3.3</td>
<td>3.8</td>
</tr>
</tbody>
</table>
associated with the tuyere gas stream.

Given that a portion of the coal is entrained in the slag and a portion of remaining tuyere stream coal passes unreacted out of the bath, a considerable excess of oxygen will be present in the tuyere gas stream. For this reason it will be assumed that the coal which does burn in this zone burns completely to CO₂ and H₂O. As mentioned earlier, the oxidation of ferrous to ferric iron will be the other major reaction taking place in the tuyere stream.

6.2.3 Wall Effects

The third dynamic zone of the furnace is the water-jacketed wall. Because temperature changes in the bath result in melting and freezing of the slag from the wall, the wall plays a role in the composition-time profiles observed during furnace operation. Furthermore the water-jacketed walls represent a significant thermal burden on the process and therefore an important consideration in the bath heat balance.

Unfortunately little is known of the behaviour of a water-jacketed wall in a slag bath. It is not known whether the melting-freezing of slag is entirely a thermal phenomenon or if it involves chemical reactions and equilibrium phase precipitation. Only a few experimental studies have been performed. These have been done simply to measure
heat transfer coefficients and no microscopic examination of the frozen slag was made. To avoid all of these problems it will be assumed that temperature changes in the bath are sufficiently slow that the wall responds in a quasi-steady state manner. In addition it will be assumed that the wall melts and freezes a constant slag composition. This avoids the problem of modelling a continuously varying slag layer composition. This refinement could be made when the phenomenon is better understood.

The heat transfer from the slag bath to the frozen slag layer has been characterized by the empirical equation

\[ \dot{q} = h_t A (T_{sl} - T_{mp}) \]  

...(6.71)

where \( T_{mp} \) is the slag melting point. By performing a steady state heat balance on the furnace wall, the following equation can be developed for the thickness of the slag layer

\[ d_{sl} = \left( \frac{g_{sl}}{h_t} \right) \left( \frac{T_{mp} - T_w}{T_{sl} - T_{mp}} \right) - \frac{d_{st}}{g_{sl}} \]  

...(6.72)

where \( g \) is thermal conductivity and \( T_w \) is the temperature of the water in the water jacket. See Appendix VI.

To solve this equation several parameters must be evaluated of which \( g_{sl} \), \( h_t \) and \( T_{mp} \) are critical. Values of \( g_{sl} \) and \( h_t \) reported in the literature are given in Table 6.6. Because the frozen slag-bath interface is highly stirred, heat transfer should be in the high end of the range quoted for \( h_t \). A value
### TABLE 6.6

**Heat Transfer Parameters**

<table>
<thead>
<tr>
<th>Reference</th>
<th>$g_{sl}$ $\frac{\text{W}}{\text{m} \cdot \text{K}}$</th>
<th>$h_t$ $\frac{\text{W}}{\text{m}^2 \cdot \text{K}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.67</td>
<td>615</td>
</tr>
<tr>
<td>43</td>
<td>1.26</td>
<td>404</td>
</tr>
<tr>
<td>139</td>
<td>1.24</td>
<td>325</td>
</tr>
<tr>
<td>141</td>
<td>--</td>
<td>335-500</td>
</tr>
</tbody>
</table>
of 600 w/m$^2$-K was assumed. An intermediate value of slag thermal conductivity, 1.5 w/m-K was assumed.

In order to avoid potential problems it will be assumed that sufficient slag is present on the wall initially, to supply whatever melting takes place. The conductivity of the steel is about 50 w/m-K. A steel thickness, $d_{st}'$, of 1 cm will be assumed. The term $d_{st}' g_{sl}/g_{st}'$ is not important because it is about two orders of magnitude smaller than the other term in Equation 6.72.

The question of the slag melting point is difficult to resolve. It would be legitimate to hold that the single-valued property $T_{mp}$ is not a valid concept. As a first approximation however, it is justified because the empirical heat transfer, Equation 6.71, was initially used to derive $h_t$ from measured data. The 'melting point' of the slag has been established to be in the range 1100°C to 1150°C. Kellogg uses a value of 1125°C. This value is consistent with the CaO-FeO-SiO$_2$ ternary and other data and therefore, will be used.

The temperature of the cooling water will be assumed to be 50°C. This is not a critical parameter.
It remains to determine what the composition of the wall slag normally is. A sample of wall material taken during an accidental shutdown of a fuming furnace at Company C was split vertically and the inner and outer sections assayed separately. The total frozen wall thickness was about 2.3 cm. This is consistent with Equation 6.72 which gives a thickness of 2.7 cm for a bath temperature of 1225°C. The assay results are given in Table 6.7.

In this sample there appears to be no significant variation through the thickness. This supports the idea that the frozen slag layer has a homogeneous composition. The most striking feature of the assays is the very high ferric iron content which is about ten times the normal bath level. This observation confirms that the tuyere gas stream is highly oxidizing. The zinc content of the wall is approximately midway between the level in slag charged and slag tapped. The lime and silica levels are reduced somewhat from their levels in the bath. This and the high level of ferric iron in the slag suggest that freezing involves a certain degree of equilibrium precipitation. In the absence of other data it will be assumed that the wall composition is 10% Zn, 17% Fe$^{2+}$, 15% Fe$^{3+}$, 10% CaO and 20% SiO$_2$. In addition since the wall slag is slightly porous, it will be assumed that it has a density equal to the liquid.
TABLE 6.7

Frozen Wall Slag Assays
(values in %)

<table>
<thead>
<tr>
<th></th>
<th>Inner Half</th>
<th>Outer Half</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>10.9</td>
<td>12.7</td>
</tr>
<tr>
<td>Pb</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>17.5</td>
<td>15.5</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>15.4</td>
<td>19.6</td>
</tr>
<tr>
<td>S</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>C</td>
<td>0.11</td>
<td>0.52</td>
</tr>
<tr>
<td>CaO</td>
<td>9.5</td>
<td>6.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>22.5</td>
<td>18.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.9</td>
<td>6.8</td>
</tr>
</tbody>
</table>
To melt the slag and heat it to bath temperature absorbs a certain quantity of heat. Grant and Barnett 44 give the heat of fusion, $\Delta H_{\text{fus}}$, as 3412000 J/kg and the slag heat capacity, $C_{p,\text{sl}}$, as 873.2 J/kg-K. Since this data is in agreement with Kellogg 43 and other sources, it will be used.

Finally since the bottom of the furnace is water cooled as well, it will be assumed to behave as the wall and be included in the wall area:

$$A_w = 2h(L+W) + LW \quad \ldots(6.73)$$

### 6.2.4 Other Considerations

The three major dynamic aspects of the process have been characterized. Before proceeding to the process model, two points must be considered.

First, it will be assumed that the surface of the bath is not a reaction site. It is anticipated that the furnace atmosphere is very turbulent and well mixed. Gases emerging from the tuyere gas stream will be rapidly mixed with gases emerging from the bath, as well as the unregulated tertiary air that leaks through the charge port and other places. The net effect will be to create an oxidizing atmosphere. Any oxidation in this region will be accounted for in the tuyere gas stream.
Second, the dynamics of furnace charging and tapping will not be addressed. During charging the behaviour of the process is strongly influenced by the following variables, (a) the ratio of solid to liquid slag charged, (b) the temperature of each charge, and (c) the time between charges to the furnace. During charging and tapping, (d) furnace mixing characteristics, and (e) the changes in injection dynamics with changes in bath depth are important variables. These are significant factors in furnace operations and are definite kinetic processes. A proper analysis of these questions would involve a study at least as long as the present one. Furthermore, the general objectives and the techniques of investigation would be quite different.

6.2.5 **Kinetic Model of the Process**

The three dynamic zones in the furnace are tied together by a kinetic process which has not yet been quantified: the partitioning of coal between the slag, the tuyere gas stream and the carry over. In addition there is a third parameter, the amount of oxygen in the tuyere stream that oxidizes ferrous to ferric iron. These factors cannot be estimated a priori and therefore must be derived from industrial data. The model must be fitted with these parameters.

If $F$ is the fraction of coal which is entrained in the slag and reacts to produce secondary bubbles, $Y$ is the fraction
of coal consumed in the tuyere gas stream and $Y_0$ is the fraction of coal that passes unconsumed through the bath (see Fig. 6.17):

$$ F + Y + Y_0 = 1 \quad \text{...(6.74)} $$

Finally, $F_{oc}$ will be defined as the fraction of oxygen in the tuyere gas stream unconsumed by coal which reacts with ferrous iron.

A kinetic model of the process can now be assembled by performing balances on the slag bath, incorporating the ideas discussed above. All rates are expressed in kg-mole/s.

6.2.5.1 Zinc Balance

Zinc is reduced from the bath in the secondary bubbles which leave the bath at residence time, $t_{res}$. If $c_{b,f}^j$ represents the final concentration of species $j$ in the secondary bubble, the rate of zinc reduction is

$$ r_{Zn}^F = \frac{c_{Zn}^b}{C_{H_2}^{b,f} + C_{H_2O}^{b,f}} \cdot \frac{F C c_{vol} v_H}{2.016} \quad \text{...(6.75)} $$

where $C$ is the coal rate (kg/s); $c_{vol}$, the weight fraction volatiles in the coal; and $v_H$, the weight fraction of hydrogen in the volatiles.
Fig. 6.17 Schematic of Coal Partition in Furnace
Zinc enters the slag as a result of wall melting:

\[
\dot{m}_{Zn} = - \frac{W_{Zn}}{65.37} \rho_{sl,s} \frac{dV_w}{dt} \quad \ldots(6.76)
\]

where \( W_{Zn} \) is the weight fraction zinc in the wall slag layer, and \( V_w \) is the wall volume.

The overall balance is then

\[
(r_{Zn}^m - r_{Zn}^r) 65.37 = \frac{d(F_{Zn}^{sl} M)}{dt} \quad \ldots(6.77)
\]

thus

\[
\frac{dF_{Zn}^{sl}}{dt} = \frac{65.37(r_{Zn}^m - r_{Zn}^r)}{M} - \frac{F_{Zn}^{sl} M}{M} \frac{dM}{dt} \quad \ldots(6.78)
\]

where \( F_{Zn}^{sl} \) is the weight fraction of species \( j \) in the slag.

6.2.5.2 Ferric Iron Balance

Ferric iron is reduced at a rate equivalent to the rate of oxygen pickup of the secondary bubbles minus the oxygen present, due to volatile oxygen and zinc oxide reduction.

\[
\dot{r}_{Fe^{3+}} = 2 \left[ \frac{(C_{CO}^{b,f} + 2C_{CO_2}^{b,f} + C_{H_2O}^{b,f})}{(C_{H_2}^{b,f} + C_{H_2O}^{b,f})} \right] \frac{FC_{vol}V_H}{2.016} \quad \ldots(6.79)
\]

\[
- \dot{r}_{Zn} - \frac{FC_{vol}V_0}{16.00}
\]
The factor 2 appears in the equation because two ferric ions are reduced for every oxygen oxidized.

Ferric iron enters the bath due to wall melting:

\[ \frac{\dot{r}_m}{\text{Fe}^{3+}} = -\frac{W_{\text{Fe}^{3+}}}{55.85} \rho_{s1,s} \frac{dV_w}{dt} \]  \ ...(6.80)

Ferric iron is also produced by ferrous oxidation at the tuyere. This requires that tuyere stream combustion be dealt with. It is assumed that the coal which burns in the tuyere (fraction Y) burns completely to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \). Therefore,

\[ \dot{r}_C = Y \left[ \frac{C(c_{\text{fC}} + c_{\text{volC}})}{12.01} + \frac{C c_{\text{volH}}}{2(2.016)} \right. \]
\[ \left. - \frac{C c_{\text{volO}}}{32.0} \right] \]  \ ...(6.81)

If \( \dot{r}_{O_2} \) is the oxygen input to the furnace, then

\[ \frac{\dot{r} \circ}{\text{Fe}^{2+}} = 4 F_{\text{OC}} (\dot{r}_{O_2} - \dot{r}_C) \]  \ ...(6.82)

The overall ferric balance is then

\[ \left[ \frac{\dot{r} \circ}{\text{Fe}^{2+}} + \frac{\dot{r}_m}{\text{Fe}^{3+}} + \frac{\dot{r} r}{\text{Fe}^{3+}} \right] 55.85 = \frac{d(F_{s1}^{\text{Fe}^{3+}} M)}{dt} \]  \ ...(6.83)

and

\[ \frac{dF_{s1}^{\text{Fe}^{3+}}}{dt} = \frac{55.85}{M} \left[ \frac{\dot{r} \circ}{\text{Fe}^{2+}} + \frac{\dot{r}_m}{\text{Fe}^{3+}} - \frac{\dot{r} r}{\text{Fe}^{2+}} \right] -F_{\text{Fe}^{3+}} \frac{dM}{dt} \]  \ ...(6.84)
6.2.5.3 Ferrous Iron Balance

The ferrous iron balance reflects the ferric balance, except for the melting/freezing term

\[ \frac{r^m_{Fe^{2+}}}{55.85} = \frac{W_{Fe^{2+}}}{55.85} \rho_{sl,s} \frac{dV_w}{dt} \quad \ldots (6.85) \]

The ferrous balance gives

\[ \frac{dF_{Fe^{2+}}}{dt} = \frac{55.85}{M} \left[ \frac{r^r_{Fe^{3+}}}{Fe^{3+}} + \frac{r^m_{Fe^{2+}}}{Fe^{2+}} - \frac{r^o_{Fe^{2+}}}{Fe^{2+}} \right] \]

\[ - \frac{F_{sl}^{Fe^{2+}}}{Fe^{2+}} \frac{dM}{dt} \quad \ldots (6.86) \]

6.2.5.4 Lime Balance

Lime enters or leaves the slag by melting or freezing on the wall.

\[ \frac{r^m_{CaO}}{56.0} = \frac{W_{CaO}}{56.0} \rho_{sl,s} \frac{dV_w}{dt} \quad \ldots (6.87) \]

Therefore

\[ \frac{dF_{sl}^{CaO}}{dt} = \frac{56.0}{M} \frac{r^m_{CaO}}{CaO} - \frac{F_{sl}^{CaO}}{CaO} \frac{dM}{dt} \quad \ldots (6.88) \]
6.2.5.5 Silica Balance

Silica participates in the wall melting and freezing

\[ \dot{r}_{SiO_2}^m = - \frac{W_{SiO_2}}{60.0} \rho_{sl,s} \frac{dV_w}{dt} \]  

(6.89)

In addition, it is the major constituent of coal ash. Assuming that the coal ash is all silica:

\[ \dot{r}_1 = \frac{F_C c_{ash}}{60.0} \left[ 1 - \frac{G^f}{\frac{c_{fc}}{12.01} + \frac{c_{volC}}{16.00}} \right] \frac{\rho c^4 r^3}{3} \]  

(6.90)

where \( r_1 \) is the rate of ash addition to the slag from the entrained coal. Performing a balance yields:

\[ \frac{dF_{SiO_2}^{sl}}{dt} = \frac{1}{M} (60.0 \dot{r}_{SiO_2}^m + YC c_{ash} + 60.0 \dot{r}_1) \]

\[ + \frac{F_{SiO_2}}{M} \frac{dM}{dt} \]  

(6.91)

6.2.5.6 Slag Wall Volume

The equation for the wall volume is:

\[ V_w = d_{sl} A_w \]  

(6.92)

Differentiating yields

\[ \frac{dV_w}{dt} = A_w \frac{d(d_{sl})}{dt} + d_{sl} \frac{dA_w}{dt} \]  

(6.93)
6.2.5.7 **Slag Wall Area**

Differentiating Equation 6.73 gives

\[
\frac{dA_w}{dt} = 2(L + W) \frac{dh}{dt} \quad \ldots (6.94)
\]

6.2.5.8 **Slag Wall Thickness**

Differentiating Equation 6.72 gives

\[
\frac{d(d_{sl})}{dt} = \frac{\left[ g_{sl} \right]}{h_{c}} \left[ \frac{(T_{mp} - T_w)}{(T_{sl} - T_{mp})^2} \right] \frac{dT_{sl}}{dt} \quad \ldots (6.95)
\]

6.2.5.9 **Slag Bath Mass Balance**

The mass of the bath changes as a result of these reactions:

\[
\frac{dM}{dt} = - \dot{r}_{\text{Zn}} \text{(81.37)} - \dot{r}_{\text{Fe}^3+} \text{(8.00)} + \dot{r}_{\text{Fe}^{2+}} \text{(8.00)}
\]

\[
+YC_c \text{ash} + \dot{r}_{l} \text{(60.0)} + \rho_{sl,s} \frac{dv_w}{dt} \quad \ldots (6.96)
\]

6.2.5.10 **Bath Height**

Differentiating Equation 6.69 gives

\[
\frac{dh}{dt} = \frac{1}{(1-\epsilon_{sl}) \rho_{sl} L(2\epsilon_{l} - \ell_{tb})} \frac{dM}{dt} \quad \ldots (6.97)
\]
6.2.5.11 Bath Heat Balance

The heat balance includes the following terms

\[ \dot{q}_w = h_t A_w (T_{sl} - T_{mp}) \quad \ldots (6.71) \]

Assuming the tuyere gas stream leaves at bath temperature:

\[ \dot{q}_{tg} = \dot{r}_{iO_2} c_{p,O_2} (T_{sl} - T_{bl}) + \dot{r}_{iN_2} c_{p,N_2} (T_{sl} - T_{bl}) \]

\[ + C (1 - c_{moist}) c_{p,coal} \]

\[ + \frac{C c_{moist}}{18.01} (\Delta H_w + c_{p,H_2O}(T_{sl} - 373.16)) \]

\[ + YC \left[ \frac{c_{fc} + c_{vol} v_c}{12.01} \Delta H_7 + \frac{c_{vol} v_H}{2.016} \Delta H_9 \right] \quad \ldots (6.98) \]

and

\[ \dot{q}^{°}_{Fe^{2+}} = \dot{r}^{°}_{Fe^{2+}} \Delta H_5/4(1.5-1/x) \quad \ldots (6.99) \]

In the secondary bubbles;

\[ \dot{q}^r = -\dot{r}^r_{Zn} (\Delta H_{10} + \Delta H_{s,ZnO}) - \dot{r}^r_{Fe^{3+}} \Delta H_5/4(1.5-1/x) \]

\[ + R_H (C_{CO}^{b,f} \Delta H_8 + C_{CO_2}^{b,f} \Delta H_7 + C_{H_2O}^{b,f} \Delta H_9) \quad \ldots (6.100) \]

where

\[ R_H = \frac{FC c_{vol} v_H}{2.016(C_{H_2}^{b,f} + C_{H_2O}^{b,f})} \quad \ldots (6.101) \]

\[ \Delta H_{s,ZnO} \] is the heat of solution of ZnO in the slag

(19680 J/kg·mole)
and
\[ \dot{q}_m = - \rho_{sl,s} \frac{dV_w}{dt} (\Delta H_{\text{fus}} + c_{p,sl}(T_{sl} - T_{mp})) \]  \hspace{1cm} (6.102)

Finally, it is assumed that due to the presence of oxide fume in the atmosphere, the water cooling of the upper furnace walls and the in flow of tertiary air, there is no net heat exchange between the bath and the free board gases.

