ASPECTS OF THE REACTION OF CO AND CO₂ WITH IRON OXIDE-CONTAINING SLAGS

by

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We accept this thesis as conforming to the required standard

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Vancouver, Canada

Date January 13, 1953
ABSTRACT

A kinetic study of reduction and oxidation slag reactions of importance to the non-ferrous smelting industry was undertaken in the laboratory by employing a thermogravimetry technique. The reduction study included ferrous-to-iron and ferric-to-ferrous reactions whereas a limited amount of data on ferrous-to-ferric and ferrous-to-magnetite reactions was also obtained for comparison. The heterogeneous gas-slag reactions were investigated using unstirred slag melts and the synthetic slags covered a wide range of melt compositions from $\text{Fe}_2\text{O}-\text{Al}_2\text{O}_3$ to $\text{Fe}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$.

The results revealed that the rate of the iron formation reaction was highest during the initial 10 minutes period and then dropped progressively with the passage of time. The melt silica content influenced the rate values to a degree and it was observed that in silica-free melts the above trend was reversed at high reaction driving force values. The latter trend is attributed to the melt movement induced by the sinking iron metal. A detailed mathematical analysis showed that during the initial period ferrous reduction rates were limited by a mixed-control regime involving gas phase mass transport and interfacial reaction. By using intrinsic rate constant, $k_c$, as a fitting parameter the predicted rates were matched with the measured data and the procedure yielded an average value of $11 \times 10^5 \text{ g/cm}^2\cdot\text{s.atm}$ at 1400 °C which is in agreement with previous work.

The results of the ferric-to-ferrous reaction showed approximately constant rate during the initial period and subsequently the rate decreased with time. Therefore, the results were analyzed using two separate mathematical models. It is proposed that this reaction operates under a gas and interfacial control regime during the initial period and subsequent to this the rate is controlled by combined gas, liquid and interfacial reaction. The intrinsic rate constant value at 1400 °C is approximately 200 times greater compared to the $\text{Fe}^{2+} \rightarrow \text{Fe}$ reaction. The apparent activation
energy value of about 44 kcal/mol is derived for the $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ reaction. By choosing the liquid phase mass-transfer coefficient, $k_L$, as a fitting parameter its values were obtained for various melts and this information was used in conjunction with the boundary layer value of 500 $\mu$m obtained by Mössbauer spectroscopy to generate oxygen anion diffusivity data. The value of apparent activation energy for diffusion, $E_D$, for lime-containing melts was found to be 53 kcal/mole.

The results obtained for both reduction reactions revealed the significance of surface active species in the melts and accommodation of this effect in the formulation and development of the mathematical models led to accurate prediction of the rate and weight loss data. In the various melts studied in this investigation silica and ferric oxide were surface active species and their individual proportion in the melts altered the available reaction area.

Mössbauer spectroscopic analyses were performed on a limited number of slag samples. A special sample holder was designed to probe an entire cross-section of the quenched slag to identify the variation in iron cations with depth. It was demonstrated for the first time that Mössbauer spectroscopy can be used to study iron distribution as a function of depth.

The limited data obtained on ferrous-to-ferric and ferrous-to-magnetite reactions revealed that the rates decreased with time in a manner similar to the reduction reactions. The weight gain-time curves for magnetite formation reaction in both simple and complex melts indicated that solid magnetite covered the melt surface and caused reduction in the rate values. The data on the ferrous-to-ferric reaction at 1300 °C indicated that the mechanisms involved in ferric-ferrous reduction and oxidation reactions are similar.
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LIST OF SYMBOLS

English symbols

A reaction area, (cm²)
A₀ melt surface area, (cm²)
ai activity of species i
Cj concentration of species j, (g.mole/cm³)
D diffusivity or diffusion coefficient, (cm²/s)
DA-B inter-diffusivity coefficient for mixture of (A + B), (cm²/s)
d crucible diameter, (cm)
ED apparent activation energy for diffusion, (kcal/mole)
f driving force, (atm)
G° standard Gibbs free energy, (cal/mole)
K(io) equilibrium constant of a reaction i
k rate constant or mass-transfer coefficient
ka apparent rate constant, (cm/s)
kₙ chemical rate constant, (cm/s)
kₙ mass transfer coefficient in gas phase, (cm/s)
kₐ mass transfer coefficient in liquid phase, (cm/s)
kₐ system dependent constants
k₂ temperature dependent rate constant
L  characteristic length, (cm)
N_i  mole fraction of species i
n_i  molar mass-transfer rate of species i, (g.mole/s)
n_j  molar quantity of species j, (g.mole)
P_i  partial pressure of species i, (atm)
R  gas constant, 1.987 (cal/K.mole)
R_T  total resistance, (R_T = 1/2 k)
r  reaction rate, (g-oxy/cm^2.s)
T  temperature, (°C or °K)
t  reaction time, (s)
V  melt volume, (cm^3)
w or W  melt weight, (g)
x  non-stoichiometric coefficient (of wüsite)

Greek symbols

α  x-ray wave length
β  SiC phase
γ  solid gamma-iron phase
γ_i  activity coefficient of species i
δ  gas phase boundary layer thickness, (cm)
\( \delta_{dl} \)  monolayer thickness, (cm)

\( \delta_i \)  boundary layer thickness in the liquid phase, (cm)

\( \mu \)  viscosity, (kg/m.s) or micro

\( \rho \)  density, (g/cm\(^3\))

\( \sigma \)  surface tension, (N/m)

\( \Gamma_i \)  excess concentration of surface active solute i, (mole/cm\(^2\))

\( \Delta \)  change or difference

\( \Sigma \)  sum or total
### Subscripts

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<td>g</td>
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### Superscripts

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<td>[n]</td>
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Chapter 1

INTRODUCTION: The Nature of Slags and Their Origin

Most pyrometallurgical processes generate slags. These slags perform a wide variety of chemical and physical functions ranging from a receptacle for gangue and unreduced oxides in primary extraction, to the reservoir of chemical reactants and absorber of extracted impurities in refining processes. Though slag generation is considered inevitable in all the ferrous and non-ferrous smelting operations, it is desirable to limit its quantity to the lowest possible value for two main reasons:

1. slag generation represents one of the "debit" items on the plant energy balance; and
2. it influences overall metal recovery values.

Both the quantity of slag and its final chemical composition are dependent on raw material assays, types of flux additions, furnace temperature, furnace atmosphere, melt oxygen potential, in addition to other prevailing operating conditions. The slags generated during smelting operations are sometimes referred to as "discard slags" because the bulk of their composition is dominated by unwanted gangue materials and oxides. The chemical composition of slags for the copper, nickel, lead and tin industries are listed in Table 1.1. For comparison the composition of iron and steelmaking slags is mentioned in the same table. A given slag will probably consist of at least 8 or 9 different oxides. However, the composition of most industrial slags is dominated by four oxides - FeO, CaO, SiO₂, and Al₂O₃. Minor quantities of other oxides rarely exceed 5 - 10% of the slag weight. Since representation of all oxides in a single diagram is virtually impossible, the slag composition on most occasions is suitably represented in ternary diagrams by choosing the dominant oxide species. The system CaO - FeO - SiO₂ is reproduced in Figure 1.1 to serve as an illustration of this.
Table 1.1 Composition of typical smelting slags.

<table>
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<th>Contained metal</th>
<th>Predominant Oxide Species, wt% range</th>
<th>Slag Temperature</th>
<th>Basicity Index</th>
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<tr>
<td>Iron Blast Furnace</td>
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<td>CaO 38-44 MgO 8-10 &quot;FeO&quot; 0.2 Al₂O₃ 10-12 SiO₂ 34-38 Other 2-3</td>
<td>1500 °C ± 50 °C</td>
<td>1.0 - 1.6</td>
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<td>Steelmaking Slags; BOF &amp; Q-BOP</td>
<td></td>
<td>CaO 45-65 MgO 2-8 Al₂O₃ 5-25 SiO₂ 10-25 Other 10-15</td>
<td>1600 °C ± 50 °C</td>
<td>2.0 - 3.5</td>
<td>[1]</td>
</tr>
<tr>
<td>Copper Reverberatory Furnace</td>
<td>1.5 (Cu)</td>
<td>CaO 5-15 MgO 0-2 Al₂O₃ 30-45 SiO₂ 8-12 Other 5</td>
<td>1220 °C ± 50 °C</td>
<td>1.0 - 1.5</td>
<td>[1-3]</td>
</tr>
<tr>
<td>Nickel Blast Furnace</td>
<td>0.2 (Ni,Co)</td>
<td>CaO 5-20 MgO 5-25 Al₂O₃ 20-50 SiO₂ 5-15 Other 3</td>
<td>1230 °C ± 50 °C</td>
<td>1.3 - 1.8</td>
<td>[2,3]</td>
</tr>
<tr>
<td>Lead Blast Furnace</td>
<td>15-20 (Zn)</td>
<td>CaO 5-18 MgO 1-2 Al₂O₃ 20-40 SiO₂ 5-10 Other 5</td>
<td>1230 °C ± 50 °C</td>
<td>1.5 - 2.0</td>
<td>[1,2]</td>
</tr>
<tr>
<td>Tin Reverberatory Furnace</td>
<td>10-15 (Sn)</td>
<td>CaO 10-15 MgO 1-2 Al₂O₃ 20-30 SiO₂ 10-15 Other 5</td>
<td>1230 °C ± 50 °C</td>
<td>1.1 - 1.9</td>
<td>[1,2]</td>
</tr>
</tbody>
</table>

Note: 1. "FeO" assay includes both ferrous and ferric oxides.
2. Basicity index = \( \frac{\text{wt}\%\text{CaO} + \frac{3}{2}\text{wt}\%\text{MgO} + \text{wt}\%\text{FeO}}{\text{wt}\%\text{SiO}_2} \)
3. In metallurgical slags, amphoteric oxides are not included in calculating Basicity Index. (ref. 4)
Figure 1.1 Location of industrial slags in the FeO-CaO-SiO₂ system (from ref. 4 and 5)

1. Basic open hearth steel furnace.
2. Acid open hearth steel furnace.
3. Basic oxygen converter.
4. Copper reverberatory.
5. Copper oxide blast furnace.
7. Tin smelting.
Based on the information in Table 1.1, the following major differences are revealed between ferrous and non-ferrous slags.

1. 
   (1) "FeO" assay: In most instances the reported assay includes both the ferrous and ferric oxides and this is represented by notation "FeO", Fe₂O or Fe₃O. In comparison with iron making slags non-ferrous slags contain a much higher proportion of "FeO". In general, the ferrous slags contain very minor quantities of ferric oxide where as in non-ferrous slags the magnetite or ferric assay may exceed 15 wt.%. The higher ferric levels in non-ferrous slags invariably lead to higher metal losses and for this reason it is important to control the ferric oxide levels of these slags at the operating temperatures.

2. Slag forming temperature: Melting points of all non-ferrous smelting slags are about 150 °C lower than iron and steelmaking slags.

3. Dollar value: This is usually related to the unit value of the contained metal. On a weight-to-weight basis each ton of either Cu, Pb, Sn or Ni produces between 2.5 - 3 tons of slag and since this slag contains some trapped metal an attempt is almost always made to recover a portion of it. On the other hand, the loss of iron metal in ferrous slags is small. Thus the dollar value of non-ferrous slags is appreciably high in comparison with ferrous slags.

1.1 Slag Treatments:

The primary reasons for the growing interest in the field of slag treatments are:

1. Increasing concern over lost metal values;

2. Growing importance of issues such as the energy of metal production;

3. Stricter and more stringent environmental regulations; and


Basically there are two ways of recovering the "contained metal" in slag: firstly, the slag can be recycled in the circuit alongside the new material and secondly, it can be processed in a separate unit operation. The choice and justification of either is governed largely by prevailing economic and operational factors, but the latter practice is generally more acceptable. [6-15]
More often than not, there are additional benefits to be gained from the employment of slag treatment practices. The "bonus" is the recovery of by-product metals - such as gold, silver and cobalt together with the main metal. For example, gold and silver are recovered with copper and cobalt is recovered with either lead, zinc, nickel or copper.

Yet another area where slag treatment can be of help is the recovery of volatile impurities. In metal recovery operations based on the hot treatment of slag viz. Electric furnace slag cleaning and slag fuming, impurities such as S, As, Sb, Zn, Pb, Se, Te, Cl and F are always volatilized to some extent. These elements are usually trapped in dust form and may require several additional treatments for isolation.

The replacement of traditional smelting processes with new, more energy efficient and environmentally acceptable processes, combined with the need to maximize recoveries has increased the need for slag treatment. Moreover with the adoption of new smelting methods, particularly where oxygen enrichment is used, non-ferrous smelting slag compositions are expected to change and this has wide implications on the recovery of both primary and by-product metal values. For these reasons it is anticipated that in the near future the role played by various slag treatments will become increasingly important.

1.2 Role of iron oxides in non-ferrous smelting operations:

The main iron removal reactions during the matte smelting operations of copper, nickel, tin, lead and zinc are:

\[
2\text{FeS}_{(\ell)} + 3\text{O}_{2(g)} = 2\text{FeO}_{(g)} + 2\text{SO}_{2(g)} \tag{1.1}
\]

\[
2\text{FeO}_{(\text{matte})} + \text{SiO}_{2(\text{flux})} = \text{Fe}_2\text{SiO}_4_{(\text{slag})} \tag{1.2}
\]

Once ferrous oxide is formed according to the reaction (1.1) it can further react to produce either metallic iron or ferric oxide depending on the oxygen potential. If conditions (thermodynamic and kinetic) are favorable to the formation of iron metal the situation can lead to several operating difficulties. On the other hand, if the oxygen partial pressure, \( P_{O_2} \), is too high, magnetite is formed as a separate phase resulting in the changes in slag properties. Invariably the slag viscosity is increased and this leads to higher metal losses.
The above facts clearly suggest that the control of oxygen potential is of paramount importance in non-ferrous smelting operations to maintain the progress of desired chemical reactions; otherwise unwanted side reactions may result. Ideally, the formation of solid magnetite should be avoided but often it is only practical to control its proportion to an optimum level. The ferric-to-ferrous ratio has a strong influence on both the physical and chemical properties of the slag melt and therefore on metal losses as well. For these reasons a clear understanding of the redox reactions taking place in non-ferrous slag melts is necessary. An added advantage of studying the iron oxide redox reaction is that the findings from such work could be extended to slags containing Mn, Cr, Sn and Ti oxides because, like iron, these metals also exhibit different valencies in oxide solution. Though some evidence in this regard [16] is available more data is needed to draw firm conclusions.
Chapter 2

LITERATURE REVIEW: Role and Status of Previous Work

Much of the early research on slag-metal reactions, in the first quarter of 20th century, was closely associated with the development of open-hearth steelmaking. During this period it was widely accepted that the interpretation and prediction of slag-metal distribution equilibria could easily be accomplished in terms of an equilibrium constant using the Law of Mass Action. For the successful application of this principle however, it was recognized that information on the nature of slags is essential together with the thermodynamic data. For this reason several researchers initiated studies to understand the nature of slag. In addition to the structure-property related research on slags, the period between 1920 and 1940 also witnessed the conception and growth of several slag models based on 'Molecular theory'. The concept of the "basicity index" or "v-ratio" emerged as a result of the molecular theory and this is considered to be of significant practical importance even today.

After 1940 slag molecular theories lost their original simplicity and became very complex with a multitude of possible compounds and dissociation constants. During the same period progress was being made in related fields - such as glasses, fused salts, molten oxides and silicates. The new data revealed that in the molten state many species dissociated to form 'ions'. [17] As a result of this evidence researchers began studies on slags to extend the newly developed ionic concepts in this field. By 1950 the concept of a completely ionized slag containing a limited number of ionic species was well established. Commensurate with this recognition of the ionic nature of slags, the importance of measuring properties related closely to structure also grew. This trend has continued to date.

Since the subject of this thesis is the reaction kinetic behavior of iron oxides it would be of interest to focus our attention primarily on past research activity in this field.
2.1 Studies involving solid iron oxides:

Origins of an active research interest in this area can be traced as far back as the early 1900s. The obvious reason for such an interest was an immediate utility and applicability of the research findings to the extraction of iron. Many developments in ironmaking techniques came about primarily as a result of the extensive research in this field. For example, between 1940 and 1980 the smelting capacity of the blast furnace has about doubled without an increase in furnace size, and coke consumption has been reduced from about 1000 kg to below 500 kg per tonne of iron produced [18]. The primary objective of all solid oxides-related research was to understand the nature of reactions taking place within an iron blast furnace. For this purpose both thermodynamic/equilibrium and kinetic studies were initiated by the researchers.

2.1.1 Equilibrium/Thermodynamic Studies:

In 1945, Darken and Gurry [19] initiated equilibrium studies on the Fe - O system using CO-CO$_2$ gas mixtures and their pioneering work culminated in the development of a phase diagram. The authors calculated activities of iron and wüstite and, in addition, determined the values of heats of magnetite formation between 1100 °C and 1400 °C which are in excellent agreement with calorimetric measurements. Later, other researchers conducted similar work [20] and as a result our understanding of various phase fields and their interrelations has improved a great deal.

2.1.2 Kinetic Studies:

Many laboratory investigations have dealt with the high temperature reduction behavior of iron oxides - hematite (Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$) and wüstite (Fe$_x$O) using either carbon or carbon monoxide as reducing agents [20, 21-26]. Comprehensive work on wüstite reduction was undertaken by Watts et al. [22], John et al. [23], Steele [24] and Childs and Wagner [25] and their research has offered valuable insights into gas-wüstite reactions.
In addition to offering explanations for the reactions taking place in the blast furnace research on solid iron oxides has paved the way for newer technology - such as direct reduction methods. Literature concerning solid iron oxide reactions is abundant [21,26], but any further review on this topic is beyond the scope of the thesis. However, some important findings of the solid iron oxide related kinetic work are summarized below:

(1) Ferric oxide, Fe$_2$O$_3$ is reduced at a higher velocity than Fe$_3$O$_4$. [21]

(2) Hydrogen at high temperatures is a better reducing agent than carbon monoxide, but is a poorer one at lower temperatures. [18]

(3) The reduction of a solid oxide to solid metal by means of hydrogen or carbon monoxide involves phase-boundary reactions as well as diffusion processes. [22,23,26]

(4) The rate of the heterogeneous gas - solid reactions is influenced by the stagnant gas boundary layer surrounding the oxide particles. [21]

2.2 Studies involving molten iron oxides:

In comparison with solid oxide reduction studies research on liquid oxides is very limited. One of the major difficulty in studying high temperature reactions involving iron oxide-containing melts is containment of the melt. In almost all studies the operating temperatures are in excess of 1200 °C and this causes serious melt containment problems if an oxide crucible is used. Although iron is commonly used as a crucible material it imposes a significant thermodynamic constraint on the experimental work. The choice of crucible material is often constrained by variables such as melt composition, melt temperature and the duration of the experiment. In addition there is one inherent difficulty which is much more problematic and complex. The origin of this lies in the temperature-composition relationship between iron and oxygen. Stoichiometric FeO (1:1) does not exist and wüstite has a variable composition depending on temperature and oxygen partial pressure. Therefore, wüstite composition is normally represented either as Fe$_{1+\gamma}$ or Fe$_x$O. Both x and y are positive non-zero numbers and their individual values are governed
by the proportion of ferric oxide. Within the wüstite phase, the Fe$^{3+}$/Fe$^{2+}$ ratio increases with increasing partial pressure of oxygen and this leads to decreasing x values. Turkdogan [1] has provided an expression for the determination of y.

In the present study however, the wüstite composition is listed as Fe$_x$O for the sake of convenience. Additional reasons for this choice are mentioned in section 2.2.1.2. Thus the non-stoichiometric coefficient, x, denotes the extent of deviation from stoichiometric FeO and its value is dependent on temperature and oxygen partial pressure. This fact necessitates extreme care in control of the experimental variables and as a corollary implies unreliability of the data in absence of such control.

The above difficulties forced investigators into trying a variety of crucible materials other than the more common ones: alumina, magnesia, spinel and iron. A few researchers employed coke and graphite crucibles. [27-31] Others resorted to using either noble metals (platinum, Pt-Rh and iridium) or expensive ceramics like zirconia, thoria and yttria. [32-36]

2.2.1 Equilibrium studies:

Research work prior to 1960 was mainly restricted to the determination of thermodynamic and physicochemical properties of these melts. As a result a wealth of information on several topics including the nature of chemical reactions, activities of compounds and phase diagrams was generated. The data was obtained for both simple and complex melt systems.

2.2.1.1 Fe$_x$O melts:

Darken and Gurry [19,37] studied equilibrium relations between the partial pressure of oxygen, temperature and oxide composition at iron saturation using controlled gas mixtures. The authors essentially looked at the following reactions:

\[ x\text{Fe}_2\text{O}_3 + CO(g) = Fe_2O_x(g) + CO(g) \]  
\[ 3\text{FeO}(g) + CO_2(g) = Fe_3O_4(g) + CO(g) \]  

In reaction (2.1) 'x' is the nonstoichiometry coefficient. The temperature-composition phase diagram, constructed mainly from their data, is shown in Figure 2.1.
Figure 2.1 Fe-O system, based on the data of Darken and Gurry [19,37]. Broken lines in single phase regions are equilibrium oxygen partial pressures in atmospheres.
Following the classical work of Darken and Gurry several other researchers looked at the phase equilibrium relations and the thermodynamics of the Fe-O system between 1000 °C - 1600 °C. For a critical assessment of the available data on the above system a paper by Spencer and Kubaschewski [38] is a very useful reference.

2.2.1.2 Pseudo-binary (Fe$_x$O-SiO$_2$) melts:

Because of its significance to both ferrous as well as non-ferrous operations, this system was a prime target for phase equilibrium and thermodynamic studies during 1940s and 1950s. [39,40] Schuhmann and Ensio [41] studied the pseudo-binary Fe$_x$O-SiO$_2$ system using iron crucibles and CO-CO$_2$ gas mixtures. The main experimental variables- temperature and silica content, were chosen to represent copper smelting slags and the primary objective of their work was determination of FeO activity. One interesting feature of Schuhmann and Ensio's data is that for a given silica percentage $a_{FeO}$ does not vary significantly with the temperature.

In 1955 Bodsworth [42] conducted research work similar to that of Schuhmann and Ensio and confirmed that the activity of ferrous oxide in Fe$_x$O-SiO$_2$ melts is essentially independent of temperature in the range 1200 °C - 1400 °C and is only a function of melt silica content. Both Bodsworth and Schuhmann and Ensio assume similar standard states for FeO and Fe namely- FeO as an ideal stoichiometric liquid and Fe as gamma-phase (f.c.c.) solid iron.

The effect of temperature, melt composition and oxygen partial pressure of the gas on the state of oxidation of iron in iron silicate melts has been measured by various investigators. [41-44] These equilibrium data for 1550 °C are collated in Figure 2.2. It is interesting to note that the data in this figure can be used for temperatures other than 1550 °C. The temperature insensitivity of the variation of Fe$^{3+}$/Fe$^{2+}$ with $P_{CO_2}/P_{CO}$ is a result of two opposing effects. First, for a given $P_{CO_2}/P_{CO}$ ratio an increase in temperature increases the equilibrium partial pressure of oxygen, and second, for a given $P_{O_2}$ and silica concentration the Fe$^{3+}$/Fe$^{2+}$ ratio decreases with increase in temperature. Darken and Gurry [19,37] and Larson and Chipman [45] have confirmed the above trend in liquid iron oxide and calcium ferrite melts respectively.
Figure 2.2 State of oxidation of iron in FeO-Fe₂O₃-SiO₂ melts at 1550 °C (from ref. 1).
In 1957 Turkdogan and Bills [46] showed that for silica saturated melts \( \log(P_{CO_2}/P_{CO}) \) is almost a linear function of \( \log(Fe^{3+}/Fe^{2+}) \) with a slope of 2. Such an observation is anticipated from the equilibrium relation for the redox reaction

\[
CO_{2(\varrho)} + 2Fe^{2+} = 2Fe^{3+} + O_2^{2-} + CO_{\varrho}
\]  

(2.3)

Although the activities or activity coefficients of individual ions cannot be determined experimentally, the state of isothermal equilibrium for the above reaction may be represented in a hypothetical manner as follows:

\[
\log \frac{P_{CO_2}}{P_{CO}} = 2 \log \frac{Fe^{3+}}{Fe^{2+}} + 2 \log \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{2+}}} + \log a_{O_2} - \log K_{(2.3)}
\]  

(2.4)

A linear relationship between \( \log(P_{CO_2}/P_{CO}) \) and \( \log(Fe^{3+}/Fe^{2+}) \) with a slope of 2 would indicate that the sum of the terms involving the activity coefficient ratio \( \gamma_{Fe^{3+}}/\gamma_{Fe^{2+}} \) and the oxygen ion activity \( a_{O_2} \) remain essentially constant in silica-saturated melts. It also follows from these observations that for silica saturated melts in the Fe\textsubscript{2}O-Si\textsubscript{2}O\textsubscript{2} system the trivalent iron does not co-polymerize with the Si-O anion group but instead remains primarily as Fe\textsuperscript{3+} cations in the melt. [1]

2.2.1.3 Pseudo-ternary (Fe\textsubscript{x}O-Si\textsubscript{2}O\textsubscript{2}-CaO) melts:

Early research work in this system dealt with the thermodynamic properties of these melts at temperatures of interest to the iron and steel industry. Though the pseudo-ternary system Fe\textsubscript{x}O-Si\textsubscript{2}O\textsubscript{2}-CaO covers the range of compositions generated in non-ferrous smelting and refining operations (see Figure 1.1) the research on melts containing a higher proportion of Fe\textsubscript{x}O did not begin until about 1955. The starting point for this research activity was determination of \( a_{FeO} \) values and later the work diversified to include determination of physicochemical properties.

In 1959 Bodsworth [42] measured the activity of ferrous oxide in iron-calcium silicate melts between 1265 °C and 1365 °C. A H\textsubscript{2}-H\textsubscript{2}O-Ar gas mixture was bubbled into the melt contained in an iron crucible and \( a_{FeO} \) was calculated from the oxygen potential of the gas phase in equilibrium.
with it. The author performed activity calculations using a method similar to that of Schuhmann and Ensio [41] and noted that lime additions enhanced $a_{\text{FeO}}$. At a fixed CaO percentage however $a_{\text{FeO}}$ decreased with increasing SiO$_2$. In other words, lower basicity ratios led to lower $a_{\text{FeO}}$ values.

In 1970 Timucin and Morris [36] studied phase equilibria and thermodynamic properties of the pseudo-ternary Fe$_x$O-SiO$_2$-CaO system at 1450 °C and 1550 °C over a range of $P_{O_2}$ from 1 to about $10^{-11}$ atm. Compositions in the pseudo-binary Fe$_x$O-CaO were studied first and then extended into the pseudo-ternary system by adding 5, 10, 15, 20 and 30 wt% SiO$_2$ to the pseudo-binary melts. In the pseudo-binary melts they observed that at constant temperature, increasing CaO contents enhanced the stability of trivalent iron, Fe$^{3+}$. This tendency decreased with increasing temperature when CaO was held constant. Additions of SiO$_2$ to pseudo-binary Fe$_x$O-CaO melts showed an opposite effect. These trends are revealed in the $n_{\text{FeO}}/(n_{\text{FeO}} + n_{\text{Fe}_x\text{O}_y})$ versus log$P_{O_2}$ plots in Figure 2.3.

2.2.1.4 Pseudo-quaternary and complex melts:

There are very few equilibrium studies on complex melts and a critical review of these has been published by Grieveson [47] and Grieveson and Pomfret [48]. In 1941 Taylor and Chipman [49] published the results of their equilibrium study in the CaO-MgO-Fe$_x$O-SiO$_2$ system at 1600 °C. Based on their experimental data the authors concluded that the effect of MgO is qualitatively equivalent to CaO (in concentrations up to at least 10 wt%) and for this reason in thermodynamic calculations magnesia can be substituted for by lime. In their subsequent study Chipman and co-workers [50] determined the activity of silica in CaO-MgO-Al$_2$O$_3$-SiO$_2$ melts by equilibrating the slag with Fe-Si-C melts saturated with graphite or SiC ($\beta$) at 1 atm pressure of CO and calculated the activities of the other oxides by Gibbs-Duhem integration.