Combining gives
\[ \dot{q}_w + \dot{q}_{tg} + \dot{q}_{\text{Fe}^2+}^{o} + \dot{q}_r + \dot{q}_m = -c_{p,sl} \frac{d(MT_{sl})}{dt} \]  \hspace{1cm} (6.103)

and
\[ \frac{dT_{sl}}{dt} = \frac{1}{M} \left[ - \frac{1}{c_{p,sl}} (\dot{q}_w + \dot{q}_{tg} + \dot{q}_{\text{Fe}^2+}^{o} + \dot{q}_r + \dot{q}_m) - T_{sl} \frac{dM}{dt} \right] \]  \hspace{1cm} (6.104)

6.2.5.12 Solution of the Model

This system of eleven equations was solved using a first order Euler method with a time step of 2 minutes. The use of a second order improved Euler method showed no significant improvement over the first order method. The program written to solve the system is reproduced in Appendix VII.
6.4 Discussion of Model Fitting

The complete model, consisting of the coal-particle-slag reaction model, residence time calculation, and bath model, was used to analyse the industrial fuming cycles presented in Chapter 5, Fig. 5.1 to 5.11. The objective was to determine those values of $F$, $Y$ and $F_{oc}$ which gave the best fit to the measured data for each individual cycle. The results of the fitting are presented in Fig. 6.18 to 6.28. In these figures, the symbols are the measured data points and the solid lines, the model predictions. The important species, Zn, $Fe^{3+}$ and $Fe^{2+}$ are presented together with the temperature profile. The predicted level of CaO is given in each to show the behaviour of an inert compound.

The model is seen to replicate the industrial data reasonably well. Two cycles however are only satisfactory. In cycle B1 the model was unable to account for furnace behaviour during the first 20 minutes. The slow fuming rate during this period is inconsistent with the remainder of the cycle. A likely explanation for this is that in the first part of the cycle, solid charge material, high in zinc, was melting into the bath. The model appears to be able to account for the rest of the cycle. However, note that 'x' must be lowered to 0.96 in order to achieve the required fuming rates in the presence of the ferric level. This may in part be due to the relatively higher levels of iron in the slag.
Fig. 6.20  Cycle A2B, Industrial Data and Model Fit
Fig. 6.21 Cycle Bl, Industrial Data and Model Fit
Fig. 6.23
Cycle B22, Industrial Data and Model Fit

Elapsed time (min)

Temperature (°C)

% Fe$^{2+}$

% Zn, Fe$^{3+}$

% CaO

Fe$^{3+}$

Zn

Fe$^{2+}$

Model:
Data:
symbols

1180

1220
Fig. 6.24 Cycle Cl, Industrial Data and Model Fit
Fig. 6.25  Cycle C2, Industrial Data and Model Fit
Fig. 6.26    Cycle D1, Industrial Data and Model Fit
Fig. 6.27  Cycle D2, Industrial Data and Model Fit
In cycle C2, Fig. 6.25, there is a serious deviation between the model and the data. A possible explanation for this run is that due to the enormous changes in the coal rate (see Fig. 5.8) the parameters \( F \), \( Y \) and \( F_{oc} \) are not constant through the cycle. At high loadings there may be a significant drop in the coal particle velocity resulting in a drop in \( F \). \( Y \) may change significantly under these conditions as well. In addition the inability to follow the ferric iron peak may reflect the existence of kinetic or thermodynamic saturation of the bath in magnetite. The large and rapid changes in temperature observed in this cycle may have resulted in wall effects that were not effectively handled by the model.

Although there are obviously improvements that could be made, the model is able to account for fuming operation under normal conditions. The model can be adjusted to match the behaviour in each of five different operations reasonably well. Predictions of zinc elimination and ferrous iron profiles are good. Predictions of ferric iron, temperature and inert behaviour are satisfactory.

What is most significant however is the consistency of the fitting parameters over the five operations. As shown in Table 6.8 the variation in \( F \) and \( Y \) is well within an expected range of uncertainty. The values of \( Y_o \), the fraction of coal un-consumed, are consistent with the mass balance calculations made in Section 6.2.2. The value of \( F \) lies in the range 0.28
<table>
<thead>
<tr>
<th>CYCLE</th>
<th>F</th>
<th>Y</th>
<th>Y₀</th>
<th>F₀c</th>
<th>X</th>
<th>% O₂ Utilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.33</td>
<td>0.55</td>
<td>0.12</td>
<td>0.16</td>
<td>0.99</td>
<td>73</td>
</tr>
<tr>
<td>A2A</td>
<td>0.28</td>
<td>0.52</td>
<td>0.20</td>
<td>0.12</td>
<td>0.99</td>
<td>71</td>
</tr>
<tr>
<td>A2B</td>
<td>0.30</td>
<td>0.57</td>
<td>0.13</td>
<td>0.13</td>
<td>1.00</td>
<td>80</td>
</tr>
<tr>
<td>B1</td>
<td>0.37</td>
<td>0.57</td>
<td>0.06</td>
<td>0.34</td>
<td>0.96</td>
<td>87</td>
</tr>
<tr>
<td>B21</td>
<td>0.37</td>
<td>0.60</td>
<td>0.03</td>
<td>0.45</td>
<td>1.00</td>
<td>92</td>
</tr>
<tr>
<td>B22</td>
<td>0.32</td>
<td>0.54</td>
<td>0.14</td>
<td>0.24</td>
<td>0.99</td>
<td>85</td>
</tr>
<tr>
<td>C1</td>
<td>0.29</td>
<td>0.54</td>
<td>0.17</td>
<td>0.04</td>
<td>1.00</td>
<td>67</td>
</tr>
<tr>
<td>C2</td>
<td>0.26</td>
<td>0.45</td>
<td>0.29</td>
<td>0.44</td>
<td>0.975</td>
<td>--</td>
</tr>
<tr>
<td>D1</td>
<td>0.37</td>
<td>0.49</td>
<td>0.14</td>
<td>0.53</td>
<td>0.99</td>
<td>92</td>
</tr>
<tr>
<td>D2</td>
<td>0.39</td>
<td>0.41</td>
<td>0.20</td>
<td>0.42</td>
<td>0.99</td>
<td>83</td>
</tr>
<tr>
<td>E1</td>
<td>0.33</td>
<td>0.62</td>
<td>0.05</td>
<td>0.29</td>
<td>1.00</td>
<td>94</td>
</tr>
</tbody>
</table>

TABLE 6.8
Model Parameters
to 0.39 (excluding C2). On average then, about 33% of the coal injected into a fuming furnace is entrained in the slag. About 55% of the coal burns in the tuyere gas stream and the balance, about 12%, passes through the bath unconsumed.

The values of $F_{QC}$, the fraction of oxygen remaining after the combustion of the tuyere coal (fraction $Y$) which reacts with ferrous iron, show a wide variation. Because there is no evident pattern to these values, it is probably not the correct way to quantify the oxidation of iron. The oxygen utilization however, calculated from $Y$ and $F_{OC}$, shows more consistent behaviour. However, there is still a significant variation between operations. If the oxygen utilization is compared to the calculated slag bath depth, a reasonable correlation can be seen. (Table 6.9.) The operation with the lowest slag depth, Company C, has the lowest oxygen utilization. Bath depth increases from C to A, then B, D and finally Company E. Average oxygen utilization also increases in this order. This suggests that the observed range of values is a reflection of a real difference due in fact to slag depth. It should be noted that in this thesis it has been assumed that there is no leakage of air from the tuyeres. It has been suggested that a leakage of 5% of the air occurs through the tuyere ball valves. 43,44,45 If this indeed is the case, the oxygen utilizations in Tables 6.7 and 6.8 would be increased by about 5%. This would give operations B, D and E utilizations in excess of 90%. Company A would have a utilization of 80% and Company C, 70%. Values
<table>
<thead>
<tr>
<th>Cycle</th>
<th>% Oxygen Utilization</th>
<th>Calculated Bath Depth h (m)</th>
<th>Quiescent Bath Depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>73</td>
<td>1.7</td>
<td>0.82</td>
</tr>
<tr>
<td>A2A</td>
<td>71</td>
<td>1.7</td>
<td>0.82</td>
</tr>
<tr>
<td>A2B</td>
<td>80</td>
<td>1.8</td>
<td>0.86</td>
</tr>
<tr>
<td>B1</td>
<td>87</td>
<td>2.0</td>
<td>0.94</td>
</tr>
<tr>
<td>B21</td>
<td>92</td>
<td>1.9</td>
<td>0.90</td>
</tr>
<tr>
<td>B22</td>
<td>85</td>
<td>1.95</td>
<td>0.92</td>
</tr>
<tr>
<td>C1</td>
<td>67</td>
<td>1.0</td>
<td>0.56</td>
</tr>
<tr>
<td>C2</td>
<td>--</td>
<td>1.0</td>
<td>0.55</td>
</tr>
<tr>
<td>D1</td>
<td>92</td>
<td>2.1</td>
<td>1.03</td>
</tr>
<tr>
<td>D2</td>
<td>83</td>
<td>2.1</td>
<td>1.04</td>
</tr>
<tr>
<td>E1</td>
<td>94</td>
<td>2.3</td>
<td>1.15</td>
</tr>
</tbody>
</table>
above 80% are consistent with measurements in copper converters. 117

The general agreement of fitted parameters within the context of a model that contains so many estimated values is strong evidence that the model is an important step in defining the kinetics of the process. Considering all of the differences in variables between operations such as slag depth, coal type, blast preheat, coal rate, furnace dimensions, slag composition and blast flow rate, the ability of the model to extract such constant parameters is confirmation of a correct conception.

It remains to assess the sensitivity of the model to important parameters and check the model against industrial observations. And finally, by an analysis of model predictions, determine the controlling kinetic processes.
CHAPTER VII

SENSITIVITY ANALYSIS AND MODEL PREDICTIONS:
KINETIC DESCRIPTION OF SLAG FUMING

In order to come to an understanding of the dynamics of the zinc slag fuming process, it is necessary to move from detailed kinetic considerations to the integrated effect of these phenomena over time. It is only from this perspective that the critical factors in furnace operation can be identified. It is therefore important that this study begin with an analysis of the sensitivity of the model to fitted parameters and parameters such as bath velocity which represent only best guesses. For purposes of this analysis, a standard case was selected which represented an 'average' of the different operations studied in this thesis. These process parameters are listed in Table 7.1

7.1 Sensitivity Analysis

The central focus of the kinetic model is the fraction of coal which is entrained in the slag, F. The sensitivity of the process to F is illustrated in Fig. 7.1. The standard case, F = 0.35, is shown as line 2. An increase in F to 0.40 brings about an increase in the fuming rate resulting in a decrease in the Zn concentration in the slag of 0.75% in 100 minutes. The increased fuming rate increases the heat load on the process and therefore brings about a greater decline in temperature. The freezing of slag resulting from this gives the Zn and Fe$^{3+}$
### TABLE 7.1

**Standard Conditions for Slag Fuming Predictions**

<table>
<thead>
<tr>
<th>Operating Parameters</th>
<th>Slag Data:</th>
<th>Coal Data:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F = 0.35$ $F_{oc} = 0.35$</td>
<td>Initial Composition</td>
<td>Assay 0.50 F.C. (wt. fr) 0.25 Vol</td>
</tr>
<tr>
<td>$Y = 0.55$</td>
<td>14% Zn</td>
<td>0.15 Ash</td>
</tr>
<tr>
<td>$Y_{o} = 0.10$</td>
<td>25% Fe$^{2+}$</td>
<td>0.10 Moist.</td>
</tr>
<tr>
<td>Furnace Dimensions</td>
<td></td>
<td>Volatile 0.50 C</td>
</tr>
<tr>
<td>$L = 4.5$ m $W = 2.5$ m</td>
<td>Initial T = 1473 K</td>
<td>Comp. 0.20 H (wt. fr) 0.20 O</td>
</tr>
<tr>
<td>Injection Dynamics</td>
<td>Initial Wt = 45 T</td>
<td>0.05 N</td>
</tr>
<tr>
<td>Bath Velocity = 1 ms$^{-1}$</td>
<td>Porosity = 30%</td>
<td>Rate = 65 kg min$^{-1}$</td>
</tr>
<tr>
<td>No. of Tuyeres = 30</td>
<td>Density = 3900 kg m$^{-3}$</td>
<td>Density = 1500 kg m$^{-3}$</td>
</tr>
<tr>
<td>Bubble Freq. = 7 s$^{-1}$</td>
<td>Viscosity = 0.50 kg m$^{-1}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Tuyere Column Void Fr = 0.60</td>
<td>$D_{FeO}$ / $D_{Fe_2O_3} = 10$</td>
<td>Blast : Air</td>
</tr>
<tr>
<td>Boudouard Reaction</td>
<td>$Fe_xO$ $x = 0.99$</td>
<td>Primary : 30 m$^3$ min$^{-1}$,STP</td>
</tr>
<tr>
<td>$A_{O} = 3.16 \times 10^{10}$ kPa$^{-1}$ s$^{-1}$</td>
<td></td>
<td>$20^\circ C$</td>
</tr>
<tr>
<td>$E_a = 196200$ kJ kg·mole$^{-1}$</td>
<td></td>
<td>Secondary :</td>
</tr>
<tr>
<td></td>
<td></td>
<td>322 m$^3$ min$^{-1}$ STP</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$20^\circ C$</td>
</tr>
</tbody>
</table>
Fig. 7.1 The Effect of 'F' on Predicted Fuming Behavior
curves a steeper slope than is seen for \( F = 0.35 \). Later in the cycle as the rate of zinc reduction slows, the thermal burden decreases and the temperature starts to rise. Melting of wall slag results, which feeds additional zinc and ferric iron into the bath giving an increased ferric level and a definite reduction in the slope of the zinc elimination curve. The leveling out of the zinc curve is also due in part to the higher ferric iron level which competes with zinc for carbon.

A decrease in \( F \) to 0.30, the lower limit of values obtained during fitting, gives slower fuming rates and an increase in the final zinc concentration of 1.5% in 100 minutes. Due to a lack of a significant change in temperature during the first half of the cycle the fuming rate is relatively constant. Toward the end however, as the thermal burden declines, the temperature starts to rise, melting of wall slag occurs which produces a slight decrease in the slope of the zinc curve.

It is apparent that the model is moderately sensitive to the value of \( F \). Since \( F \) essentially represents the amount of reductant which is available to the slag this effect is not surprising. If the values of \( F \) at each operation are examined, see Table 6.7, it can be seen that with the exception of cycle B22, the values are reasonably consistent at each operation. The variation in \( F \) may then reflect to some extent, variations in injection conditions. It is interesting to note that the operations with the higher values of \( F \), i.e. B and D, are also
those with the higher blast intensities expressed as blast volume flow rate at bath temperature per unit area of furnace cross-section. Some differences in $F$ are therefore to be expected and the observed variations are probably legitimate.

The effect of the fraction of coal combusted, $Y$, on the process, all other variables constant, is shown in Fig. 7.2. Over the range 0.45 to 0.65 $Y$ has a significant influence on fuming. Increasing $Y$ to 0.65 increases fuming rates, resulting in a decrease of 1.7% in the final zinc concentration in 100 minutes. Decreasing $Y$ to 0.45 results in a 2% increase in zinc concentration in 100 minutes of fuming. $Y$ also has a significant influence on bath temperature, but most important is the effect on ferric iron levels. Owing to the manner in which the model is formulated a constant fraction of the oxygen remaining after coal combustion, $F_{OC}$, reacts with ferrous iron in the slag. Increasing $Y$ therefore has the effect of consuming more oxygen in the tuyere stream and reducing the amount available for ferrous oxidation. Thus increasing $Y$ reduces the ferric level in the bath and therefore the amount of ferric iron competing with zinc for reduction. Zinc reduction is thereby increased. Reducing $Y$ has the opposite effect.

A majority of the fitted $Y$ values ended up in the range 0.5-0.6 (see Table 6.7) so in most cases, the variations are not as dramatic as illustrated in Fig. 7.2. Furthermore, as discussed in Section 6.4, the model has indicated that a better
Fig. 7.2 The Effect of 'Y' on Predicted Fuming Behavior
way of handling the oxygen utilization in the tuyere gas stream may be to express it as a function of bath depth. This would then require a partition to be made between coal combustion and ferrous iron oxidation. If a relatively constant fraction of the coal is combusted \((Y = 0.55)\) then the difference between the oxygen used for combustion and the overall utilization would oxidize ferrous iron.

The same questions are raised by an analysis of the effect of \(F_{OC}\). The effect of \(F_{OC}\) is similar. Increasing \(F_{OC}\) from the standard condition, \(F_{OC} = 0.30\), to 0.45 increases the temperature and level of ferric iron in the bath. See Fig. 7.3. The fuming rate is consequently slowed. Decreasing \(F_{OC}\) to 0.15 decreases the ferric iron, allowing more rapid reduction of zinc, resulting in significant cooling of the bath. In the latter part of the run when zinc reduction rate decreases, the temperature starts to rise, melting of wall slag begins and material high in zinc enters the bath, producing a noticeable decrease in the slope of the zinc elimination curve.

The effect of \(F_{OC}\) is essentially the same as that of \(Y\), and the same considerations apply. As discussed in Section 6.4, \(F_{OC}\) is probably not the best way of representing ferrous iron oxidation. Instead, total oxygen utilization as a function of slag depth seems to be a more realistic parameter. To quantify this effect however, would require a special set of industrial experiments.
Fig. 7.3 The Effect of $F_{oc}$ on Predicted Fuming Behavior
In addition to the fitted parameters \( F, Y \) and \( F_{oc} \), there are several model parameters which could at best only be good guesses. These include the slag bath circulation velocity, \( v_{sl} \); the coal particle radius or coal particle clustering effect, \( r_p \); the non-stoichiometry of ferrous oxide, \( x \); and the relative diffusivity of ferrous and ferric iron which was set to 10, ferrous to ferric. It is important to examine the effect of these variables.

The results of changing bath circulation velocity, which is essentially to change the secondary bubble residence time, are illustrated in Fig. 7.4. The standard case, \( v_{sl} = 1.0 \) m/s, is shown as line 2. Increasing bath velocity by 50% (decreasing residence time by a third) has only a slight negative effect on zinc elimination. Decreasing bath velocity by 50% (increasing residence time by a factor of two) again has only a small effect on zinc elimination, this time a slight positive effect. A significant difference is found however, in the ferric iron levels. In the case of a higher bath velocity, shorter residence time, the ferric iron level is higher.

It was suggested in the development of the model that due to the fact that the coal particles are not wetted by the slag, they will tend to cluster together. A clustering, the equivalent of a particle with a radius of 80 \( \mu m \) was assumed. This represents a clustering of eight particles of 40 \( \mu m \) radius or about 32 particles of 25 \( \mu m \) radius (approximately the weight
Fig. 7.4  The Effect of Slag Velocity 'v_{sl}' on Predicted Fuming Behavior
mean size of pulverized coal). The effect of this clustering on the zinc elimination curve is negligible. See Fig. 7.5. Again there is a significant effect on the ferric iron level. The larger the coal particles or the greater the clustering, the higher will be the resulting ferric iron level.

The effect of the non-stoichiometry factor, $x$ in $\text{Fe}_x\text{O}$, is shown in Fig. 7.6. Again over a significant range the effect on zinc fuming rates and recovery is small. The temperature of the slag is essentially the same over the course of the cycle. Again however, the ferric iron level responds. The larger the value of $x$, the lower is the ferric iron level. This is in accord with the earlier discussion on the effect of $x$. Increasing $x$ moves the slag towards a lower ferric iron level at equilibrium.

Turning to the influence of the ratio of ferrous to ferric iron diffusivity, $D$, the effect is again small, as seen in Fig. 7.7. The ferric iron level is the only variable influenced by this change.

It can now be appreciated why the value of $F$ is relatively constant and consistent from operation to operation. This is due to the fact that few of these variables have any significant influence on the zinc elimination curve or zinc reduction curve. Thus variations in slag velocity, blast intensity or coal particle clustering which might vary from one operation to another will not affect zinc elimination unless they have some
Fig. 7.5
The Effect of Coal Particle Size 'r' on Predicted Fuming Behavior

% Zn

% Fe³⁺

Elapsed time (min)

F=0.35, Y=0.55

F=0.15

40

80

120

27

8
Fig. 7.6 The Effect of the Non-Stoichiometry Factor 'x' (Fe\_xO) on Predicted Fuming Behavior
Fig. 7.7 The Effect of the Diffusivity Ratio 'D' $(D_{FeO}/D_{Fe_2O_3})$ on Predicted Fuming Behavior
effect on F. On the other hand, the fitted values of $Y$ and $F_{oc}$ (or oxygen utilization) which therefore essentially fit the ferric iron level in the bath to F are more scattered because they are fairly sensitive to estimates of $v_{sl}$, $r_p$, $x$ and $D$. It therefore is a vindication of the model and the estimates made of these parameters that the scatter in $Y$ and $F_{oc}$ (or oxygen utilization) are as small as they are.

To explain the sensitivity of the ferric iron level to these variables and the relative insensitivity of the zinc fuming rate is to understand the process.

7.2 Kinetic Description of the Process

The coal particle-slag reaction is the basis of the description of process kinetics. This reaction is illustrated by Fig. 7.8. In the lower part of this figure the fuming efficiency, expressed as the ratio of zinc to total furnace coal, is graphed against the residence time of the entrained coal in the bath. The upper part of the figure, the bath heat balance, expressed as the rate of bath temperature change, is graphed against the entrained coal residence time. These curves are drawn for a particular bath composition which is assumed to be fixed over the indicated residence time. The standard slag composition is given in Table 7.2. The standard values of other parameters are given in Table 7.1.
Fig. 7.8 The Effect of Slag Zn Concentration on Fuming Efficiency and Furnace Heat Balance as a Function of Particle Residence Time
### TABLE 7.2

**STANDARD SLAG COMPOSITION FOR FUMING EFFICIENCY CALCULATION**

<table>
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<td>Al$_2$O$_3$</td>
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The most striking feature of the fuming efficiency curve is that there is a maximum. For the standard curve, 8% Zn, 2% Fe$^{3+}$ at 1200°C, a peak efficiency of 0.95 Zn/coal occurs at a residence time of 1.3 seconds. Up to this point zinc is diffusing into the secondary bubble and being reduced. Its concentration in the secondary bubble gas phase is increasing. At the same time, ferric iron is also diffusing to the bubble and undergoing reduction. Since zinc oxide diffusion is faster than ferric diffusion, zinc reduction proceeds more rapidly and zinc builds up in the bubble. The zinc and carbon dioxide partial pressures increase until the equilibrium interfacial concentration of zinc oxide is equal to the bulk concentration, see Equation 6.45. At this point zinc reduction ceases. Ferric reduction however, continues to higher oxygen partial pressures in the bubble because ferric reduction is thermodynamically favoured over zinc reduction (see Fig. 1.2). As ferric reduction proceeds, the carbon monoxide concentration decreases and the carbon dioxide concentration increases.

As the CO$_2$/CO ratio increases the interfacial zinc concentration becomes greater than the bath concentration. Zinc therefore is oxidized from the gas phase onto the interface and diffuses away from the bubble. The zinc content of the secondary bubble declines and hence the decline in fuming efficiency. This process will continue until the bubble is in equilibrium with the slag, which occurs after a period of 10 seconds or more.
The bath heat balance mirrors this curve. The bath heat balance declines from the start to a maximum heat loss at the peak of the zinc fuming efficiency curve. Following this point, the heat balance gradually becomes more favourable because the heat of ferric reduction is less than the heat of zinc oxidation.

In Fig. 7.8, the effect of a declining zinc concentration at a constant ferric iron level is examined. Increasing the zinc concentration shifts the peak to a shorter residence time and higher efficiencies, and decreasing the zinc concentration reduces the efficiency with a peak at a longer residence time.

In Fig. 7.9, the effect of the ferric iron level is shown and is seen to be dramatic. At 3% ferric iron the efficiency peak is relatively steep on both sides. At 1%, a very high efficiency is achieved over a longer residence time.

The rate controlling processes in the coal particle-slag reaction can best be identified by studying Figs. 7.10 and 7.11. In Fig. 7.10 the effect of the Boudouard Reaction pre-exponential constant, $A_0$, on the reaction is seen. In Fig. 7.11, the effect of the inter-diffusivities of zinc oxide and ferric oxide are shown. In the period up to the maximum zinc efficiency the Boudouard Reaction is rate controlling as evidenced by the strong influence of this factor on the efficiency curve. The zinc inter-diffusivity has a small effect and ferric diffusivity
The Effect of Slag Fe$^{3+}$ Concentration on Fuming Efficiency and Furnace Heat Balance as a Function of Particle Residence Time
Fig. 7.10  The Effect of Coal Reactivity on Fuming Efficiency and Furnace Heat Balance as a Function of Particle Residence Time
Fig. 7.11  The Effect of ZnO and Fe$_2$O$_3$ Diffusivities on Fuming Efficiency as a Function of Particle Residence Time
only begins to become important in the region of the maximum. Following the maximum however, ferric diffusion is clearly the rate controlling process at the higher Boudouard Reaction rates.

The consequences of this reaction scheme is the explanation of the process dynamics. The process naturally seeks a level of dynamic equilibrium in which the rate processes such as heat transfer, are balanced. The critical balance in zinc slag fuming is the ferric iron equilibrium.

Due to the sensitivity of the reduction reaction at any fixed residence time to the ferric iron level (see Fig. 7.9), the process rapidly responds to any change in the ferric iron level. It responds to ensure that the rate of ferric reduction exactly balances ferric input to the bath by ferrous oxidation and net wall melting. Variables such as $Y$ and $F_{oc}$ which control the rate of ferric iron generation have a direct influence on the process. If the ferric input rate to the process is increased, the zinc reduction suffers.

Variables such as $v_{sl}$, $r_p$, $x$ and $D$ affect the rate at which ferric iron can be reduced. For example, consider the slag bath velocity, $v_{sl}$. Assume that the process is at steady state at 8% Zn and 2% $\text{Fe}^{3+}$. If $v_{sl}$ is increased, the residence time decreases and the process moves up towards the peak along line 2 in Fig. 7.9. This immediately means that there is less ferric iron reduction. The ferric input therefore gets ahead
of the ferric reduction and the ferric content of the bath increases. The fuming efficiency curve therefore shifts downward towards the $3\% \text{ Fe}^{3+}$ line in the figure. It will shift to compensate exactly for the decrease in residence time. At this point the fuming rate will return to its original value.

The reason for this is very interesting. As implied above, the initial period of secondary bubble residence time is involved almost exclusively with reducing zinc. Following this period, reduction of ferric iron takes place essentially by displacing zinc from the bubble. The char carbon has been almost entirely consumed during the period of zinc dominated reduction. Therefore, to reduce a given amount of ferric iron, a fixed amount of zinc must be displaced whether the residence time is short or long, or the ferric diffusivity is large or small. The ferric iron level simply adjusts to the point where reduction equals net input.

The zinc fuming rate therefore depends on the rate of ferrous oxidation. Hence decreasing $F_{OC}$ or increasing $Y$ should be beneficial to the process, as illustrated in Fig. 7.2 and 7.3.

7.3 Model Predictions

The model will be used to analyse the consequences of changes in different variables for batch fuming and the
implications it holds for continuous fuming.

7.3.1 Batch Fuming

As shown in Fig. 7.12 and implied by Fig. 7.10, an increase in coal reactivity above a certain level is somewhat beneficial to the process. By increasing the reactivity of the coal, the ratio of zinc to iron reduced, when zinc reduction stops, is increased, see Fig. 7.10. Given then that a fixed amount of zinc must be displaced by ferric iron, the amount of zinc will be higher in the case of the more reactive coal.

It is important to appreciate that when dealing with coal it is unrealistic to expect to be able to change one variable independent of another. An increase in reactivity is likely to be accompanied by an increase in volatile and perhaps ash content. However, in the absence of good data, it would be unwise to extrapolate by making unwarranted assumptions.

The predicted effect of coal composition is shown in Fig. 7.13. Line 2 represents the standard case. Line 1 represents the replacement of 10% volatiles with fixed carbon, and line 3 represents 10% replacement of fixed carbon with volatiles. The ash content and reactivity were held constant. Although at intermediate times the higher fixed carbon coal gives a better performance, overall the coals turn out to be equal. This is
Fig. 7.12  The Effect of Coal Reactivity on Predicted Fuming Behavior
Fig. 7.13  The Effect of Coal Composition on Predicted Fuming Behavior
in agreement with the observations of Yurko\textsuperscript{26} and McNaughton\textsuperscript{28} who found that the efficiency of bituminous and sub-bituminous coal is equal, provided the ash content is constant. The higher fixed carbon curve intersects the others at low zinc levels due to melting and the introduction of additional ferric iron into the bath. Initially due to the lower fuel value the bath cools off more rapidly, removing ferric from the bath and allowing somewhat greater fuming rates.

The effect of reducing the ash content of the standard coal and replacing it with fixed carbon is quite significant. In the first place, it increases the amount of combustion in the tuyere gas stream, decreasing the rate of ferrous oxidation. Second, it increases the rate of carbon input to the bath, somewhat equivalent to increasing F. As a function of both effects, the fuming rate increases. These results are in agreement with the statements of McNaughton\textsuperscript{28} and Yurko\textsuperscript{26}. The data collected by Blaskett\textsuperscript{14} tends to support this result, although he explained it in terms of volatile content.

The effect of bath weight is shown in Fig. 7.14. Assuming that bath depth has no effect on oxygen utilization, lower bath weights, not unexpectedly, show better fuming rates. This is simply a function of the smaller bath mass. Any effect on the residence time, through changes in bath depth, is compensated for by changes in the ferric iron level.
Fig. 7.14 The Effect of Bath Weight on Predicted Fuming Behavior
In Fig. 7.15 the influence of two blast parameters, preheat and oxygen enrichment are explored. In both cases the overall oxygen to carbon ratio into the furnace was held constant. The results of the model are in reasonable agreement with McNaughton although the blowing times are different. This would be in part due to the higher initial zinc level and perhaps a lower value of F. The important fact however, is that the difference in the zinc between the standard case and 25% oxygen enrichment in model is 1.3% at about the same zinc levels that McNaughton observed a difference of 2.0%. The model predicts a temperature difference of 75°C between the two cases, while McNaughton observed a difference of 85°C. Thus the model appears to be consistent with industrial observation.

The model also predicts that blast preheat will be beneficial, in agreement with Blaskett. The model does not predict as great an improvement as Blaskett notes, but no data is presented and it is impossible to make a quantitative comparison.

Since the ferrous oxidation rate is the same in each case, the important effect is wall melting and absolute temperature. A unit rise in temperature at a lower temperature results in a greater increment in melting than at a higher temperature. (See Equation 6.95). Thus in the standard case at a relatively low temperature, the temperature rise at the end of the cycle puts significantly more ferric iron into the bath. Fuming rate
Fig. 7.15  The Effect of Preheat and Oxygen Enrichment of Blast on Predicted Fuming Behavior
drops more significantly as a consequence. Furthermore, as shown in Fig. 7.16, increased temperatures at a given residence time and ferric content (2% Fe\(^{3+}\)) tend to increase fuming efficiency.

### 7.3.2 Consequences of the Model for Slag Fuming

The model suggests that to improve the process, attention should be paid primarily to \(F\) and \(Y\) and \(F_{oc}\). To increase fuming rates the fraction of coal entrained in the slag should be increased. As shown in Fig. 7.1 a significant improvement in fuming efficiency can be achieved in this manner. Probably the easiest way to effect this improvement would be to use higher blast pressures and coarser coal.

Of equal importance is control of ferrous iron oxidation. If this is high, then fuming rates are going to be slow. The best way to reduce ferrous iron oxidation would be to achieve more complete combustion of the tuyere coal. This might involve using a finer coal grind for tuyere coal, although coarse coal would still be preferred for entrainment.

Care must be taken to balance \(F\) against \(Y\) so that the heat balance is satisfied. Alternatively, a temperature profile which does not drop too close to the melting point is important. Oxygen enrichment could be an important factor in maintaining a heat balance that did not allow the temperature to drop during
Fig. 7.16 The Effect of Bath Temperature on Fuming Efficiency and Bath Heat Balance as a Function of Particle Residence Time
the initial stages of reduction. See Fig. 7.15.

An interesting idea in this regard is pre-combustion of the coal-air mixture. As mentioned earlier, this technique has been used in the U.S.S.R. to effect fuming with natural gas. Pre-combustion of the coal would reduce the carry over of coal, and reduce the oxidation of ferrous iron.

The operating scheme discussed above basically implies that the reduction and heat balance requirements of the furnace be fulfilled separately. One set of high pressure tuyeres, using high loading ratios and inert gas, would be used to inject the coal for slag reduction. A second set of tuyeres, operating at low pressure, would burn natural gas or pulverized coal to make up the heat balance. Pre-combustion or pre-ignition of the mixture would be used to ensure efficient use of the fuel and to prevent free oxygen from entering the furnace and reacting with the slag.