Sommerville and Bell [51] measured the activity of FeO$_{\alpha}$ in the quaternary FeO-CaO-SiO$_2$-TiO$_2$ and FeO-MnO-SiO$_2$-TiO$_2$ melts at 1450 °C at iron saturation and
Figure 2.3 Effects of temperature and melt compositions on the relative stability of Fe$^{3+}$ cations (from ref. 36). (a) effect of temperature in Fe$_2$O-CaO melts at two levels of CaO; (b) effect of silica content in Fe$_2$O-CaO-SiO$_2$ melts.
represented their results as a series of iso-activity curves on ternary and pseudo-ternary diagrams. The authors initiated the work primarily to study the reduction behavior of titania in the slags and therefore the data is not of much relevance to the present thesis.

Using an emf technique Filipovska and Bell [35] measured the activities of FeO and ZnO in FeO-CaO-SiO₂-ZnO and FeO-CaO-Al₂O₃-SiO₂-ZnO systems. The iron saturated slags were equilibrated with CO-CO₂ mixtures at 1250 °C and liquid silver was used as the zinc and oxygen transfer medium. The authors calculated \( \gamma_{FeO} \) and \( \gamma_{ZnO} \) values and found that addition of CaO to the slag increased the activity coefficients of both FeO and ZnO. They observe that for a given alumina content the activity ratio \( \frac{\gamma_{FeO}}{\gamma_{ZnO}} \) decreases with an increase in the basicity (or molar CaO/SiO₂) ratio; and the ratio increases with increase in Al₂O₃ content, but this effect is small. It is interesting to note that similar observations were made in a separate study by Richards and Thorne [52].

2.2.2 Kinetic studies:

In order to extend the utility of the equilibrium and thermodynamic data to practical situations in industry information on kinetics and transport properties is essential. With this in mind many researchers initiated work to cover a broad spectrum of slag compositions - ferrous as well as non-ferrous. An overview of research work relating to iron oxide-containing melts is presented below.

2.2.2.1 FeₓO melts:

Grieveson and Turkelvog [33] in 1964 investigated the rates of oxidation and reduction of the pure molten oxide contained in iridium crucibles at 1550 °C using CO-CO₂ gas mixtures. For unstirred melts, about 3 mm deep, the reaction rates were controlled by interdiffusion of iron and oxygen within the melt. Their data fitted Fick's Second Law equation solved for unidirectional diffusion in a finite medium and based on these calculations the authors proposed a value of interdiffusion coefficients for oxygen and iron atoms as \( 5 \pm 1.0 \times 10^{-5} \) cm² s⁻¹. Additionally, the authors observed that the rate of reduction was slightly higher (about 10-20%) than the oxidation
rate and they attributed this result to density changes and convection currents in the melts.

In 1969 Mori and Suzuki [53] studied ferric oxide reduction reaction (reverse of reaction 2.3) using CO-CO$_2$ mixtures within the temperature range 1430 °C to 1530 °C and substantiated findings of the earlier work by Grieveson and Turdogan [33]. In addition, they found that at a constant temperature the diffusivity of iron and oxygen atoms decreased with an increase in the $\frac{F_{\text{Fe}^3+}}{F_{\text{Fe}^2+}}$ ratio and this phenomenon becomes more conspicuous at higher Fe$^{3+}$ contents ($\frac{F_{\text{Fe}^3+}}{F_{\text{Fe}^2+}} > 0.25$). The authors interpreted their results in terms of the difference in the cation-oxygen attraction between Fe$^{3+}$ and Fe$^{2+}$. They predicted that since oxygen ions are much more closely attracted to Fe$^{3+}$ than to Fe$^{2+}$, the melt becomes more ordered into a rigid structure at higher Fe$^{3+}$ contents. Consequently the ion mobility decreases and this leads to a decrease in diffusivity at a higher Fe$^{3+}$ content. Although the results obtained in these studies are in agreement, it is unfortunate that the authors did not extend their work to study the effect of gas flow rate.

Kato, Sasaki and Soma [54] in 1977 performed experiments to study the rate of reduction of molten iron oxide to liquid iron. The reaction

$$FeO_{(s)} + CO_{(g)} = Fe_{(l)} + CO_{2(g)}$$

(2.5) was studied at 1600 °C using alumina crucibles. The reductant CO was blown normally onto the surface of the melt through an alumina tube (5 mm ID), the tip of which was held about 10 mm above the liquid surface. For the gas flow rates investigated, 0.6-16 Nl/min, the reduction rate was proportional to square root of gas flow rate and the rate controlling step was mass transfer in the gas film (suggesting a relatively fast rate for the reaction on the surface of the melt). Evidently, mass transfer in the oxide melt did not impede the rate of reaction (2.5) in these experiments, presumably because of the forced convection induced by the flow of gas across the surface.

In 1981 Tsukihashi et al. [55] published the results of their work on the reduction of molten ferrous oxide to solid iron in the temperature range 1450 °C to 1600 °C. The main objective of their work was determination of the rate constant, $k_c$, for the chemical reaction (2.5). They report two $k_c$ values, 19.4 cm/s and 9.3 cm/s; the former for the formation of liquid Fe at 1600 °C and
the latter for the formation of solid Fe at 1450 °C. They devised a novel set up, consisting of a fluidized bed transport reactor and a high temperature furnace, to overcome the effects of the gas phase boundary layer surrounding the molten iron oxide droplets. This approach to the study of reaction kinetics is both interesting and commendable. However, the $k_c$ value obtained by them at 1600 °C (19.4 cm/s) is much lower than the value of 1350 cm/s reported earlier by Kato et al. [54]. Perhaps the main reason for this disagreement lies in the estimation of $k_g$ values by both groups. Furthermore Tsukihashi et al. [55] did not considered the effects of the following important parameters on the rate of the reduction reaction:

1. the presence of either magnetite or Fe$^{3+}$ in the FeO powder;
2. particle diameter and particle dispersion;
3. nucleation, growth and cohesion of iron in the FeO droplets; and
4. prereduction;

which could have led to the observed discrepancy in the $k_c$ value.

In 1986 Nagasaka, Iguchi and Ban-ya [56] studied liquid wüstite reduction reaction using Ar-CO, CO-CO$_2$ and Ar-CO-CO$_2$ mixtures at 1400 °C. The reduction gas mixture was jetted onto the melt surface through a steel nozzle whose tip was about 10 mm above the melt surface. During all their experiments the melts were held in a shallow iron crucible (17 mm ID). The authors measured the reduction rates by monitoring the melt weight loss using a thermogravimetric set up. Assuming steady state conditions they define the reduction rate as

$$ r = -\left(\frac{dw}{dt}\right) \frac{1}{A} \tag{2.6} $$

where 

- $w$ = weight of sample (g)
- $A$ = gas-liquid interfacial area (cm$^2$)
- $t$ = reduction time (s)

and based on the results observe the following relation

$$ r = k_a \cdot (P_{CO} - P_{CO_2})/0.242 \tag{2.7} $$
where $k_A$ is the apparent rate constant ($g/cm^2 \cdot s \cdot atm$) and 0.242 is the equilibrium $(P_{CO}/P_{CO})$ ratio.

Figure 2.4 is reproduced from their publication showing the variation of percent reduction with time. The profile of reduction curves drawn for different gas mixtures reveal that equation (2.7) is not strictly valid in all the runs for the duration of the experiment. According to the authors, the eventual decrease in the reduction rate at higher $P_{CO}$ values results from the coverage of the melt surface by metallic iron.

In 1984 Ban-Ya, Iguchi and Nagasaka [57] studied molten iron oxide reduction at 1450 °C using $H_2$-inert gas mixtures. They observed that the chemical reaction:

$$Fe_xO_{(q)} + H_2_{(q)} = xFe_{(q)} + H_2O_{(q)}$$

was extremely fast and the reduction rate was controlled by mass transfer in the gas phase. Reaction (2.8) was examined using $N_2-H_2$, $Ar-H_2$, and $He-H_2$ mixtures at low flow rates (4-7 litres/min) whereas the experimental work at high flow rates (7-28 litres/min) utilized only $He-H_2$ mixtures. The apparent rate constant, $k_A$, of the chemical reaction (2.8) at the surface was estimated as $0.6 \times 10^{-2}$ ($g/cm^2 \cdot s \cdot atm$) for the high flow rate data.

Researchers have also studied iron oxide reduction reactions using solid carbon or carbon in iron as reductants. Table 2.1 summarizes available information on the activation energy values and reduction rates obtained using these reductants. Some of the important points that emerge from the data in this table are given below.

1. The activation energy for the reduction of molten iron oxide averages about 40 kcal/mole (167 kJ/mole) using either carbon or carbon in iron as a reductant and the equivalence of this value with that of Boudouard reaction implies rate control via this reaction.
2. The activation energy decreases with the addition of CaO and $Al_2O_3$.
3. Use of carbon in iron as a reductant yields higher reduction rates.
4. With either solid carbon or carbon in the iron as a reductant, the reduction rates of ferric oxide are higher in comparison with ferrous oxide.
Figure 2.4 Reduction curves of pure liquid Fe$_2$O from Nagasaki et al. (ref.56).
Table 2.1  Kinetic studies on the reduction of iron oxides and iron oxide-containing melts using carbon and carbon dissolved in iron as reductants.

<table>
<thead>
<tr>
<th>Author (Year)</th>
<th>Reductant</th>
<th>Iron oxide</th>
<th>Temp.</th>
<th>Area</th>
<th>Reduction rate x 10⁴</th>
<th>Activation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>--------------</td>
<td>-----------</td>
<td>------------</td>
<td>-------</td>
<td>------</td>
<td>----------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Kondokov et al. (1960)</td>
<td>Graphite crucible</td>
<td>FeO 0.3 g</td>
<td>1450</td>
<td>-</td>
<td>4.81</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1600</td>
<td>-</td>
<td>5.53</td>
<td></td>
</tr>
<tr>
<td>Sugata et al. (1972)</td>
<td>Graphite rod</td>
<td>SiO₂-69% FeO</td>
<td>1350</td>
<td>31.4</td>
<td>0.09</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-78% FeO</td>
<td>1400</td>
<td>28.6</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-69% FeO</td>
<td>1450</td>
<td>31.4</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>Takahashi et al. (1975)</td>
<td>Graphite crucible</td>
<td>Fe₂O₃ ore 12 g</td>
<td>1410</td>
<td>-30</td>
<td>0.20</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1570</td>
<td>-30</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>Sasaki et al. (1978)</td>
<td>Graphite crucible</td>
<td>FeO 10 g</td>
<td>1400</td>
<td>=25</td>
<td>0.11</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1500</td>
<td>=25</td>
<td>0.26</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1600</td>
<td>=25</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CaO-SiO₂-80% FeO</td>
<td>1400</td>
<td>=25</td>
<td>0.50</td>
<td>20-30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1500</td>
<td>=25</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1600</td>
<td>=25</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>Sato et al. (1986)</td>
<td>Graphite rod</td>
<td>Molten FeO in alumina crucible</td>
<td>1470</td>
<td>=7</td>
<td>0.42</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1520</td>
<td>=7</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1620</td>
<td>=7</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Dancy (1951)</td>
<td>Carbon in molten iron</td>
<td>FeO 0.5 g</td>
<td>1430</td>
<td>=1</td>
<td>31.73</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1500</td>
<td>=1</td>
<td>34.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1610</td>
<td>=1</td>
<td>86.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe₃O₄ 0.5 g</td>
<td>1580</td>
<td>=1</td>
<td>34.80</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1650</td>
<td>=1</td>
<td>48.99</td>
<td></td>
</tr>
<tr>
<td>Mac Rae (1965)</td>
<td>C in iron</td>
<td>Fe₂O₃ 3 g</td>
<td>1335</td>
<td>=3</td>
<td>4.03</td>
<td>27-44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1450</td>
<td>=3</td>
<td>8.80</td>
<td></td>
</tr>
<tr>
<td>Lloyd et al. (1975)</td>
<td>4.15 Wt% C in iron</td>
<td>Fe₂O₃ 0.7 g</td>
<td>1400</td>
<td>0.54</td>
<td>7.94</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1600</td>
<td>0.44</td>
<td>50.12</td>
<td></td>
</tr>
<tr>
<td>Sato et al. (1986)</td>
<td>C in iron</td>
<td>Molten FeO 50 g</td>
<td>1470</td>
<td>19.6</td>
<td>1.19</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1520</td>
<td>19.6</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1620</td>
<td>19.6</td>
<td>3.30</td>
<td></td>
</tr>
</tbody>
</table>
Sato et al. [29] in 1987 published their work on molten iron oxide reduction by carbon. They obtained reduction rate data using solid carbon and carbon dissolved in iron as reductants in the temperatures ranging from 1420 °C to 1620 °C. The reaction

\[ FeO_{(s)} + C_{(s)} = Fe_{(s)} + CO_{(g)} \] (2.9)

was studied in alumina and steel crucibles and the reduction rates were calculated from the measured CO gas evolution. The reduction rates of molten iron oxide by the solid carbon were \(0.12 \times 10^{-2}\) and \(0.46 \times 10^{-2}\) (g/cm\(^2\)•s) at 1420 °C and 1620 °C respectively. The activation energy for the reaction was 75 kcal/mol using a steel crucible; but a lower value of 31 kcal/mol was obtained when an alumina crucible was used. Higher reduction rates were obtained when using carbon dissolved in iron as a reductant. The reported values at 1420 °C and 1620 °C were \(0.61 \times 10^{-2}\) and \(1.8 \times 10^{-2}\) (g/cm\(^2\)•s) respectively. A comparison with the data of Ban-ya et al. [57] reveals that the reduction rates for both the hydrogen and carbon dissolved in iron are comparable; however the reduction rate obtained using solid carbon is lower.

Finally some remarks concerning the effect of the reaction product on oxidation and reduction rates are in order. According to Grieve son and Turkdogan [33] the reduction reaction product, ferrous oxide, induces convection currents because of its higher density in comparison with underlying ferric oxide melt and as expected the reduction rate is enhanced. The study by Nagasaka et al. [56], however, claims the opposite effect i.e. a decrease in the reduction rate after the production of much heavier solid iron. Although these authors offer no further explanation of this phenomenon, the information is sufficient to force one to consider the role of physicochemical factors such as surface tension and viscosity in the overall scheme.

2.2.2.2 Pseudo-binary Fe\(_x\)O-SiO\(_2\) melts:

Kinetic information concerning Fe\(_x\)O-SiO\(_2\) melts is sparse in comparison with the equivalent thermodynamic/equilibrium data. The earliest reported work, 1966, is by Krainer, Beer and Brandl [128]. These authors used graphite and coke crucibles to study the ferrous oxide reduction rate in the 1300 °C - 1500 °C temperature range by employing a thermogravimetric technique. Based on the experimental observations it was proposed that the overall reaction
\[ \textit{FeO}_{\text{slag}} + \text{C}_{\text{crucible}} = \textit{Fe}^0_{\text{gas}} + \text{CO}_{\text{gas}} \]  

was the result of two consecutive reactions taking place at different sites.

\[ \text{slag/gas: FeO}_{\text{slag}} + \text{CO}_{\text{gas}} = \textit{Fe}^0_{\text{gas}} + \text{CO}_{2\text{gas}} \]  

\[ \text{gas/crucible: CO}_{2\text{gas}} + \text{C}_{\text{crucible}} = 2\text{CO}_{\text{gas}} \]

From a consideration of the activation energy value and other relevant observations the authors concluded that the overall rate was controlled by reaction (2.11).

Shalimov, Boronenkov and Lyamkin [30] conducted research to identify the effects of FeO concentration, temperature and pressure on reduction reaction (2.10). They report a reduction activation energy value of 190 kJ/mole and observe that in the 0.125 to 2 atm. pressure range the rate reaches a maximum at about 1 atm. Based on the findings of the work the authors conclude that between 1300 °C and 1450 °C ferrous oxide reduction by carbon is controlled by chemical adsorption at the gas-slag boundary.

Davies, Hazelden and Smith [31] used both coal and graphite crucibles to hold Fe_xO-SiO_2 melts and studied ferrous oxide reduction between 1400 °C and 1500 °C, at Fe_xO contents greater than 60%. From the data obtained using graphite crucibles they calculated an apparent activation energy of 280 kJ/mole which is approximately 30% higher than that reported by Shalimov et al. [30]. By duplicating the experiments in coal crucibles they obtained results similar to that for graphite crucibles and concluded that the form of the reductant material does not affect the ferrous reduction rate. However, after critical evaluation of their data, the authors failed to arrive at a firm conclusion regarding the rate limiting step(s).

Instead of using carbon or graphite as a reductant material several researchers [58-60] used carbon dissolved in iron to study the ferrous oxide reduction reaction. This choice was popular because the findings of the work were of potential importance to the steelmaking industry. Many investigators studied the reaction

\[ \textit{FeO}_{\text{slag}} + [C]_{\text{Fe}} = \textit{Fe}_{\text{slag/metal}} + \text{CO}_{\text{gas}} \]  

Moreover, similar to reaction (2.10) above, reaction (2.13) can also be represented as the sum of two reactions taking place at slag/gas and gas/metal interfaces.
Opinions concerning the reduction mechanism and the rate limiting steps for reaction (2.13) are varied. For example, in their study Philbrook and Kirkbride [59] observed that the rate was controlled by an interfacial chemical reaction (2.11); but Kondakov et al. [60] concluded that the carbon solution reaction (2.12) is rate limiting. Though the findings of various researchers do not agree on one single rate controlling step for either of reactions (2.10) and (2.13), the literature does identify several other factors - such as silica reduction in melts, chemisorption of surface active elements, interfacial movement and gas evolution, that influence the overall reaction rate. Grieveson [47] and Pomfret and Grieveson [48] have published excellent reviews of the important investigations in the field.

The use of gaseous reductants is favoured in the studies involving pseudo-binary melts because of the general consensus amongst the researchers that even when solid carbonaceous reductants are used to reduce slags it is possible that in many cases the reduction occurs through gaseous intermediates. In 1986 Nagasaka et al. [56] published the results of their research on slag reduction at 1400 °C using gas mixtures containing CO. Their rate data for Fe$_2$O and Fe$_3$O-SiO$_2$ melts reveal a linear relationship between rate (g-oxygen/cm$^2$.s) and log $P_{\text{CO}}$ (atm.). It was observed from these plots that the a range of linear relationship for pseudo-binary melts was much narrower (0.003-0.02 atm.) in comparison with the pure FeO melt (0.003-0.1 atm). They also noted that for each individual melt there was a critical $P_{\text{CO}}$ value at which the curve started flattening out (indicating breakdown of the linear relationship) and these critical values decreased with increasing silica content in the melt. The authors propose that the deviation is caused by the effect of mass transfer in the liquid phase. By conducting additional experiments Nagasaka et al. established conditions under which gas phase resistance was minimal and obtained all their data by operating within this range. With this knowledge of the effects of mass transfer in both the gas and liquid phases the authors derived an empirical formula to calculate the rate of the chemical reaction on the surface.
Sasaki and Belton [61] measured interfacial rate constants for the gas-slag reaction using H\textsubscript{2}O and CO gas mixtures at 1250 °C. Silica-saturated melts were chosen for the study because the relatively low rates of reaction of CO\textsubscript{2} and CO had been established and because the data relating Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratios as a function of oxygen activity was readily available from the work of Michal and Schuhmann [62]. Based on their experimental findings the authors concluded that the apparent first order rate constant for the reaction of H\textsubscript{2} exceeded that for CO by a factor of about 53 and similarly the apparent rate constant for the reaction of H\textsubscript{2}O exceeded that for CO\textsubscript{2} by a factor of about 20. Moreover, their data suggests that both the oxidation and reduction rates are significantly influenced by the constitution of the melt.

El-Rahaiby, Sasaki, Gaskell and Belton [34] measured the rates of dissociation of CO\textsubscript{2} by an isotope exchange technique on liquid slags to establish interfacial rate constants for these reactions. Sun et al. [63] have performed similar work using calcium ferrite melts. The melts were exposed to CO\textsubscript{2}-CO gas mixtures enriched in \textsuperscript{14}CO\textsubscript{2} to promote the following isotope exchange reaction:

\begin{equation}
\text{\textsuperscript{14}CO}_2 + \text{\textsuperscript{12}CO} = \text{\textsuperscript{12}CO}_2 + \text{\textsuperscript{14}CO} \tag{2.14}
\end{equation}

by consecutive steps involving the dissociation and reforming of CO\textsubscript{2} molecules at the surface. For the melt temperatures ranging between 1240 °C and 1480 °C the following relationship between the apparent rate constant, \(k_a\), and the gas composition was observed by the authors:

\begin{equation}
k_a = k_a^o(P_{\text{CO}_2}/P_{\text{CO}})^{\frac{1}{1}} \tag{2.15}
\end{equation}

in which \(k_a^o\) is a temperature dependent constant for each melt. From their data the authors derived several equations relating \(k_a^o\) to temperature.

2.2.2.3 Pseudo-ternary Fe\textsubscript{x}O-Si\textsubscript{2}O\textsubscript{3}-CaO melts:

In 1986 Nagasaka et al. [56] published results of their kinetic study at 1400 °C using pseudo-ternary melts held in iron crucibles. Based on the weight loss data the authors derived an empirical equation for liquid ferrous oxide reduction to solid iron:
\[ r = \left( \frac{N_{Fe}^2}{N_{Fe}^3} \right)^{\frac{1}{2}} \left( \frac{P_{CO} - P_{CO_2}}{K_c} \right) \exp \left( \frac{-33000}{RT} + 2.86 \right) \]

where \( r \) is the rate in g-oxy/cm\(^2\).s and \( K_c \) is the equilibrium \( (P_{CO_2}/P_{CO}) \) ratio for the backward reaction (2.1). i.e. \( Fe_xO + CO = xFe + CO_2 \).

El-Rahaiby et al. [34] measured the rates of dissociation of \( CO_2 \) on liquid calcium iron silicates between 1240 °C and 1400 °C using an isotope exchange technique. Apart from the reduction study by Nagasaka et al. [56], this is the only other reported kinetic work involving the pseudo-ternary \( Fe_xO\)-SiO\(_2\)-CaO system. The results of a series of experiments on melts which contained initially 5 to 80 mol % iron oxide at gas flow rates of 240-340 ml/min are presented in Figure 2.5. This figure reveals that the results for pseudo-ternary melts lie within those obtained for pseudo-binary systems, viz. \( Fe_xO\)-CaO and \( Fe_xO\)-SiO\(_2\). In general the apparent rate constant values for the ternary melts are closer to the \( Fe_xO\)-SiO\(_2\) binary throughout the temperature range.

El-Rahaiby et al. proposed a redox equilibria on the surface of the form:

\[ CO_{2(d)} + 2Fe^{2+}_{(mel)} = CO_{2-}^{2-}_{(ad)} + 2Fe^{3+}_{(mel)} \quad (2.17) \]

Based on the observed variations of the apparent first order rate constant with oxygen activity values a charge transfer reaction was suggested. According to this hypothesis, the overall reaction of \( CO_2 \) with oxidizable oxide melts involves charge transfer to produce \( O^{2-} \) ions as follows:

\[ CO_{2-}^{2-}_{(ad)} = CO_{(d)} + O^{2-} \quad (2.18) \]

By assuming the weakly \( CO_{2-}^{2-}_{(ad)} \) (in equation 2.17) to be in equilibrium with \( CO_{2(d)} \), the authors obtain an expression for the surface concentration of former species:

\[ \Gamma_{CO_{2-}^{2-}} = m \cdot P_{CO_2} \cdot (Fe^{2+}/Fe^{3+})^2 \quad (2.19) \]

where \( m \) is a temperature dependent constant. Their results suggest that the rate of dissociation is proportional to \( \Gamma_{CO_{2-}^{2-}} \). El-Rahaiby et al. [34] comment that though their data offers good
Figure 2.5 Arrhenius plot of the apparent rate constants for pseudo ternary (Fe₂O₃-CaO-SiO₂) melts containing equal mole fractions of CaO and SiO₂ at an equilibrium CO₂/CO ratio of 1. (ref. 34)
evidence in support of the hypothesized charge transfer model (expressed in terms of the concentrations of donors and acceptors), more rate data together with the appropriate thermodynamic data are required before making firm conclusions in this regard.

2.2.2.4 Pseudo-quaternary melts:

In 1985 Fine, Meyer, Janke and Engell [64] studied the kinetics of molten iron oxide reduction at 1873 °K in the FeO-CaO-MgO-SiO₂ system using CO as a reductant. The gas was jetted onto the melt surface (in a manner similar to that described by Nagasaka et al. [56]) and the product gases were analyzed with the help of an infrared gas analyzer. The authors fitted their results to an empirical rate equation

\[
\text{rate} = \frac{dn_{\text{FeO}}}{dt} = -kAa_{\text{FeO}}\Delta P_{\text{CO}}
\]  

(2.20)

where \(k\), \(m\) and \(n\) are constants and \(A\) is gas-melt interfacial area. The rate is expressed as \(\text{mol FeO} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}\) and the quantity \(\Delta P_{\text{CO}}\) equals the inlet minus the equilibrium partial pressure of CO (for the ferrous oxide reduction reaction). The authors calculated \(a_{\text{FeO}}\) values using a 4th order polynomial equation in terms of \(X_{\text{FeO}}\) (obtained by Turkdogan and Pearson [65]) for a Fe₂O-CaO-MgO-MnO-SiO₂-P₂O₅ system.

In a recent study Kim, Gränzdörffer and Fine [66] report that with increasing SiO₂ contents the rate of reduction of ferrous oxide is decreased. Their experimental set up and data analysis were similar to that used by Fine et al. [64] and the slag compositions were within the Fe₂O-CaO-MgO-SiO₂ system. The authors accounted for the "excess surface coverage" by silica in these melts and derived the following rate expression

\[
\frac{r}{A_o} = k\left[1 - 0.7(a_{\text{SiO}_2})^{1/3}\right]\left(a_{\text{FeO}}P_{\text{CO}} - a_{\text{Fe}_2\text{P}_{\text{CO}_2}}/K\right)
\]

(2.21)

The authors assume that the surface area available for the reduction reaction (A) is related to the total gas-melt area \(A_o\) by

\[
\frac{A}{A_o} = \left[1 - 0.7(a_{\text{SiO}_2})^{1/3}\right]
\]

(2.22)
Equation (2.22) was derived by the authors based on available surface tension data for Fe$_4$O-SiO$_2$ melts. [67] The validity of the rate law represented by the equation (2.21) was determined using the data for all experiments with $P_{CO}$ values of 0.05 atm. or less. The best-fit straight line through the data yielded a rate constant, $k$, of $4.2 \times 10^{-5}$ (mol/cm$^2$ s atm). Using their own data in conjunction with the earlier reported data by Nagasaka et al. [56] and Belton and coworkers [34,61,68] the authors derived an activation energy value of 135 kJ/mol for ferrous oxide reduction using CO reductant. Additionally, Kim et al. [66] report the following relationship between their rate constant $k$ and the one reported earlier by Ban-ya and coworkers [56]:

$$k_a = k a_{FeO} \left[ 1 - 0.7(a_{SiO_2})^{1/2} \right]$$

(2.23)

This relationship is shown in Figure 2.6.

2.2.2.5 Complex melts:

Many Russian researchers report the use of industrial slags in their kinetic investigations [28,69-72]. As a direct consequence of this choice they had to consider several different reactions taking place in their melts and this has caused numerous difficulties in the data interpretation. Although the chemical reaction of primary importance in these studies was reduction of ZnO to Zn, their results strongly suggest an important contribution by a transient iron phase and its oxide species in the overall reduction scheme.

2.3 Industrial/Large scale work:

In general there is no adequate foundation for direct extrapolation of information from the laboratory to an industrial process and for this reason it is important to perform either large-scale experimental work or pilot plant studies. In spite of the potential benefits emanating from such research activity the reported data concerning this topic is very limited.