7.3.3 Continuous Fuming

The curves of residence time versus fuming efficiency are directly applicable to continuous fuming. These diagrams could be used to define operating points where the heat balance is just satisfied \((dT_{sl}/dt = 0)\). For example, in Fig. 7.17, the effect of substituting fixed carbon for volatiles on continuous fuming can be assessed. Thus, although higher fixed carbon
Fig. 7.17 The Effect of Coal Composition on Fuming Efficiency and Bath Heat Balance as a Function of Particle Residence Time
coals yield more efficient fuming, the heat balance is not satisfied. In this case, the highest efficiency is 0.94 for 50% fixed carbon coal at a residence time of 1.1 seconds. A technique of controlling residence time such as varying bath depth would have to be available.

In Fig. 7.18, the effect of particle size or clustering is examined. From this figure it is apparent that increasing particle size is of significant benefit at the zero heat balance point. Although there are zero points at longer residence times, the highest zinc efficiency is found at the shorter residence times.

From an analysis of Fig. 7.16, it is apparent that intermediate temperatures, say 1200°C, represent the most efficient fuming point. At higher temperatures the zero heat balance point occurs at a much lower residence time where the fuming efficiency is significantly lower. At lower temperatures, the efficiency never rises very high. Finally from Fig. 7.10, coal reactivity does not seem to be an important variable, as long as the reactivity is the assumed value or greater.
Fig. 7.18 The Effect of Particle Size \( r_p \) on Fuming Efficiency and Bath Heat Balance as a Function of Particle Residence Time
CHAPTER VIII

SUMMARY AND CONCLUSIONS

8.1 Summary

The results of industrial measurements at five different operations has demonstrated that the equilibrium model of slag fuming is not generally applicable. Tuyere back-pressure measurements revealed that the predominant mode of gas behaviour was bubbling. Analysis of slag samples has shown that, as expected from injection dynamics, a portion of the coal injected into the furnace enters the slag.

A model of the direct coal particle-slag reaction was developed assuming mass transfer control in the slag phase and a finite Boudouard Reaction rate on the internal char particle. This model was incorporated into a model of the slag bath, involving balances on the species \( \text{Zn}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{CaO}, \text{SiO}_2 \) and including the behaviour of the water-jacketed wall. Fitting of the process model to industrial data showed that the fraction of coal entering the bath was consistently about 35%. Roughly 55% of the coal is combusted in the tuyere gas stream and 10% passes through the bath unconsumed. Oxygen utilization in the tuyere gas stream ranged from 70-95%, dependent on slag depth.
The slag fuming process is kinetically controlled, essentially by two parameters: the fraction of coal which is entrained in the slag, and the rate of ferrous iron oxidation. The rate of ferric reduction balances ferric iron inputs to the bath by displacing previously reduced zinc from the entrained secondary bubbles. An increase in process efficiency can therefore only result from increasing the entrainment of coal in the bath or reducing the oxidation of ferrous iron. The former objective may be achieved by higher injection pressures. The latter may be achieved by more complete combustion of tuyere coal by using finer coal grinds or pre-combustion.

The implications for continuous fuming are important. Improved efficiencies could result from using coarser ground and higher fixed carbon coals, and by operating at intermediate temperatures, about 1200°C.

8.2 Suggestions for Further Work

This thesis has served as an attempt to define a very complex system with an enormous number of inter-related processes. The information available on each of these is very poor. In order to better characterize the slag fuming process, it would be important to study:

(a) the whole field of submerged coal combustion;
(b) the coal particle-slag reaction as a function of parameters such as temperature, surface tension, coal and slag composition;
(c) the physio-chemical properties of these slag systems, and;
(d) the physical entrainment of pulverized coal in slag;

In addition, further industrial tests could be performed, including:

(e) experimental studies on the efficiency of high pressure injection for coal entrainment;
(f) experimental studies on continuous fuming to verify the predictions of the model;
(g) further sampling in fuming furnaces to study the slag-coal reaction zone;
(h) the measurement of slag circulation velocities in fuming furnaces, and;
(i) further sampling and analysis of water-jacketed wall effects.
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APPENDIX I

WET FERROUS IRON ASSAY TECHNIQUE
Weigh a suitable weight of sample into a clean, dry 250 ml erlenmeyer flask. Add 2 gm calcium carbonate, 100 ml distilled water and 25 ml HCl. Cover, and digest on a bare plate until the sample is decomposed.

Remove from the hot plate, one at a time. Add a pinch of calcium carbonate and stopper tightly with a rubber stopper. Cool to room temperature in a water bath.

Add 5 ml phosphoric acid, and titrate with standard dichromate solution (0.005 gm Fe/ml K_2Cr_2O_7) using sodium diphenylamine sulphonate as indicator.

**NOTE:**

In complex materials containing other oxidizing or reducing agents, the exact determination of Fe^{++} is one fraught with uncertainties.
APPENDIX II

FUMING CYCLE SAMPLING DATA
COMPANY A CYCLE NO.1

BATH WEIGHT: 49668.0 KG

COAL COMPOSITION: WEIGHT FRACTION

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<th>Fe*** (%)</th>
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* Estimated
COMPANY A CYCLE No.2B

BATH WEIGHT: 52344.6 KG

COAL COMPOSITION: WEIGHT FRACTION

**FIXED CARBON:** 0.428  **VOLATILES:** 0.365  **ASH:** 0.097  **MOISTURE:** 0.110

**COAL VOLATILES:** WEIGHT FRACTION*  
CARBON: 0.400  HYDROGEN: 0.168  OXYGEN: 0.177  NITROGEN: 0.050

| TIME (MIN) | TEMP* (°C) | Zn (%) | Fe* (%) | Fe** (%) | CARBON (%) | SULFUR (%) | LEAD (%) | CaO (%) | SiO2 (%) | Al2O3 (%) | MgO (%) | STP STP STP TEMP | PRIMARY BLAST SECOND BLAST SECOND BLAST RATE |
|------------|------------|--------|---------|----------|-------------|-------------|----------|--------|---------|-----------|---------|----------------|------------------------|------------------------------------------|
| 0.0        | 1200.0     | 4.3    | 24.6    | 0.3      | 0.44        | 1.1         | 0.1      | 22.9   | 33.3    | 5.9       | 2.3     | 0.3            | 5.2        | 104.4                    | 1.16                                      |
| 10.0       | 1200.0     | 3.4    | 24.3    | 0.1      | 0.33        | 1.1         | 0.08     | 23.5   | 34.9    | 6.0       | 2.4     | 0.3            | 5.2        | 104.4                    | 1.16                                      |
| 20.0       | 1200.0     | 2.5    | 24.8    | 0.1      | 0.44        | 1.2         | 0.14     | 23.2   | 34.7    | 6.3       | 2.2     | 0.3            | 5.2        | 104.4                    | 1.16                                      |
| 30.0       | 1200.0     | 1.9    | 24.9    | 0.2      | 0.44        | 1.2         | 0.09     | 23.5   | 35.2    | 6.2       | 2.3     | 0.3            | 5.2        | 104.4                    | 1.16                                      |
| 40.0       | 1200.0     | 1.3    | 24.9    | 0.1      | 0.54        | 1.2         | 0.06     | 23.8   | 36.1    | 6.4       | 2.3     | 0.3            | 5.2        | 104.4                    | 1.16                                      |
| 50.0       | 1200.0     | 0.8    | 25.2    | 0.0      | 0.65        | 1.2         | 0.05     | 23.9   | 36.2    | 6.4       | 2.2     | 0.3            | 5.2        | 104.4                    | 1.16                                      |
| 60.0       | 1200.0     | 0.9    | 23.6    | 1.1      | 0.88        | 1.3         | 0.18     | 23.5   | 37.3    | 6.4       | 2.3     | 0.3            | 5.2        | 104.4                    | 1.16                                      |

* Estimated
COMPANY B CYCLE NO. 1
BATH WEIGHT: 40823.0 KG

COAL COMPOSITION: WEIGHT FRACTION

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* Estimated

** Not Assayed
COMPANY B CYCLE NO.21

BATH WEIGHT: 3990.4 KG

COAL COMPOSITION: WEIGHT FRACTION*

- FIXED CARBON: 0.499
- VOLATILES: 0.335
- ASH: 0.067
- MOISTURE: 0.099

COAL VOLATILES: WEIGHT FRACTION

- CARBON: 0.400
- HYDROGEN: 0.168
- OXYGEN: 0.177
- NITROGEN: 0.050

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* Estimated
COMPANY B CYCLE NO. 22

BATH WEIGHT: 40097.6 KG

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COAL VOLATILES: WEIGHT FRACTION

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COMPANY C CYCLE NO.1
BATH WEIGHT: 52617.0 KG
COAL COMPOSITION: WEIGHT FRACTION

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** Not Assayed
COMPANY C CYCLE NO. 3
BATH WEIGHT: 52072.4 KG
COAL COMPOSITION: WEIGHT FRACTION

- FIXED CARBON: 0.600
- VOLATILES: 0.235
- ASH: 0.165
- MOISTURE: 0.0

COAL VOLATILES: WEIGHT FRACTION

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 COMPANY D CYCLE NO. 1

BATH WEIGHT: 44964.0 KG

COAL COMPOSITION: WEIGHT FRACTION

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Data taken from reference 45
COMPANY D CYCLE NO.2
BATH WEIGHT: 45320.0 KG
COAL COMPOSITION: WEIGHT FRACTION

FIXED CARBON: 0.597  VOLATILES: 0.195  ASH: 0.181  MOISTURE: 0.027

COAL VOLATILES: WEIGHT FRACTION

CARBON: 0.545  HYDROGEN: 0.201  OXYGEN: 0.193  NITROGEN: 0.050

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<th>Fe⁺⁺</th>
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<td>%</td>
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Data taken from reference 45
COMPANY E  CYCLE NO.1
BATH WEIGHT: 70000.0 KG
COAL COMPOSITION: WEIGHT FRACTION

FIXED CARBON: 0.540  VOLATILES: 0.236  ASH: 0.180  MOISTURE: 0.072

COAL VOLATILES: WEIGHT FRACTION*

CARBON: 0.400  HYDROGEN: 0.168  OXYGEN: 0.177  NITROGEN: 0.050

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<th>Fe³⁺ (%)</th>
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* Estimated
APPENDIX III

EQUILIBRIUM FUMING RATE CALCULATION METHOD
The equilibrium fuming rate is calculated assuming that the coal-air mixture injected into the furnace comes to chemical and thermal equilibrium with the slag. The slag bath is assumed to be an infinite reservoir with a fixed temperature and fixed activities of ZnO, FeO, and Fe$_3$O$_4$. The fuming rate can then be calculated as outlined below:

The reaction:

$$3\text{FeO} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{Fe}_3\text{O}_4 \quad \ldots(\text{III.1})$$

$$K_6 = \frac{a_{\text{Fe}_3\text{O}_4}^3}{a_{\text{Fe}^\bullet\text{O}_2}^{\frac{1}{2}}} \quad \ldots(\text{III.2})$$

at equilibrium immediately dictates the oxygen potential in the gas leaving the slag surface.

From the slag composition the mole fractions of Fe$_3$O$_4$ and FeO, $N_{\text{FeO}}$ respectively, can be calculated. Using the given activity coefficients then;

$$P_{\text{O}_2} = \frac{\gamma_{\text{Fe}_3\text{O}_4}^3 N_{\text{Fe}_3\text{O}_4}^3}{K_6 \gamma_{\text{FeO}} N_{\text{FeO}}^3} \quad \ldots(\text{III.2})$$

'K$_6$' is calculated from free energy data for slag temperature. Then the zinc partial pressure in the gas can be determined from the equation:

$$\text{ZnO} \leftrightarrow \text{Zn}^{(g)} + \frac{1}{2}\text{O}_2 \quad \ldots(\text{III.3})$$
Again calculating the mole fraction ZnO, N_{ZnO}, from the slag composition and taking the activity coefficient from the given data:

\[
P_{Zn} = \frac{\gamma_{ZnO} N_{ZnO} K_2^{-1}}{P_{O_2}^{-\frac{1}{2}}} \quad \text{(III.5)}
\]

Having established the oxygen potential, a calculation can be performed to check whether or not solid carbon will be present at equilibrium. Using the equation:

\[
2C + O_2 \not\Rightarrow 2CO \quad \text{(III.6)}
\]

\[
K_8^2 = \frac{P_{CO}^2}{P_{O_2}^{-\frac{1}{2}} a_C^2} \quad \text{(III.7)}
\]

let \( C_1 \) = the amount of CO formed (kg·moles);

\( n_T \) = total kg·moles of gas

\( P_T \) = total pressure

then;

\[
P_{CO}^2 = K_8^2 P_{O_2}^{-\frac{1}{2}} a_C^2
\]

\[
\frac{C_1^2}{n_T} P_T^2 = K_8^2 P_{O_2}^{-\frac{1}{2}} a_C^2
\]

\[
C_1 = \frac{n_T a_C (K_8^2 P_{O_2})^{\frac{1}{2}}}{P_T} \quad \text{(III.8)}
\]
Likewise for the equation:

\[
C + O_2 \rightarrow CO_2
\]

...(III.9)

\[
K_7 = \frac{PCO_2}{P_{O_2}^aC}
\]

...(III.10)

let \( C_2 \) = the amount of \( CO_2 \) formed (kg·moles)

\( n_T \) = total kg·moles of gas

\( P_T \) = total pressure

then;

\[
PCO_2 = K_7P_{O_2}^aC
\]

\[
\frac{C_2}{n_T} P_T = K_7P_{O_2}^aC
\]

\[
C_2 = \frac{n_T^aC K_7P_{O_2}}{P_T}
\]

...(III.11)

Initially \( n_T \) is assumed to be the total amount of nitrogen in the gas stream in a certain unit time (e.g. 1 second). The activity of carbon is assumed to be unity. If the sum of 'C' and 'C_2' exceeds the carbon input to the furnace as coal in that unit time then no solid carbon exists at equilibrium. This is the situation under conditions normally encountered in a fuming furnace.

If all of the carbon is consumed, assuming it initially appears as CO, then the quantities of CO and \( CO_2 \) per unit time can be calculated. Using the equation:
\[2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2\] ...(III.12)

\[K_e = \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}^2 P_{\text{O}_2}}\]

Let \(n_{\text{CO}}\) = the amount of CO initially present (kg-moles)
\(\Delta x\) = the amount of CO consumed (kg-moles)

(the amount of \(\text{CO}_2\) formed)

then;

\[P_{O_2} = \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}^2 K_e}\]

\[P_{O_2} = \frac{\frac{\Delta x}{n_T}^2}{\frac{n_{\text{CO}} - \Delta x}{n_T}^2 K_e}\]

thus

\[P_{O_2} = \frac{\Delta x^2}{(n_{\text{CO}} - \Delta x)^2 K_e}\]

Solving for \(\Delta x\) gives

\[\Delta x = \frac{n_{\text{CO}} (P_{O_2} K_e + (P_{O_2} K_e)^{\frac{1}{2}})}{(1 - P_{O_2} K_e)}\] ...(III.13)

In a similar manner the distribution of hydrogen between \(\text{H}_2\) and \(\text{H}_2\text{O}\) can be determined. Using the equation

\[2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}\] ...(III.14)

\[K_9 = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}}\]
let \( n_{H_2} \) = the amount of \( H_2 \) from coal volatiles (kg·moles)
\( n_{H_2O} \) = the amount of moisture associated with coal (kg·moles)
\( \Delta y \) = the amount of \( H_2 \) consumed (kg·moles)

Therefore;

\[
P_{O_2} = \frac{(n_{H_2O} + \Delta y)^2}{(n_{H_2} - \Delta y)^2 k_9}
\]

and

\[
\Delta y = 2 \frac{-b + (b^2 - 4ac)^{\frac{1}{2}}}{2a} \quad \ldots (III.15)
\]

where;

\[
a = 4(P_{O_2} k_9^2 - 1)
\]
\[
b = -4 \left( n_{H_2O} + n_{H_2} P_{O_2} k_9^2 \right)
\]
\[
c = n_{H_2}^2 P_{O_2} k_9^2 - n_{H_2O}^2
\]

Finally the amount of zinc vapour in the equilibrium gas stream is calculated. If

\( n_{Zn} \) = the amount of zinc vapour (kg·moles) present in the gas per unit time

then;

\[
P_{Zn} = \frac{n_{Zn}}{n_T} P_T
\]
\[
n_{Zn} = \frac{n_T P_{Zn}}{P_T} \quad \ldots (III.16)
\]

An oxygen balance is also performed but under normal circumstances the oxygen partial pressure is so low that the quantity of oxygen present at equilibrium is negligible.
Using the quantities \( n_{CO}, \Delta x, n_{H_2}, n_{H_2O}, \Delta y, n_{Zn}, \) and \( n_{N_2}, \) the quantity of nitrogen present per unit time, a new total molar quantity, \( n_T, \) can be calculated. With this value the calculation can be repeated from Equation III.6. Iterations are performed in this manner until the change in \( n_T \) is negligible.

The zinc fuming rate can then be calculated from the final total molar flow rate \( n_T \) per unit time and \( P_{Zn}. \) The net rate of ferric reduction can be determined from an oxygen balance on the gas stream taking into account the oxygen derived from the air, coal and zinc oxide.

The observed fuming rate can be calculated in the following manner. If 'Z' represents the weight of zinc in the slag bath and 'W' is the weight of the bath at a particular point, then:

\[
Z = \left(\frac{\%Zn}{100}\right) \cdot W \quad \text{...(III.17)}
\]

Therefore;

\[
\frac{dz}{dt} = \frac{1}{100} W \frac{d(\%Zn)}{dt} + (\%Zn) \frac{dW}{dt} \quad \text{...(III.18)}
\]

where

\[
\frac{dz}{dt} = \text{actual fuming rate (kg/s)}
\]

\[
\frac{d(\%Zn)}{dt} = (\%Zn) \text{ change with time (kg/s)}
\]

(measured from zinc elimination curve)

Assuming that the main mass change in the bath weight is due to the removal of zinc oxide, then
\[
\frac{dw}{dt} = \frac{81.37}{65.37} \frac{dz}{dt} 
\]

Substituting Equation III.19 into III.18 gives the actual fuming rate as a function of bath weight, zinc content of the bath (\%Zn) and percent fuming rate:

\[
\frac{dz}{dt} = \frac{w \cdot \frac{d(\%Zn)}{dt}}{100 - (\%Zn) \cdot \frac{81.37}{65.37}} \hspace{1cm} \text{..(III.20)}
\]

The actual molar fuming rate is then

\[
\frac{-dz}{dt}/\frac{65.37}{\text{kg.mole Zn/s}}
\]

This quantity is termed 'observed fuming rate' in Fig. 5.12 through 5.14.

The net ferric reduction rate can be calculated in a similar way. If \( f_3 \) is the mass of ferric iron in the bath, i.e.

\[
f_3 = \frac{(\%Fe^{3+})}{100} \cdot w \hspace{1cm} \text{..(III.21)}
\]

then

\[
\frac{df_3}{dt} = \frac{1}{100} \cdot w \frac{d(\%Fe^{3+})}{dt} + (\%Fe^{3+}) \cdot \frac{81.37}{65.37} \frac{dz}{dt} \hspace{1cm} \text{..(III.22)}
\]

For ferrous iron;

\[
\frac{df_2}{dt} = \frac{1}{100} \cdot w \frac{d(\%Fe^{2+})}{dt} + (\%Fe^{2+}) \cdot \frac{81.37}{65.37} \frac{dz}{dt} \hspace{1cm} \text{..(III.23)}
\]

where \( f_2 \) = mass of ferrous iron in the bath (kg).
These quantities should be related by the iron balance

\[
\frac{df_2}{dt} = -\frac{df_3}{dt} \quad \text{...(III.24)}
\]

These quantities were converted to molar rates and the average graphed as 'net observed ferric reduction rate' in Fig. 15.15.

A listing of the computer program written to perform this calculation is given on the following pages.
IMPLICIT REAL*8 (A-Z)

INTEGER WFL,I,INT,JT,JT1,IX,J,N

REAL*4 STAR,BLNK,WARN(20),NAME(2),R1,R2,GB1,GB2,KEL1,KEL2
1,HATCH

DIMENSION TEST(4),H(12),COAL(20),PAIR(20),PP(20),SAIR(20)
1,SP(20),BATH(20),Z(20),C(20),FE2(20),FE3(20),CAO(20),
2SIO2(20),AL2O3(20),DELTAT(20),OXY(20),OXYP(20),COMET(9),
3CHR(4),WR(4),FUMRT(20,7),INPTT(20),FERED(20,7)

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1BLNK/' '/,R1/'RICH'/,R2/'ARDS'/,GB1/'G & '/,GB2/'B '/,
2KEL1/'KELL'/,KEL2/'OOG '/,HATCH/'##'/,STAR/'**'/

READ (7,43) IX,OX,BX,CX
READ (7,45) INT
READ (7,47) OBJ
READ (7,53) BTHWTI
READ (7,48) (COMET(I), I=1,9)
READ (7,49) TEST(1),TEST(2),TEST(3),TEST(4)
READ (7,51) N,JT

N = 1 RICHARDS DATA
2 GRANT AND BARNETT DATA
3 KELLOGG DATA

READ (7,54) C1,C2,C3,C4,V1,V2,V3,V4
READ (7,50) WX,FE3ST
JT1=JT-1
READ (7,55) (COAL(J), J=1,JT)
READ (7,57) (PAIR(J), J=1,JT)
READ (7,59) (PP(J), J=1,JT)
READ (7,57) (SAIR(J), J=1,JT)
READ (7,59) (SP(J), J=1,JT)
READ (7,65) (INPTT(J), J=1,JT)
READ (7,57) (OXY(J), J=1,JT)
READ (7,59) (OXYP(J), J=1,JT)
READ (7,65) (BATH(J), J=1,JT)
READ (7,69) (Z(J), J=1,JT)
READ (7,69) (C(J), J=1,JT)
READ (7,69) (FE2(J), J=1,JT)
READ (7,69) (FE3(J), J=1,JT)
READ (7,69) (CAO(J), J=1,JT)
READ (7,69) (SIO2(J), J=1,JT)
READ (7,69) (AL2O3(J), J=1,JT)
READ (7,71) (DELTAT(J), J=1,JT)
READ (7,73) FURLEN,FURWID
READ (7,75) SLMPT
READ (7,75) BMM

43 FORMAT (I2,1X,A4,F8.1,1X,A4)
45 FORMAT (I2)
47 FORMAT (A4)
48 FORMAT (9A4)
49 FORMAT (20A4)
50 FORMAT (F5.3,1X,F4.2)
51 FORMAT (2I2)
52 FORMAT (20F6.4)
53 FORMAT (20F8.1)
54 FORMAT (20F7.3)
55 FORMAT (20F8.3)
56 FORMAT (20F8.3)
57 FORMAT (20F7.4)
58 FORMAT (20F6.3)
59 FORMAT (2F6.2)
60 FORMAT (F6.1)

C

IF (N .EQ. 2 .OR. N .EQ. 3) WX=1.0
NAME(1)=R1
NAME(2)=R2
IF (N .EQ. 2) NAME(1)=GB1
IF (N .EQ. 2) NAME(2)=GB2
IF (N .EQ. 3) NAME(1)=KEL1
IF (N .EQ. 3) NAME(2)=KEL2

C

DO 1000 INT=1,JT
WFL=0
ZNO=Z(INT)*81.37/65.37
CA=CA0(INT)
SI=SI02(INT)
AL=AL203(INT)
WX1=3.0*WX-2.0
WX2=2.0*(1.0-WX)
IF (WX .LT. 1.0) GOTO 77
FE04=FE3(INT)*231.54/(2.0*55.85)
FE0=FE2(INT)*71.85/55.85
MF2=FE0/71.85
MF3=FE04/231.54
GOTO 79

77 MF3=(1.0/55.85)*(FE2(INT)-WX1/WX2*FE3(INT))/
     (1.0-2.0*WX1/WX2)
MF2=(FE3(INT)/55.85-2.0*MF3)/WX2
IF (MF3 .LE. 0.0) WFL=1
IF (MF3 .GT. 0.0) GOTO 78
MF2=(FE3(INT)+FE2(INT))/(WX*55.85)

78 FE0=MF2*(WX*55.85+16.00)
FE04=MF3*231.54
GOTO 79

C

79 M2=ZNO/81.37
MS=SI/60.09
MC=CA/56.08
MA=AL/101.96
UNK=100.0-(ZNO+SI+CA+AL+FE0+FE04)
MUNK=UNK/60.0
MT=M2+MS+MC+MA+MF2+MF3+MUNK
MFZ=M2/MT
MFS=MS/MT
MFC=MC/MT
MFA=MA/MT
MFF2=MF2/MT
MFF3=MF3/MT
CSS=MC/MS

\[ MF3G = FE3(INT)/(2.0*55.85) \]
\[ MF2G = (FE2(INT)-55.85*MF3G)/(0.945*55.85) \]
\[ FEOG = MF2G*68.78 \]
\[ FE3O4G = MF3G*231.54 \]
\[ UNKG = 100.0-(ZNO+SI+CA+AL+FEOG+FE3O4G) \]
\[ MUNKG = UNKG/60.0 \]
\[ MTG = MZ+MS+MC+MA+MF2G+MF3G+MUNKG \]
\[ MF2G = MZ/MTG \]
\[ MFF2G = MF2G/MTG \]
\[ MFF3G = MF3G/MTG \]

BTK = BATHT(INT) + 273.16
\[ LNZ = (16390.0*CSS-12031.0)/BTK-10.694*CSS+8.8317 \]
IF (N . EQ. 2) LNZ = 2331.0/BTK
IF (N . EQ. 3) LNZ = 920.0/BTK
\[ ACZNO = DEXP(LNZ) \]

\[ LNFE2 = (3310.0*CSS+1656.5)/BTK-1.887*CSS-0.6394 \]
IF (N . EQ. 2) LNFE2 = 1501.0/BTK
IF (N . EQ. 3) LNFE2 = 1501.0/BTK
\[ ACFEO = DEXP(LNFE2) \]
\[ LNFE3 = 8495.0/BTK-2.653 \]
IF (N . EQ. 2 . OR. N . EQ. 3) LNFE3 = 8495.0/BTK-2.653
\[ ACFE3O = DEXP(LNFE3) \]
\[ AFE = 1.0 \]

PAIRA = PAIR(INT)
PPA = PP(INT)
SAIRA = SAIR(INT)
SPA = SP(INT)
INPTTA = INPTT(INT)
GP = PAIRA*PPA/101.325*(273.16/(INPTTA+273.16))
GS = SAIRA*SPA/101.325*(273.16/(INPTTA+273.16))
G = GP + GS
\[ OXYA = OXY(INT) \]
\[ OXYPA = OXYP(INT) \]
\[ OIN = 0.209*g/(0.08205*273.16) + (OXYA*OXYPA/101.325)/(0.08205*273.0) \]

COALA = COAL(INT)
CARB = COALA*C1/12.01
VOLTH = COALA*C2*V2/1.008
VOLTO = COALA*C2*V3/16.0
VOLTC = COALA*C2*V1/12.01
VOLTN = COALA*C2*V4/14.007
HSC = VOLTH/(CARB+VOLTC)
NSC = VOLTN/(CARB+VOLTC)
OSC = VOLTO/(CARB + VOLTC)

E = R * BTK
G0 = -228781.1 - 171.5 * BTK
K0 = DEXP(-1.0 * G0/E)
G1 = -395346.2 - 0.5439 * BTK
K1 = DEXP(-1.0 * G1/E)
GA = -561911.3 + 170.4 * BTK
KA = DEXP(-1.0 * GA/E)
G2 = -494967.2 + 111.7 * BTK
K2 = DEXP(-1.0 * G2/E)
G5 = -624420.0 + 250.2 * BTK
IF (N .EQ. 2 .OR. N .EQ. 3) G5 = -600026.0 + 213.84 * BTK
C2
G5 = -582580.0 + 260.0 * BTK
K5 = DEXP(-1.0 * G5/E)
G6 = -920480.0 + 396.6 * BTK
IF (N .EQ. 2 .OR. N .EQ. 3) G6 = -925736.0 + 398.8 * BTK
K6 = DEXP(-1.0 * G6/E)
X1 = ACFEO**3/ACFE30
KK = DEXP(-1.0 * GA/E)

80 NH2O = COALA * C4/18.016
NCO2 = 0.0
NCO = 0.0
NN2 = VOLTN/2.0
ANN2 = NN2 + 0.791 * G/(0.08205 * 273.16)
NC = CARB + VOLTC
NO2 = VOLTO/2.0
ANO2 = NO2 + OIN
NH2 = (VOLTH)/2.0

IF (FE3(INT) .GT. 0.0) GOTO 81
FUMRT(INT, 6) = 999999.9
FUMRT(INT, 7) = 9999.9
GOTO 82
81 FUMRT(INT, 6) = FE2(INT)**2 * Z(INT)/FE3(INT)**2
FUMRT(INT, 7) = MFF2**3 * MFZ/MFF3

82 MFF2O = MFF2

C1
X1 = ACFEO**3.168/ACFE30
C1
PO2 = MFF3**2/(X1**2 * MFF2**6.3358 * K5)
PO2D = (ACFEO * MFF2 / (AFE * KK))**2.0
IF (WFL .NE. 1) GOTO 83
PO2C = 0.0
GOTO 84
83 PO2C = ((ACFEO * MFF3)**2.0/((ACFEO * MFF2)**2.0/6.0/WX)**K5)
1**((1.0/(4.0 - 3.0/WX)))
84 IF (PO2C .GT. PO2D) PO2 = PO2C
IF (PO2D .GE. PO2C) PO2 = PO2D

85 DO 900 I = 2, 5
IF (I .EQ. 3) NN2 = ANN2
IF (I .EQ. 3) NO2 = ANO2
IF (I .LT. 4) GOTO 97
KA=DEXP(67451.0/BTK-20.484)
K2=DEXP(60201.0/BTK-13.768)
K5=DEXP(31118.5/BTK-11.884)
K6=DEXP(111952.0/BTK-48.322)
ACZNO=3.401
PO2A=(ACFE0*MFF2/(AFE*KK))**2.0
IF (MFF3G .LE. 0.0) PO2=PO2A
IF (MFF3G .LE. 0.0) GOTO 95
X1=4.187
PO2B=(MFF3G/(X1*MFF2G**3.1746*K5))**2.42307
IF (PO2B .GT. PO2A) PO2=PO2B
IF (PO2A .GT. PO2B) PO2=PO2A
95 NH20=COALA*C4/18.016
NCO2=0.0
NCO=0.0
NN2=VOLTN/2.0
NC=CARB+VOLTC
NO2=VOLTO/2.0
NH2=(VOLTH)/2.0
MFZ=MFZG
MFF2=MFF2G
MFF3=MFF3G
IF (I .EQ. 5) NN2=ANN2
IF (I .EQ. 5) NO2=AN02
C
97 NT=NCO+NCO2+NH2+NH2O+NO2+NN2
NTOLD=NT
NTI=NT
DF=0.0
PZN=ACZNO*MFZ/(PO2*K6)**0.5
C
100 NCOP=0.0
DXA=0.0
DX0=0.0
DX1=0.0
IF (NC .LE. 0.0) GOTO 190
DX0=2.0*NT*AC*(K0*PO2)**0.5/PT
C
WRITE (6,98) I,P02,NT,AC,K1,PT
98 FORMAT (3X,I 2,5(5X,D12.5) )
DX1=NT*AC*K1*PO2/PT
IF (NC .GT. 2.0*DX0+DX1) GOTO 290
DX0=0.0
DX1=0.0
NCOP=NC
GOTO 200
190 NCOP=0.0
200 NCOT=NCOP+NCO
DXA=NCOT*(-1.0*PO2*KA+(PO2*KA)**0.5)/(2.0*(1.0-PO2*KA))
GOTO 300
290 NCOP=0.0
NCOT=NCO
300 DXP=DX0+DX1+DXA+NCOP/2.0
C
WRITE (6,301) NT,DF,DX0,DX1,DXA
301 FORMAT (2(E13.5,5X),/,'DX ',3(E13.5))
A11=4.0*(PO2*K2-1.0)
\begin{align*}
B_{11} &= -4.0 \times (\text{NH}_2 \text{O} + \text{NH}_2 \text{PO}_2 \text{K}_2) \\
C_{11} &= \text{NH}_2 \text{**} 2\times \text{PO}_2 \text{K}_2 - \text{NH}_2 \text{O} \times 2 \\
B_{12} &= (B_{11} \times 2 - 4.0 \times A_{11} \times C_{11}) \\
\text{IF} (B_{12} \lt .LT. 0.0) \quad B_{12} &= 0.0 \\
D_Y &= (1.0 \times B_{11} - (B_{12}) \times 0.5) / (2.0 \times A_{11}) \\
D_M &= -1.0 \times N_T \times P_Z/N / (2.0 \times P_T) \\
N_T &= N_T I + D_XO - D_XA + N_C O/P / 2.0 - 3.0 \times D_M - D_F - D_Y \\
D_F P &= -1.0 \times N_T \times P_O_2 / P_T + (N_O_2 - D_XP - D_Y - D_M) \\
C_H &= D_A B S((A_F P - D_F) / D_F P) \\
\text{IF} (C_H \leq 0.000001) \quad \text{GOTO} 500 \\
D_F &= D_F P \\
\text{GOTO} 400 \\
\text{GOTO} 500 \\
N_T N_E W &= N_T \\
\text{IF} (D_A B S((N_T N_E W - N_T O L D) / N_T O L D) \LT. 0.000001) \quad \text{GOTO} 600 \\
N_T O L D &= N_T \\
\text{GOTO} 100 \\
F_Z N &= P_Z N \\
F_H 2 &= (\text{NH}_2 - 2.0 \times D_Y) / N_T N_E W \\
F_H 2 O &= (\text{NH}_2 O + 2.0 \times D_Y) / N_T N_E W \\
F_N 2 &= N_N 2 / N_T N_E W \\
F_P O_2 &= P_O_2 / P_T \times N_T N_E W \\
F_C O &= (N_C O T - 2.0 \times D_XA + 2.0 \times D_XO) / N_T N_E W \\
F_C O_2 &= (N_C O_2 + 2.0 \times D_XA + D_X1) / N_T N_E W \\
\text{WRITE} (8, 630) \quad \text{INT, I} \\
630 \text{FORMAT} (5X, '(I12, I12)') / \\
840 \text{WRITE} (8, 650) \quad F_Z N, F_C O, F_C O_2, F_H 2, F_H 2 O, F_P O_2, F_N 2 \\
\text{WRITE} (8, 655) \quad N_T N_E W \\
655 \text{FORMAT} (9N14.6) \\
660 \text{WRITE} (8, 660) \quad K_0, K_1, K_A, K_2, K_5, K_6 \\
\text{WRITE} (8, 670) \quad P_O_2, A_C Z N_0, X_1 \\
670 \text{WRITE} (8, 680) \quad M_F 2, M_F F 2, M_F F 3 \\
680 \text{FORMAT} (8, 690) \quad N_C, N_O_2, N_H_2, N_N 2, N_C O \\
680 \text{FORMAT} (8, 690) \quad N_C=', E13.6, 3X, 'N_O_2=', E13.6, 3X, 'N_H_2=', E13.6, 3X, 'N_N 2=', E13.6, 3X, 'N_C O=', E13.6, 3X) \\
700 \text{WRITE} (8, 680) \quad N_T N_E W=2.0 \times N_O_2 - N_H_2 O \\
700 \text{WRITE} (8, 680) \quad F_E R E D(\text{INT, I})=2.0 \times O_F E R \\
900 \text{CONTINUE} \\
\text{IF} (\text{INT} \EQ. 1) \quad \text{GOTO} 930 \\
\text{IF} (\text{INT} \EQ. \text{JT}) \quad \text{GOTO} 940 \\
Z_1 &= Z(\text{INT} - 1) \\
Z_2 &= Z(\text{INT} + 1) \\
F_2 2 &= F_E 2(\text{INT} + 1) \\
F_2 1 &= F_E 2(\text{INT} - 1) \\
F_3 1 &= F_E 3(\text{INT} - 1) \\
F_3 2 &= F_E 3(\text{INT} + 1) \\
D_T &= D_E L_T A T(\text{INT}) + D_E L_T A T(\text{INT} - 1)
GO TO 950
930 Z1=Z(INT)
    Z2=Z(INT+1)
    F21=FE2(INT)
    F22=FE2(INT+1)
    F31=FE3(INT)
    F32=FE3(INT+1)
    DT=DELTAT(INT)
    GO TO 950
940 Z1=Z(INT-1)
    Z2=Z(INT)
    F21=FE2(INT-1)
    F22=FE2(INT)
    F31=FE3(INT-1)
    F32=FE3(INT)
    DT=DELTAT(INT-1)