During 1981 and 1982 Richards, Brimacombe and Toop [9,73,74] performed industrial trials on zinc fuming furnaces at Cominco's plant in British Columbia. Based on their measurements and subsequent mathematical analysis the authors concluded that the reaction between coal and the slag is controlled by diffusion of the reactant species (e.g. Fe$_2$O$_3$ and ZnO)
Figure 2.6 Relationship between the apparent rate constants obtained in two separate investigations. (from ref. 56, 66)
in the slag phase and/or carbon gasification (Boudouard reaction). In a separate set of trials Lehner and Lindgren [75] studied fluid flow phenomenon in Boliden's zinc fuming plant. Chemical analyses of the dust samples extracted above the turbulent slag bath, revealed about 8.8% carbon in them and this observation was in good agreement with the measurements of Richards et al. [74] Based on the results obtained in their investigation the authors conclude that zinc fuming rates were influenced mainly by the coal and air feed rates and coal-to-air ratio.

In addition to the above publications on industrial trials there are others that report on large scale laboratory work. In 1979 Floyd and Conochie [76] published results of their experiments using 500 gm batches of slag in aluminosilicate crucibles. The kinetics of Sn removal was studied by injecting either a solid or gaseous reductant into the molten slag. The authors report the following important conclusions:

(1) Reduction rates obtained using the CO were lower than those using H₂.
(2) Rapid reduction of slag occurs when the injected reductants are partly burned with co-injected air; and
(3) SnO reduction reactions involve the participation of both metallic iron and iron oxides.

In 1981 Schmitt and Wuth [77] reported the results of top blowing experiments in complex non-ferrous slags. The melts were held in 0.1 m diameter crucibles and the charge weights ranged between 0.5 and 1.5 kg. The authors analyzed their data using a "surface renewal model" and calculated overall mass transfer coefficients assuming liquid phase control. The values of the overall mass transfer coefficient, \(k_a\) (defined by the authors as \(k_a = k_{oo}(\frac{A}{V})\)) ranged between \(10^{-4}\) and \(3 \times 10^3\) sec\(^{-1}\) and these were found to be in agreement with the theoretically predicted values.

Malone et al. [78] in their reduction kinetic study of copper and zinc oxide bearing slags using carbon have considered several concurrent reactions. For example carbon, CO, Fe and FeO can all participate in the reduction of copper and zinc oxides. The authors classified the reactions via carbon as direct reduction reactions and those via either CO, Fe or FeO were termed
indirect reduction. Based on the evidence of microscopic analysis they suggest that in the Fe$_2$O-SiO$_2$-CaO pseudo-ternary system containing either copper or zinc oxides reduction via metallic Fe may not occur.

2.4 Critical assessment of published work:

It is commonly stated that those who have worked in the field of high-temperature chemical metallurgy have devoted too much time to establishing the equilibrium properties of their phases and too little time studying the rates at which reactions within and between phases proceed. The information in the foregoing paragraphs offers some evidence in support of this opinion. Since the 1960s however, the interest in the field of slag reaction kinetics has grown steadily and this has resulted in an improvement of our understanding of this area.

Researchers have tried a variety of crucible materials including graphite, coal, iron, alumina, zirconia, MgO, BeO, platinum, iridium and Pt-Rh, to hold oxide melts. However, only a few have commented on the effects of crucible contamination on the overall reaction behavior. A few researchers attempted to overcome the contamination problem by selecting solid carbon or graphite as a crucible material. However, this choice introduced another problem - namely nucleation of gas bubbles. This caused discrepancies in the results between various investigators and as a result no unequivocal conclusion was drawn regarding the overall rate controlling step(s). Since three phases - solid, liquid and gas are involved in the reaction between iron-oxide bearing slags and solid carbon, mass transport and chemical processes may both play a part in controlling the rate of reaction (2.9). It should be also be noted that the above reaction is strongly endothermic and hence in general terms, heat transfer might also be important in maintaining the reaction [31,79].

Additionally there are conflicting opinions concerning the presence and/or participation of iron in the reduction reactions in iron oxide-containing melts. Many Russian researchers [69-72] have speculated on the presence of an intermediate (or transient) iron phase. According to these authors both ferrous oxide and metallic iron can act as reductants to reduce zinc oxide but none of the authors have provided evidence or proof to substantiate their claim. On the contrary, based
on their research Melone et al. [78] have concluded that in the reduction of copper and zinc oxides the reduction via metallic iron does not occur. Therefore it is important to undertake additional studies to identify the role played by the iron phase and to further improve our understanding of the complexities of slag reactions.

Limited data on the ferrous reduction reaction shows that lower rates are obtained at higher silica levels in the melts and the trend is reversed with the addition of lime. [56] Further analysis has attributed such results to the changes in the apparent rate constants. The results have also been interpreted in terms of changes in the surface electrochemical potential of the melts and the same model has been proposed for the oxidation reaction. [80] Based on the work of Sun et al.[63], Sasaki et al. [68] and El-Rahaiby and co-workers [34] Belton [80] has concluded that the rate of oxidation reaction is governed by the dissociation of CO$_2$ at the melt surface. The author has also shown that the results of the oxidation of liquid iron oxide, conducted by Turkdogan and Grieveson [33], can be interpreted by assuming dissociation of CO$_2$ adsorbed on the surface to be the rate-controlling step. In general however the fundamental reasons behind the observed variations in the apparent rate constants in these melts are not understood with certainty and therefore more research work is needed.

The important points that emerge from the literature survey are outlined below:

(1) Most reduction kinetic studies have been done at iron saturation.

(2) The effects of crucible dissolution on the reaction rates, if any, are not clearly identified.

(3) In many cases, the data is fitted to empirical rate expressions.

(4) Bulk of the kinetic data has been obtained by jetting a gaseous mixture onto the melt surface; but equivalent information concerning unstirred melts is very meagre.

(5) The work of Kim et al. [66] highlighted the potentially important role played by surface silica coverage for the first time.

(6) The importance of charge transfer reactions in the iron oxide-containing slag melts has been suggested; but no conclusive evidence in its support is available.
(7) The role played by the physicochemical properties of the melts (e.g. density, viscosity and surface tension) in gas-slag reactions is not understood with certainty.

(8) No systematic studies are reported for comparing relative rates of oxidation and reduction reactions in non-ferrous slag systems.
Chapter 3
Objectives and Scope

From the information provided in the two previous chapters it is clear that our understanding of slag-related reactions in general, and redox reactions involving iron oxide species in particular, is far from complete. Because gas-slag reactions are of practical importance to many non-ferrous industries, it is important to obtain as much useful information on them as possible. The understanding of gas-slag reactions is vital for either developing new pyrometallurgical operations or improving existing ones. Since much of the previous research work (thermodynamic and kinetic) deals with gas-slag-metal reactions of importance to ironmaking and steelmaking industries, it is also necessary to extend this research activity into the non-ferrous field. Moreover, new rate data is needed to confirm and verify certain aspects of earlier studies.

3.1 Objectives

The primary objective of the work is to obtain quantitative data on the reduction and oxidation reactions in simple melts containing iron oxides at temperatures between 1200 °C and 1400 °C by CO and CO$_2$. The secondary objective is to investigate the nature of the ferric-to-ferrous reaction in melt compositions away from both iron and magnetite saturation. The tertiary objective is to evaluate the effects of solid reaction products, namely iron metal and magnetite, on the gas-slag reaction rates.

3.2 Scope of the experimental work

The choice of synthetic slags, as opposed to industrial slags, is made for the present study for the following reasons:

(1) By working on pure oxide melts it is hoped to restrict the number of parameters that affect reduction rates to a minimum.

(2) Once the basic data on pure oxide melts is generated it will be easier to extend the investigation to evaluate the effects of individual oxides on overall reaction rates.
Industrial slags usually contain several impurities that may strongly affect the reaction under review. There is a possibility that these impurities e.g. S, Bi, As, Sb, and Sn, may lead to side reactions and surface effects which would pose difficulties in the analysis and interpretation of the rate data.

The temperature range of primary interest to the non-ferrous industry is chosen so that the data could be directly applied to practical situations. Use of gaseous reductants is preferred because earlier research has shown that even when solid reductants are employed the reduction reactions usually involve participation of an intermediate gaseous reactant species. Unstirred melts were exposed to gas mixtures containing different proportions of CO and CO$_2$. The gas mixture was not jetted onto the melt surface to avoid the possibility of melt surface movement due to the velocity of impinging gases. Moreover, it is believed that the reaction area estimates for unstirred melts would be more reliable than the ones for a jetting setup.

Admittedly, the stagnant system goes to the other extreme when compared to jetting arrangement and it is anticipated that the gas phase resistance would affect the reaction rates to a degree. However, the main advantage of the stagnant system is that the gas phase contribution can be easily characterized and thereby the roles played by other interfacial and liquid phase mass transfer effects, if any, could be identified.

A comprehensive experimental scheme includes a reduction reaction study at iron saturation in both simple and complex melts. A few magnetite saturation experiments are performed to compare the effects of solid phases on reaction rates. But perhaps the most important feature of this work is the study of the ferric-to-ferrous reaction in lime-free and lime-containing melts away from both iron and magnetite saturation. No such study using unstirred melts is previously reported in the literature.

The experimental variables - temperature, melt composition, melt weight, ferric-to-total iron ratio, basicity, gas composition and crucible material, are chosen to generate sufficient data for a critical analysis of several important issues including the occurrence of charge transfer
reactions in slag melts, extent of crucible dissolution and its effect on the overall reaction rate, role of the gas-slag interface and effect of melt ferric level on rate phenomena. Further details on the variables employed in this investigation are outlined in Chapter 4.

The data generated is analyzed with the help of mathematical models to distinguish different stages of the reduction reactions. These models are used to evaluate the roles played by gas-phase mass transfer, liquid-phase mass transfer and interfacial phenomenon. Based on the findings of the work several comments are made concerning reaction rate phenomena in gas-slag melts.

As an aid to the interpretation of results a Mössbauer technique is used for identification of compositional gradients in the melts. To further support these results some X-ray diffraction and scanning electron microscopic work is also done.
Chapter 4

EXPERIMENTAL WORK: Techniques and Methodology

In order to determine the rate of gas-slag reactions the change in concentration of a particular component in either the gas or slag phase must be determined with time either directly or indirectly. Chromatography or infrared spectroscopy is used commonly for monitoring changes in the product gas composition; on the other hand the choice of thermogravimetry is often made when information on the melt weight changes is required on a continuous basis. However, simultaneous use of the two techniques, one for gas composition measurement and the other to monitor slag weight changes is very rare (only one reported use [81]) and the same was attempted in this investigation. A solid electrolyte oxygen probe was installed to monitor gas composition and the slag weight changes were recorded continuously using a precision balance.

4.1 Apparatus:

The experimental apparatus essentially consists of three major components:

(1) Gas purification system;
(2) Reaction chamber; and
(3) Data acquisition system.

Figure 4.1 shows general arrangement of the above apparatus.

Argon, carbon monoxide and carbon dioxide were used in the preparation of various gas mixtures. All three gases were purified and metered prior to mixing. A schematic of the purification set up is shown in Figure 4.2.

The reaction chamber consists of an alumina tube (length 90 cm, i.d. 3.8 cm, o.d. 4.5 cm) within a super kanthal furnace. The top of the alumina tube was closed with a metallic flange which had two openings - one on the side for the zirconia solid electrolyte and the other in the centre for the alumina hanger. Through the central opening the product gases left the reaction chamber. The lower end of the alumina tube was closed using a flange and a copper chamber assembly. An inlet for the reactant gas mixture was provided in the copper chamber.
Figure 4.1 Schematic diagram of the apparatus used in this study.
Figure 4.2 Schematic diagram of the gas purification system. (a) shows arrangement of argon, carbon monoxide and carbon dioxide purification trains, (b) indicates components used in individual train.
The bottom end of this chamber could be opened and closed using a screwable cap. Loading and unloading of the weighed slag crucibles was done from this end. Thermocouple A, located approximately in the middle of the furnace, touched the reactor tube from outside and its emf output in conjunction with 'celetray' controller was used to maintain the furnace temperature at the set level.

The data acquisition system was made up of the following: balance and its bi-directional interface, DAS-8 and EXP-16 boards, Junction/grounding box, pH meter, chart recorder and an IBM PC-XT. Additional details are provided in Appendix I.

4.2 Raw materials:

Ferrous oxide, FeO of 99.9% purity (80 mesh pass) was obtained from Kojundo Chemical Laboratory Ltd, (Japan). Calcium oxide and silica were of AR (Analytical Reagent) grade and ferric oxide assaying a minimum of 99% purity was used in the preparation of slag melts. Both the CaO and SiO₂ powders (-200 mesh size) were thoroughly dried by heating to 1000 °C and later an appropriate precaution was taken to store them to avoid any moisture pick up.

All the gases used were of commercial/industrial quality and for the elimination of impurities in these the individual gases were channelled through specially designed purification trains prior to their entry into the reaction chamber. The slag melts were contained in alumina crucibles on most occasions; however, magnesia (MgO) and spinel (MgO-Al₂O₃) crucibles were also tried in several runs to study the effect of crucible dissolution on the reaction rate.

4.3 Preparatory work:

To supplement the weight measurement data a scheme was planned in which changes in the gas phase oxygen potential would be continuously monitored and recorded. For this purpose a solid electrolyte probe was fabricated and installed in the reaction chamber. (See Figure 4.1) While testing and calibrating the probe it was observed that the output was very sensitive to two parameters namely - gas velocity and carbon monoxide content of the gas mixtures. Accurate and meaningful probe readings could only be obtained using CO-CO₂ gas mixtures in which the
$P_{\text{CO}}/P_{\text{CO}_2}$ ratio was about 9 or more. Upon exposure to the argon-oxygen mixtures the probe response did not correspond to the expected emf output. Increase in the gas velocities of these mixtures produced the results in the right direction however the data did not yield the reliable and exact oxygen partial pressure values. Though the observed trends are consistent with those reported by Estell and Flengas [82] in the context of the present work these results implied that the probe output could not be utilized for correlating the weight changes arising from the gas-slag reactions.

Prior to the commencement of actual experiments several preparatory steps were necessary and a few important ones are briefly described below.

**4.3.1 Flow meter calibration:**

After leaving the cooling coils (see Figure 4.2) the three gases entered the rotameter tubes. Passage of the gases via cooling coils (made from 7 mm copper tubing and immersed in a water bath) ensured gas supply to the flow meters at a constant ambient temperature. Individual flow meters (for Ar, CO and CO$_2$) were calibrated by adding a linear mass flow meter unit at the exit end of the rotameter. During the calibration run gas entered the purification train and then passed through rotameter-mass flow meter arrangement. For a constant rotameter float reading (which was controlled and adjusted using a precision needle valve) the corresponding flow reading in the mass flow meter was recorded. Later the flow rate was altered by opening/closing the needle valve at the inlet end of the rotameter tube and when the float reading stabilized the mass flow meter rate was read. The procedure was repeated to cover an entire scale (5 to 100 mm) of the rotameter tube. To supplement the above data which essentially represented high flow rates additional measurements were made using a dry gas meter. An average of three readings was taken to be the rotameter flow rate. A typical set of data obtained during argon calibration is listed in Table 4.1.

To calibrate low flow rate (#610 tube) rotameters a 'soap bubble' technique was employed; and similar to the high flow rate rotameter (#604 tube) calibration, further confirmation of the data were obtained by repeating the calibration trials using a mass flow meter.
Table 4.1 Flow rate calibration results for argon gas.

<table>
<thead>
<tr>
<th>Rotameter Scale Reading</th>
<th>Calibrated flow rate</th>
<th>Measured flow rate as per</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stainless steel float</td>
<td>Pyrex float</td>
</tr>
<tr>
<td>mm</td>
<td>mm</td>
<td>cc/sec</td>
</tr>
<tr>
<td>1.5</td>
<td>8</td>
<td>3.75</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>4.45</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>5.75</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>6.5</td>
</tr>
<tr>
<td>6</td>
<td>13</td>
<td>8.0</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>13.0</td>
</tr>
<tr>
<td>15</td>
<td>31</td>
<td>22.0</td>
</tr>
<tr>
<td>20</td>
<td>39</td>
<td>25.5</td>
</tr>
<tr>
<td>25</td>
<td>49</td>
<td>42.0</td>
</tr>
<tr>
<td>30</td>
<td>59</td>
<td>46.5</td>
</tr>
<tr>
<td>35</td>
<td>65</td>
<td>53.5</td>
</tr>
<tr>
<td>40</td>
<td>78</td>
<td>62.0</td>
</tr>
<tr>
<td>45</td>
<td>87</td>
<td>68.0</td>
</tr>
<tr>
<td>50</td>
<td>97</td>
<td>77.5</td>
</tr>
<tr>
<td>55</td>
<td>108</td>
<td>87.0</td>
</tr>
<tr>
<td>60</td>
<td>119</td>
<td>94.5</td>
</tr>
<tr>
<td>65</td>
<td>127</td>
<td>104.0</td>
</tr>
<tr>
<td>70</td>
<td>137</td>
<td>109.0</td>
</tr>
<tr>
<td>75</td>
<td>147</td>
<td>118.0</td>
</tr>
</tbody>
</table>
In each individual case the calibration data was finalized when the flow rates for a particular flow meter reading could be reproduced using two independent techniques. The accuracy of both "high flow rate" and "low flow rate" type rotameters is estimated to be ± 5%. All the flow meters were obtained from Matheson Gas Company of Canada.

4.3.2 Furnace temperature profile:

The alumina reactor tube was heated by the super kanthal elements. A Pt/Pt-10%Rh thermocouple was placed approximately in the middle of the hot zone and its junction touched the outside wall of the alumina tube. Signal from this thermocouple was channelled to a regulator for controlling the furnace temperature at a set level. However, it was necessary to generate precise information on the temperature profile within the reactor tube and for this reason an additional thermocouple was constructed to measure the profile of the furnace maintained at 1400 °C. The newly made thermocouple was traversed through the length of the reactor tube (lying within the furnace) at fixed intervals of 10 mm. At each interval the emf response was read on the chart recorder and based on this information temperature profile of the reactor tube was obtained. Care was taken to hold the hot junction in the centre of the reactor tube and a steady flow of argon gas was maintained during these measurements. The procedure was repeated for other furnace temperature settings at 1300 °C and 1200 °C. The data revealed the hottest zone within the reactor tube to be approximately 40 mm in length. This information was later utilized to position the crucible.

4.3.3 Activity calculations:

In the present study the activity values were derived using the model developed by Kellogg and Goel. [83,84] A computer program was written based primarily on the data supplied by Goel and Kellogg [83] to calculate activity values of various oxide species in iron oxide-containing silica melts (FeO-Fe₂O₃-SiO₂). Prior to its adoption calculations were made to check the validity of the model. For this purpose the composition of a ternary peritectic was chosen in the Fe-O-SiO₂ system; and based on the wt. pct values of SiO₂, Fe₂O₃ and FeO species (25.0, 11.5 and 63.5...
respectively) and the temperature of 1163 °C the computer program was run to calculate activities of hypothetical species, FeO and FeO$_{1.5}$. These values were in turn utilized to predict the activity of solid Fe$_3$O$_4$ according to following reaction:

$$2\text{FeO}_{1.5(\text{hyp})} + \text{FeO}_{(\text{hyp})} = \text{Fe}_3\text{O}_4(\text{actual}) \quad (4.1)$$

The following relationship between the equilibrium constant, $K_{(4.1)}^*$, and temperature for the above reaction (4.1) was arrived at using the data in the literature [84]

$$\ln K_{(4.1)}^* = \frac{17837.63}{T} - 15.08 - 0.54 \cdot (10^{-3}) \cdot T + \frac{(1.28)(10^5)}{T^2} + (1.2) \cdot \ln T \quad (4.2)$$

Substitution of the peritectic temperature, T, value of 1436 °K yielded a $K_{(4.1)}^*$ value and based on this the $a_{\text{Fe}_3\text{O}_4}$ was found to be 1.0338, which is in close agreement with the theoretical value of 1. Similar calculations were repeated to find the correlation between the predicted and theoretical activity values of fayalite species. The calculated value of 0.9936 matched well with the expected theoretical value of unity. In addition the data obtained on silica activity were found to be consistent with those reported by Timucin and Morris [36] and Schuhmann and Ensio [41]. A few additional details concerning the model are presented in Appendix I.

To generate activity data in the complex FeO-Fe$_2$O$_3$-SiO$_2$-CaO-Al$_2$O$_3$ system an additional computer programme was written. Before using the model predicted activity values in thermodynamic calculations a comparison was made with the activity values reported by other researchers. Table 4.2 is prepared to illustrate the proximity of the predicted ferrous oxide activity values with those obtained from other sources. Though the table does not list the silica activity data the accuracy of the predicted values was within ± 5% of those reported in the literature. [36,41] Based on these findings it was concluded that Kellogg’s model provides a satisfactory prediction of the measured activity data.
Table 4.2 Comparison of $a_{FeO}$ values calculated using Kellogg's model with the other researchers.

<table>
<thead>
<tr>
<th>Slag composition, wt%</th>
<th>Temp.</th>
<th>Kellogg's model</th>
<th>Estimated $a_{FeO}$ values** based on other sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>Fe$_2$O$_3$</td>
<td>SiO$_2$</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>63.8</td>
<td>0.4</td>
<td>35.8</td>
<td>-</td>
</tr>
<tr>
<td>71.6</td>
<td>1.0</td>
<td>27.4</td>
<td>-</td>
</tr>
<tr>
<td>77.8</td>
<td>3.8</td>
<td>18.4</td>
<td>-</td>
</tr>
<tr>
<td>50.0</td>
<td>-</td>
<td>27.8</td>
<td>-</td>
</tr>
<tr>
<td>40.0</td>
<td>-</td>
<td>33.3</td>
<td>-</td>
</tr>
<tr>
<td>46.7</td>
<td>-</td>
<td>36.3</td>
<td>-</td>
</tr>
<tr>
<td>56.3</td>
<td>3.6</td>
<td>31.4</td>
<td>-</td>
</tr>
<tr>
<td>47.8</td>
<td>6.2</td>
<td>22.1</td>
<td>-</td>
</tr>
<tr>
<td>51.9</td>
<td>1.0</td>
<td>27.3</td>
<td>-</td>
</tr>
<tr>
<td>40.0</td>
<td>-</td>
<td>30.0</td>
<td>8.0</td>
</tr>
<tr>
<td>39.0</td>
<td>-</td>
<td>20.0</td>
<td>21.0</td>
</tr>
<tr>
<td>30.0</td>
<td>-</td>
<td>24.0</td>
<td>21.0</td>
</tr>
</tbody>
</table>

Note:  
(1) * slag composition rounded to nearest digit.  
(2) ** Estimated values are accurate within ± 5%.
4.3.4 Data acquisition trials:

Three important parameters - oxygen probe output, furnace temperature and crucible weight, were monitored during all the experiments and their permanent record was kept using the on-line computer. The hardware - DAS-8 and EXP-16 boards and IBM PC-XT was used in conjunction with the data acquisition software 'Labtech notebook' which allowed simultaneous display of the data being stored on the computer hard drive. A brief description of the data acquisition system is provided in Appendix II.

4.4 Experimental procedure:

A thoroughly dried and clean alumina crucible was weighed accurately using a precision balance. The crucible was reweighed after placing a known amount of ferrous oxide powder (or its mixture with silica, calcium oxide and ferric oxide). After recording the weights, the crucible was attached to the alumina hanger assembly using a solid alumina pin. To do this the bottom cap of the copper chamber was unscrewed. Once the crucible was suspended, the hanger assembly was raised slightly within the copper chamber and the cap reattached. At this point, purging of the reactor tube with the gas mixture commenced. After about 5-10 minutes all the air was driven out and the operation of raising the crucible within the reaction tube was started. The crucible was raised slowly from its lowest position in the copper chamber to the reaction site at a rate of about 45 °C/min. During this heating period the proportion of CO and CO\(_2\) was controlled in the Ar-CO-CO\(_2\) mixture so as to eliminate unwanted side reactions. At the end of the heating period, which averaged approximately 35 minutes, the alumina hanger was attached to the middle hanger (Figure 4.1). The middle hanger was held by the top steel hanger which in turn was suspended from the balance. Prior to this the balance was calibrated by following the recommended procedure and other preparatory steps were taken to record the balance output. The weight of the crucible-hanger assembly was logged after 10 seconds and, in addition, the record of furnace temperature (using thermocouple A) was stored on the computer hard drive. During this period melting of oxide mixture and its homogenization was permitted. The duration of the melting
period varied from 1-3 hours depending on the reaction temperature.

At the end of the melting period the gas mixture was altered to promote the desired chemical reaction. The flow rates employed during the reaction periods were approximately 5 times higher than those during the heating and melting periods. The increased flow rates caused an abrupt weight change at the beginning of the reaction period. The phenomenon was attributed to the drag effect (as the reactant gases travelled from bottom to the top) and its duration was observed to be less than 2 minutes. Following this period, the flow rate related fluctuations in weights were minimal and the melt weight changes corresponding to the chemical reaction alone were recorded.

At the end of the reaction period, which varied from 2-7 hours depending on both the temperature and the type of reaction studied, the alumina hanger was detached from the middle hanger and was connected to a movable arm of the hanger raising/lowering device. By operating this device powered by a small D.C. motor the arm was lowered rapidly until the crucible reached the copper chamber. During this quenching procedure the crucible was brought from its reaction site in the alumina reactor tube to the copper chamber at an ambient temperature in less than 20 seconds. The arrangement enabled smooth and reliable quenching operation without inducing any melt turbulence. The reactant gas supply to the reactor chamber was maintained at least 30 minutes into the quenching period to ensure complete cooling down. Later, the gas supply was stopped and the crucible was taken out for reweighing.

Though the melt weight data were collected only during the melting and reaction periods, the melt weight change in the heating period could be calculated using the following equation:

\[ \Delta W_{\text{heating}} = (\text{Initial wt.} - \text{Final wt.}) - \Delta W_{\text{melting}} - \Delta W_{\text{reaction}} \]  

(4.3)

By substitution of all the known values, the weight change during heating can be calculated readily. This data was useful to ascertain if side reactions were taking place prior to the reaction period.
In all the runs slag weighed about 3 grams and the melt depth averaged between 3 to 4 mm depending on the melt density and the crucible diameter.

4.5 Experimental variables:

To cover all aspects of the oxidation and reduction reactions under review the following variables were studied during this work.

(1) Temperature; (2) Melt composition; (3) Gas composition; (4) Crucible material; and (5) Melt surface area.

4.6 Laboratory methods:

In addition to the weight gain/loss data obtained using thermogravimetry, the information on slag composition was necessary to interpret the effects of various operating variables on the rate data. For this purpose it was essential to perform chemical analysis of the melts. To supplement the observations and findings of the experimental data use was made of conventional techniques such as electron microscopy and X-ray diffraction; but in addition to this Mössbauer spectroscopy was employed to verify the presence of iron ion gradients with melt depth.

4.6.1 Chemical analysis of slag melts:

A total of 29 samples including the Fe₂O starting material were analyzed for the determination of the following: (1) ferrous oxide; (2) total iron; (3) silica; (4) calcium oxide; (5) magnesium oxide; and (6) alumina. The ferric oxide proportion in the slags was derived from the total Fe and ferrous oxide assays by difference. All the assays were performed by the Cominco assay laboratory at Trail, B.C. The methods of analyses used in the determination of various components are listed below.

(1) Ferrous oxide: Atomic Absorption (AA) and Volumetric - SnCl₂;
(2) Total Fe: Potassium Dichromate method and Atomic Absorption;
(3) Silica, (SiO₂): Colorimetric - Molybdenum Blue;
(4) Calcium oxide, (CaO): Volumetric - EDTA;
(5) Magnesium oxide, (MgO): Volumetric - EDTA and Atomic Absorption;
(6) Alumina, (Al₂O₃): Volumetric - EDTA.

4.6.2 SEM analysis:

Our kinetic data indicated that silica is surface active in the melts i.e. its surface concentration is moderately higher than the bulk composition. Though there is clear evidence in support of this in the literature [67], measurements were made of silicon with depth using the electron probe on the SEM. In addition, the average value obtained from such analyses was compared with the wet chemical assay for confirmation. An example of this is provided in Table 4.3 where Al₂O₃, MgO and SiO₂ assays obtained by SEM and wet chemical analyses are compared. To a limited extent the SEM was also used to observe and identify various glassy phases in the quenched slags.

4.6.3 Mössbauer spectroscopy analysis:

This technique has been used primarily to study the distribution of iron cations in the slag bulk. However, in the present study an attempt is made to use this technique to trace Fe³⁺ and Fe²⁺ gradients away from the reaction interface. A special sample holder was designed for this purpose and the Mössbauer spectra were obtained in quenched slags at various depths. Details of this work are provided in Chapter 7.

4.6.4 X-ray diffraction analysis:

A powder diffraction pattern was obtained on the ferrous oxide raw material to test for the presence of iron metal and magnetite. Peaks of iron (fcc) and magnetite were identified using two separate radiations i.e. CuKα and FeKα. This qualitative analysis was later supplemented by the wet chemical analysis and based on both the measurements individual proportions of Fe and Fe₂O₃ were estimated to be approximately 4 wt pct.

Additionally the presence of crystalline phases, if any, in the quenched slag samples was tested for using X-ray diffractometer.
Table 4.3 Slag chemical compositions obtained by wet chemical methods and SEM-EDX.

<table>
<thead>
<tr>
<th>Exp</th>
<th>Slag</th>
<th>Chemical composition, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Melt type</td>
<td>Wet chemical assay</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FeO</td>
</tr>
<tr>
<td>123</td>
<td>Fe₃O₄-Al₂O₃</td>
<td>93.5</td>
</tr>
<tr>
<td>124</td>
<td>Fe₃O-MgO</td>
<td>97.3</td>
</tr>
<tr>
<td>125</td>
<td>Fe₃O-SiO₂-Al₂O₃</td>
<td>56.5</td>
</tr>
<tr>
<td>126</td>
<td>Fe₃O-Al₂O₃-MgO</td>
<td>93.5</td>
</tr>
</tbody>
</table>
Chapter 5

Results and Preliminary Analysis

The analysis of the accumulated data is based primarily on the weight change observed during an individual run. The weight of the alumina hanger assembly (i.e. hanger rod, crucible and pin) within the furnace and two steel hangers outside of the reactor tube (see Figure 4.1) did not change during the experiment and therefore changes in the balance readings were attributed only to the passage of oxygen in and out of the slag due to the gas-melt reactions. From the recorded data weight versus time curves could be plotted and slope of these curves represented reaction rates.

It is felt that presentation of the results in either tabular or graphical form alone may not be sufficient to develop an understanding of the rate phenomenon because several different factors are responsible for the observed rates. It is therefore important to identify the contributions to the rate from individual parameters and then study their combined behaviour. Furthermore, such an approach is helpful in the development of a mathematical model. For these reasons preliminary discussion of the results is included in this chapter.

5.1 Ferrous-to-iron reduction study between 1200 °C and 1400 °C:

The ferrous oxide raw material, Fe₃O₄, used in the preparation of the melts contained ~ 4 wt% ferric oxide and therefore the reduction reaction under review can be written as

\[
\text{Wüstite}_{(\text{plag})} + CO_{(g)} = Fe(\gamma)_{(s)} + CO_{2(g)}
\]  (5.1)

By performing wet chemical analysis of the ferrous oxide material it was possible to estimate the value of the non-stoichiometry coefficient, x, as 0.98 ± 0.01. Additional confirmation of this was obtained using Mössbauer spectroscopy as discussed in chapter 7. Since the value of x is close to unity, the standard state of wüstite (ferrous oxide) is assumed to be the ideal stoichiometric liquid. In many publications [37,40-43,56,57] the authors have assumed this standard state to list free energy change data for reaction (5.1).
5.1.1 Fe₂O melts at 1400 °C:

Experiments were conducted at 1400 °C to identify the effects of various parameters such as gas composition, melt surface area, melt composition and gas flow rate on the iron formation reaction. Alumina crucibles were used and the extent of crucible dissolution was determined from wet chemical analyses of the quenched slag samples. The results showed about 6-6.5 wt% Al₂O₃ in these slags which is in close agreement with its equilibrium value according to the Fe₂O-Al₂O₃ phase diagram. [86,87]

5.1.1.1 Effect of gas composition:

Three gas mixtures: Ar-CO, CO-CO₂ and Ar-CO-CO₂ were used. In each case, variation in the melt weight with respect to time was found to be linear. In some cases however an increase in the slope could be detected after an initial period. This increase is attributed to melt movement induced by the metallic iron. Figure 5.1 shows several weight-time curves obtained using CO-CO₂ and Ar-CO mixtures.

It can be seen from the plots in this figure that for low values of P_{CO} the slope is constant throughout the reduction period; however at higher values of P_{CO} (≥ 0.6 atm) in either Ar-CO or CO-CO₂ the slope increases after a certain point in the reduction period. Therefore, for comparing data amongst different runs only the initial, linear reduction period (approximately 10 minutes) is considered for all runs. The reduction rate is derived using following equation

\[ r = \frac{1}{A_o} \frac{dW}{dt} \tag{5.2} \]

where \( W \) is sample weight in grams, \( t \) is reaction time in seconds and \( A_o \) is the gas-melt surface area in cm².

Alternately, the rate can also be expressed as

\[ Rate = \text{(rate constant)} \times (\text{Driving force}) \tag{5.3} \]

and

\[ \text{(gms/cm}^2\text{s)} \text{ (gms/cm}^2\text{s atm)} \text{ (atm)} \]
Figure 5.1  Variation of the melt weight with time during ferrous-to-iron reaction study at 1400 °C (a) Expt #2A; (b) Expt #8; (c) Expt #1; and (d) Expt #7.
\[ f = P_{CO}^b - \frac{(P_{CO_2}^b)}{(K_{5.1}^{eq}a_{FeO})} \]  

(5.4)

where \( f \) is the reaction driving force, \( P_{CO}^b \) and \( P_{CO_2}^b \) are the bulk partial pressures of the reactant gases, \( K_{5.1}^{eq} \) is the equilibrium constant for the reaction (5.1) and \( a_{FeO} \) is the ferrous oxide activity in the melt. Additional details on the derivation of equation (5.4) are given in chapter 6.

The reaction rate values obtained for various runs are listed in Table 5.1 along with the relevant experimental parameters. In addition a separate column is prepared to indicate the weight gained by an individual melt prior to the reduction period. This information concerning the weight gain was considered essential to verify the absence of any solid phases in the melt (either wüstite or magnetite) prior to the reaction period. According to the Fe-O phase diagram (Figure 2.1), at 1400 °C liquid wüstite can contain only 24 wt% oxygen. Any additional oxygen in the melt results in the precipitation of a solid phase. Oxygen levels between 24 and 25.5 wt % lead to solid wüstite formation and when the level exceeds 25.5 wt% magnetite is formed. Therefore to avoid the presence of either of the solid phases it was necessary to hold the gas phase \( P_{O_2} \) below 10\(^{-8}\) atm (calculated from the thermodynamic data) during the heating and melting periods. The data in Table 5.1 reveals that in all the melts studied the melt oxygen content was below this threshold value of 24 wt% (calculated using the initial assay and equation 4.6). In the absence of precise \( P_{O_2} \) control during the heating and melting periods the possibility of oxidation is more likely.

The reduction rate values in Table 5.1 reveal that the rate increases with an increase in \( P_{CO} \). This relationship is shown graphically in Figure 5.2. Based on this figure an equilibrium \( P_{CO_2}/P_{CO} \) ratio for reaction (5.1) is determined for comparison with its theoretical value (derived using free energy data and assuming unit activities of wüstite and Fe). The line OB (x-axis) represents zero reduction rate and therefore the equilibrium point lies on this line. Along the line AB the \( P_{CO_2}/P_{CO} \) ratio changes. Since the point A is obtained by extrapolation of the rate data it represents the highest rate at \( P_{CO} = 1 \) atm. Therefore, as we move away from point A the \( P_{CO_2}/P_{CO} \) ratio increases.

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Table 5.1 Reduction rate data for Fe$_2$O-Al$_2$O$_3$ melts at 1400 °C.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Initial Melt Weight</th>
<th>Weight gain</th>
<th>Melt oxygen* prior to reduction reaction</th>
<th>Gas mixture</th>
<th>Reduction rate during initial 10 minute period</th>
<th>D.F.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g</td>
<td>mg</td>
<td>wt%</td>
<td>$P_{CO}$</td>
<td>$P_{CO_2}$</td>
<td>$P_{\alpha}$</td>
</tr>
<tr>
<td>1</td>
<td>4.0595</td>
<td>5</td>
<td>13</td>
<td>22.15</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>2.5022</td>
<td>28</td>
<td>8</td>
<td>23.16</td>
<td>0.18</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>2.0761</td>
<td>25</td>
<td>2</td>
<td>23.00</td>
<td>0.61</td>
<td>-</td>
</tr>
<tr>
<td>16A</td>
<td>2.9675</td>
<td>2</td>
<td>1</td>
<td>21.80</td>
<td>0.73</td>
<td>-</td>
</tr>
<tr>
<td>2A</td>
<td>2.5160</td>
<td>19</td>
<td>10</td>
<td>22.85</td>
<td>0.96</td>
<td>0.04</td>
</tr>
<tr>
<td>5</td>
<td>2.4380</td>
<td>30</td>
<td>5</td>
<td>22.71</td>
<td>0.88</td>
<td>0.12</td>
</tr>
<tr>
<td>8</td>
<td>2.4740</td>
<td>34</td>
<td>2</td>
<td>23.16</td>
<td>0.87</td>
<td>0.13</td>
</tr>
<tr>
<td>19A</td>
<td>2.3640</td>
<td>6</td>
<td>1</td>
<td>22.00</td>
<td>0.94</td>
<td>0.06</td>
</tr>
<tr>
<td>7A</td>
<td>2.5220</td>
<td>25</td>
<td>7</td>
<td>23.00</td>
<td>0.53</td>
<td>0.13</td>
</tr>
<tr>
<td>9</td>
<td>2.5450</td>
<td>35</td>
<td>3</td>
<td>23.19</td>
<td>0.65</td>
<td>0.13</td>
</tr>
<tr>
<td>19B</td>
<td>2.3640</td>
<td>6</td>
<td>1</td>
<td>22.00</td>
<td>0.69</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Note:
1. * Assuming all weight gain was oxygen.
2. According to Fe-O phase diagram (Figure 2.1) oxygen levels exceeding 24% by wt. lead to either solid wustite or magnetite formation.
3. During heating (~35 minutes) and melting (60 minutes) periods Ar-CO-CO$_2$ mixture was used.
4. Ferrous oxide raw material contained 21.7 wt% oxygen.
Figure 5.2 Relation between the initial reduction rates and $P_{\text{CO}}$ for the Fe$_2$O-Al$_2$O$_3$ melts at 1400 °C.
and the rate decreases until at point B on the x-axis the gas is incapable of reducing the slag. At this point then the gas is in equilibrium with the wüstite. In Figure 5.2, the point B is located at 0.80 atm and therefore assuming CO-CO₂ mixture at 1 atm the $P_{CO_2}$ value would be 0.20 atm. The lines OA and AB are obtained by performing linear regression analysis on the results of Ar-CO and CO-CO₂ gas mixture runs respectively. Thus, the experimentally determined value of the equilibrium $P_{CO_2}/P_{CO}$ ratio is 0.25. Thermodynamic calculation reveals a value of 0.264 for the equilibrium constant, $K_{eq}$, assuming unit activities of wüstite and Fe species. In our melts however, $a_{FeO}$ is less than 1 (due to the dissolution of alumina in the melt) and therefore the value of the equilibrium $P_{CO_2}/P_{CO}$ ratio is obtained by multiplying 0.264 by the $a_{FeO}$. For Fe₂O-Al₂O₃ melts at Al₂O₃ saturation an $a_{FeO}$ value of 0.96 is obtained using Kellogg’s model [83,84] and its multiplication with 0.264 yields an equilibrium $P_{CO_2}/P_{CO}$ value of 0.253. This agrees well with both the experimentally derived value of 0.25 and the previously reported values by Ban-ya and Watanabe (0.251) and Darken and Gurry (0.263) for the equilibrium $P_{CO_2}/P_{CO}$ ratios.

5.1.1.2 Effect of surface area:

To identify the role of surface area it was necessary to conduct experiments in alumina crucibles with different diameters using the same reaction driving force value (as per equation 5.4). Accordingly, three experiments (#6, #113 and #121) were performed using a Ar-CO mixture with $P_{CO} = 0.18$ atm. The results obtained are listed in Table 5.2. The data reveals three different weight loss values for the initial reduction period of approximately 10 minutes. However, for all the three experiments a rate value of $6.5 \pm 0.5 \times 10^4$ g-oxygen/cm²s was obtained.

5.1.1.3 Effect of crucible height:

Experimental results showed that the rate values were dependent on the crucible height. (Table 5.2) Critical analyses of the data suggested that this effect is attributed to the increased diffusion length in the taller crucibles. If we consider the distance between the crucible top and the melt surface as a gas phase boundary layer for molecular diffusion then the thickness of this
Table 5.2 Reduction rates for Fe$_2$O melts held in magnesia, alumina and spinel (MgO-Al$_2$O$_3$) crucibles and exposed to Ar-CO mixture ($P_{CO} = 0.18$ atm) at 1400 °C.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Crucible</th>
<th>Gas-melt area</th>
<th>Diffusion length, δ</th>
<th>Melt oxygen prior to reduction period</th>
<th>Weight loss during first 10 minutes</th>
<th>Reduction rate during the initial 10 minutes</th>
<th>Crucible dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Alumina</td>
<td>2.64 cm$^2$</td>
<td>2.60 cm</td>
<td>23.16 wt%</td>
<td>11.0 mg</td>
<td>6.8 x 10$^{-6}$</td>
<td>6.5% Al$_2$O$_3$</td>
</tr>
<tr>
<td>113</td>
<td>Alumina</td>
<td>2.08 cm$^2$</td>
<td>2.63 cm</td>
<td>22.00 wt%</td>
<td>7.5 mg</td>
<td>6.0 x 10$^{-6}$</td>
<td>6.5% Al$_2$O$_3$</td>
</tr>
<tr>
<td>121</td>
<td>Alumina</td>
<td>0.39 cm$^2$</td>
<td>2.60 cm</td>
<td>21.90 wt%</td>
<td>1.6 mg</td>
<td>6.8 x 10$^{-6}$</td>
<td>6.5% Al$_2$O$_3$</td>
</tr>
<tr>
<td>114</td>
<td>Alumina</td>
<td>1.80 cm$^2$</td>
<td>2.20 cm</td>
<td>22.00 wt%</td>
<td>8.0 mg</td>
<td>7.4 x 10$^{-6}$</td>
<td>6.5% Al$_2$O$_3$</td>
</tr>
<tr>
<td>122</td>
<td>Alumina</td>
<td>0.39 cm$^2$</td>
<td>4.50 cm</td>
<td>21.80 wt%</td>
<td>1.0 mg</td>
<td>4.3 x 10$^{-6}$</td>
<td>6.5% Al$_2$O$_3$</td>
</tr>
<tr>
<td>120</td>
<td>Spinel</td>
<td>1.23 cm$^2$</td>
<td>2.70 cm</td>
<td>21.80 wt%</td>
<td>3.5 mg</td>
<td>4.7 x 10$^{-6}$</td>
<td>4.5% Al$_2$O$_3$, 2.0% MgO</td>
</tr>
<tr>
<td>117</td>
<td>Magnesia</td>
<td>3.78 cm$^2$</td>
<td>2.70 cm</td>
<td>21.79 wt%</td>
<td>10.6 mg</td>
<td>4.7 x 10$^{-4}$</td>
<td>2.7% MgO</td>
</tr>
<tr>
<td>118</td>
<td>Magnesia</td>
<td>1.84 cm$^2$</td>
<td>2.40 cm</td>
<td>21.70 wt%</td>
<td>5.6 mg</td>
<td>5.1 x 10$^{-4}$</td>
<td>2.7% MgO</td>
</tr>
<tr>
<td>119</td>
<td>Magnesia</td>
<td>3.66 cm$^2$</td>
<td>1.90 cm</td>
<td>21.80 wt%</td>
<td>14.3 mg</td>
<td>6.5 x 10$^{-4}$</td>
<td>2.7% MgO</td>
</tr>
<tr>
<td>116</td>
<td>Alumina</td>
<td>2.09 cm$^2$</td>
<td>2.60 cm</td>
<td>21.95 wt%</td>
<td>7.5 mg</td>
<td>6.0 x 10$^{-4}$</td>
<td>6.5% Al$_2$O$_3$</td>
</tr>
<tr>
<td>115</td>
<td>Alumina</td>
<td>2.12 cm$^2$</td>
<td>2.74 cm</td>
<td>21.85 wt%</td>
<td>7.0 mg</td>
<td>5.7 x 10$^{-6}$</td>
<td>6.5% Al$_2$O$_3$</td>
</tr>
</tbody>
</table>

Note: Diffusion length, δ, refers to the distance between the melt surface and the crucible top. Taller crucibles and lower melt heights lead to higher δ values.
layer is one of the rate controlling parameters. Any experimental variable that alters the gas phase boundary, e.g. melt height and crucible height, can potentially affect the overall reduction rate. Analysis of the experimental data has revealed that the value of gas phase mass transfer coefficient

\[ k_s = \frac{D_{A-B}}{\delta} \]  \hspace{1cm} (5.5)

is in close agreement with the theoretically predicted value given by equation (5.5). In the above equation \( D_{A-B} \) is the diffusivity of reactant gaseous species and \( \delta \) is the gas phase boundary layer thickness. Binary diffusivity values (i.e. diffusion coefficients for the binary system) were determined using the Fuller, Schettler and Giddings relation \[88\] and for the calculation of ternary diffusion coefficients the procedure prescribed by Bird, Stewart and Lightfoot \[89\] was followed.

Experiments performed using both alumina and magnesia crucibles revealed that when the value of gas phase boundary layer, \( \delta \) (cm), decreased an increase in the \( k_s \) value (according to equation 5.5) caused a corresponding increase in the rate. To highlight this trend a plot of rate versus \( \delta \) is shown in Figure 5.3. Results obtained using alumina and magnesia crucibles are plotted separately because the extent of crucible dissolution is different in each case.

5.1.1.4 Effect of gas flow rate:

In the experiments #116, #115 and #113, the Ar-CO mixtures were proportioned to yield a \( P_{CO} \) of 0.18 atm and the overall flow rates were maintained at 10.6, 26.0 and 36.5 cc/sec respectively. Apart from this difference in the gas flow rates all the other experimental parameters—melt weight, crucible material and height, duration of heating, melting and reduction periods etc. were same for these runs. Analysis of the data revealed a rate value of \( 6 \pm 0.5 \times 10^{-6} \) g-oxygen/cm\(^2\)s for all the three runs. (Table 5.2) Additionally, the weight-time curves for three experiments are shown in Figure 5.4 and from the similarity in their slopes it is evident that within the scatter of the experimental data the reduction rates for these runs are equal.
Figure 5.3 Relation between reduction rate and gas phase boundary layer, $\delta$. 
Fe₂O₃-Al₂O₃ melts at 1400 °C

<table>
<thead>
<tr>
<th>Expt</th>
<th>Flow rate (cc/sec)</th>
<th>Slope (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#113</td>
<td>36.5</td>
<td>6.3 x 10⁻²</td>
</tr>
<tr>
<td>#115</td>
<td>26.0</td>
<td>6.0 x 10⁻²</td>
</tr>
<tr>
<td>#116</td>
<td>10.6</td>
<td>6.1 x 10⁻²</td>
</tr>
</tbody>
</table>

Ar-CO mixture; Pco = 0.18 atm

Figure 5.4 Weight loss-time relationships for the experiments designed to study the effect of flow rate.
5.1.1.5 Effect of excess oxygen:

The data in Tables 5.1 and 5.2 shows that in all the melts the oxygen level prior to the reduction period was kept below 24 wt% using controlled Ar-CO-CO$_2$ mixtures to avoid the formation of solid phases: wüstite and magnetite. The weight gain data generated during a few preliminary experiments revealed that in absence of precise $P_{O_2}$ control during the heating and melting periods ferrous oxide oxidation is unavoidable. It was felt that under such circumstance the resultant weight gain might lead to higher reduction rate (during the subsequent reaction period). To test this hypothesis and, in general, to better understand the role played by excess oxygen in the melt (i.e amounts exceeding 24 wt%), a special experiment was designed in which ferrous oxide was deliberately heated and melted in an argon atmosphere.

Nagasaka et al. [56] employed a purified argon atmosphere during the heating and melting periods. Moreover they report sample heating rates of ~5 °C/min. It was decided to simulate these conditions in experiment #12 and obtain the rate data for comparison. A 93 mg weight gain was seen during the heating and melting under these conditions. In a controlled Ar-CO-CO$_2$ atmosphere employed in a total of 11 experiments (Table 5.1) the weight gain was a maximum of 38 mg. A direct consequence of this excess melt oxygen was an increase in the initial reduction rate. Table 5.3 provides a few additional details concerning the experimental parameters and observed reduction rates for the experiments #1 and #12. Comparison of the rates for experiments #1 and #12 reveal about a 3-fold increase in the value of the latter due largely to the excess oxygen level of 24.95 wt.% in the melt. Because only one experiment was performed to study the effect of excess oxygen no firm conclusion is drawn on the role played by this parameter on the rate phenomenon.

However, an important point that emerges from the above data concerns the validity and reliability of the rate values for reaction (5.1) obtained under these conditions. If the melt oxygen level exceeds 24 wt% prior to the reaction then the resultant data does not yield true rate values for the reduction reaction represented by equation (5.1) due to the presence of either solid wüstite
Table 5.3  Rate comparison between two Fe₃O-Al₂O₃ melts with varying oxygen contents.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Gas-melt area</th>
<th>Heating period</th>
<th>Melting period</th>
<th>Gas mixture used during heating and melting periods</th>
<th>Melt oxygen at the end of melting period</th>
<th>Reduction rate during initial period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Duration</td>
<td>Wt. gain</td>
<td>Duration</td>
<td>Wt. gain</td>
<td>Wt%</td>
</tr>
<tr>
<td>#</td>
<td>cm²</td>
<td>Min</td>
<td>mg</td>
<td>Min</td>
<td>mg</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>2.42</td>
<td>175</td>
<td>64</td>
<td>60</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.68</td>
<td>35</td>
<td>5</td>
<td>60</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>

Gas mixture used during heating and melting periods: Ar-CO-CO₂
or magnetite in the melt. Additionally it is possible that a concurrent ferric-to-ferrous side reaction is taking place due to the higher ferric levels in the melt. Using controlled Ar-CO-CO$_2$ mixtures during the heating and melting periods therefore significantly enhances the reliability of the data.

5.1.2 Pseudo binary melts at 1400 °C:

After obtaining information on the Fe$_x$O system further experiments were performed in the Fe$_x$O-SiO$_2$ and Fe$_x$O-CaO systems to identify the contributions made by acidic and basic oxide species to the reaction rates. The results obtained at 1400 °C for these systems are presented below.

5.1.2.1 Fe$_x$O-SiO$_2$ melts:

Four melt compositions were studied to identify the effects of silica on the reduction rate: 5.4, 15.5, 24.6 and 29.3 mole% silica. An additional set of experiments was performed in which ferric oxide was added to give an initial ferric-to-total iron ratio of 0.18 in the resultant mixture with silica contents of 16.6, 25.9 and 31.8 mole%. In all of the tests the slag mixture weighed 3 grams and the melts were held in alumina crucibles.

5.1.2.1.1 Effect of silica:

Chemical analysis of the quenched slags revealed that the extent of crucible dissolution increased with the silica content of the melt and the weight loss data indicated lower rate values compared to the Fe$_x$O melts. In the melts with the lowest silica content (5.4 mole%) the alumina assayed 9.6 mole% whereas for the melts with the highest silica level (29.3 mole%) the alumina assayed 15.2 mole%. The weight-time curves for the low silica melts were similar to those obtained in the Fe$_x$O melts, i.e. the slope did not change appreciably with time. On the other hand, in the melts with the highest silica the form of the weight-time curve altered. The slope was highest in the beginning and as the reduction reaction proceeded the curve flattened off indicating the slowing down of reaction (5.1). To highlight these facts Figure 5.5 was prepared.
Figure 5.5 Effect of silica content on the weight-time relation in three Fe$_2$O-SiO$_2$-Al$_2$O$_3$ melts (a) 5.4 mole % silica (b) 15.5 mole % silica (c) and (d) 24.6 mole % silica.
The weight-time data obtained for the Fe$_x$O-SiO$_2$-Al$_2$O$_3$ melts is shown in Figure 5.5. The results suggest that the onset of change in the slope is governed primarily by the silica content of the melts. More important though is the fact that the curves in this figure clearly show that when the melts of different compositions are exposed to the same reducing gas mixture different rates are obtained. Comparison of curves (b) and (c) in Figure 5.5 reveal the above trend. The figure also shows that when two melts of same compositions (curves c and d) are exposed to a different gas mixtures the one exposed to a higher $P_{\text{CO}}$ yields the higher rate. These observations indicate that both melt and gas compositions govern the rates in the Fe$_x$O-SiO$_2$-Al$_2$O$_3$ system.

In all the silica-containing melts changes in the individual weight-time curves indicated variations in the rate values with time and to understand the nature of these changes it was necessary to compare the data obtained in all the experiments. It was felt that if the rate value is derived for an initial period ($t < 10$ minutes) then the influence of physicochemical factors as well as the reaction product would be minimal and the comparison amongst different runs would be valid. Moreover such a comparison for various Fe$_x$O-Al$_2$O$_3$, Fe$_x$O-MgO-Al$_2$O$_3$ and FeO-MgO runs was found to yield a useful and reliable information and therefore the same procedure was adopted for the Fe$_x$O-SiO$_2$-Al$_2$O$_3$ melts. Table 5.4 lists the rate data for all the Fe$_x$O-SiO$_2$-Al$_2$O$_3$ melts. The data reveals that as the silica proportion in the melt increases the reduction rate decreases.

To further explain the qualitative effect of silica the results are plotted in Figure 5.6 with the observed reduction rate on y-axis and the reaction driving force (equation 5.4) on x-axis. Three important features of this figure are: (1) Data points for all the Fe$_x$O-SiO$_2$-Al$_2$O$_3$ melts lie below the best fit line drawn through Fe$_x$O-Al$_2$O$_3$ melts; (2) The rate values for a particular melt composition lie on the straight line; and (3) all the five lines (one for Fe$_x$O-Al$_2$O$_3$ and four for Fe$_x$O-SiO$_2$-Al$_2$O$_3$) converge at the origin, indicating zero rate at zero driving force.