C
950 BTHWT=BTHWTI*(CAO(1)/CAO(INT)+SIO2(1)/SIO2(INT))/2.0
    DZDT=(Z2-Z1)/DT*BTHWT/(100.0-Z(INT)*1.2448)
    FUMRT(INT,1)=-1.0*DZDT/65.37
    FERED(INT,1)=(1.0/100.0)*((F22-F21)/DT*BTHWT+FE2(INT)*
    DZDT*1.2448))/55.85
    FERED(INT,6)=-(1.0/100.0)*((F32-F31)/DT*BTHWT+FE3(INT)*
    DZDT*1.2448))/55.85
    FERED(INT,7)=(FERED(INT,1)+FERED(INT,6))/2.0

C
    IF (WFL .EQ. 1)  WARN(INT)=STAR
    IF (WFL .EQ. 0)  WARN(INT)=BLNK

C
1000 CONTINUE
    WRITE (6,1001) (TEST(I), I=1,4)
1001 FORMAT (' ',10X,4A4,/)  
    WRITE (6,1002) WX
1002 FORMAT ('/',12X,'FEXO X=',F5.3,///
    112X,'REDUCTION RATES (KGMOLES/MIN)',///)
    WRITE (6,1003) NAME(1),NAME(2)
1003 FORMAT (3X,'PT',4X,'ACTUAL',6X,2A4,1X,'DATA',6X,
    1 'GRANT DATA',7X,'(FE2+)(ZN2+)/',4X,'(FEO)(ZNO)/',///
    219X,'COAL',4X,'COAL+AIR',5X,'COAL',4X,'COAL+AIR',7X,
    3 '(FE3+)',12X,'(FE3O4)',///)
    DO 1100 INT=1,JT
    WRITE (6,1005) INT,(FUMRT(INT,J), J=1,3),WARN(INT),
1105 FORMAT (3X,12,3X,F7.4,3X,F7.4,2X,F7.4,1X,A1,2X,F7.4,
    12X,F7.4,5X,F9.2,8X,F9.4,/)  
    WRITE (6,1010) HATCH,FERED(INT,1),(FERED(INT,J), J=2,5),
1010 FORMAT (3X,A2,2X,F8.4,3X,F8.4,2X,F8.4,4X,F8.4,2X,F8.4,
    130X,F8.4,///,7X,F8.4,/)  
    DO 1100 CONTINUE
1110 FORMAT (6,1110)
1110 FORMAT (30X,'* : METALLIC IRON SHOULD BE PRESENT',///
    130X,'## : FE3+ REDUCTION',///)
    STOP
END
APPENDIX IV

RADIATION HEAT TRANSFER TO A

COAL PARTICLE IN A TUYERE BUBBLE
As the coal particle traverses the tuyere bubble, it is heated by radiation. The situation is schematically illustrated in Fig. IV.1. To simplify the problem it will be assumed that both the coal particle and the tuyere bubble are spherical, and that the particle is stationary in the centre of the bubble.

Performing a heat balance on the particle:

\[ \dot{q}_p = \sigma F_{2-1} (T_{sl}^4 - T_p^4) A_{sl} \]  \( \text{...(IV.1)} \)

The rate of heat accumulation is then

\[ \sigma F_{2-1} (T_{sl}^4 - T_p^4) A_{sl} = \frac{4\pi}{3} r_p^3 \rho_c c_p, c \frac{dT_p}{dt} \]  \( \text{...(IV.2)} \)

where \( c_p, c \) is the specific heat of coal. This assumes that there is negligible resistance to heat flow (maximum heating rate). This equation becomes

\[ \frac{dT_p}{T_{sl}^4 - T_p^4} = \frac{\sigma F_{2-1} A_{sl}}{\frac{4\pi}{3} r_p^3 \rho_c c_p, c} \frac{dT_p}{dt} \]  \( \text{...(IV.3)} \)

Let

\[ \beta = \frac{\sigma F_{2-1} A_{sl}}{\frac{4\pi}{3} r_p^3 \rho_c c_p, c} \]  \( \text{...(IV.4)} \)

The time required to heat the particle from \( T_i \) to \( T_f \) is

\[ \int_{T_i}^{T_f} \frac{dT_p}{T_{sl}^4 - T_p^4} = \int_0^t \beta dt \]  \( \text{...(IV.5)} \)
Fig. IV.1 Coal Particle-Tuyere Bubble Geometry
giving

\[ t = \frac{1}{\beta} \left[ \frac{1}{4T_{sl}} \ln \left( \frac{T_{sl} + T_p}{T_{sl} - T_p} \right) + \frac{1}{2T_{sl}} \arctan \left( \frac{T_p}{T_{sl}} \right) \right] \frac{T_f}{T_i} \]  

\[ \text{...(IV.6)} \]

From Kreith 142

\[ F_2 - 1 = \frac{A_p}{A_{sl}} \epsilon_1 \]  

\[ \text{...(IV.7)} \]

Substituting this into Equation IV.4 gives

\[ \beta = \frac{3\sigma \epsilon_1}{4r_p \rho C c_{p,c}} \]  

\[ \text{...(IV.8)} \]

Evaluating parameters:

(a) \( \epsilon_1 \approx 0.7 \), from Kreith 143 for graphite at room temperature, source temperature 1200°C

(b) \( \sigma = \text{Stefan Boltzmann constant} = 5.671(10^{-8}) \text{ J/s-m}^2\text{-K}^4 \)

(c) \( \rho C = 1500 \text{ kg/m}^3 \) reference (109)

(d) \( c_{p,c} = 1340 \text{ J/kg·K} \), reference (109)

(e) \( r_p = 40 \mu \text{m} \)

Therefore \( \beta = 3.70(10^{-10}) \text{ K}^{-3}\text{s}^{-1} \)

Assuming an initial temperature of 20°C and final temperature of 600°C, evaluation of Equation IV.6 gives

\[ t = 350 \text{ ms} \]
APPENDIX V

FUMING FURNACE MASS BALANCE
There are nine different components to the fuming furnace mass balance at Company C:

1 : initial slag
2 : final slag
3 : lead blast furnace dust
4 : coal ash carry over
5 : slag carry over
6 : coal carry over
7 : flue clinker
8 : boiler ash
9 : fume

Lead blast furnace dust (component 3) is blown into the slag fuming system and therefore must be included in the balance. If \( W_{x,j} \) is the weight fraction of \( j \) in component \( x \) and \( M_x \) is the mass of component \( x \), a mass balance over the furnace gives:

\[
W_{1,j} M_1 + W_{3,j} M_3 + W_{4,j} M_4 + W_{5,j} M_5 + W_{6,j} M_6 = W_{2,j} M_2 + W_{7,j} M_7 + W_{8,j} M_8 + W_{9,j} M_9 \quad \ldots (V.1)
\]

Due to uncertainties in chemical assays, only balances on particular species have any validity. The following species were selected for the balance: Zn, SiO2, Fe and C.

Several other equations are available relating various quantities in Equation V.1. The initial bath weight \( (M_1) \) and
the amount of blast furnace dust \((M_3)\) are numbers which are relatively easy to obtain. Finally, from historical data, the following relationships were obtained

\[
0.75 M_1 < M_2 < 0.96 M_1 \quad \cdots (V.2)
\]

and

\[
0.02 M_9 < M_7 + M_8 < 0.20 M_9 \quad \cdots (V.3)
\]

Equation V.2 relates the final bath weight to the initial weight. Equation V.3 is a relation between the fume, ash and clinker.

Since this system of equations contains inequalities it cannot be solved for a specific solution. Instead only the range in which a particular variable lies can be determined. A linear programming routine developed by the U.B.C. Computing Centre was used.

The assays on each component are presented in Table V.1. Note that the slag bath was not assumed to be a source of Fe, SiO\(_2\) or C, except through component 5, slag carry over. Thus any discrepancy between the charge and tail mass of non-fumed components was ignored. The slag carry over assay was estimated as the average of the charge and tail assays. In order to determine the coal carry over as coal ash, the silica content of the coal ash was set to the silica content of the coal. Finally the carbon content of the coal was assumed to be fixed carbon content because devolatilization is likely
<table>
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<th>Cycle</th>
<th>Components</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<td>14.1</td>
<td>4.5</td>
<td>14.8</td>
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<td>9.3</td>
<td>-</td>
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<td>-</td>
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<td>-</td>
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<td>-</td>
<td>29</td>
<td>-</td>
<td>4.3</td>
<td>1.6</td>
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</tr>
<tr>
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<td>C</td>
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<td>-</td>
<td>-</td>
<td>0.1</td>
<td>62</td>
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<td>-</td>
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<td>-</td>
<td>36.5</td>
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<td>-</td>
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<td>4.4</td>
<td>1.5</td>
<td>0.1</td>
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<td>-</td>
<td>-</td>
<td>0.1</td>
<td>62</td>
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<td>0.3</td>
<td>0.9</td>
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<td>4.3</td>
<td>14.8</td>
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<td>9.0</td>
<td>-</td>
<td>49.8</td>
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<td>9.6</td>
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<td>-</td>
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<td>-</td>
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<td>61</td>
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<td>10.1</td>
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<td>-</td>
<td>30.1</td>
<td>-</td>
<td>3.9</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
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<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
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<td>0.3</td>
<td>1.5</td>
<td>1.7</td>
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<tr>
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<td>14.8</td>
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<td>9.4</td>
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<td>38</td>
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<td>9.6</td>
<td>4.0</td>
<td>1.9</td>
<td>0.7</td>
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<tr>
<td></td>
<td>Fe²</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
<td>29.5</td>
<td>-</td>
<td>3.9</td>
<td>1.2</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>61</td>
<td>-</td>
<td>0.3</td>
<td>1.2</td>
<td>1.5</td>
</tr>
</tbody>
</table>
to have occurred by the time the coal reaches the fume.

Bath weight, blast furnace dust weight and coal weight to the furnace over the mass balance period are reported in Table V.2.
### TABLE V.2

**Mass Balance Components**

<table>
<thead>
<tr>
<th>Cycle</th>
<th>t (min)</th>
<th>$M_1$ (kg)</th>
<th>$M_3$ (kg)</th>
<th>Total Coal (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C41</td>
<td>140</td>
<td>52000</td>
<td>3730</td>
<td>8590</td>
</tr>
<tr>
<td>C42</td>
<td>75</td>
<td>52000</td>
<td>2000</td>
<td>6350</td>
</tr>
<tr>
<td>C43</td>
<td>125</td>
<td>52000</td>
<td>3330</td>
<td>9560</td>
</tr>
<tr>
<td>C44</td>
<td>150</td>
<td>52000</td>
<td>4000</td>
<td>10400</td>
</tr>
<tr>
<td>C51</td>
<td>120</td>
<td>52000</td>
<td>4130</td>
<td>7140</td>
</tr>
<tr>
<td>C52</td>
<td>125</td>
<td>52000</td>
<td>3860</td>
<td>7510</td>
</tr>
<tr>
<td>C53</td>
<td>140</td>
<td>52000</td>
<td>3730</td>
<td>8850</td>
</tr>
</tbody>
</table>
APPENDIX VI

FURNACE WALL HEAT TRANSFER MODEL
The transfer of heat through the wall of the slag fuming furnace can be simply modelled if we assume the wall structure shown in Fig. VI.1 and neglect any contact resistance at the interface between the slag and the steel.

The following equations express the heat transfer in this system:

\[ \dot{q}_{\text{bath}} = h_t A(T_{sl} - T_{mp}) \]  \hspace{1cm} \text{(VI.1)}

\[ \dot{q}_{sl} = \left(\frac{g_{sl}}{d_{sl}}\right) A(T_{mp} - T_I) \]  \hspace{1cm} \text{(VI.2)}

\[ \dot{q}_{st} = \left(\frac{g_{st}}{d_{st}}\right) A(T_I - T_W) \]  \hspace{1cm} \text{(VI.3)}

At steady state

\[ \dot{q}_{\text{bath}} = \dot{q}_{sl} = \dot{q}_{st} \]  \hspace{1cm} \text{(VI.4)}

Solving the above system of four equations to eliminate \( T_I \), and the heat flow terms gives

\[ d_{sl} = \frac{g_{sl}}{h_t} \left(\frac{T_{mp} - T_W}{T_{sl} - T_{mp}}\right) - \frac{d_{st} g_{sl}}{q_{st}} \]  \hspace{1cm} \text{(VI.5)}
Fig. VI.1  Fuming Furnace Wall Structure
APPENDIX VII

SLAG FUMING MODEL PROGRAM
IMPLICIT REAL*8 (A-Z)

REAL*4 OX,CX

INTEGER JFLAG,JCOUNT,JC,STEP,STEP2,LFLAG,STEPC,STEP3,IFL,
1JCNT2,JCNT3,MST,INT,J,JT,JI1,I,IX,INTS,PH,CTR,N,KFL

DIMENSION TEST(4),HM(12),COALM(20),PAIR(20),PP(20),
1SP(20),BATHT(20),ZM(20),C(20),FE2M(20),FE3M(20),CAOM(20),
2AL2O3M(20),DELTAT(20),OXY(20),OXYP(20),COMET(9),CHR(4),
3INPTT(20),SI02M(20),FZNM(20),FCOM(20),FCO2M(20),FH2M(20),
4FH2OM(20),FCM(20),SM(20),Y(11),F(11),T(11),S(11),G(11),
5SAIR(20),WR(4)

EXTERNAL FUNC

COMMON C1S,C2,C3,C4,V1,V2,V3,V4,ZN,FE2,FE3X,CAO,SIO2,
1AL2O3,TEMP,INTR,PT,TRES,ACZNO,ACIR1,DR,DELT1,DELT2,DELT1,
2A0,EA,RO,ZNOF,DFEOF,DFE3F,
3WX,PYRRT,INT,JCOUNT,JCNT2,JCNT3,MST,STEPC,PH,CTR

DATA HZNOS/19680.0000/,HZNO/460240.000/,HCO/-114390.55/,
1HC02/-395346.20/,HH2O/-247483.60/,HFE2O/329615.50/,
2HVOL/-430.000000/,RC/0.0820500000/,RHOC/1500.000/,
3RHOSL/3900.0000/,VIS/0.5000000/,KSL/1.5000/,HC/600.0/,
4STT/373.0/,GE/'<'/,LE/'<'/,EQ/'='/,HFUS/341200.0/,5CP/1357.000000/,CPV/1192.4/,PI/3.141592654/

READ (7,43) IX,OX,BX,CX
READ (7,45) INTS
READ (7,47) OBJ
READ (7,53) BTHWT1
READ (7,48) (COMET(I), I=1,5)
READ (7,49) (TEST(I),TEST(2)
READ (7,51) IN,JT,CTR

IN : 1 = NO DATA PRINTED
2 = ALL DATA PRINTED

CTR : 1 = WALL EFFECT
2 = NO WALL EFFECTS
3 = ZN/COAL, HEAT BALANCE PROFILES
4 = 2ND ORDER BATH MODEL

READ (7,54) C1,C2,C3,C4,V1,V2,V3,V4
READ (7,50) WX,FE3ST
JT1=JT-1
READ (7,55) (COALM(J), J=1,JT1)
READ (7,57) (PAIR(J), J=1,JT)
READ (7,59) (PP(J), J=1,JT)
READ (7,57) (SAIR(J), J=1,JT)
READ (7,59) (SP(J), J=1,JT)
READ (7,65) (INPTT(J), J=1,JT)
READ (7,57) (OXY(J), J=1,JT)
READ (7,59) (OXYP(J), J=1,JT)
READ (7,65) (BATHT(J), J=1,JT)
READ (7,69) (ZM(J), J=1,JT)
READ (7,69) (C(J), J=1,JT)
READ (7,69) (FE2M(J), J=1,JT)
READ (7,69) (FE3M(J), J=1,JT)
READ (7,69) (CAOM(J), J=1,JT)
READ (7,69) (SI02M(J), J=1,JT)
READ (7,69) (AL203M(J), J=1,JT)
READ (7,71) (DELTAT(J), J=1,JT1)
READ (7,73) (FURLEN,FURWID,NTUY
READ (7,75) (SLMPT,PORO,TCP
READ (7,76) (VBATH,BFREQ
READ (7,69) (CHCAO,CHSIO,CHFEO,CHFEM,CHZNO
READ (7,69) (WCAO,WSIO2,WFE0,WFE,M,WZNO