Yet another important point emerges from Figure 5.6. According to this figure, for a fixed reaction driving force different rates result from differences in the melt composition. In general, as the silica content is increased the reaction rate decreased. Such behaviour suggests that the
Table 5.4 Reduction rate data for Fe$_2$O-SiO$_2$-Al$_2$O$_3$ melts at 1400 °C. (Fe$^{3+}$/ΣFe ratio < 0.05)

<table>
<thead>
<tr>
<th>Expt</th>
<th>Final melt composition, mole %</th>
<th>Reduction gas mixture @ latm</th>
<th>Wt. change prior to reduction period, mg</th>
<th>$a_{FeO}$ std. state liq.</th>
<th>Reduction rate$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FeO</td>
<td>Fe$_2$O$_3$</td>
<td>SiO$_2$</td>
<td>Al$_2$O$_3$</td>
<td>$P_{CO}$</td>
</tr>
<tr>
<td>26</td>
<td>83.4</td>
<td>1.6</td>
<td>5.4</td>
<td>9.6</td>
<td>0.98</td>
</tr>
<tr>
<td>27</td>
<td>0.11</td>
<td>-</td>
<td>0.89</td>
<td>6</td>
<td>0.92</td>
</tr>
<tr>
<td>28</td>
<td>0.87</td>
<td>0.13</td>
<td>-</td>
<td>8</td>
<td>0.92</td>
</tr>
<tr>
<td>130</td>
<td>73.2</td>
<td>1.4</td>
<td>13.6</td>
<td>11.8</td>
<td>0.18</td>
</tr>
<tr>
<td>23</td>
<td>70.7</td>
<td>1.3</td>
<td>15.5</td>
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<tr>
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</tr>
<tr>
<td>25</td>
<td>0.98</td>
<td>0.02</td>
<td>-</td>
<td>11</td>
<td>0.70</td>
</tr>
<tr>
<td>20</td>
<td>60.1</td>
<td>1.5</td>
<td>24.6</td>
<td>13.8</td>
<td>0.98</td>
</tr>
<tr>
<td>22</td>
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<td>-</td>
<td>0.85</td>
<td>4</td>
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</tr>
<tr>
<td>18</td>
<td>0.95</td>
<td>0.05</td>
<td>-</td>
<td>8</td>
<td>0.55</td>
</tr>
<tr>
<td>21</td>
<td>0.11</td>
<td>-</td>
<td>0.89</td>
<td>9</td>
<td>0.55</td>
</tr>
<tr>
<td>29</td>
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<td>29.3</td>
<td>15.2</td>
<td>0.98</td>
</tr>
<tr>
<td>30</td>
<td>0.11</td>
<td>-</td>
<td>0.89</td>
<td>1</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Note: (1) $a_{FeO}$ values are derived using Kellogg’s model.
(2) Highest reduction rate data is obtained for the initial 10 minutes reduction period.
(3) The high weight gain for experiment #14 is due to argon usage during heating and melting periods. (In all other experiments Ar-CO-CO$_2$ mixture was employed during the heating and melting periods).
Figure 5.6 Plots of initial reduction rate versus gas phase driving force (as per equation 5.4) for several Fe$_2$O-SiO$_2$-Al$_2$O$_3$ melts at 1400 °C.
values of the rate constant (in equation 5.3) are dependent on the melt silica level and can be clearly identified by this experimental procedure. The dependence of the apparent rate constant, $k_a$, on the melt composition has been discussed in some detail by Nagasaka et al. [56] and Belton et al. [80] and its relationship with the overall rate constant in this study is pursued further in the next chapter.

The rate values obtained in this work in both $\text{Fe}_x\text{O-}\text{Al}_2\text{O}_3$ and $\text{Fe}_x\text{O-SiO}_2\text{-Al}_2\text{O}_3$ systems are much lower than those reported earlier by Nagasaka et al. [56] The two most important reasons for this difference are: (1) by jetting the reducing gas mixtures onto the melt surface Nagasaka et al. avoided restrictions imposed by the gas phase mass transport on the rate phenomenon however no such attempt was made in this study; and (2) type of crucibles used to contain the melts were different in two investigations. Further information on these critical issues is provided in the next chapter.

5.1.2.1.2 Effect of excess oxygen:

Experiment #14 was performed to assess the effect of excess oxygen on the reduction rate in silica-containing melts and for this purpose the procedure followed during the experiment #12 ($\text{Fe}_x\text{O-}\text{Al}_2\text{O}_3$ melt) was repeated. As a result of argon usage prior to the reaction period a weight gain of about 89 mg was recorded, which is roughly 7 times more than the equivalent gain in weight using the $\text{Ar-CO-CO}_2$ gas mixture, and a correspondent higher rate value of $2.5 \times 10^{-5}$ g-oxygen/cm²s was recorded during the subsequent reduction period. For comparison with the other melts of similar composition (experiments #18, #20, #21 and #22) this data point is shown in Figure 5.6. The location of the point clearly indicates an enhancement in the rate.

For further confirmation of the above effect three additional experiments were performed in which the reaction gas mixture was deliberately altered in the middle of the reaction period to promote an oxidation reaction for a short while. The reduction reaction was then resumed using the same gas mixture as before. In these experiments oxidation reactions were controlled using different $P_{\text{CO}}/P_{\text{CO}_2}$ ratios. In the experiment #28 (melt silica ~5.4 mole%) the $P_{\text{CO}}/P_{\text{CO}_2}$ ratio of 1.7 was maintained to promote a reoxidation of reduced metallic iron to liquid ferrous oxide; and
the reaction was allowed to continue until the weight gain value (92 mg) exceeded that of weight loss (75 mg) prior to the oxidation period. In the experiment #29 (silica ~29.3 mole%) however, the reoxidation was allowed so that the weight gain (39 mg) during the oxidation nearly equalled the weight loss (36 mg). On the other hand in the experiment #30, an Ar-CO$_2$ mixture was employed during the oxidation period to promote magnetite formation according to reactions

$$Fe_{(g)} + CO_{2(g)} = FeO_{(slag)} + CO_{(g)} \quad (5.6)$$

$$3FeO_{(slag)} + CO_{2(g)} = Fe_3O_4(s) + CO_{(g)} \quad (5.7)$$

Comparison of the weight loss data between the two reduction periods- one prior to and the other after the oxidation period, revealed that the rates were higher for the latter reduction period and the difference in rates increased with the increase in the level of melt oxygen. Table 5.5 is prepared to highlight this fact.

Fine et al. [64] have reported findings similar to those described above. The authors did not attempt oxidation of the melt surface similar to the procedure described above but instead interrupted the reduction reaction by an introduction of argon into the reaction chamber. They observed enhancement in the rate after resumption of the reduction reaction in their "stop and go" experiments. Based on this finding Fine et al. concluded that the higher rates were caused by the reoxidation of iron species. Our observations are consistent with their reported findings. It is interesting to note that though Fine et al. used the jetting procedure yet found the same effect.

5.1.2.2 Fe$_2$O-CaO melts:

A total of 7 experiments were conducted in the Fe$_2$O-CaO system at 1400 °C using alumina crucibles. Experiments #10, #11 and #93A were designed to study the effect of replacement of silica by lime on a weight-to-weight basis in melts containing a very small proportion of ferric oxide (Fe$^{3+}$/$\Sigma$Fe ratio < 0.05); whereas experiment #13 aimed to identify the effect of excess melt oxygen. In the experiments #87, #88 and #89 the lime content was progressively increased to characterize its effects on the reduction reaction rate at a Fe$^{3+}$/\Sigma$Fe ratio of approximately 0.2.
Table 5.5 Rate comparison for the reduction-oxidation-reduction runs.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Melt silica</th>
<th>Reduction gas mixture @ 1 atm</th>
<th>$P_{co}/P_{co_2}$ ratios</th>
<th>Weight gain</th>
<th>$a_{r,o}$</th>
<th>Reduction rate, g-oxy/cm².sec</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$P_{co}$</td>
<td>$P_{co_2}$</td>
<td>$P_{Ar}$</td>
<td>Equilibrium values</td>
</tr>
<tr>
<td>#</td>
<td>mole%</td>
<td>atm</td>
<td>atm</td>
<td>atm</td>
<td>atm</td>
<td>mg</td>
</tr>
<tr>
<td>28</td>
<td>5.4</td>
<td>0.87</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
<td>4.2</td>
</tr>
<tr>
<td>29</td>
<td>29.3</td>
<td>0.98</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>11.0</td>
</tr>
<tr>
<td>30</td>
<td>29.3</td>
<td>0.11</td>
<td>0.89</td>
<td>-</td>
<td>-</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Note:  
(1) During the oxidation period of #28 Fe₆₀ → FeOₓ₁₀ reaction is promoted and the weight gain exceeds the loss during previous reduction.  
(2) In the experiment #29, the weight gain during oxidation was nearly same as the loss during previous reduction.  
(3) Magnetite formation is promoted during the oxidation period of experiment #30 and the weight gain exceeds the loss during previous reduction.
Results of chemical analysis revealed that crucible dissolution in the lime-containing melts was much higher compared to the silica-containing melts. The alumina assay averaged about 23 ± 4 mole% in the Fe₂O-CaO-Al₂O₃ melts; whereas in the case of the Fe₂O-SiO₂-Al₂O₃ melts the equivalent value was about 13 mole%. The weight loss data indicated that despite the higher levels of alumina contamination the reduction rates for the Fe₂O-CaO-Al₂O₃ melts (Fe³⁺/ΣFe ratio < 0.05) are higher than the Fe₂O-SiO₂-Al₂O₃ melts (Fe³⁺/ΣFe ratio < 0.05) but lower than the Fe₂O-Al₂O₃ melts. This is shown in Figure 5.7. The rate data for all the 7 experiments is listed in Table 5.6 together with the relevant details concerning experimental parameters. For comparison equivalent data for the Fe₂O-SiO₂-Al₂O₃ melts is also included in this table.

The rate data for the melts containing relatively higher level of ferric oxide (Fe³⁺/ΣFe ratio > 0.05) reveals that a progressive increase in the melt lime content from 16.3 to 28.2 mole% leads only to a moderate reduction in the rates. It can be argued that within the scatter of the experimental data the above trend is hardly discernible. However further scrutiny of the data reveals that a possible cause for this trend could be traced back to the alumina dissolution in the melts. It is particularly interesting to compare the results of increasing lime content with the equivalent data in Fe₂O-SiO₂-Al₂O₃ melts. Such a comparison reveals a distinct reduction in the rate values in the latter due to increasing silica levels. This is a very important observation and its full significance is understood only after a critical examination of the rate data using a mathematical modelling analysis.

Moreover, when compared to the work of Nagasaka et al. [56] the observed rates are lower by about a factor of 5 for reaction driving force values below 0.1 atm. Reasons for such discrepancy in the data are the same as those mentioned for the Fe₂O-SiO₂-Al₂O₃ melts.

The effect of excess oxygen in the Fe₂O-CaO-Al₂O₃ melt was similar to the one observed in the Fe₂O-Al₂O₃ and Fe₂O-SiO₂-Al₂O₃ melts, namely a higher rate with higher oxygen levels.
Figure 5.7 Rate versus gas phase driving force plots for pseudo-binary melts- Fe₂O-SiO₂ and Fe₂O-CaO, held in alumina crucibles at 1400 °C.
Table 5.6 Reduction rate data for Fe₂O₃-CaO-Al₂O₃ melts at 1400 °C.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Final melt composition, mole %</th>
<th>Reduction gas mixture @ 1 atm</th>
<th>$a_{FeO}$</th>
<th>$\frac{Fe^3}{\Sigma Fe}$</th>
<th>Reduction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FeO</td>
<td>Fe₂O₃</td>
<td>CaO</td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>10</td>
<td>49.9</td>
<td>0.9</td>
<td>21.8</td>
<td>-</td>
<td>27.4</td>
</tr>
<tr>
<td>11</td>
<td>49.6</td>
<td>1.2</td>
<td>21.8</td>
<td>-</td>
<td>27.4</td>
</tr>
<tr>
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<td>49.6</td>
<td>1.2</td>
<td>21.8</td>
<td>-</td>
<td>27.4</td>
</tr>
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<td>21</td>
<td>60.1</td>
<td>1.5</td>
<td>-</td>
<td>24.6</td>
<td>13.8</td>
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<td>87</td>
<td>57.8</td>
<td>6.8</td>
<td>16.3</td>
<td>-</td>
<td>19.1</td>
</tr>
<tr>
<td>88</td>
<td>47.1</td>
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<td>23.9</td>
<td>-</td>
<td>23.5</td>
</tr>
<tr>
<td>89</td>
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<td>5.5</td>
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<td>-</td>
<td>26.8</td>
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<td>90</td>
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<td>7.1</td>
<td>-</td>
<td>16.6</td>
<td>12.5</td>
</tr>
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<td>49.1</td>
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<td>20.4</td>
<td>-</td>
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<tr>
<td>14</td>
<td>58.9</td>
<td>2.4</td>
<td>-</td>
<td>24.7</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Note: 
(1) Effects of silica surface coverage and $a_{FeO}$ terms on the rates are revealed by comparing data for #11 and #21. 
(2) Comparison of rates for #10 and #11 indicates the role of gas phase control. 
(3) Rate data for three experiments #90, #91 and #92, shows that as the silica content of the melt goes up the rate decreases in a dramatic fashion however, a similar comparison for #87, #88 and #89 reveals that with the increase in the melt lime content the corresponding rate decrease is only moderate. 
(4) Rate comparison between #13 and #10 reveals the effect of higher ferric level or the excess melt oxygen.
5.1.3 Pseudo ternary melts between 1200 °C and 1400 °C:

5.1.3.1 Effect of melt and gas composition:

The experimental data revealed that for ternary Fe,O-CaO-SiO₂ melts held in alumina crucibles at 1400 °C, as in previous cases, the initial rate is controlled by both gas and liquid compositions. To highlight these facts the experimental rate data is listed in Table 5.7 and the plot of initial rate versus reaction driving force is presented in Figure 5.8 (a). Comparison with the previous work by Nagasaka et al. reveals, as in previous cases, that the measured rates are much lower due primarily to the contributions from gas phase resistance and the surface blockage effects by the non-reactant species of the melts.

5.1.3.2 Effect of ferric oxide:

The rate data showed that in the presence of ferric oxide the oxygen removal rates were higher. Illustration of this is shown Figure 5.8(b). The location of line A representing melts with higher ferric-to-total ratio (approximately 0.19) clearly demonstrates the rate enhancement phenomenon. The same figure shows that a point corresponding to the melt with a ferric-to-total iron ratio of about 0.14 (Expt. #40) lies closer to the line A (and above the line representing melts with lowest Fe³⁺/ΣFe ratio). Nagasaka et al. [56] also report similar observations concerning the rate enhancement effect of ferric oxide.

5.1.3.3 Effect of excess melt oxygen:

Experiment #15 was designed to assess the effect of excess oxygen. To induce higher oxygen levels the melt the procedure followed was similar to the one employed during experiments #12, #13, and #14. Higher rate value was obtained under these conditions (Table 5.7). The experimental data point is shown in Figure 5.8(a) and its location clearly shows this rate enhancement effect.
Table 5.7 Reduction rate data for Fe₂O₃-SiO₂-CaO-Al₂O₃ melts between 1200 and 1400 °C.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Final melt composition, mole %</th>
<th>Reduction gas mixture @ 1 atm</th>
<th>a_{Fe₂O₃}</th>
<th>Fe^{3+}</th>
<th>Reduction rate</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FeO</td>
<td>Fe₂O₃</td>
<td>CaO</td>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>P_{CO}</td>
</tr>
<tr>
<td>31</td>
<td>40.3</td>
<td>1.0</td>
<td>14.9</td>
<td>27.6</td>
<td>16.2</td>
<td>0.95</td>
</tr>
<tr>
<td>32</td>
<td>1.8</td>
<td></td>
<td>0.82</td>
<td>0.60</td>
<td>0.05</td>
<td>0.7 x 10⁻⁶</td>
</tr>
<tr>
<td>33</td>
<td>31.7</td>
<td>0.8</td>
<td>19.1</td>
<td>31.0</td>
<td>17.4</td>
<td>0.95</td>
</tr>
<tr>
<td>34</td>
<td>0.18</td>
<td></td>
<td>0.82</td>
<td>0.41</td>
<td>0.05</td>
<td>0.4 x 10⁻⁶</td>
</tr>
<tr>
<td>35</td>
<td>35.9</td>
<td>0.9</td>
<td>19.3</td>
<td>27.1</td>
<td>16.8</td>
<td>0.95</td>
</tr>
<tr>
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<td>0.18</td>
<td></td>
<td>0.82</td>
<td>0.57</td>
<td>0.05</td>
<td>0.4 x 10⁻⁶</td>
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<tr>
<td>37</td>
<td>0.18</td>
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<td>0.82</td>
<td>0.57</td>
<td>0.05</td>
<td>0.6 x 10⁻⁶</td>
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<td>0.7 x 10⁻⁶</td>
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<td>32.9</td>
<td>15.6</td>
<td>0.95</td>
</tr>
<tr>
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<td>2.4</td>
<td>19.5</td>
<td>32.0</td>
<td>17.0</td>
<td>0.18</td>
</tr>
<tr>
<td>76</td>
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<td>7.9</td>
<td>0.18</td>
</tr>
<tr>
<td>51</td>
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<td>0.8</td>
<td>21.5</td>
<td>30.1</td>
<td>7.4</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Figure 5.8 Plots of initial reduction rate versus gas phase driving force for pseudo-ternary melts held in alumina crucibles at 1400 °C (a) shows location of pseudo-ternary melts relative to pseudo-binary melts and (b) illustrates the effect of melt ferric content.
5.1.3.4 Effect of temperature:

Though most of the data was obtained at 1400 °C using the alumina crucibles, two additional experiments were performed— one at 1200 °C and the other at 1300 °C, to study the effect of temperature on the rate phenomena. Melt composition and rate data for experiments #51 (1200 °C) and #76 (1300 °C) is provided in Table 5.7 and the results show that the rates are similar.

It is interesting to examine the results of experiments #51 and #76 by comparing them with the melts of similar starting compositions but reduced at 1400 °C. Accordingly, these experiments (#51 and #76) are compared with the experiments #37 and #32 respectively. In all four runs, a melt weighing 3 grams was exposed to an Ar-CO mixture ($P_{CO} = 0.18$ atm.) during the reduction period. Comparison between #51 and #37 reveals that in spite of the lower reaction temperature of the former melt the rate value obtained is moderately higher than the latter. This is attributed to the lower alumina dissolution at 1200 °C and the resultant higher value of $a_{FeO}$. Also at the lower reaction temperature the value of equilibrium constant for reaction (5.1), $K_{eq}^{(5.1)}$, is higher and this would result in a higher reaction driving force value according to equation (5.4). From the comparison of the rate data between the experiments #76 (1300 °C) and #32 (1400 °C) a similar trend is observed namely, a moderately higher rate at lower temperature.

5.2 Ferric-to-ferrous reduction study between 1200 °C and 1400 °C:

$Fe^{3+} \rightarrow Fe^{2+}$ reduction was studied using Ar-CO-CO$_2$ mixtures. This reaction is represented as:

$$Fe_2O_3(slag)_{(q)} + CO_{(g)} = 2FeO(slag)_{(q)} + CO_2(g)$$  \hspace{1cm} (5.8)

To ensure the forward progress of the above reaction however, it was of paramount importance to choose the appropriate $P_{CO_2}/P_{CO}$ ratios and avoid either the reduction or the oxidation of the ferrous oxide species. Thermodynamic calculations were performed prior to each run and the range of $P_{CO_2}/P_{CO}$ was determined where $a_{Fe}$ and $a_{FeO_{2}}$ would be less than 1. Both lime-containing and lime-free melts were used in the alumina crucibles and the reduction runs were performed at 1200 °C, 1300 °C and 1400 °C.
5.2.1 Pseudo binary Fe₂O-SiO₂ melts:

The results indicated that the rate was highest during the initial period and it decreased progressively with the passage of time. Table 5.8 lists the measured initial rate values for all the melts studied. Comparison of ferric-to-ferrous rates with the earlier ferrous-to-iron reduction data (Table 5.4) reveals that the former values are lower by a factor of 10 or more for the equivalent melt silica contents. Figure 5.9(a) shows the rate versus reaction driving force relationship for the melts at 1400 °C. The reaction driving force expression for the ferric-to-ferrous reaction is:

\[
f = P_{CO}^{b} - \frac{P_{CO_{2}}^{b}a_{FeO}^{2}}{a_{Fe_{2}O_{3}}K_{Fe_{2}O_{3}}^{s}} \text{ (atm)}
\]

(5.9)

where \(K_{Fe_{2}O_{3}}^{s}\) is the equilibrium constant of reaction (5.8). Details on the derivation of the above equation are provided in Chapter 6.

The main feature of the plots in Figures 5.9(a), 5.9(b) and 5.9(c) is that they all show an increase in the rate with an increase in the reaction driving force. This trend can also be seen in Figures 5.6 - 5.8. Comparison of plots in Figures 5.8(b) and 5.9(b) reveals higher rates at higher ferric levels for both iron formation and \(Fe^{3+} \rightarrow Fe^{2+}\) reactions.

To study the effect of temperature four additional experiments were performed at lower temperatures- two each at 1200 and 1300 °C. From the observed rate values listed in Table 5.8 and the plot of initial rate versus reaction driving force in Figure 5.9(c) the trend of decreasing reduction rate with decreasing reaction temperature is evident. Yet another observation concerns the weight-time curves. In all the runs these curves revealed reduction in the slope with time and such behavior implied the importance of an additional liquid phase resistance after the initial period. Further details on the time dependence of the rate are discussed in Chapter 6.
Table 5.8 Ferric-to-ferrous reaction study in Fe₂O₃-SiO₂-Al₂O₃ melts between 1200 and 1400 °C.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Final melt composition, mole %</th>
<th>Reduction gas mixture @ 1 atm</th>
<th>$a_{FeO}$</th>
<th>$a_{Fe₂O₃}$</th>
<th>$F_e^{3+}/\Sigma F_e$</th>
<th>Reduction rate</th>
<th>Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>FeO</td>
<td>Fe₂O₃</td>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>$P_{CO}$</td>
<td>$P_{CO₂}$</td>
<td>$P_{Ar}$</td>
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<td>78.7</td>
<td>7.0</td>
<td>6.5</td>
<td>7.8</td>
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<td>0.027</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>0.031</td>
<td>0.027</td>
<td>0.942</td>
</tr>
<tr>
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<td>6.0</td>
<td>16.6</td>
<td>10.0</td>
<td>0.022</td>
<td>0.025</td>
<td>0.943</td>
</tr>
<tr>
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<td>0.041</td>
<td>0.942</td>
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<td>0.014</td>
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<tr>
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<td>0.014</td>
<td>0.038</td>
<td>0.945</td>
</tr>
<tr>
<td>82</td>
<td>51.3</td>
<td>4.6</td>
<td>31.3</td>
<td>12.8</td>
<td>0.008</td>
<td>0.042</td>
<td>0.950</td>
</tr>
<tr>
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<td></td>
<td>0.053</td>
<td>0.014</td>
<td>0.15</td>
</tr>
<tr>
<td>84</td>
<td>55.6</td>
<td>7.2</td>
<td>26.8</td>
<td>10.4</td>
<td>0.010</td>
<td>0.045</td>
<td>0.945</td>
</tr>
<tr>
<td>100</td>
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<td></td>
<td></td>
<td>0.046</td>
<td>0.024</td>
<td>0.21</td>
</tr>
<tr>
<td>99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.006</td>
<td>0.043</td>
<td>0.951</td>
</tr>
<tr>
<td>137</td>
<td>57.2</td>
<td>8.8</td>
<td>29.1</td>
<td>4.9</td>
<td>0.019</td>
<td>0.128</td>
<td>0.853</td>
</tr>
<tr>
<td>138</td>
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<td></td>
<td></td>
<td></td>
<td>0.019</td>
<td>0.128</td>
<td>0.853</td>
</tr>
<tr>
<td>141</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.018</td>
<td>0.037</td>
<td>0.951</td>
</tr>
<tr>
<td>142</td>
<td>58.5</td>
<td>9.0</td>
<td>29.5</td>
<td>3.0</td>
<td>0.018</td>
<td>0.037</td>
<td>0.945</td>
</tr>
</tbody>
</table>

Note: Activities of ferrous and ferric oxides are derived using Kellogg's model assuming liquid standard states for both the species.
Figure 5.9 Plots of initial rate versus gas phase driving force (equation 5.9) for ferric-to-ferrous reaction in Fe₂O₃-SiO₂-Al₂O₃ melts (a) shows effect of silica at a constant Fe³⁺/ΣFe ratio; (b) shows effect of ferric level and (c) shows effects of temperature and Fe³⁺/ΣFe ratio.
5.2.2 Pseudo ternary Fe$_{x}$O-SiO$_2$-CaO melts:

The data obtained at three temperatures- 1400 °C, 1300 °C and 1200 °C is listed in Tables 5.9, 5.10 and 5.11 respectively and the plots of initial rate versus reaction driving force (equation 5.9) are shown in Figure 5.10. The observed rate values for 1400 °C runs suggest that the higher lime-to-silica ratio leads to higher rate values. Location of the melts with a higher molar ratio of 0.71 in Figure 5.10(a) supports this hypothesis. It is interesting to note that above trend was not repeated for lower temperature runs at 1200 and 1300 °C. (Figures 5.10b and 5.10c) These results indicate that at lower temperatures the role played by the melt lime-to-silica ratio is perhaps masked by the other important physicochemical properties such as surface tension, viscosity and density. Although the above conclusions are only tentative, as they are based on very limited data, the results do indicate a possible trend.

A few experiments were done to study the effect of ferric level on the rate phenomenon. The results revealed a trend of higher rate values with the higher melt ferric contents. The data obtained at 1200 °C is shown in Figure 5.10(c) and the increasing slopes of the lines with increasing Fe$^{3+}$/ΣFe ratios clearly presents a strong evidence of the expected behaviour. Also in Figure 5.10(b) the location of a point corresponding to a melt Fe$^{3+}$/ΣFe ratio of about 0.2 (expt. #139) supports the above finding.

5.3 Ferrous-to-ferric oxidation study at 1300 °C:

A few oxidation experiments were performed for comparison with the ferric-ferrous reduction data. The weight gain data revealed the highest oxidation rates in the initial period followed by a progressive drop with time. Such a trend suggests that once the ferric oxide species is formed (reverse of reaction 5.8) it preferentially occupies sites at the surface region and the behaviour leads to the lowering of the oxidation rate. An illustration of this is provided in Figure 5.11.
Table 5.9 Ferric-to-ferrous reaction study at 1400 °C in Fe₂O₃-SiO₂-CaO-Al₂O₃ melts. ($Fe^{3+}/ΣFe = 0.15$)

<table>
<thead>
<tr>
<th>Expt</th>
<th>Final melt composition, mole %</th>
<th>Reduction gas mixture @ 1 atm</th>
<th>$a_{FeO}$</th>
<th>$a_{Fe₂O₃}$</th>
<th>Reduction rate g·oxy/cm²·sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>FeO</td>
<td>Fe₂O₃</td>
<td>CaO</td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>41</td>
<td>29.3</td>
<td>2.6</td>
<td>20.0</td>
<td>32.6</td>
<td>15.5</td>
</tr>
<tr>
<td>42</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>46</td>
<td>37.1</td>
<td>3.3</td>
<td>15.5</td>
<td>29.0</td>
<td>15.1</td>
</tr>
<tr>
<td>47</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>33.1</td>
<td>2.9</td>
<td>20.3</td>
<td>28.4</td>
<td>15.3</td>
</tr>
<tr>
<td>48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Activities of ferrous and ferric oxides are calculated using Kellogg's model (assuming liquid standard state for both the species).
Table 5.10  Ferric-to-ferrous reaction study at 1300 °C in Fe₂O-SiO₂-CaO-Al₂O₃ melts.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Final melt composition, mole %</th>
<th>Reduction gas mixture @ 1 atm</th>
<th>a₉FeO</th>
<th>a₉Fe₂O₃</th>
<th>Fe³⁺/ΣFe</th>
<th>Reduction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td>40.3 3.6 16.6 31.4 8.1</td>
<td>0.030 0.022 0.948 0.51</td>
<td>0.012</td>
<td>0.15</td>
<td>3.8 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>0.018 0.031 0.951 0.51</td>
<td>0.012</td>
<td>0.15</td>
<td>2.1 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td></td>
<td>0.029 0.044 0.927 0.51</td>
<td>0.012</td>
<td>0.15</td>
<td>4.0 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>35.7 3.2 21.5 30.6 9.0</td>
<td>0.029 0.044 0.927 0.52</td>
<td>0.013</td>
<td>0.15</td>
<td>3.5 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td></td>
<td>0.029 0.044 0.927 0.52</td>
<td>0.013</td>
<td>0.15</td>
<td>3.2 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>139</td>
<td>34.3 4.3 22.3 31.1 8.0</td>
<td>0.033 0.099 0.868 0.48</td>
<td>0.020</td>
<td>0.20</td>
<td>5.1 x 10⁷</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.11  Ferric-to-ferrous reaction study at 1200 °C in Fe₂O₃-SiO₂-CaO-Al₂O₃ melts.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Final melt composition, mole %</th>
<th>Reduction gas mixture @ 1 atm</th>
<th>$a_{FeO}$</th>
<th>$a_{Fe₂O₃}$</th>
<th>$\frac{Fe^{3+}}{\Sigma Fe}$</th>
<th>Reduction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>FeO</td>
<td>Fe₂O₃</td>
<td>CaO</td>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>$P_{CO}$</td>
</tr>
<tr>
<td>52A</td>
<td>32.9</td>
<td>2.9</td>
<td>22.1</td>
<td>36.7</td>
<td>5.4</td>
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</tr>
<tr>
<td>63</td>
<td>0.042</td>
<td>0.063</td>
<td>0.895</td>
<td>0.42</td>
<td>0.013</td>
<td>0.15</td>
</tr>
<tr>
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<td>0.932</td>
<td>0.42</td>
<td>0.013</td>
<td>0.15</td>
</tr>
<tr>
<td>54</td>
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<td>0.940</td>
<td>0.42</td>
<td>0.013</td>
<td>0.15</td>
</tr>
<tr>
<td>108</td>
<td>0.017</td>
<td>0.036</td>
<td>0.947</td>
<td>0.42</td>
<td>0.013</td>
<td>0.15</td>
</tr>
<tr>
<td>55</td>
<td>0.029</td>
<td>0.044</td>
<td>0.927</td>
<td>0.53</td>
<td>0.011</td>
<td>0.15</td>
</tr>
<tr>
<td>106</td>
<td>0.026</td>
<td>0.039</td>
<td>0.927</td>
<td>0.53</td>
<td>0.011</td>
<td>0.15</td>
</tr>
<tr>
<td>56</td>
<td>0.030</td>
<td>0.022</td>
<td>0.948</td>
<td>0.53</td>
<td>0.011</td>
<td>0.15</td>
</tr>
<tr>
<td>57</td>
<td>0.029</td>
<td>0.043</td>
<td>0.928</td>
<td>0.49</td>
<td>0.013</td>
<td>0.15</td>
</tr>
<tr>
<td>58</td>
<td>0.030</td>
<td>0.022</td>
<td>0.948</td>
<td>0.49</td>
<td>0.013</td>
<td>0.15</td>
</tr>
<tr>
<td>107</td>
<td>0.029</td>
<td>0.036</td>
<td>0.942</td>
<td>0.46</td>
<td>0.021</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Figure 5.10  Rate versus driving force (equation 5.9) plots for ferric-to-ferrous reaction in Fe₃O₄-SiO₂-CaO-Al₂O₃ melts (a) 1400 °C runs; (b) 1300 °C runs; and (c) 1200 °C runs.
Figure 5.11  Weight gain curves for ferrous-to-ferric reaction at 1300 °C (a) melt $Fe^{2+}/\Sigma Fe$ ratio 0.05 (b)$Fe^{3+}/\Sigma Fe$ ratio 0.10.
The values of the highest oxidation rate at \( t \to 0 \) for the five runs are listed in Table 5.12. Some important experimental details are also provided in the same table. The limited data generated in this work is considered insufficient for carrying out a detailed mathematical analysis, however the available data suggests that a model similar to that for the ferric-ferrous reaction can adequately describe the overall oxidation reaction. The ferrous-to-ferric reaction

\[
2Fe_{0(\text{slag})} + CO_{2(g)} = Fe_{2O(\text{slag})} + CO_{(g)}
\]

is essentially the reverse of reaction (5.8) for which the following equation can be derived for the reaction driving force at \( t \to 0 \),

\[
f = P_{CO}^{b} \frac{a_{Fe}^{P_{CO}} P_{CO}^{b}}{K_{5.10}^{*} a_{Fe}^{P_{CO}}} \text{(atm)}
\]

where \( K_{5.10}^{*} \) is the equilibrium constant for the reaction (5.10). In Figure 5.12 the initial oxidation rates (Table 5.12) are plotted against the driving force values derived using equation (5.11). The relationship indicates that like ferric-to-ferrous reaction the ferrous-to-ferric reaction also is controlled by both gas and melt compositions. In addition, from the nature of the weight-versus-time curves in the Figure 5.11 it can be inferred that with the passage of time additional factors such as surface blockage, mass transport in the liquid phase and physicochemical properties of the melt such as surface tension, diffusivity and density become increasingly important in dictating the progress of the reaction.

5.4 Ferrous-to-magnetite oxidation study at 1400 °C:

The results of all the previous runs suggest that after an initial period the rates are influenced either by melt physicochemical properties or the diffusion of both product and reactant species in the melt. In the case of iron saturation runs in ferrous oxide melts the sinking metal may have induced melt movement and caused a moderate increase in the rates at higher \( P_{CO} \) values (Figure 5.1). On the other hand in silica-containing melts the above trend was reversed.
Table 5.12 Ferrous-to-ferric reaction study at 1300 °C in FeO-SiO$_2$-CaO-Al$_2$O$_3$ melts.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Melt composition, mole %</th>
<th>Reduction gas mixture @ 1 atm</th>
<th>$a_{FeO}$</th>
<th>$a_{FeO_2}$</th>
<th>$\frac{Fe^3+}{\Sigma Fe}$</th>
<th>Reduction rate g-oxy/cm$^2$.sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>74</td>
<td>35.1 0.9 20.7 34.6 8.7</td>
<td>0.017 0.035 0.948</td>
<td>0.54</td>
<td>0.001</td>
<td>0.05</td>
<td>$2.5 \times 10^{-7}$</td>
</tr>
<tr>
<td>75</td>
<td>44.1 1.2 16.2 30.6 7.9</td>
<td>0.014 0.044 0.942</td>
<td>0.62</td>
<td>0.001</td>
<td>0.05</td>
<td>$5.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>72</td>
<td>0.018 0.035 0.947</td>
<td>0.62</td>
<td>0.001</td>
<td>0.05</td>
<td>$3.8 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>39.0 1.1 20.7 29.7 9.5</td>
<td>0.018 0.035 0.947</td>
<td>0.64</td>
<td>0.001</td>
<td>0.05</td>
<td>$4.5 \times 10^{-7}$</td>
</tr>
<tr>
<td>71</td>
<td>42.3 2.4 16.2 31.1 8.0</td>
<td>0.013 0.025 0.964</td>
<td>0.57</td>
<td>0.005</td>
<td>0.10</td>
<td>$&lt; 1.0 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
Ferrous-to-ferric reaction study
Pseudo ternary melts at 1300 °C

<table>
<thead>
<tr>
<th>Ferric-to-total Fe ratio = 0.1</th>
<th>Ferric-to-total Fe ratio = 0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basicity = 0.7</td>
<td>Basicity = 0.6</td>
</tr>
<tr>
<td></td>
<td>Basicity = 0.53</td>
</tr>
</tbody>
</table>

Figure 5.12  Relation between initial oxidation rate and gas phase driving force (equation 5.11) for Fe₂O-SiO₂-CaO-Al₂O₃ melts at 1300 °C.
possibly due to the increased melt viscosity (Figure 5.5). To further understand the role played by the solid reaction products an additional set of experiments was done in which the magnetite was formed according to reaction (5.7).

5.4.1 Simple Fe_2O-Fe_2O_3 melts:

Results of ferrous oxidation to magnetite for two runs (#131 and #132) are illustrated in Figure 5.13. Both the curves reveal an initial linear portion representing the highest rate values followed by the progressive flattening of the curves indicating a slowing down of the oxidation reaction. It is believed that after about 10 minutes or so the surface of the melt is increasingly covered by magnetite and this leads to a reduction in the available area for the gas-melt reaction. Microscopic as well as a visual examination of the melt surfaces after quenching support the above hypothesis.

5.4.2 Complex Fe_2O-SiO_2-CaO-Fe_2O_3 melts:

Figure 5.14 illustrates the results obtained in experiments #44 and #45. The form of weight-time curves for these two experiments is essentially similar to the ones shown in Figure 5.13 for the ferrous oxide melts in alumina crucibles. Hence we can draw similar conclusions, i.e. the highest weight gain is observed during the initial period when the melt coverage by magnetite is minimal; however with the passage of time the weight gain values are progressively lowered due to the increasing magnetite coverage of the melt.

It is interesting to note that the weight-time curves for both simple and complex melts have a few common features: (1) for a particular melt composition the initial slope of the curve varies with the gas composition; (2) at a higher P_{CO}/P_{CO} ratio the slope is steeper and vice versa; (3) when the P_{CO_2}/P_{CO} is low the higher initial rate is maintained for a relatively longer duration. All these features suggest that once the magnetite is formed at the gas-melt interface it does not sink below the surface and such behavior demonstrates an important role played by the melt physicochemical properties in this type of system.
Figure 5.13  Weight gain curves for ferrous-to-magnetite reaction in Fe$_x$O-Al$_2$O$_3$ melts exposed to different Ar-CO$_2$ mixtures at 1400 °C (a) $P_{CO_2} = 0.12\text{atm}$ and (b) $P_{CO_2} = 0.72\text{atm}$.
Figure 5.14 Weight gain curves for ferrous-to-magnetite reaction in Fe₂O₃-SiO₂-CaO-Al₂O₃ melts at 1400 °C.
Chapter 6
Discussion

6.1 Ferrous-to-iron study:

6.1.1 Findings of present work

A detailed analysis of the weight-time behaviour has revealed two trends— one showing decreasing rate with time and the other showing an opposite pattern. A majority of the data conformed to the former category. However the fact that the rates did increase with time in few runs (Figure 5.1) indicated that melt movement induced by the sinking iron was a distinct possibility. A close examination of individual weight-time curves for various melts indicated that the onset of the change in slopes varied with both the melt and gas compositions. (Figure 5.5) On the contrary, it was observed that the slopes of weight-time plots for all the runs remained essentially unchanged during the initial reduction period of about 10 minutes (Figures 5.1 and 5.5). Therefore it was felt that a meaningful comparison amongst different runs would be more valid for the initial period (when the influence of physicochemical factors as well as the reaction product would be minimal) and based on this additional useful information concerning the chemical reaction was generated.

Rate data was obtained for the initial period for all the melts using equation (5.2) and comparison amongst individual melts highlighted a few important trends, namely— decreasing rates with increasing silica (Table 5.4), decreasing rates with decreasing $P_{CO}$ (Table 5.1), decreasing rates with increasing distance between the crucible top and the melt surface (Table 5.2 and Figure 5.3) and higher rates with higher melt oxygen contents (Tables 5.3 and 5.5). These observations implied that the rate of reduction reaction is governed by both gas and melt compositions. It is worth noting that these findings concerning the effects of silica and $P_{CO}$ on the reduction rates are consistent with those reported earlier by Nagasaka et al. [56].

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Yet another finding that was in agreement with the work of Nagasaka et al. concerned with the rate enhancement due to higher ferric levels in the melt. Examination of the Fe-O phase diagram (Figure 2.1) reveals that the level of oxygen in the melt also governs its constitution and at higher O/Fe ratios the formation of solid wüstite and magnetite is favored. The role of these factors on the ferrous oxide reduction is not clearly understood. Nagasaka et al. addressed this issue in their work and observed that the apparent rate constant, $k_a$, was exceedingly influenced by the melt $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. The authors noted that $k_a$ values decreased with silica and that lime had the opposite effect. Since the overall rates obtained in the present study were influenced by the gas phase mass transfer the results cannot be compared directly with the data reported by either Nagasaka et al. or Kim et al. [66]. However, with the help of mathematical analysis an attempt is made to link all the three sets of data and offer an explanation on the common observations concerning ferric oxide and silica effects on the rate phenomena. The mathematical scheme provided an independent means of calculating intrinsic rate data at different temperatures. It will be shown later that the intrinsic rate values obtained thus are in agreement with other studies.

6.1.2 Mathematical Analysis

Several other possibilities were examined before finalizing a mixed gas phase mass transfer and chemical reaction control model. However it was noted that the observed results could be satisfactorily explained in terms of the proposed model alone. Before discussing the mathematical formulation of a mixed control model a few important reasons for the failure of other models are outlined below.

6.1.2.1 Justification of the proposed model

It was expected that in any mathematical modelling scheme, gas phase mass transfer cannot be overlooked due to the choice of a stagnant system. However, the main advantage of such an arrangement is that the gas phase contribution can be easily characterized and thereby the roles played by other interfacial and liquid mass transfer effects, if any, could be identified. For this
reason, in the mathematical analysis a gas phase control model was used as a starting point. A rate expression was formulated on the assumptions of an instantaneous chemical reaction and no liquid phase mass transfer resistance. The predicted rate data was then compared to the measured values and it was noted the model was applicable only to the simple Fe$_x$O-Al$_2$O$_3$ melts. For all other 36 melts in the pseudo binary and ternary systems the model over-predicted the rates. To highlight these facts Figures 6.1 and 6.2 are prepared.

Figure 6.1(a) shows an agreement between the predicted and observed rate values for 11 runs in the Fe$_x$O-Al$_2$O$_3$ system however, a similar comparison for the melts in Fe$_x$O-SiO$_2$-Al$_2$O$_3$ system in Figure 6.1(b) reveals distinct differences between the two sets of data. Rate versus driving force plots in Figures 6.2(a) and 6.2(b) also show a clear disagreement between the model predicted and measured rate data for the melts in Fe$_x$O-CaO-Al$_2$O$_3$ and Fe$_x$O-CaO-SiO$_2$-Al$_2$O$_3$ systems respectively. In a few cases in the latter system the model overpredicted the rates by as high as 8 to 10 times and therefore the gas phase control model was abandoned. Yet another reason that supported this decision was the fact that in all four special experiments in which excess oxygen was present in the melt the resultant rates were greater than the equivalent data for melts exposed to the same reducing gas mixture but contained no excess oxygen.

The liquid phase control model was written next and again no agreement between the measured and predicted data could be reached. This model was discarded because the measured rate data showed clearly that for any given melt composition, rate values changed with a change in gas composition. (Tables 5.1, 5.4, 5.6 and 5.7)

An unsteady state liquid diffusion model was considered as a third possibility. In the model formulation, quasi-steady state was assumed in the gas phase together with unsteady state in the liquid. The diffusion of reactant species in the liquid was assumed to follow Ficks Second Law and the heterogeneous reaction was considered to be fast and not rate limiting. Essentially the situation was considered to be equivalent to the evaporation from a liquid surface for the derivation of the governing equations.
Figure 6.1 Comparison of model predicted and measured rate data for the melts at 1400 °C. Model predicted values are derived assuming only gas phase control. (a) Fe$_2$O-Al$_2$O$_3$ Melts; (b) Fe$_2$O-SiO$_2$-Al$_2$O$_3$ melts.
Figure 6.2 Comparison of model predicted and measured rate data for the melts at 1400 °C. Model predicted values are derived assuming only gas phase control. (a) Fe₃O-CaO-Al₂O₃ Melts; (b) Fe₅O-CaO-SiO₂-Al₂O₃ melts.
With these equations a relationship between the fraction reacted (ratio of moles of oxygen reacted at time \( t \) to the total moles available for reaction) and \( \sqrt{\left(D_{t/L}L^2\right)} \) was obtained. An illustration of this is shown in Figure 6.3. None of the data from the present work complied with the trends of the lines shown in this figure and therefore the model was abandoned.

Finally, a gas and liquid mass transfer model was tried. For predicting rates using this model an expression was developed in which all parameters except \( k_L \) (liquid phase mass transfer coefficient) were known. Therefore, by choosing appropriate values for \( k_L \) calculated rates could be matched with the measured data. The predicted values of \( k_L \) thus obtained could not be compared with any other data because of lack of such information in the literature. Therefore alternate methodology had to be explored to test the validity of the \( k_L \) data. It was thought that if the predicted values varied according to the melt composition in some expected manner then perhaps the model could be validated on this ground. For example, based on the viscosity and diffusivity data in the literature one expects an increase in \( k_L \) with the addition of basic oxides and an opposite trend after the addition of an acidic oxide like silica. Upon close examination of the fitted \( k_L \) for various melt systems the above trends were not evidenced. To highlight this behavior Table 6.1 is prepared.

Further scrutiny of the fitted \( k_L \) data was carried out before rejecting the gas + liquid model. Using the simple relationship,

\[
k_L = \frac{D_{O^2^-}}{\delta}
\]

the boundary layer thicknesses were calculated for various melts and an anomalous result was obtained. It was noted that for a few lime and silica-containing melts the predicted boundary layer values exceeded the actual melt height. Illustration of this is shown in Table 6.2. The oxygen diffusivity values for use in the equation (6.31) were obtained assuming diffusion analog of Walden’s rule [1,90] i.e. \( D_{O^2^-} \cdot \mu = \text{constant} \). The value of the constant was derived using Sutherland equation [91].
Figure 6.3 A plot of fraction reacted versus $\sqrt{D \cdot t/L_i^2}$ obtained using unsteady model. (from ref. 92) The hatched portion shows the approximate range of the measured data and $\lambda_i$ is the dimensionless parameter. $\Lambda = \frac{D_{tot} \cdot L_i \cdot K^*}{D_{tot} (a_2 - L_1)}$. 
Table 6.1  Values of fitted liquid phase mass transfer coefficients, $k_L$, obtained in the ferrous reduction study at 1400 °C using gas and liquid mass transfer control model.

<table>
<thead>
<tr>
<th>Melt type</th>
<th>Silica</th>
<th>Lime</th>
<th>Fitted $k_L$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fe_2O - Al_2O_3$</td>
<td>- mole%</td>
<td>- mole%</td>
<td>10.0 x 10^{-3}</td>
</tr>
<tr>
<td>$Fe_2O - MgO$</td>
<td>- mole%</td>
<td>- mole%</td>
<td>7.0 x 10^{-3}</td>
</tr>
<tr>
<td>$Fe_2O - MgO - Al_2O_3$</td>
<td>- mole%</td>
<td>- mole%</td>
<td>2.5 x 10^{-3}</td>
</tr>
<tr>
<td>$Fe_2O - CaO - Al_2O_3$</td>
<td>- mole%</td>
<td>- mole%</td>
<td>7.5 x 10^{-3}</td>
</tr>
<tr>
<td>$Fe_2O - SiO_2 - Al_2O_3$</td>
<td>~5 mole%</td>
<td>- mole%</td>
<td>5.0 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>~16 mole%</td>
<td>- mole%</td>
<td>2.5 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>~25 mole%</td>
<td>- mole%</td>
<td>1.3 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>~29 mole%</td>
<td>- mole%</td>
<td>1.0 x 10^{-3}</td>
</tr>
<tr>
<td>$Fe_2O - SiO_2 - CaO - Al_2O_3$</td>
<td>~28 mole%</td>
<td>~15 mole%</td>
<td>1.2 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>~31 mole%</td>
<td>~19 mole%</td>
<td>0.85 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>~27 mole%</td>
<td>~19 mole%</td>
<td>1.3 x 10^{-4}</td>
</tr>
</tbody>
</table>
Table 6.2  Predicted boundary layer thicknesses using gas and liquid mass transfer control model.

<table>
<thead>
<tr>
<th>Melt type</th>
<th>Expt</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Fitted kₖ</th>
<th>Predicted δ</th>
<th>Melt height</th>
<th>Available oxygen for the reduction</th>
<th>Oxygen in the predicted δ</th>
<th>Oxygen removed in the initial period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₆-Al₃O₃</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>10 x 10⁻⁵</td>
<td>4.2 x 10⁴</td>
<td>200</td>
<td>3645</td>
<td>818</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>2A</td>
<td>-</td>
<td>-</td>
<td>10 x 10⁻³</td>
<td>4.2 x 10⁴</td>
<td>200</td>
<td>2410</td>
<td>508</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>-</td>
<td>~5</td>
<td>5 x 10⁻⁴</td>
<td>3.5 x 10⁴</td>
<td>400</td>
<td>2910</td>
<td>540</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-</td>
<td>~14</td>
<td>2.5 x 10⁻⁵</td>
<td>3.0 x 10⁴</td>
<td>600</td>
<td>3290</td>
<td>461</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-</td>
<td>~25</td>
<td>1.5 x 10⁻⁴</td>
<td>2.5 x 10⁴</td>
<td>665</td>
<td>3075</td>
<td>406</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td>-</td>
<td>~29</td>
<td>1.0 x 10⁻⁵</td>
<td>2 x 10⁴</td>
<td>1000</td>
<td>2900</td>
<td>357</td>
<td>123</td>
</tr>
<tr>
<td>Fe₃O₆-CaO-Al₂O₃</td>
<td>10</td>
<td>~17</td>
<td>-</td>
<td>7.5 x 10⁻⁵</td>
<td>7 x 10⁴</td>
<td>933</td>
<td>3860</td>
<td>315</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>~15</td>
<td>~27</td>
<td>1.2 x 10⁻⁵</td>
<td>4 x 10⁴</td>
<td>3330</td>
<td>3235</td>
<td>274</td>
<td>274</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>~19</td>
<td>~31</td>
<td>0.9 x 10⁻⁵</td>
<td>4 x 10⁴</td>
<td>4440</td>
<td>3345</td>
<td>218</td>
<td>218</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>~19</td>
<td>~27</td>
<td>1.3 x 10⁻⁵</td>
<td>4 x 10⁴</td>
<td>3080</td>
<td>3280</td>
<td>245</td>
<td>230</td>
</tr>
</tbody>
</table>

Note:  Boundary layer thicknesses, δ, are predicted using equation (6.37).
In the above calculations equation (6.1) was used for estimating boundary layer thicknesses however the same equation can be employed for the determination of \( k_L \) values by fixing the boundary layer thicknesses. The information obtained thus can then be compared with the set of fitted \( k_L \) values derived independently from the gas + liquid model. The data listed in Table 6.3 shows a lack of agreement between the two sets of \( k_L \) values. The results implied that the predicted \( k_L \) values using the gas and liquid control model were inconsistent. On the contrary, using a mixed gas and interfacial reaction control model more meaningful data was generated and therefore this model was finally accepted.

### 6.1.2.2 Mixed control model formulation

The reduction of ferrous oxide in the slag melt was carried out using the carbon monoxide-containing gaseous mixtures. Schematic representation of this arrangement is illustrated in Figure 6.4 to show the directions of movement of reactant and product gaseous species relative to the melt surface and the gas and liquid phase resistances to the reduction reaction (5.1). The theoretical value of the gas phase mass transfer coefficient, \( k_g \), can be calculated for stagnant conditions using equation (5.5) i.e. \( D_{co} \cdot \delta / \delta \) where \( \delta \) represents the distance between crucible top and gas-melt surface. The present model formulation is restricted to the initial 10 minute period during which the role played by \( k_L \) is assumed to be of little consequence.

For the ferrous oxide reduction reaction (5.1) we can write the following flux equations:

\[
\dot{n}_{CO} = A_o \cdot k_g (C_{CO}^* - C_{CO}) \quad \text{mole/s} \quad (6.2)
\]

\[
\dot{n}_{CO_2} = A_o \cdot k_g (C_{CO_2}^* - C_{CO_2}^b) \quad \text{mole/s} \quad (6.3)
\]

where \( A_o \) is the gas-melt area in \( \text{cm}^2 \), \( k_g \) is gas phase mass transfer coefficient, in \( \text{cm/s} \) and concentrations of gaseous species are in \( \text{mole/cm}^3 \). The superscripts * and b refer to interfacial and bulk concentrations respectively.
Table 6.3 Comparison of $k_L$ values obtained from two independent sources.

<table>
<thead>
<tr>
<th>Melt</th>
<th>silica</th>
<th>$D_{O_{2}^{-}}$</th>
<th>$D_{O_{2}^{-}} \cdot \mu$</th>
<th>Expt.</th>
<th>$k_L^*$</th>
<th>$k_L$ values estimated using equation (6.1) at different $\delta$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mole%</td>
<td>cm$^2$/s x 10$^6$</td>
<td>N x 10$^{11}$ #</td>
<td>cm/s</td>
<td>$\delta = 110 \mu m$</td>
<td>$\delta = 500 \mu m$</td>
</tr>
<tr>
<td>Lime-free melts</td>
<td>~ 5</td>
<td>3.5</td>
<td>1.22 #26</td>
<td>5 x 10$^5$</td>
<td>18.2 x 10$^5$</td>
<td>4.0 x 10$^5$</td>
</tr>
<tr>
<td></td>
<td>~ 29</td>
<td>2</td>
<td>1.22 #29</td>
<td>5 x 10$^3$</td>
<td>9.1 x 10$^5$</td>
<td>2.0 x 10$^5$</td>
</tr>
<tr>
<td>Lime-containing melts</td>
<td>~27</td>
<td>4</td>
<td>1.02 #31</td>
<td>1.2 x 10$^5$</td>
<td>36.4 x 10$^5$</td>
<td>8.0 x 10$^5$</td>
</tr>
<tr>
<td>(~ 15 mole% lime)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>~ 29</td>
<td>4</td>
<td>1.02 #32</td>
<td>1.2 x 10$^5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lime-containing melts</td>
<td>~ 29</td>
<td>4</td>
<td>1.02 #35</td>
<td>1.3 x 10$^5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(~ 19 mole% lime)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note:  
1. Fitted $k_L^*$ values using gas and liquid mass transfer control model.  
2. Boundary layer, $\delta$, value of 110 $\mu m$ as per McCarron and Belton [94].  
3. Boundary layer, $\delta = 500 \mu m$ based on Mössbauer data in the present work.  
4. Boundary layer thickness value of 860 $\mu m$ as per M. E. Fraser and A. Mitchell [93].  
5. According to Sutherland equation $D_{O_{2}^{-}} \cdot \mu = \frac{k_L^* \cdot T}{4e \cdot \delta_{O_{2}^{-}}}$ [91].
Figure 6.4  Schematic representation of (a) movement of gaseous species relative to melt surface; (b) gas and liquid phase resistances to the reduction reaction.
The rate of the chemical reaction can be written as

\[ r = k_c \cdot A \cdot \left( a_{FeO} \cdot C_{CO}^* - \frac{C_{CO_2}^*}{K^*} \right) \tag{6.4} \]

where \( k_c \) is intrinsic rate constant of reduction reaction in cm/s, \( K^* \) is equilibrium constant of wüstite reduction reaction and \( A \) is the available reaction area in cm\(^2\). Equation (6.4) can be readily derived on the assumption of a reversible ferrous-to-iron reaction. Thus, individual rate expressions were written for the forward and backward reactions and the overall expression was obtained by subtraction of the latter from the former. Kim et al. [66] have followed a similar procedure for deriving the rate expression for the melts at 1600 °C. It is worth noting here that the reaction driving force term used by Nagasaka et al. [56] can also be obtained using the above principle.

The following assumptions are made in the model formulation:

1. steady state conditions prevail during the reduction reaction;
2. at the crucible top the composition of gaseous species (Ar, CO and CO\(_2\)) equals their bulk composition in the alumina reaction chamber;
3. diffusion of product and reactant gaseous species takes place under stagnant conditions;
4. \( D_{CO_{-gas}} = D_{CO_2_{-gas}} \)

At steady state

\[ r = \dot{n}_{CO} = \dot{n}_{CO_2} \tag{6.5} \]

By mathematical manipulation the two interfacial concentration terms can be eliminated to yield

\[ \frac{r}{A_o} = \frac{1}{A_o} \cdot \frac{A_1 + A_2}{k_{FeO} + k_{FeO}^*} \left( \frac{C_{CO}^b}{C_{CO_2}^b} - \frac{C_{CO_2}^b}{a_{FeO}K^*} \right) \tag{6.6} \]

moles \( cm^2.s \)

and the same can be expressed in the practical form as

\[ \frac{r}{A_o} = \frac{16/(R \cdot T)}{k_{FeO} + k_{FeO}^*} \left( \frac{p_{CO}^b}{p_{CO_2}^b} - \frac{p_{CO_2}^b}{a_{FeO}K^*} \right) \tag{6.7} \]

\( g \) \( cm^2.s \)
The term in the first bracket represents the overall rate constant in \( g/cm^2\cdot atm\cdot s \) and the second term is the reaction driving force in atm. The area ratio, \( A/A_0 \), represents the fractional coverage due to the reactant species. It will be shown later that this ratio varies from melt to melt and generally lower values are obtained when a non-reactant surface active species like silica is present.