C

43 FORMAT (I2,1X,A4,F8.1,1X,A4)
45 FORMAT (I2).
47 FORMAT (A8)
48 FORMAT (6A8)
49 FORMAT (10A8)
50 FORMAT (F5.3,1X,F4.2)
51 FORMAT (212,1X,I1)
54 FORMAT (20F6.4)
53 FORMAT (20F8.1)
55 FORMAT (20F7.3)
57 FORMAT (20F7.3)
59 FORMAT (20F8.3)
65 FORMAT (20F8.3)
69 FORMAT (20F7.4)
71 FORMAT (20F6.3)
73 FORMAT (2(F5.2,1X),F3.0)
75 FORMAT (F6.1,1X,F4.1,1X,F5.3)
76 FORMAT (F5.2,1X,F5.1)
77 FORMAT (20(F7.5,1X))
79 FORMAT (3(F5.3,1X))
83 FORMAT (3(F7.3,1X))

C

READ (7,77) (FZNM(J), J=1,JT1)
READ (7,77) (FCOM(J), J=1,JT1)
READ (7,77) (FCO2M(J), J=1,JT1)
READ (7,77) (FH2M(J), J=1,JT1)
READ (7,77) (FH20M(J), J=1,JT1)
READ (7,77) (FCM(J), J=1,JT1)

C

READ (7,79) FF,YY
READ (7,79) FOC
READ (7,83) TSR,TEND,TP

C

THIRD=1.0/3.0
KFL=0
RHOSLF=RHOSL*(1.0-PORO/100.0)
INT=INTS-1
C1S=C1
YO=1.0-FF-YY
TS2=0.0
TT=0.0
90 INT=INT+1
TN=TT+DELTAT(INT)
IF (TS2 .EQ. 0.0) TS=TSR
IF (TS2 .NE. 0.0) TS=TS2
IF (TS2 .NE. 0.0) TS2=0.0

C
BAREA=FURLEN*FURWID
PAIRA=(PAIR(INT)+PAIR(INT+1))/2.0
PPA=(PP(INT)+PP(INT+1))/2.0
SAIRA=(SAIR(INT)+SAIR(INT+1))/2.0
SPA=(SP(INT)+SP(INT+1))/2.0
INPT=(INPTT(INT)+INPTT(INT))/2.0+273.16
GP=PAIRA*PPA/101.325*(273.16/(INPT))
GS=SAIRA*SPA/101.325*(273.16/(INPT))
GG=GP+GS
OXYA=(OXY(INT)+OXY(INT))/2.0
OXYP=(OXYP(INT)+OXYP(INT+1))/2.0
OIN=0.209*GG/(0.08205*273.16) + (OXYA*OXYP/101.325)/(0.08205*273.0)
COAL=COALM(INT)
HCOALC=(C1+C2*V1)/12.01*HCO2+(C2*V2)/2.016*HH2O-HVOL

O2=(C1+C2*V1)/12.01+0.5*(C2*V2)/2.016-(C2*V3)/32.00

C
O2C=O2*YY*COAL
IF (O2C .GE. OIN) YY=OIN/(O2*COAL)
HTOX=HCOALC*YY*COAL

C
IF (TT .GT. 0.0) GOTO 430

C
SLMPT=SLMPT+273.16
ZN2=ZM(INT)
FE22=FE2M(INT)-3.484*SM(INT)
FE32=FE3M(INT)+3.484*SM(INT)
CAO2=CAOM(INT)
SIO22=SIO2M(INT)
AL2O32=AL2O3M(INT)
BTHWT2=BTHWT1

C
BTHWT2=BATHT(INT)+273.16

C
********** READ INPUT DATA FOR PARTICLE CONSUMPTION MODEL
C
READ (8,101) INTR,TEMP,PT
101 FORMAT (D9.3,1X,F6.1,1X,F6.3,1X,F7.4)
READ (8,105) ACZNO,ACIR1
105 FORMAT (F6.3,1X,F6.3)
READ (8,111) DZNOF,DFEOF,DFE3F,DR
111 FORMAT (F9.5,1X,F9.5,1X,F9.5,1X,F7.3)
C
IF STEPC = 1 NO BOUDOUARD REACTION
C
READ (8,115) DELT1,DELT2,E
115 FORMAT (//,D9.3,1X,D9.3,1X,D9.3)
READ (8,121) A0,EA,RO
121 FORMAT (D9.3,1X,D9.3,1X,F4.1)
READ (8,125) JCOUNT,JCNT2,JCNT3,MST
125 FORMAT (I 5,1X,I 5,1X,I 5,1X,I 5)
READ (8,131) PYRRT
131 FORMAT (D9.3)

C
IF (IN .EQ. 1) GOTO 400

C
WRITE (6,199)
199 FORMAT (' 1' ,20X,'FUMING CYCLE PREDICTION',10X,
1' VERSION 7',///)

C
WRITE (6,201) TEST(1),TEST(2)
201 FORMAT (30X,'COMPANY:',2X,2A8,//)

C
IF (CTR .EQ. 2) WRITE (6,202)
202 FORMAT (35X,'### NO WALL EFFECT ###',//)

C
IF (CTR .EQ. 3) WRITE (6,203)
203 FORMAT (35X,'### ZN/COAL & DT/DT VS TRES PROFILES
1 ###',//)

C
WRITE (6,205)
205 FORMAT (20X,'COAL',40X,'AIR',//)

C
WRITE (6,207) COAL,PAIRA,PPA
207 FORMAT (25X,'COAL RATE:',2X,F5.2,2X,'KG/MIN',16X,'PRIMARY
1 AIR',4X,F7.2,2X,'M<3>/MIN',//,90X,F6.1,2X,'KPASCALS')

C
WRITE (6,209) C1,C2,SAIRA,C3,SPA,C4
209 FORMAT (24X,'COAL ASSAY:',2X,F5.3,2X,'FIXED CARBON',//,
137X,F5.3,2X,'VOLATILES',12X,'SECONDARY AIR',3X,F7.2,2X,
2'M<3>/MIN',//,37X,F5.3,2X,'ASH',35X,F6.1,2X,'KPASCALS',//,
337X,F5.3,2X,'MOISTURE')

C
WRITE (6,211) V1,INPT,V2,V3
211 FORMAT (20X,'VOLATILE ASSAY:',2X,F5.3,2X,'C',28X,'TEMP:',
14X,F6.1,2X,'DEG K',//,37X,F5.3,2X,'H',//,37X,F5.3,2X,'O',
2//)

C
ZNOI=ZM(INT)*81.37/65.37
WRITE (6,213) ZM(INT),BTHT2,ZNOI,CAOM(INT),BTHWT1,
1SI02M(INT),AL203M(INT),SLMPT
213 FORMAT (20X,'SLAG ASSAY (PER CENT)',20X,
1'BATH DATA (INITIAL)',//,36X,'INITIAL',5X,
2'/',30X,'ZN',5X,F5.2,20X,'TEMP',9X,F6.1,2X,'DEG K',//,29X,
3'ZNOI',1(5X,F5.2),//,29X,'CAO',5X,F5.2,20X,'BATH WT',5X,
4F8.1,1X,'KG',//,28X,'SI02',1(5X,F5.2),/,
527X,'AL203',5X,F5.2,20X,'SLAG MPT',5X,F6.1,2X,'DEG K')

C
WRITE (6,215) FE22,FE32,FE3ST,WX
C
WRITE (6,220) FURLEN,NTUY,FURWID
220 FORMAT (/,'FURNACE LENGTH = ',F6.2,1X,'M',/,'NUMBER OF TUYERES = ',F3.0,/,'FURNACE WIDTH = ',
2F6.2,1X,'M',/)
C
WRITE (6,225) BFREQ,VBATH,TCP
225 FORMAT (/,,'BUBBLE FREQUENCY = ',F5.1,1X,'SEC-1',/,,'BATH VELOCITY = ',F5.2,1X,'M/SEC',/,'TUYERE',
2'COLUMN VOID FRACTION = ',F5.3,/)
400  WRITE (6,410)  
410  FORMAT ('//,7X,'T',10X,'ZN',10X,'FE3+',7X,'FE2+',7X, \\
1'TEMP',12X,'BATH WT',7X,'CAO',8X,'ZN FR',7X,'FE3 R', \\
27X,'FE2 O',//)  
C
   IF (CTR .EQ. 3) GOTO 416  
   WRITE (6,415)  
415  FORMAT (15X,'RHOSLM',10X,'ACZNO',5X,'ACIR1',8X,'TRES')  
C
416  WRITE (6,417)  
417  FORMAT (9X,'FZN',10X,'FCO',10X,'FCO2',9X,'FH2',10X, \\
1'FH20',9X,'FN2',10X,'FC',11X,'PH')  
C
   IF (CTR .EQ. 3) WRITE (6,418)  
418  FORMAT (5X,'T',9X,'ZFR',8X,'ZNP',7X,'ZN/COAL',5X, \\
1'DT/DT',//)  
   WRITE (6,610) TT,ZN2,FE32,FE22,BTHT2,BTHWT2,CA02  
420  CONTINUE  
   IF (TS2 .EQ. 0.0) TS=TSR  
430  CONTINUE  
   ZN1=ZN2  
   FE21=FE22  
   FE31=FE32  
   CAO1=CAO2  
   SI021=SI022  
   AL2031=AL2032  
   BTHT1=BTHT2  
   BTHWT1=BTHWT2  
C
   FE2=FE21  
   ZN=ZN1  
   FE3=FE31  
   CAO=CAO1  
   SI02=SI021  
   AL203=AL2031  
C
C
   FE3X=FE3  
   IF (FE3 .GT. FE3ST) FE3X=FE3ST  
C
   TEMP=BTHT1  
C
   VBUBB=(GG/60.0)*(1.0/NTUY)*(TEMP/273.16)*(1.0/BFREQ)  
   DBUBB=(6.0*VBUBB/PI)**THIRD  
   SLGH=BTHT1/(RHOSLF*FURLEN*(FURWID-2.0*TCP*DBUBB))  
   XPATH=SLGH+(FURWID-2.0*DBUBB)/4.0  
   TRES=XPATH/VBATH  
C
   WRITE (6,435)  
435  FORMAT (6,435)  
435  FORMAT ('//,3X,'-----------------------------', \\
1'-----------------------------')  
C
   X=0.0  
   PH=0  
   N=11  
C
\[ \text{PARTOI} = 4.0 \pi / 3.0 \times \text{INTR} \times 3.0 \times \text{RHOC} \]

\begin{verbatim}
CALL FUNC (X, Y, F)
YT = Y(1) + Y(2) + Y(3) + Y(4) + Y(5) + Y(6)
FZN = Y(1) / YT
FCO = Y(2) / YT
FCO2 = Y(3) / YT
FH2 = Y(4) / YT
FH20 = Y(5) / YT
FN2 = Y(6) / YT
FC = Y(7) * 12.01 / PARTOI

IF (CTR .EQ. 3) WRITE (6, 440) FZN, FCO, FCO2, FH2, FH20, FN2, FC

IF (CTR .EQ. 3) TRES = 0.0
432 IF (CTR .EQ. 3) TRES = TRES + DELT2

Z = TRES
H = DELT1
HMIN = 1.0D-04 * H

438 CALL DRKC(N, X, Z, Y, F, H, HMIN, E, FUNC, G, S, T)

C1 = C1S
YT = Y(1) + Y(2) + Y(3) + Y(4) + Y(5) + Y(6)
FZN = Y(1) / YT
FCO = Y(2) / YT
FCO2 = Y(3) / YT
FH2 = Y(4) / YT
FH20 = Y(5) / YT
FN2 = Y(6) / YT
FC = Y(11) * 12.01 / PARTOI

WRITE (6, 440) FZN, FCO, FCO2, FH2, FH20, FN2, FC, PH

440 FORMAT (10X, 7(F7.5, 5X), I1)

WALLA1 = SLGH * 2.0 * (FURLEN + FURWID) + BAREA
WALLA = WALLA1
IF (CTR .EQ. 2) WALLA = 0.0

ZFR = FZN / (FCO + FCO2) * FF * COAL * (C1 + C2 * V1 - FC) / 12.01
ZNTP = ZFR * TS / 65.37
ZNTPC = ZNP / (COAL * TS)
FE3R = 2.0 * (FCO + 2.0 * FCO2 + FH2O) / (FCO + FCO2) * FF * COAL * (C1 + C2 * V1 - FC) / 12.01 - ZFR - FF * COAL * C2 * V3 / 16.00
FEOO = 4.0 * FOC * (OIN - O2C)
IF (FEOO .LT. 0.0) WRITE (6, 451)

451 FORMAT (' FEOO < 0.0', //)

IF (FEOO .LT. 0.0) FEOO = 0.0
COP = FCO / (FCO + FCO2) * FF * COAL * (C1 + C2 * V1 - FC) / 12.01
CO2P = COP * FCO2 / FCO
H20P = COP * FH2O / FCO

HRRED = ZFR * (-1.0 * HZNOS + HZNO) + COP * HCO + CO2P * HCO2 + H20P * HH2O + FE3R / 2.0 * HFE2O
\end{verbatim}
\[ HFEOO = FEOO \times (-1.0 \times HFEO) / 2.0 \]

\[ QH1 = -1.0 \times (GP \times (BTHT1 - 293.0) \times CP + GS \times (BTHT1 - INPT)) \]
\[ + 1 \times CP + C4 \times COAL / 18.0 \times (45200000.0 + 41840.0 \times (BTHT1 - 373.16)) + \]
\[ 2 \times COAL \times 2050200.0 + HC \times 60.0 \times WALLA1 \times (BTHT1 - SLMPT) + \]
\[ 3 \times (HRED + HTOX + HFEOO) \times 1000.0 \]
\[ QA = QH1 \times TS / (CPV \times BTHWT1) \]
\[ QB = 1.0 \times KSL \times WALLA \times RHOSL \times (SLMPT - STT) / (HC \times CPV \times BTHWT1) \]
\[ A11 = 1.0 \times QB \times CPV / (BTHT1 - SLMPT) \]
\[ B11 = -2.0 \times QB \times SLMPT \times CPV / (BTHT1 - SLMPT) - SLMPT - BTHT1 - QA \]
\[ C11 = SLMPT**2 \times QB \times CPV / (BTHT1 - SLMPT) + SLMPT \times (BTHT1 + QA \]
\[ - QB \times CPV + QB \times HFUS / (BTHT1 - SLMPT) \]
\[ BTHT2 = (-1.0 \times B11 + (B11**2 - 4.0 \times A11 \times C11)**0.5) / (2.0 \times A11) \]

\[ DTPDT = (BTHT2 - BTHT1) / TS \]
\[ IF (CTR . EQ. 3) WRITE (6,435) \]
\[ IF (CTR . EQ. 3) WRITE (6,500) X,ZFR,ZNP,ZNCTL,DTPDT \]
\[ IF (CTR . EQ. 3) WRITE (6,435) \]
\[ IF (CTR . EQ. 3 .AND. X .GT. TEND) GOTO 700 \]
\[ IF (CTR . EQ. 3) GOTO 432 \]

\[ WALLC = -1.0 \times (KSL / HC) \times (SLMPT - STT) \times (1.0 / (BTHT2 - SLMPT)) \]
\[ - 1.0 / (BTHT1 - SLMPT) \]
\[ WALLA \times RHOSL \]

\[ WRITE (6,515) WALLC \]
\[ 515 FORMAT (10X,'WALLC = ',F7.2) \]

\[ WRITE (6,435) \]

\[ BTHWT2 = BTHWT1 - ZFR \times TS \times 81.37 - FE3R / 2.0 \times TS \times 16.00 + FEOO / 2.0 \]
\[ + TS \times 16.00 + WALLC \times COAL \times TS \times C3 \]
\[ ZN2 = (ZN1 / 100.0 \times BTHWT1 - ZFR \times TS \times 65.37 + WZNO \times WALLC \times 0.8034 / \]
\[ 1100.0) / BTHWT2 \times 100.0 \]
\[ FE32 = (FE31 / 100.0 \times BTHWT1 + FEOO \times TS \times 55.85 - FE3R \times TS \times 55.85 + \]
\[ WFEM \times WALLC \times 0.4824 / 100.0) / BTHWT2 \times 100.0 \]
\[ FE22 = (FE21 / 100.0 \times BTHWT1 + FE3R \times TS \times 55.85 - FEOO \times TS \times 55.85 + \]
\[ 1 \times (WFEO \times 0.7773 + WFEM \times 0.2412) \times WALLC / 100.0) / BTHWT2 \times 100.0 \]

\[ CAO2 = (CAO1 \times BTHWT1 + WCAO \times WALLC) / BTHWT2 \]
\[ SI022 = (SI021 \times BTHWT1 + WSI02 \times WALLC) / BTHWT2 \]
\[ AL2032 = (AL2031 \times BTHWT1 + 5.0 \times WALLC) / BTHWT2 \]

\[ IF (CTR . NE. 4) GOTO 580 \]
\[ IF (KFL . EQ. 1) GOTO 540 \]
\[ IF (KFL . EQ. 2) GOTO 580 \]
\[ ZNS = ZN1 \]
\[ FE2S = FE21 \]
\[ FE3S = FE31 \]
\[ CAOS = CAO1 \]
\[ SI02S = SI021 \]
\[ AL203S = AL2031 \]
ZFR1 = ZFR
FE3R1 = FE3R
FEOO1 = FEOO
HRED1 = HRED
HFEOO1 = HFEOO
BTHTS = BTHT1
BTHWTS = BTHWT1
KFL = 1
GOTO 430