Equation (6.7) can also be expressed as

\[
\frac{w_t}{A_0 t} = \left( \frac{1}{k_1 a_{FeO}} + \frac{1}{k_2 a_{FeO}} + \frac{1}{k_3 a_{FeO}} \right) \left( \frac{p_{CO}^b}{a_{FeO} K^*} - \frac{p_{CO_2}^b}{a_{FeO} K^*} \right) \frac{g}{cm^2 s}
\]

where \( w_t \) is oxygen loss (g) and \( t \) is reduction time (s).

In the right hand side of equations (6.7) and (6.8) all the terms except \( k_0 \) and \( A/A_0 \) are known and therefore once the fractional coverage data is obtained \( k_0 \) remains the only unknown. Fitting of the experimental data to the model will thus yield the value of \( k_0 \). This can then be compared to the results of other researchers. Therefore it is important to derive an expression for the \( A/A_0 \) term and understand its significance.

Since the term "A" represents the gas-melt area available for the reaction (5.1) and \( A_0 \) is the total melt area exposed to the gas their ratio corresponds to a dimensionless area parameter. In the simplest case of a pure ferrous oxide melt being held in an iron crucible the cross sectional area \( A_0 \) would equal the reaction area and therefore the \( A/A_0 \) ratio would have the highest value of 1. However when molten ferrous oxide reacts with the container material (e.g. alumina) the dissolved species is expected to block some reaction sites and effectively lower the reaction area by way of a dilution effect. Addition of an acidic oxide species like silica or phosphorus pentoxide to the melt may essentially have a similar effect however, due to the surface active nature of these species an additional contribution may result via an excess surface concentration effect. It is worth mentioning here that Kim et al. [66] have employed similar approach for the determination of the reaction area. The authors studied ferrous reduction reaction using the melts from the FeO-CaO-SiO2-MgO system and developed the fractional coverage expression for their melts.
Alternately it is also possible to view the melt surface coverage by oxygen anions, $O^{2-}$, [80,34,68] and the reduction reaction as

\[ CO + O^{2-} = CO_2^{2-} \]  \hspace{1cm} (6.9)

and

\[ Fe^{2+} + CO_2^{2-} = Fe + CO_2 \]  \hspace{1cm} (6.10)

In this sense the area term $A$ will account for the $O^{2-}$ coverage. When the surface is occupied by the $O^{2-}$ anions alone then the fractional coverage will be unity. Because acidic oxides are glass formers they promote complex anion formation and lock up $O^{2-}$ ions which otherwise would be available for the reaction (6.9). This is equivalent to saying that any oxygen atom attached to silicon atom/s is not a free $O^{2-}$ anion and this is consistent with the polymerization model proposed by C.R. Masson [129]. Addition of basic oxides to the melt may have no significant effect on the area term "A" and one expects that in the presence of ferric oxide the area would increase because ferric anions can release the oxygen for continuation of reaction (6.9).

A scheme was developed to quantify the fractional coverage parameter, $A/A_0$, in terms of two separate phenomena, namely - the dilution effect and the excess surface concentration effect. According to the proposed scheme, reaction (6.9) is dependent on the availability of both the free $O^{2-}$ anions (those associated with basic oxides) and the number of ferric anions that can provide $O^{2-}$ (i.e. $O^{2-}$ associated with any complex anion that can release oxygen). Therefore the available reaction sites or the $A/A_0$ term can be represented as

\[ \text{available reaction sites} = 1 - \text{net unavailable sites} \]  \hspace{1cm} (6.11)

where the net unavailable sites are those covered by anion species other than $O^{2-}$. Three complex anion species have been considered previously [95,96,97] - $FeO_3^{3-}$, $AlO_3^{3-}$ and $SiO_4^{4-}$. It is appreciated that in any polymeric melt the oxygen coordination of various cations is governed by various factors - such as proportions of basic and acidic oxides and ionic radii of cations. Therefore it is very difficult to assign a particular formula to the complex anions in such melts. In the presence of amphoteric oxides (ferric oxide and alumina) in the melts further complications arise in the identification of the coordination states of $Fe^{3+}$ and $Al^{3+}$. Although from the knowledge
of the coordination states these cations should be coordinated 6-fold the facts mentioned above suggest that the oxygen coordination of Fe$^{3+}$ and Al$^{3+}$ may vary from tetrahedral to octahedral in the complex melts. Such predictions have been confirmed, to a limited extent in the case of Fe$^{3+}$ cations, by the Mössbauer spectroscopy analysis of the quenched slags. [98,99] Researchers have noted that coordination of Al$^{3+}$ decreases from six to four with increasing basicity. [100] Under the circumstance the complex $\text{AlO}_4^{3-}$ anions are formed in these melts. In view of the above difficulties the selection of $\text{FeO}_3^{2-},\text{AlO}_3^{2-}$ as anion complexes is made for convenience only.

It is important to note that whether $\text{SiO}_4^{4-}$ is polymerized or not the calculation will give the approximate area coverage because it is based on SiO$_2$. Of the three anions, the latter two do not take part in the reaction (i.e. they do not release oxygen) whereas the ferric anions behave differently. These can release oxygen from their coordination and therefore their contribution results in the decrease in the net (or actual) unavailable sites. Table 6.4 is prepared to highlight this effect. The same table shows how the melt composition affects the fractional coverage term. The following assumptions were made in the derivation of various expressions listed in Table 6.4.

1. alumina is not surface active;
2. alumina and ferric oxide are present in some form of cation-anion complexes but these can be represented by $\text{AlO}_{1.5}$ and $\text{FeO}_{1.5}$ species respectively; (this choice can be justified on the basis that in both alumina and ferric oxides the ratio of cations to anions is 1:1.5.)
3. volume fraction of the individual species equals the mole fraction; and
4. in the ferrous oxide melts both silica and ferric oxide are surface active and the excess surface concentration of the latter is controlled to an extent by the melt silica content.
Table 6.4  Expressions for the available reaction sites.

<table>
<thead>
<tr>
<th>Melt type</th>
<th>Fractional sites covered by anions other than $O^{2-}$</th>
<th>Net or actual unavailable sites for reaction</th>
<th>available sites</th>
<th>= 1 - net unavailable sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure FeO</td>
<td>$\text{FeO}_3^{2-}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{AlO}_3^{2-}$</td>
<td></td>
<td>$N_{\text{FeO}<em>{1.5}} - N</em>{\text{FeO}<em>{1.5}} - N</em>{\text{FeO}_{1.5}}$</td>
<td>$1 - N_{\text{AlO}<em>{1.5}} + N</em>{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}$</td>
<td>$N_{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
<td></td>
<td>$1$</td>
<td></td>
</tr>
<tr>
<td>$\text{Fe}<em>2\text{O} - \text{AlO}</em>{1.5}$</td>
<td>$N_{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
<td>$N_{\text{AlO}_{1.5}}$</td>
<td>$N_{\text{AlO}<em>{1.5}} - N</em>{\text{FeO}<em>{1.5}} - N</em>{\text{FeO}_{1.5}}$</td>
<td>$1 - N_{\text{AlO}<em>{1.5}} + N</em>{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
</tr>
<tr>
<td>$\text{Fe}<em>2\text{O} - \text{MgO} - \text{AlO}</em>{1.5}$</td>
<td>$N_{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
<td>$N_{\text{AlO}_{1.5}}$</td>
<td>$N_{\text{AlO}<em>{1.5}} - N</em>{\text{FeO}<em>{1.5}} - N</em>{\text{FeO}_{1.5}}$</td>
<td>$1 - N_{\text{AlO}<em>{1.5}} + N</em>{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O} - \text{MgO}$</td>
<td>$N_{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
<td>$N_{\text{AlO}_{1.5}}$</td>
<td>$N_{\text{AlO}<em>{1.5}} - N</em>{\text{FeO}<em>{1.5}} - N</em>{\text{FeO}_{1.5}}$</td>
<td>$1 - N_{\text{AlO}<em>{1.5}} + N</em>{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
</tr>
<tr>
<td>$\text{Fe}<em>2\text{O} - \text{CaO} - \text{AlO}</em>{1.5}$</td>
<td>$N_{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
<td>$N_{\text{AlO}_{1.5}}$</td>
<td>$N_{\text{AlO}<em>{1.5}} - N</em>{\text{FeO}<em>{1.5}} - N</em>{\text{FeO}_{1.5}}$</td>
<td>$1 - N_{\text{AlO}<em>{1.5}} + N</em>{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O} - \text{SiO}<em>2 - \text{AlO}</em>{1.5}$</td>
<td>$N_{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
<td>$N_{\text{AlO}<em>{1.5}} + N</em>{\text{SiO}<em>2} + N</em>{\text{SO}_2}$</td>
<td>$-N_{\text{FeO}<em>{1.5}} - N</em>{\text{FeO}_{1.5}}$</td>
<td>$1 - N_{\text{AlO}<em>{1.5}} - N</em>{\text{SiO}<em>2} - N</em>{\text{SO}<em>2} + N</em>{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O} - \text{SiO}<em>2 - \text{CaO} - \text{AlO}</em>{1.5}$</td>
<td>$N_{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
<td>$N_{\text{AlO}<em>{1.5}} + N</em>{\text{SiO}<em>2} + N</em>{\text{SO}_2}$</td>
<td>$-N_{\text{FeO}<em>{1.5}} - N</em>{\text{FeO}_{1.5}}$</td>
<td>$1 - N_{\text{AlO}<em>{1.5}} - N</em>{\text{SiO}<em>2} - N</em>{\text{SO}<em>2} + N</em>{\text{FeO}<em>{1.5}} + N</em>{\text{FeO}_{1.5}}$</td>
</tr>
</tbody>
</table>

Note:  
(1) Decrease in net unavailable sites is caused by the ferric anions as they can provide $O^{2-}$ for the reduction reaction. Moreover, due to their surface active they can displace some of the alumina anions.  
(2) The available reaction sites parameter is equivalent to the $A/A_o$ ratio.
Based on the above scheme the following general expression was developed

\[ \frac{A}{A_0} = 1 - N_{Al_{2}O_{3}} - N_{SiO_{2}} - N^{XS}_{SiO_{2}} + N_{Fe_{2}O_{3}} + N^{XS}_{Fe_{2}O_{3}} \] (6.12)

where \( N_i \) is the mole fraction of species \( i \) and the superscript XS is the excess concentration of the surface active species. It was easy to calculate the mole fraction of species that are not surface active. However for the silica and ferric oxide species additional expressions were necessary to quantify the excess surface concentration. This task posed a special challenge because our melts did not qualify strictly for an approach using Gibbs adsorption isotherm equation

\[ \Gamma_i = -\frac{1}{RT} \left( \frac{\partial \sigma}{\partial \ln a_i} \right) \frac{mole}{cm^2} \] (6.13)

in which \( \Gamma_i \) is the excess quantity of solute \( i \) per unit area of interface (mole/cm\(^2\)), \( R \) is the gas constant (cal/K.mole), \( \sigma \) is the surface tension (cal/cm\(^2\)) and \( a_i \) is the activity of \( i \) in the melt. Two important reasons for the inadequacy of above equation for the present situation are: (1) the Gibbs adsorption equation was developed for a binary system whereas our melts contained at least three or more oxide species; and (2) equation (6.13) accounts for the excess surface concentration of a single surface active species whereas in the melts in this study both ferric oxide and silica are surface active species. Furthermore it is possible that other physicochemical properties such as density and viscosity of the melt may independently alter the excess surface concentration. It is appreciated that in ionic melts the situation is further complicated due to the nature of various ionic species and therefore quantitative estimation of surface active species becomes more difficult in such melts.

In spite of these limitations a large number of workers have used this equation to explain lowering of surface tension values of the melts due to addition of solute to these melts and therefore an attempt has been made in the thesis to apply the concept of the Gibbs adsorption isotherm equation. In this regard a reference by Kim et al. [66] is of particular interest to this work because these authors also studied the ferrous reduction reaction and they report the same approach for
the determination of the reaction area in the Fe₂O-CaO-SiO₂-MgO system. In a separate study Pal et al. [101] estimate the lowering of the reaction area due to P₂O₅ coverage using a similar technique. In the present study the concept of the Gibbs adsorption isotherm is employed (to an extent, in an indirect way) to arrive at the excess surface concentration data in agreement with the observed surface tension behavior in complex melts. The basis for this is briefly discussed below.

P. Kozakevitch and other researchers [67,102,103] have shown that silica lowers the surface tension of ferrous oxide melts. Therefore, the excess concentration of silica at the surface can be determined using Gibbs adsorption isotherm. The results of such calculation are shown in Figure 6.5. The plots of excess silica versus \( a_{\text{SiO}_2} \) and surface tension (\( \sigma \)) versus log \( a_{\text{SiO}_2} \) for FeO-SiO₂ system highlight the relationships between the parameters in equation (6.13). A critical point that emerges from Figure 6.5(b) is that the melt surface tension, \( \sigma \), varies in a non-linear fashion with respect to the activity of silica. To further confirm of this trend available surface tension data was utilized in the preparation of surface tension-activity plots for other melts such as - FeO-Fe₂O₃, Fe₆O-CaO, Fe₆O-SiO₂-Al₂O₃ and Fe₆O-SiO₂-CaO-Al₂O₃. These are shown in Figure 6.6. Comparison of curves in this figure with the curve in Figure 6.5(b) reveals some interesting features. All the four curves in Figure 6.6 are concave-up whereas the one in the latter figure is convex. The activity range of silica in Figures 6.5(a) and 6.5(b) is widely different and most likely the curve for silica in the former figure is equivalent to the bottom end of \( \sigma \) versus log \( a_{\text{SiO}_2} \) curve in the latter figure. The convex-concave pattern is typical of such plots and in fact in the case of many solutes the convex curve is normally followed by a linear region, which in turn is followed by the concave region. However, without going into further details it would suffice to state at this stage that the curves from Figures 6.5 and 6.6 clearly show a consistent non-linear behavior. The important thing in the present case is to develop a method for estimating excess surface concentrations in complex melts.
Figure 6.5 Surface tension - composition relationship. (a) shows variations in surface tension values of wüstite melt due to additions of Fe$_2$O$_3$, SiO$_2$ and P$_2$O$_5$ (ref. 103); (b) surface tension-activity and excess surface concentration-activity relationships for Fe$_x$O-SiO$_2$ melts at 1400 °C (ref.67).
Figure 6.6 Surface tension-activity relationships for various melts at 1400 °C.
Due to the paucity of surface tension data in the literature, it is difficult to establish the exact relationship between the activity of the solute and the surface tension for a particular melt system. Under the circumstance, it can be assumed that $\Gamma_i$ bears some functional relationship with $\sigma$ and in turn $\sigma$ and $a_i$ vary together with composition. Based on this assumption it is possible to develop an expression relating excess concentration and the solute activity. As a first step we can write

$$\Gamma_i = \alpha \cdot (a_i)^n \quad (6.14)$$

where $\alpha$ and $n$ are constants. The above equation can be expressed as

$$\log \Gamma_i = \log \alpha + n \cdot \log a_i \quad (6.15)$$

Therefore, from the plots of $\log \Gamma_i$ versus $\log a_i$ the values of $\alpha$ and $n$ can be evaluated.

Based on the knowledge of these two parameters the moles of excess silica at the surface could be calculated by combining equation (6.14) with the following relationship

$$\text{excess moles of silica} = \Gamma_{\text{SO}_2} \cdot A_o \quad (6.16)$$

However, in order to arrive at an overall coverage value the excess silica moles are added to the term representing surface silica moles due to the dilution effect in the following manner

$$\text{moles of silica on surface} = (\Gamma_{\text{SO}_2} \cdot A_o + \delta_{st} \cdot A_o \cdot C_{\text{SiO}_2}) \quad (6.17)$$

where $\delta_{st}$ is the monolayer thickness (cm), $C_{\text{SiO}_2}$ is the bulk silica concentration (moles/cm$^3$) and $A_o$ is the melt surface area (cm$^2$). The above equation can be alternatively expressed in terms of area coverage due to silica as

$$\frac{A}{A_o - A} = \frac{\Gamma_{\text{SiO}_2} \cdot A_o}{(\delta_{st} \cdot \rho_{st})} + \frac{\delta_{st} \cdot A_o \cdot C_{\text{SiO}_2}}{(\delta_{st} \cdot \rho_{st})} \quad (6.18)$$

where $\rho_{st}$ is the density of slag expressed as moles/cm$^3$. After dividing both sides of equation (6.18) by $A_o$ and rearranging we get

$$\frac{A}{A_o} = 1 - \frac{\Gamma_{\text{SO}_2}}{\rho_{st} \cdot \delta_{st} \cdot \rho_{st}} \quad (6.19)$$
where \( A/A_o \) is the fractional area available for the reaction. The second term on the right hand side of the above equation can be expressed in terms of volume fraction

\[
\frac{C_{\text{SiO}_2}}{\rho_{dl}} = \frac{(C_{\text{SiO}_2})(V_{dl}/\rho_{dl})}{V_{dl}} \tag{6.20}
\]

The above can be alternatively be stated as

\[
\frac{A}{A_o} = 1 - N_{\text{SiO}_2} - \frac{\Gamma_{\text{SiO}_2}}{\rho_{dl} \cdot \delta_{dl}} \tag{6.21}
\]

in which substitution for \( \Gamma_{\text{SiO}_2} \) can be made according to equation (6.14) to yield

\[
\frac{A}{A_o} = 1 - N_{\text{SiO}_2} - \frac{\alpha \cdot (a_{\text{SiO}_2})^n}{\rho_{dl} \cdot \delta_{dl}} \tag{6.22}
\]

For the melt density calculations mole/cm\(^3\) units were chosen and an estimation of \( \delta_{dl} \), (monolayer thickness of an adsorbed silica) was obtained using the information published by F.D. Richardson. [105] Values of \( n \) and \( \alpha \) were derived from the log \( \Gamma_{\text{SiO}_2} \) versus log \( a_{\text{SiO}_2} \) plot shown in Figure 6.7. Calculation based on the \( \alpha, \rho_{dl}, \delta_{dl} \), and \( n \) values of \( 6.92(10^{-10}) \) (moles/cm\(^3\)), 3.7 (g/cm\(^3\)), 5(10\(^{-8}\)) (cm) and 0.5 respectively yields the following expression for the binary FeO-SiO\(_2\) melts at 1400 °C:

\[
\frac{A}{A_o} = 1 - N_{\text{SiO}_2} - 0.76(a_{\text{SiO}_2})^{0.5} \tag{6.23}
\]

Some support for the form of equations presented above can be obtained from the work of Kim et al. [66] who have proposed the following relationship

\[
\frac{(A_o - A)}{A_o} = 0.7(a_{\text{SiO}_2})^{0.33} \tag{6.24}
\]

to evaluate the fractional surface coverage due to silica at 1600 °C. Although there are some differences between the set of equations proposed in this work and that by Kim et al. both clearly highlight the role played by the fractional coverage phenomenon on the reduction rates.
Figure 6.7  \( \log \Gamma_{\text{SiO}_2} \) versus \( \log a_{\text{SiO}_2} \) plot for FeO-SiO\(_2\) melts.
Equation (6.23) is strictly applicable to the melts without ferric oxide. Since the melts used in the present work contained minor proportions of ferric oxide, this equation was further modified to account for the excess surface concentration by ferric oxide. However the procedure for the derivation of excess surface concentrations in the melts containing two surface active solutes is not readily available in the literature and therefore it was decided to infer some useful information from the available sources.

As was seen earlier, in the calculation of excess surface concentrations (using equation 6.14) the log $\Gamma_i$ - log $a_i$ plots are essential because without these $\alpha$ and n values of the surface active species cannot be determined. For the FeO-SiO$_2$, FeO-Fe$_2$O$_3$ and FeO-Fe$_2$O$_3$-CaO melt systems such plots were prepared using the available surface tension and thermodynamic activity data. This is shown in Figure 6.8. It is important to remember that in each of the above three systems only one surface active species is present and therefore different trends are expected in the presence of two surface active oxide species. It is not unreasonable to assume that for the melts containing two surface active oxides the slopes of the lines would alter within the individual limits set by the two solutes. Support for this hypothesis is obtained from the surface tension-mole% solute plots shown in Figure 6.9. The slopes of the lines in this figure clearly imply that the surface activity of SiO$_2$ is most marked in the melts containing <5% Fe$_2$O$_3$ and in addition the effect of ferric oxide on the surface tension diminishes with increasing silica levels. (Figure 6.9b) These trends suggest that the excess surface concentration of ferric oxide would decrease with increase in the melt silica content and vice versa and therefore the log $\Gamma_i$ - log $a_i$ plots for the melts containing two surface active species are expected to fall between the limits set by the two. The behaviour also hinted that the $\alpha$ and n values would be largely dependent on the silica level of the melts.
Figure 6.8  Log $\Gamma_i$ versus log $a_i$ plots for FeO-$\text{Fe}_2\text{O}_3$, FeO-$\text{SiO}_2$ and FeO-$\text{Fe}_2\text{O}_3$-$\text{CaO}$ melts at 1400 °C (where $i$ represents ferric oxide and silica species).
Figure 6.9 Surface tension variations in pseudo-binary Fe₂O₃-SiO₂ melts (ref.102) (a) shows effect of silica at various levels of ferric oxide (b) shows effect of ferric oxide in melts containing > 21 mass% silica.
Based primarily on these observations the following empirical relationships were developed for the calculation of \( \alpha \) and \( n \) coefficients for ferric oxide species in silica-containing melts:

\[
\alpha = 0.3 + N_{\text{SiO}_2} \quad (6.25)
\]
\[
n = 0.25 + 0.6(N_{\text{SiO}_2}) \quad (6.26)
\]

For silica-free melts \( \alpha \) and \( n \) values correspond to 0.3 and 0.25 respectively and these represent the intercept and slope of the line 1 in Figure 6.9. Due to paucity of the surface tension data more points could not be added to line 1. However, based on the shapes of curves in Figure 6.5(a) it is assumed that the behavior of ferric oxide is similar to silica and therefore the line 1 can be extrapolated. Additional calculations revealed that the coverage parameter is more sensitive to the \( n \) values. Thus for Fe\(_2\)O-SiO\(_2\) melts the fractional coverage expression is written as:

\[
\frac{A}{A_0} = 1 - N_{\text{SiO}_2} - 0.76(a_{\text{SiO}_2})^{0.5} + N_{\text{FeO}_1} + (0.3 + N_{\text{SiO}_2})\{a_{\text{FeO}_1}\}^{0.25 + 0.6(N_{\text{SiO}_2})} \quad (6.27)
\]

The contribution of ferric oxide is added to the R.H.S. of the above equation because this species provides oxygen atoms for the reduction reaction and therefore is treated as a reactant species. By the extension of this logic, it is necessary to subtract the mole fraction contributions by any species that does not release an oxygen atom. Therefore, for Fe\(_2\)O-SiO\(_2\)-Al\(_2\)O\(_3\) melts the above equation transforms to

\[
\frac{A}{A_0} = 1 - N_{\text{SiO}_2} - 0.76(a_{\text{SiO}_2})^{0.5} - N_{\text{AlO}_1} + N_{\text{FeO}_1} + (0.3 + N_{\text{SiO}_2})\{a_{\text{FeO}_1}\}^{0.25 + 0.6(N_{\text{SiO}_2})} \quad (6.28)
\]

Equations (6.27) and (6.28) are applicable to melt compositions within the pseudo ternary Fe\(_2\)O-SiO\(_2\)-Al\(_2\)O\(_3\) system at 1400 °C. Addition of a basic oxide (e.g. CaO and MgO) to the melt does not alter the form of these equations and therefore the same equations are applicable to either Fe\(_2\)O-SiO\(_2\)-CaO-Al\(_2\)O\(_3\) or Fe\(_2\)O-SiO\(_2\)-MgO-Al\(_2\)O\(_3\) melt systems.

The discussion so far has covered the effect of melt silica and ferric oxide contents on the fractional coverage parameter, \( \frac{A}{A_0} \), at a constant temperature of 1400 °C. The role played by the temperature is discussed next.
It is possible to modify the fractional coverage expression for the Fe$_x$O-SiO$_2$-CaO-Al$_2$O$_3$ system obtained at 1400 °C (i.e equation 6.28) to arrive at similar expressions for 1300 °C and 1200 °C melts by substituting appropriate values of coefficient ($\alpha$) and exponent (n) for the $a_{\text{SiO}_2}$ and $a_{\text{Fe}_2\text{O}_3}$ terms. However, this task could not be undertaken due to the lack of surface tension data at lower temperatures and an alternate approach had to be found to complete the task. A clue was taken from the work of P. Kozakevitch [106] who has performed a few calculations on the temperature dependence of the surface tension in metal solutions. The author has concluded that at lower temperatures the solute becomes more surface active. In other words, the slope, $d\alpha/dC$, is steeper at lower temperatures. An illustration of this is shown in Figure 6.10. Such a trend implied changes in the values of exponent (n) for both surface active species. Also it was appreciated that for a particular activity value the decrease in n (or exponent) value led to higher coverages. Based on the above information the following equations are proposed for the complex melts at 1300 °C and 1200 °C.

\[
\frac{A}{A_0} = 1 + N_{\text{FeO}_{1.5}} + (0.3 + N_{\text{SiO}_2}) \left[ a_{\text{Fe}_2\text{O}_3} \right]^{0.15 + 0.4 \left[ N_{\text{SiO}_2} \right]} - N_{\text{SiO}_2} - 0.76(a_{\text{SiO}_2})^{0.4} - N_{\text{AlO}_{1.5}} \tag{6.29}
\]

\[
\frac{A}{A_0} = 1 + N_{\text{FeO}_{1.3}} + (0.3 + N_{\text{SiO}_2}) \left[ a_{\text{Fe}_2\text{O}_3} \right]^{0.1 + 0.4 \left[ N_{\text{SiO}_2} \right]} - N_{\text{SiO}_2} - 0.76(a_{\text{SiO}_2})^{0.35} - N_{\text{AlO}_{1.5}} \tag{6.30}
\]

The $\alpha$ and n values of the ferric oxide and silica species in the above equations are to some extent fitted to the experimental results. However, their individual trends are consistent with the melt behaviour expected at lower temperatures [106]. It is worth mentioning here that the approach chosen for the derivation of equations (6.29) and (6.30) was the only available option due to the paucity of melt surface tension data at lower temperatures.
Figure 6.10 Surface tension of solutions of a surface-active solute at different temperatures, $t_1$, $t_2$ and $t_3$. (ref.106)
Before discussing the application of the above model, it is important to clarify a few points concerning the fractional coverage expressions. Firstly, it should be appreciated that the expressions are derived by the combination of both theoretical and published data on the surface tension of the melts. Support for this approach was obtained from the work published by Pal et al. [101] and Kim et al. [66] who have accounted for the blockage effects of P$_2$O$_5$ and SiO$_2$ species respectively. Secondly, the form of the fractional coverage expressions shows that their values decrease with the increasing proportions of silica or other non-reactant species. Based on this trend, it is easier to appreciate the reasons behind the decreasing apparent rate constant values reported in the literature [56,34,68]. Thus, the $A/A_o$ expressions were very useful in interpreting the nature of the apparent rate constant. Another advantage of this approach is that the rates can be predicted for untested melts for which $k_s$ values are not available and finally the technique allows characterization of important reaction resistances to study their effect on the rate phenomenon.

6.1.2.3 Application

6.1.2.3.1 Calculation of $k_c$

In the equation (6.7) all parameters except $k_c$ are known and therefore by choosing this as a fitting parameter the calculated rates were matched with the measured data. To illustrate this procedure Tables 6.5-6.8 are prepared. Tables 6.5 and 6.6 list the information on the melt composition, activity and $A/A_o$ for various melts studied in this work. Comparison of measured and fitted rates for the pseudo binary and pseudo ternary melts at 1400 °C is shown in Table 6.7, whereas the data obtained for the complex melts at three reaction temperatures is listed in Table 6.8. Both Tables 6.7 and 6.8 contain additional information on reaction resistances and relevant data on the driving force and overall rate constants for the selected melt compositions.