C
540 ZN1 = ZNS
FE21 = FE2S
FE31 = FE3S
CA01 = CAOS
SI021 = SI02S
AL2031 = AL203S
BTHWT1 = BTHWTS
ZFR = (ZFR + ZFR1)/2.0
FE3R = (FE3R + FE3R1)/2.0
FEOO = (FEOO + FEOO1)/2.0
HRED = (HRED + HRED1)/2.0
HFEOO = (HFEOO + HFEOO1)/2.0
BTHT1 = BTHTS
KFL = 2
GOTO 480

C
580 KFL = 0
TT = TT + TS
TTT = TT + TS
IF (TT + TS .GT. TN) TS2 = TTT - TN
IF (TT + TS .GT. TN) TS = TN - TT
IF (TT .GE. TN) GOTO 630
IF (TT .GE. TP) GOTO 600
GOTO 650

C
600 WRITE (6, 610) TT, ZN2, FE32, FE22, BTHT2, BTHWT2, CAO2, ZFR, 1FE3R, FEOO
610 FORMAT (/ , 3X, 5(F7.2, 5X), 5X, F7.1, 5X, 4(F7.2, 5X), //)

C
TPS = TP
TP = TT + 1.0
IF (TP .LT. TPS + TS) TP = TPS + TS
GOTO 650
630 WRITE (6, 631) TT, ZN2, FE32, FE22, BTHT2, BTHWT2, CAO2, ZFR, 1FE3R, FEOO
631 FORMAT (/ , 3X, 5(F7.2, 5X), 5X, F7.1, 5X, 4(F7.2, 5X), //)

IF (TT .LT. TEND) GOTO 90

C
650 IF (TT .LT. TEND) GOTO 420
WRITE (6, 610) TT, ZN2, FE32, FE22, BTHT2, BTHWT2, CAO2, ZFR, 1FE3R, FEOO

C
700 CONTINUE
STOP
END
SUBROUTINE FUNC(X,Y,F)

**********************************************************************
* COAL PARTICLE - SLAG REACTION ANALYSIS *
* ZNO AND FE2O3 REDUCTION ON COAL PARTICLE BUBBLE *
* WITH MASS TRANSFER OF THESE SPECIES (AND FEO) *
* AND BOUDOUARD REACTION AS THE RATE CONTROLLING *
* STEPS *
* INCLUDING PYROLYSIS *
**********************************************************************

IMPLICIT REAL*8 (A-Z)

INTEGER JFLAG,JCOUNT,JC,STEP,STEP2,LFLAG,STEPC,STEP3,IFL,
1JCNT2,JCNT3,MST,INT,RFL,PH,CTR,II

DIMENSION Y(11),F(11)

COMMON C1S,C2,C3,C4,V1,V2,V3,V4,ZN,FE2,FE3X,CAO,SIO2,
1AL2O3,TEMP,INTR,PT,TRES,ACZNO,ACIR1,DR,DELT1,DELT2,DELTI,
2A0,EA,RO,DZNOF,DFEOF,DFE3F,
3WX,PYRRT,INT,JCOUNT,JCNT2,JCNT3,MST,STEPC,PH,CTR

DATA PI/3.141592654/,RHOC/1500.000000/,RHOSL/3900.00
100000/,G/9.81000000/,VIS/0.50000000/,AC/1.00000000/,
2RC/0.08205000000/,RJ/8.31440000000/

********** CALCULATION OF SLAG MOLAR DENSITY FOR CONVERSION
OF ACTIVITY LEVELS TO MOLAL CONCENTRATIONS

UNKNOWN SPECIES (UNK) MOLECULAR WT = 60.0

M-X = KG-MOLES X (PER 100 WT UNITS)
X = % X
C-X-B = BULK CONCENTRATION X (KG-MOLES/M3)
RHOSL = SLAG DENSITY (KG/M3)

PCO2I=0.0
IF (X .GT. 0.0 .OR. PH .EQ. 2) GOTO 90
WX1=3.0*WX-2.0
WX2=2.0*(1.0-WX)
25 FE3=FE3X
MZNO=ZN/65.37
MFE2O3 = FE2/(WX1*55.85)
MFE3O4 = (1.0/55.85)*(WX2*FE2-WX1*FE3)/(WX2-2.0*WX1)
MFE2O2 = (FE2/55.85-MFE3O4)/WX1

C
MCAO = CAO/56.06
MSIO2 = SI02/60.09
MAL2O3 = AL2O3/101.96
WTT = MZNO*81.37 + MFEO* (WX*55.85 + 16.00) + MFE2O3*159.7+ CAO + MSIO2 + AL2O3
UNK = 100.0-WTT
MUNK = UNK/60.0
ZNO = MZNO*81.37
FE0 = MFE0*71.85
FE2O3 = MFE2O3*159.7
CZNOB = RHOSL* MZNO/100.0
CFEOB = RHOSL* MFE0/100.0
CFE2O3B = RHOSL* MFE2O3/100.0
CFE3O4B = RHOSL* MFE3O4/100.0
CCAOB = RHOSL* MCAO/100.0
CSI02B = RHOSL* MSIO2/100.0
CAl2O3B = RHOSL* MAL2O3/100.0
CUNKB = RHOSL* MUNK/100.0
RHOSL = CZNOB + CFEOB + CFE2O3B + CCAOB + CSI02B + CAL2O3B + CUNKB

C
CS = MCAO/MSIO2
LNACF = (3310.0*CS + 1656.5)/TEMP - 1.887*CS - 0.6394
LNACZ = (16390.0*CS - 12030.0)/TEMP - 10.894*CS + 8.8317
ACZNO = DEXP(LNACZ)
ACFEO = DEXP(LNACF)
ACFE3O = DEXP(8495.0/TEMP - 2.653)
AC1 = ACFE3O/ACFEO**((3.0/WX)

C
MFFEO = CFEOB/RHOSL
MFFE2O = CFE2O3B/RHOSL
MFFE02 = CFEO2/RHOSL
MFFE3O = CFE3O4/RHOSL

C
E = RJ*TEMP
G5 = -624420.0 + 250.2*TEMP
K5 = DEXP(-1.0*G5/E)
G7 = -582580.0 + 260.6*TEMP
K7 = DEXP(-1.0*G7/E)

C
ACIR2 = (K7/K5)**0.5*ACIR1*(MFFE0**2)/(MFFE0-MFFE2O)**3
AC1 = MFFE0**(4.0/WX)*K7/MFFE2O**2
AC2 = (ACIR1**2*MFFE3O**2/K5/MFFE2O**2*(6.0/WX))
AC3 = AC2**((3.0-2.0/WX)/(4.0-3.0/WX))
ACIR2 = (AC1*AC3)**0.5

C
DBASE = 10.0**((-5450.0/TEMP - 1.93-4.0)
DZNO = DZNOF*DBASE
DFEO = DFEOF*DBASE
DFE2O3 = DFE3F*DFEO/DR
W = A0*DEXP(-1.0*EA/(RJ*TEMP))
**REDUCTION PHASE I: REDUCTION IN THE PRESENCE OF COAL PARTICLE**

******* TITLES PRINTED

******* FREE ENERGY DATA AND EQUILIBRIUM CONSTANTS

\[ E = R J \times T E M P \]
\[ G_0 = -228781.1 - 171.5 \times T E M P \]
\[ K_0 = D E X P \left( -1.0 \times G_0 / E \right) \]
\[ G_6 = -920480.0 + 396.6 \times T E M P \]
\[ K_6 = D E X P \left( -1.0 \times G_6 / E \right) \]

\[ \text{H}_2\text{O} + \text{CO} = \text{CO}_2 + \text{H}_2 \]
\[ G_F = -33472.05 + 29.35 \times T E M P \]
\[ K_F = D E X P \left( -1.0 \times G_F / E \right) \]
\[ G_D = 212756.4 - 142.45 \times T E M P \]
\[ K_D = D E X P \left( -1.0 \times G_D / E \right) \]
\[ G_G = 179284.35 - 113.1 \times T E M P \]
\[ K_G = D E X P \left( -1.0 \times G_G / E \right) \]

\[ \text{C}_2 \text{GH} = 18179.0 - 52.7 \times T E M P \]
\[ \text{GH} = 8870.1 - 35.95 \times T E M P \]
\[ K_H = D E X P \left( -1.0 \times G_H / E \right) \]

\[ \text{C} + \text{CO}_2 = 2\text{CO} \]
\[ G_J = 166565.1 - 170.96 \times T E M P \]
\[ K_J = D E X P \left( -1.0 \times G_J / E \right) \]

\[ \text{EXP}^{23} = 2.0 / 3.0 \]
\[ \text{EXP}^{13} = 1.0 / 3.0 \]

******* INITIAL VALUE CALCULATIONS

\[ \text{RHOB} = \text{BUBBLE DENSITY} \]
\[ \text{PARTOI} = \text{INITIAL PARTICLE WT} \]
\[ \text{CC} = \text{CONTAINED C (WT)} \]
\[ \text{T} = \text{ELAPSED TIME} \]
\[ \text{P-X} = \text{PARTIAL PRESSURE X} \]
\[ \text{G-X} = \text{KG-MOLES X IN GAS PHASE} \]

\[ \text{IF (PH .EQ. 2 .OR. X .GT. 0.0) GOTO 90} \]

******* PYROLYSIS

\[ \text{PARTOI}=4.0*\pi/3.0*\text{INTR}**3*\text{RHOC} \]
GC0 = PARTOI * C2 * V3 / 16.00
GH2 = PARTOI * C2 * V2 / 2.016
GN2 = PARTOI * C2 * V4 / 28.014
GTN = GC0 + GH2 + GN2
VCO2 = 0.0
VH2O = 0.0
VH2 = GH2
VCO = GC0

VT = VH2 + VCO + VH2O + VCO2 + GN2
VCO2P = VCO ** 2 * PT / (VT * AC * KJ)
VH2OP = VH2 * VCO2P / (VCO * KF)
IF (DABS((VH2OP - VH2O) / VH2OP) .LT. 0.000000001) GOTO 65
VH2O = VH2OP
VCO2 = VCO2P
VH2 = GH2 - VH2O
VCO = GC0 - 2.0 * VCO2 - VH2O
GOTO 61

65 RHOG = PT / (RC * TEMP)
GASV = VT / RHOG
PCO = GC0 / GTN * PT

C =
CU = GC0 * 12.01
PARTN = PARTOI - PARTOI * (C2 * V3 * 28.01 / 16.00 + C2 * V2 + C2 * V4)
C1 = C1S
C1 = (PARTOI * C1 + PARTOI * C2 * V1 - CU) / PARTN
COALV = PARTN / RHOC

Y(1) = 0.0
Y(2) = VCO / VT * RHOG
Y(3) = VCO2P / VT * PT * RHOG
Y(4) = VH2 / VT * RHOG * PT
Y(5) = VH2O / VT * PT * RHOG
Y(6) = GN2 / VT * RHOG
Y(7) = (3.0 * (GASV + COALV) / (4.0 * PI)) ** EXP13
Y(8) = (3.0 * COALV / (4.0 * PI)) ** EXP13
Y(9) = PARTN
Y(10) = GASV
Y(11) = PARTN * C1 / 12.01

C =
COCR = 1.0 / C1
T = (TEMP - 298.0) / PYRRT
WRITE (6, 85) RHOSLM, ACZNO, ACIR1, TRES
85 FORMAT (15X, F7.3, 8X, F5.2, 5X, F5.2)
PH = 2
GOTO 900

90 YT = Y(1) + Y(2) + Y(3) + Y(4) + Y(5) + Y(6)
PZN = Y(1) / YT * PT
PCO2 = Y(3) / YT * PT
PH2O = Y(5) / YT * PT
PCO = Y(2) / YT * PT
PH2 = Y(4) / YT * PT
PN2 = Y(6) / YT * PT
RHOG = PT / (RC * TEMP)
GASWT = Y(10) * (Y(1) * 65.37 + Y(2) * 28.01 + Y(3) * 44.01 + Y(4) * 12.016 + Y(5) * 18.016 + Y(6) * 28.014)
RHOB = (GASWT + Y(9)) / (4.0 / 3.0 * PI * Y(7) ** 3)
LFLAG=0

*************** PARTICLE CONSUMPTION STEPS 101 - 310

AR = BUBBLE SURFACE AREA
UTS = BUBBLE RISE VELOCITY
PE-X = PECLET NO. OF SPECIES X
SH-X = SHERWOOD NO. OF X
K-X = MASS TRANSFER COEFFICIENT OF X
N-X = MOLAR TRANSFER RATE OF X

CZNOI = INTERFACIAL ZNO CONCENTRATION

101 AR=4.0*PI*Y(7)**2
PO2=PCO**2/(AC**2*K0)
UTS=G*(2.0*Y(7))**2*(RHOSL-RHOB)/(18.0*VIS)
IF (UTS .LT. 0.0) WRITE (6,103) GASWT,RHOB,Y(9),RHOSL,
 1G,UTS
PEZNO=2.0*Y(7)*UTS/DZNO
PEFEO=2.0*Y(7)*UTS/DFEO
PEFE2O=2.0*Y(7)*UTS/DFE2O3
IF (PEZNO .LT. 0.0 .OR. PEFE2O .LT. 0.0 .OR. PEFEO .LT. 0.0) WRITE (6,103) PEZNO,PEFE2O,PEFEO,UTS,Y(7)
103 FORMAT (5X,6(D12.5,5X))
SHZNO=1.0+(1.0+PEZNO)**EXP13
SHFEO=1.0+(1.0+PEFEO)**EXP13
SHFE2O=1.0+(1.0+PEFE2O)**EXP13
KZNO=SHZNO*DZNO/(2.0*Y(7))
KFEO=SHFEO*DFEO/(2.0*Y(7))
KFE2O3=SHFE2O*DFE2O3/(2.0*Y(7))

110 CZNOI=(PZN*PCO2/(KG*ACZNO/RHOSLM*PCO))

NZNO=KZNO*AR*(CZN0B-CZNOI)

IF (PCO2  .GT. 0.0) GOTO 115
NFE20A=KFE2O3*AR*CFE20B
NFE203=NFE20A
IF (PCO2 .EQ. 0.0) GOTO 120

KHP=KH*ACIR2*RHOSLM

115 KHP=KH*ACIR2*RHOSLM**(2.0/WX-1.0)

A=PCO2
B1=(KFEO*AR/4.0)
B2=(KHP*PCO*KFEO+4.0*KFE2O3*CFE2OB*PCO2)/KFE2O3
B=B1*B2
CA=(KFEO**2*AR**2)/(4.0)
CB=CFE2OB**2*PCO2-KHP*PCO*CFE2OB
C=CA*CB
NFE20B = (-1.0*B + (B**2 - 4.0*A*C)**0.5) / (2.0*A)
NFE8 = NFE20B
BOT = NFE8 / 2.0
TOP = NFE8 * 2.0
N1 = (1.0/KHP) * (PCO2/PCO)**(3.0 - 2.0/WX)
N2 = 2.0/WX * NFE8/KFEO/AR + CFEOB
IF (N2 .LE. 0.0) WRITE (6, 111) (Y(ll), 11 = 1,11)
111 FORMAT (5X, 5(D12.5, 3X))
N3 = N2**(2.0/WX)
NFE9 = AR*KFE203*(CFE20B-N1*N3)
CK = (NFE8-NFE9)/NFE8
IF (DABS(CK) .LT. 0.00001) GOTO 118
NFE8 = NFE9
GOTO 116
112 IF (CK .GT. 0.0) GOTO 117
BOT = NFE8
NFE8 = (BOT + TOP)/2.0
GOTO 116
117 TOP = NFE8
NFE8 = (BOT + TOP)/2.0
GOTO 116
118 NFE20B = NFE8
119 NFE203 = NFE20B
120 IF (RO .NE. 0.0) GOTO 200
BOURD = A0*DEXP(-1.0*EA/(RJ*TEMP))
GOTO 250
200 BOURD = A0*DEXP(-1.0*EA/(RJ*TEMP))*(PCO2-PCO2I)**RO
250 F(1) = 1.0/Y(10)*(NZNO-Y(1)*F(10))
F(2) = 1.0/Y(10)*(2.0*BOURD*Y(11)-NZNO-NFE203-Y(2)*F(10))
F(3) = 1.0/Y(10)*(NZNO+NFE203-BOURD*Y(11)-Y(3)*F(10))
F(4) = 1.0/(Y(3)**2+Y(3)*Y(2)*KF)*(Y(3)*(GH2/Y(10)-Y(4))*Y(2)*KF*F(3)
+2GH2/Y(10)**2*F(10))
F(5) = -1.0*GH2/Y(10)**2*F(10) - F(4)
F(6) = -1.0*Y(6)/Y(10)*F(10)
F(7) = 1.0/(4.0*PI*Y(8)**2*RHOC)
F(8) = F(9)/(4.0*PI*Y(8)**2*RHOC)
F(9) = -1.0*BOURD*12.01*Y(11)*COCR
F(10) = 1.0/RHOG*(NZNO+BOURD*Y(11))
F(11) = -1.0*BOURD*Y(11)
900 CONTINUE
C
RETURN
END