It can be seen from the information in these tables that for the melts at 1400 °C the fitted $k_c$ values range between $9 \times 10^{-5}$ and $13 \times 10^{-5}$ gm/cm$^2$.s.atm, whereas for the 1300 and 1200 °C melts the values obtained are $7 \times 10^{-5}$ and $3.5 \times 10^{-5}$ gm/cm$^2$.s.atm. respectively.
Table 6.5  Melt compositions of various pseudo binary and pseudo ternary melts and the activity data for FeO, Fe$_2$O$_3$ and SiO$_2$.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Melt composition as mole fraction (N$_i$)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>$a_{FeO}$</th>
<th>$a_{Fe_2O_3}$</th>
<th>$a_{SiO_2}$</th>
<th>A/A$_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>FeO</td>
<td>Fe$_{0.5}$</td>
<td>SiO$_2$</td>
<td>CaO</td>
<td>MgO</td>
<td>AlO$_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,6,7A,2A,</td>
<td>0.87</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.08</td>
<td>0.96</td>
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<tr>
<td>19A,113,115</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>117,118</td>
<td>0.92</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
<td>0.06</td>
<td>0.97</td>
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<tr>
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<td>-</td>
<td>0.03</td>
<td>0.06</td>
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<td>0.70</td>
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<td>0.17</td>
<td>-</td>
<td>0.03</td>
<td>0.20</td>
<td>0.70</td>
<td>5x10$^{-3}$</td>
<td>-</td>
<td>0.61</td>
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<td>-</td>
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<td>0.17</td>
<td>0.92</td>
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<td>0.57</td>
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<td>130</td>
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<td>0.03</td>
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<td>-</td>
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<td>-</td>
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<td>0.22</td>
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<td>-</td>
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<tr>
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<td>0.35</td>
<td>1x10$^3$</td>
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<td>0.09</td>
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</table>

Note:  
(1) Melt compositions at 1400 °C.  
(2) A/A$_0$ values are calculated using equation (6.33).  
(3) Standard state for FeO and Fe$_2$O$_3$ is liquid whereas that for SiO$_2$ is solid.
Table 6.6 Melt compositions of complex melts (Fe₂O₃-CaO-SiO₂-Al₂O₃ system) and the activity data for FeO, Fe₂O₃ and SiO₂ species at 1200 °C, 1300 °C and 1400 °C.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Temp.</th>
<th>Melt composition as mole fraction (N₁)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>°C</td>
<td>FeO</td>
<td>FeO₁₃</td>
<td>SiO₂</td>
<td>CaO</td>
<td>AlO₁₃</td>
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<tr>
<td>31,32</td>
<td>1400</td>
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<td>0.02</td>
<td>0.23</td>
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<td>0.28</td>
</tr>
<tr>
<td>33,34</td>
<td>1400</td>
<td>0.27</td>
<td>0.01</td>
<td>0.26</td>
<td>0.16</td>
<td>0.30</td>
</tr>
<tr>
<td>35,36,37</td>
<td>1400</td>
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<td>0.23</td>
<td>0.17</td>
<td>0.29</td>
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<td>0.14</td>
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<td>1200</td>
<td>0.37</td>
<td>0.01</td>
<td>0.28</td>
<td>0.20</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Note: (1) A/A₀ values are calculated using equation (6.28).
Table 6.7 Comparison of measured and predicted rates for the pseudo binary and pseudo ternary melts at 1400 °C. (Fe<sup>3+</sup>/ΣFe < 0.05)

<table>
<thead>
<tr>
<th>Melt type</th>
<th>Expt</th>
<th>Reaction resistance (cm&lt;sup&gt;2&lt;/sup&gt; • s • atm)/g</th>
<th>Overall rate constant</th>
<th>Reaction driving force</th>
<th>Predicted rate</th>
<th>Measured rate</th>
<th>Fitted k&lt;sub&gt;e&lt;/sub&gt; value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#</td>
<td>1/ν&lt;sub&gt;k&lt;/sub&gt; 1/ν&lt;sub&gt;α&lt;/sub&gt;</td>
<td>1/ν&lt;sub&gt;α&lt;/sub&gt;</td>
<td>g/cm&lt;sup&gt;2&lt;/sup&gt; • s • atm</td>
<td>am</td>
<td>g/cm&lt;sup&gt;3&lt;/sup&gt; • s</td>
<td>g/cm&lt;sup&gt;3&lt;/sup&gt; • s • atm</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;0-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2A</td>
<td>5720 22570 8013</td>
<td>2.75 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>0.80</td>
<td>22.0 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>25.5 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>13 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>7A</td>
<td>6129 24183 11574</td>
<td>2.39 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>0.017</td>
<td>4.0 x 10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>4.0 x 10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>9 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>19A</td>
<td>5720 22570 8013</td>
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<td>19.3 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>22.2 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>13 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>113</td>
<td>5363 21160 8013</td>
<td>2.90 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>0.18</td>
<td>5.2 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>6.0 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>13 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>115</td>
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<td>5.0 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>5.7 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>13 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;0-MgO</td>
<td>117</td>
<td>5720 22110 11339</td>
<td>2.55 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.18</td>
<td>4.6 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>4.7 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>9 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>118</td>
<td>5047 19509 10204</td>
<td>2.88 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
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<td>5.2 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<td>10 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;0-MgO-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>5720 22338 10309</td>
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<td>4.7 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<td>Fe&lt;sub&gt;2&lt;/sub&gt;0-CaO-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10</td>
<td>5720 30954 21290</td>
<td>1.72 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>0.75</td>
<td>12.9 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<tr>
<td></td>
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<td>0.18</td>
<td>3.1 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>2.8 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>11 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
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<tr>
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<td>5363 31251 27571</td>
<td>1.56 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>0.03</td>
<td>4.7 x 10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>4.0 x 10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>9 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;0-SiO&lt;sub&gt;2&lt;/sub&gt;-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>26</td>
<td>6600 27175 19069</td>
<td>1.89 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>0.76</td>
<td>17.0 x 10&lt;sup&gt;-6&lt;/sup&gt;</td>
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<td>10 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
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<td></td>
<td>130</td>
<td>4767 24075 33670</td>
<td>1.60 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.18</td>
<td>2.9 x 10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>2.6 x 10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>11 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
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<tr>
<td></td>
<td>29</td>
<td>5363 58038 244200</td>
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<td>0.76</td>
<td>2.5 x 10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>2.8 x 10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>13 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Note: (1) Overall rate constant = \( \frac{1}{\frac{1}{k} + \frac{1}{k_e} + \frac{1}{k_{eq}}} \)

(2) Equilibrium constant, \( K_e = 0.264 \).

(3) Values of gas phase mass transfer coefficient, \( k_e \), are calculated using equation (5.5).
Table 6.8 Comparison of measured and predicted rates for complex melts between 1200 °C and 1400 °C. (Fe<sup>3+</sup>/ΣFe < 0.05)

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Temp. °C</th>
<th>Reaction resistance (cm&lt;sup&gt;3&lt;/sup&gt;·s·atm)/g</th>
<th>Overall rate constant (k&lt;sub&gt;0&lt;/sub&gt;)&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Reaction driving force</th>
<th>Predicted rate</th>
<th>Measured rate</th>
<th>Fitted k&lt;sub&gt;a&lt;/sub&gt; value</th>
<th>Fitted l&lt;sub&gt;c&lt;/sub&gt;, value</th>
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</thead>
<tbody>
<tr>
<td>31</td>
<td>1400</td>
<td>6600</td>
<td>37880</td>
<td>210438</td>
<td>3.92 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>0.66</td>
<td>2.6 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>2.2 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td>32</td>
<td>1400</td>
<td>6600</td>
<td>37880</td>
<td>210438</td>
<td>3.92 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>0.18</td>
<td>7.1 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>7.0 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
<tr>
<td>33</td>
<td>1400</td>
<td>6600</td>
<td>60978</td>
<td>369549</td>
<td>2.29 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>0.49</td>
<td>1.1 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>1.0 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
<tr>
<td>34</td>
<td>1400</td>
<td>6600</td>
<td>60978</td>
<td>369549</td>
<td>2.29 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>0.18</td>
<td>4.1 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>4.0 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
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<td>6600</td>
<td>43862</td>
<td>216591</td>
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<td>2.3 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>2.0 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
<tr>
<td>36</td>
<td>1400</td>
<td>6600</td>
<td>43862</td>
<td>216591</td>
<td>3.74 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>0.18</td>
<td>6.7 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>4.0 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
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<td>37</td>
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<td>6600</td>
<td>43862</td>
<td>216591</td>
<td>3.74 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>0.18</td>
<td>6.7 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>6.0 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
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<td>6723</td>
<td>32388</td>
<td>97847</td>
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<td>0.18</td>
<td>1.1 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>0.9 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
<tr>
<td>51</td>
<td>1200</td>
<td>6868</td>
<td>23488</td>
<td>190985</td>
<td>4.52 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>0.18</td>
<td>8.1 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>8.0 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Note: (1) Overall rate constant = \( \frac{1}{\frac{1}{k_a} + \frac{1}{k_{\text{gas}}} + \frac{1}{k_{\text{FeO}}} + \frac{1}{k_{\Delta x}}} \)

(2) Values of k<sub>a</sub> are 0.264, 0.33 and 0.43 at reaction temperatures of 1400 °C, 1300 °C and 1200 °C respectively.

(3) Values of gas phase mass transfer coefficient, k<sub>gas</sub>, are calculated using equation (5.5).
Only one experiment each was performed at 1200 and 1300 °C and therefore the \( k_c \) values obtained from these experiments have a large element of uncertainty associated with them. However, the fitted values show a right trend namely - decreasing \( k_c \) with decreasing reaction temperature.

Since the \( k_c \) values for the 1400 °C runs varied consistently between \( 9 \times 10^{-5} \) and \( 13 \times 10^{-5} \) g/cm\(^2\).s.atm an average value of \( 11 \times 10^{-5} \) was fixed to represent all the data at this temperature and the value was used in conjunction with those at 1200 °C and 1300 °C temperatures for construction of Arrehinus plot (Figure 6.11). Additional calculations were performed to arrive at the activation energy value of about 28 kcal/mole. This agrees well with the earlier reported values by Nagasaka et al. (33,000 cal/mole), Kim et al. (32,000 cal/mole) and Tsukuhashi et al. (31,400 cal/mole).

6.1.2.3.2 Interpretation of the rate constant term

The data listed in Tables 6.7 and 6.8 reveals that individual values of the overall rate constants are dictated by three reaction resistances - \( 1/k_g \), \( 1/(k_g \cdot K^* \cdot a_{FeO}) \) and \( 1/(k_c \cdot A/A_o \cdot a_{FeO}) \).

In a situation where gas phase mass transfer is not rate limiting the first two resistances are negligible (because of the higher \( k_g \) value) and the resultant rate constant term would then equal the reciprocal of the remaining resistance. In the literature this term is often referred to as an apparent rate constant. Thus when the gas phase resistance is neglected the apparent rate constant can be represented as:

\[
k_a = k_c \cdot \frac{A}{A_o} \cdot a_{FeO}
\]  

(6.31)

The above equation implies that the apparent rate constant values are dependent on the individual values of \( A/A_o \) and \( a_{FeO} \). Any changes in the melt compositions are therefore expected to alter the apparent rate constant values. Thus with this approach it is possible to appreciate the reasons behind the reported variations in the apparent rate constants. [56,64] Further discussion on this topic is pursued in section 6.3.
Ferrous-to-iron reaction study
between 1200 and 1400 °C

Arrhenius plot of $\ln k_e$ versus $1/T$

Activation energy ~ 28142 cal/mole

Figure 6.11 Arrhenius plot of $\ln k_e$ versus $1/T$ for ferrous reduction study.
6.1.3 Reaction resistances

The data listed in Tables 6.7 and 6.8 shows the reaction resistances for the melts studied. It can be seen that the gas phase contribution comes from two terms containing $k_g$ parameter whereas the remaining resistance is offered by the chemical reaction. The data shows that in the case of simple melts, without lime and silica, the gas phase contribution to the total resistance is between 70 to 80% and therefore in these melts the reduction reaction is controlled by the gas phase. However, with the addition of lime and silica the gas phase contribution decreases with a commensurate increase in the chemical reaction resistance term. This result is attributed to the decrease in the fractional coverage parameter and the lower ferrous oxide activity. The effect is more pronounced with the addition of silica. For example, in the melt containing lowest silica (expt. #26) in the Fe$_2$O-SiO$_2$-Al$_2$O$_3$ system the gas phase contribution is nearly 64% whereas the equivalent value for the high silica melt (expt. #29) is about 21%. The same trend is observed in the complex melts containing both lime and silica.

The above pattern of behaviour implied that the rates were not governed by the gas phase transport alone. Although this conclusion was drawn earlier based on the discrepancy between the predicted rates, assuming gas phase control model, and the measured rate data (Figures 6.1 and 6.2) the description in the foregoing paragraph offers further explanation for such behaviour.

6.1.4 Effect of melt composition

The measured rate data clearly showed that increasing additions of silica led to consistently lower rate values. (Table 5.4 and Figure 5.6) Nagasaka et al. [56] report similar observation in their study. Though these investigators employed a jetting set up their findings concerning the effect of silica are not different. Nagasaka et al. account for the decreasing rates in terms of reduction in the apparent rate constant values due to silica. In the present work, based on the detailed mathematical analysis an explanation to the silica effect was sought in terms of its surface active properties.
Equation (6.7) implied that the lower reduction rates could also result from the decrease in the $a_{FeO}$ values which are caused by the addition of silica to the melt. However, the observed rates were much lower than the ones predicted on the assumption of activity contribution alone. For example, the measured rate for the lowest silica-containing melt (~5 mole%) was about 6 times higher than the one recorded for the highest silica (~29 mole%) melt using the same reduction gas mixture. However, the $a_{FeO}$ value for the former melt was only about 2 times greater than the latter. Such a pattern of behaviour supported the idea that in addition to the activity effect which acted via driving force term an additional contribution may come from the overall rate constant term. Therefore, this idea was pursued further by quantifying the silica effect in terms of the fractional coverage parameter, $A/A_0$. Also the same concept was extended further to include the role played by amphoteric oxide species like ferric oxide and alumina.

With the help of a mathematical expression the role played by the melt composition can be appreciated without much difficulty. For example, equation (6.28) clearly shows that as the melt silica and alumina levels increase the fractional coverage parameter values decrease. As per equation (6.7), this in turn leads to lower apparent rate constant values and therefore lower rates are predicted. Thus both the activity and surface coverage effects are considered in the mathematical modelling scheme.

### 6.1.5 Effect of excess melt oxygen

Special experiments (#12-#15) were conducted to study the effect of excess oxygen in the melts and the data showed higher reduction rates. This trend was consistent in both simple and complex melts. According to Fe-O phase diagram (Figure 2.1) higher oxygen contents lead to higher ferric levels and therefore it is easier to appreciate the fact that in our study higher rates were obtained at higher ferric levels. (Tables 5.5 and 5.7 and Figures 5.6 and 5.8) Nagasaka et al. [56] report a similar finding in their work.
The authors observed that ferrous reduction rates were exceedingly influenced by the ferric-to-ferrous ratio expressed as $N_{Fe^3+/Fe^{2+}}$ and proposed the following empirical relationship between this ratio and the composition dependent apparent rate constant

$$k_a = 8.4 \times 10^{-4} \left( N_{Fe^3+/Fe^{2+}} \right)^{1/3} \frac{g}{cm^2.s.atm} \quad (6.32)$$

The above relation shows that the value of apparent rate constant would increase commensurate with the melt ferric levels and this would lead to the higher rates. Due to the empirical nature of the expression however the fundamental reasons underlying the rate enhancement phenomenon were not addressed by the authors.

From the expression derived by Nagasaka et al. one can see that the values of apparent rate constant are dependent on the state of oxidation of the melt. Other researchers [68,34] have also noted similar trend while studying the interfacial rates of oxidation in various melt systems. Belton [80] have proposed a model involving dissociation of a doubly charged (negative) CO$_2$ molecule according to:

$$CO_2 + 2Fe^{2+} = CO_2^{-}(ad) + 2Fe^{3+} \quad (6.33)$$

and

$$CO_2^{-} = CO + O^{2-} \quad (6.34)$$

to explain the trends observed in the oxidation studies. Later, using the same model and the principle of microscopic reversibility the author has explained the results obtained in reduction studies by both Nagasaka et al. [56] and Tsukuhashi et al. [55]. This fact suggested that in the reduction of ferrous iron the ferric-ferrous reaction is critical.

To further test this possibility additional experiments were performed where the $Fe^{3+}/\Sigma Fe$ ratio of the melts was higher (between 0.14 and 0.19) than the normal melts in which this ratio was about 0.05. (Table 6.7 and 6.8) When the measured rates were compared with the predicted data, using the model developed earlier (i.e. gas phase mass transfer and interfacial reaction model assuming $Fe^{2+} \rightarrow Fe$ reaction), poor agreement was noticed.
Table 6.9 shows comparison of measured and predicted rates for the high ferric oxide-containing melts. The data highlights two important points: (1) in most cases the predicted values are lower; and (2) highest discrepancy is noted for Fe$_x$O-SiO$_2$-Al$_2$O$_3$ melts. The same table lists the data for the over-oxidized melts (Experiments #12-#15) and again these numbers reveal a poor agreement between the predicted and measured data. Lower predicted values in Table 6.9 suggest two things: (1) the model is wrong for these conditions or (2) a faster concurrent reaction is taking place in these melts. The former possibility was discarded because the model could make reasonable predictions in the case of low ferric oxide-containing melts.

Additional support for the concurrent ferric-ferrous reaction was obtained by comparing the model predicted rates, assuming $Fe^{3+} \rightarrow Fe^{2+}$ reaction, with the measured data. A mixed gas + reaction control model was formulated for this purpose and the resultant rate comparison revealed an agreement between the two sets of data. The main reason for the success of the model was found to be the consideration of a simultaneous ferric-to-ferrous reaction which led to higher overall rate constant values compared to the equivalent data obtained assuming ferrous-to-iron reaction. This comparison is shown in Table 6.10. Upon further investigation it was noted that the value of intrinsic rate constant for the ferric-to-ferrous reaction was nearly 200 times greater than the equivalent value for the ferrous-to-iron reaction. Additional details on this are provided in section 6.2.

The above results were interesting because they suggested that perhaps the mechanisms involved in ferric and ferrous reduction reactions are different. Kinetic studies on the solid iron oxides have revealed different rates for the ferric oxide and magnetite reduction [21] and therefore the above idea was not discarded. However, according to the model suggested by Belton [80], in the melts, the ferric-to-ferrous and ferrous-to-iron reactions are not separate.
Table 6.9 Comparison of model predicted and measured rates for ferrous-to-iron reaction.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Melt composition, mole fraction (N&lt;sub&gt;i&lt;/sub&gt;)</th>
<th>$\frac{Fe^{2+}}{ΣFe}$</th>
<th>Measured rate</th>
<th>Predicted rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FeO</td>
<td>$FeO_{1.3}$</td>
<td>CaO</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
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<td>0.460</td>
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<td>0.157</td>
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<td>14</td>
<td>0.505</td>
<td>0.041</td>
<td>-</td>
<td>0.213</td>
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<tr>
<td>15</td>
<td>0.352</td>
<td>0.040</td>
<td>0.124</td>
<td>0.240</td>
</tr>
</tbody>
</table>

Note: (1) gas and interfacial reaction model formulated for the ferrous-to-iron reaction.
(2) Predicted rates are based on a $k_c$ value of $11 \times 10^{-7}$ $g/cm^2.s.atm$.
(3) * Melts contain excess oxygen.
Table 6.10  Comparison of overall rate constants for the melts with higher ferric oxide. (Fe$^{3+}$/$\Sigma$Fe > 0.05)

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Overall rate constant Fe$^{3+}$ $\rightarrow$ Fe reaction</th>
<th>Overall rate constant Fe$^{2+}$ $\rightarrow$ Fe$^{3+}$ reaction</th>
<th>Melt type</th>
<th>Fe$^{3+}$ $\rightarrow$ Fe$^{2+}$ reaction rate, gm/cm$^2$.s.atm</th>
</tr>
</thead>
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<td>12</td>
<td>2.34 x 10$^{-5}$</td>
<td>1.28 x 10$^4$</td>
<td>Fe$_3$O-Al$_2$O$_3$</td>
<td>12.8 x 10$^{-7}$</td>
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<td>87</td>
<td>1.94 x 10$^{-5}$</td>
<td>3.54 x 10$^{-5}$</td>
<td>Fe$_3$O-CaO-Al$_2$O$_3$</td>
<td>10.6 x 10$^{-7}$</td>
</tr>
<tr>
<td>88</td>
<td>1.63 x 10$^{-5}$</td>
<td>2.44 x 10$^{-5}$</td>
<td>Fe$_3$O-CaO-Al$_2$O$_3$</td>
<td>8.1 x 10$^{-7}$</td>
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<td>89</td>
<td>1.88 x 10$^{-3}$</td>
<td>4.57 x 10$^{-3}$</td>
<td>Fe$_3$O-CaO-Al$_2$O$_3$</td>
<td>7.3 x 10$^{-7}$</td>
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<tr>
<td>90</td>
<td>1.49 x 10$^{-3}$</td>
<td>5.39 x 10$^{-3}$</td>
<td>Fe$_3$O-SiO$_2$-Al$_2$O$_3$</td>
<td>1.6 x 10$^{-4}$</td>
</tr>
<tr>
<td>91</td>
<td>0.91 x 10$^{-3}$</td>
<td>3.84 x 10$^{-3}$</td>
<td>Fe$_3$O-SiO$_2$-Al$_2$O$_3$</td>
<td>1.1 x 10$^{-4}$</td>
</tr>
<tr>
<td>14</td>
<td>8.84 x 10$^{-6}$</td>
<td>3.05 x 10$^{-6}$</td>
<td>Fe$_3$O-SiO$_2$-Al$_2$O$_3$</td>
<td>22.9 x 10$^{-7}$</td>
</tr>
<tr>
<td>15</td>
<td>9.52 x 10$^{-6}$</td>
<td>2.90 x 10$^{-6}$</td>
<td>Fe$_3$O-CaO-SiO$_2$-Al$_2$O$_3$</td>
<td>21.8 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

Note: (1) For the Fe$^{2+}$ $\rightarrow$ Fe reaction overall rate constant =  \[ \frac{1}{k_1 + k_2 + k_{3Ti} + k_{5Fe} + k_{7Fe} + k_{9Fe}} \]

(2) For the Fe$^{3+}$ $\rightarrow$ Fe$^{2+}$ reaction overall rate constant =  \[ \frac{1}{k_1 + k_2 + k_{3Ti} + k_{5Fe} + k_{7Fe} + k_{9Fe}} \]

(3) All the melts at 1400 °C.
(4) Fitted $k_e$ value for the ferric-to-ferrous reaction averaged 0.025 (g/cm$^2$.s.atm)
(5) Fitted $k_e$ value for the iron formation reaction averaged 11 x 10$^{-5}$ (g/cm$^2$.s.atm).
Based on the studies by Sun et al. [63], Sasaki et al. [68] and El-Rahaiby et al. [34] Belton has proposed the following empirical relation:

\[ k_a = k' (Fe^{3+}/Fe^{2+})^{-2} \]  

(6.35)  

where \( k' \) is a system and temperature dependent constant. Using the available ferrous-to-ferric oxidation data, Belton has shown that equation (6.35) is consistent with a rational rate law based on the dissociation of an adsorbed \( CO_2^- \). By plotting \( \log k_a \) versus \( \log Fe^{3+}/Fe^{2+} \) for various melts (Figure 6.12a) the value of the slope was found to be -2, as predicted by the above equation, and this validated the proposed model. For the ferrous reduction reaction Belton’s model would predict the dependence of apparent rate constant as follows:

\[ k_a = m (Fe^{3+}/Fe^{2+})^2 \]  

(6.36)  

where \( m \) is a system and temperature dependent constant. However, Nagasaka et al. [56] report a different relation:

\[ k_a = k_r \left\{ \left( \frac{N_2^{2+}}{N_2^{3+}} \right)^2 / \left( \frac{N_2^{2+}}{N_2^{3+}} \right)^{3/3} \right\} \]  

(6.37)  

where \( k_r \) is the empirical rate constant. Equation (6.37) suggests a complex dependence of \( k_a \) on the melt ferric-ferrous proportions and implies some uncertainty in the application of Belton’s model to the reduction data. To further support this point Figure 6.12(b) is shown. This plot of \( k_a \) versus \( P_{CO_2}/P_{CO} \) shows the results of oxidation study on the lime ferrite melt (Ca/Fe = 0.3). Belton agrees that there are uncertainties in these measurements and has shown one result from the reduction study by Nagasaka et al. in the same figure. Although location of the reduction point is in reasonable agreement with the plot it is difficult to confirm whether the same trend will continue for other melts containing either lower or higher lime contents. Such behaviour implies that the mechanisms of oxidation and reduction reactions may be different. It is felt that more data is needed to either confirm or deny such a possibility.
Figure 6.12 Variations in apparent rate constants observed in oxidation studies using isotope exchange technique (ref. 80); (a) dependence on the melt Fe$^{3+}$/Fe$^{2+}$ ratio; (b) variation of $k_a$ as a function of oxygen activity for the reaction of CO$_2$ with a calcium ferrite melt (Ca/Fe = 0.3).
6.1.6 Reaction mechanism

The ferrous reduction reaction in the present work was controlled by a mixed gas phase mass transfer and interfacial reaction. In the melts with $Fe^{3+}/\Sigma Fe < 0.05$ the ferrous reduction reaction can be represented as

$$Fe^{2+} + CO_2^2- = Fe + CO_2 \quad (6.38)$$

However, in the melts with $Fe^{3+}/\Sigma Fe$ exceeding 0.05 additional reactions involving either $Fe^{3+}$ or other ferric ion species are significant.

The above scheme does not contradict the formation of $CO_2^2-$ as per reaction (6.9) suggested by Belton [80] and in addition is consistent with the findings of Kim et al. [66] concerning the silica coverage effect. The suggestion on participation of ferric anion species is essentially an extension of the idea proposed earlier by Gaskell [96] and such participation by ferric anions does not exclude the presence of a charge transfer reaction (reverse of reaction 6.33) involving ferric and ferrous cations. The presence of $Fe^{3+}$ ions in both the tetrahedral (anions) and octahedral (cations) coordination is justifiable on the grounds of amphoteric nature of ferric oxide species.

6.2 Ferric-to-ferrous study

Although a certain amount of data on the ferrous-to-iron reaction can be found in the literature very little information is available on the $Fe^{3+} \rightarrow Fe^{2+}$ reaction. Since the present work suggested the possibility of this reaction during the ferrous reduction, several additional experiments were performed to study the ferric-ferrous reduction reaction. These experiments were conducted at three temperatures - 1200 °C, 1300 °C and 1400 °C and a wide range of slag compositions was covered. Extreme care was exercised in both the selection and control of the reactant gas mixtures to avoid precipitation of either Fe or $Fe_2O_4$ species during reduction. In other words, the ferric-to-ferrous study was conducted in melts away from iron and magnetite saturation ($a_{Fe}$ and $a_{Fe_2O_4} < 1$). It is worth mentioning here that no such work has been reported in the past.
6.2.1 Mathematical analysis

To account for the two distinct stages observed during the reduction period two separate models were written. A mixed gas phase mass transfer and reaction control model described the highest initial rates whereas in the second model a liquid phase contribution was added to the existing reaction resistances to explain the slowing down of rate with time.

6.2.1.1 Model formulation

6.2.1.1.1 Constant initial rate

The procedure used in the derivation of a rate expression is essentially similar to the one described earlier in the ferrous reduction study. The flux equations (6.2) and (6.3), for the CO and CO$_2$ species respectively, remain the same. However, the rate equation (6.4) is modified because the reactant and product species in the liquid phase are different. The rate per unit area for the ferric oxide reduction (reaction 5.8) can be written as

$$r = k'_c \cdot A \cdot \left( a_{Fe_2O_3} \cdot C_{CO}^* - \frac{C_{CO_2}^*}{K} \right) \text{ moles/cm}^2\cdot\text{s}$$

where $k'_c$ is the intrinsic rate constant of ferric-to-ferrous reaction in cm/s and $K$ is the equilibrium constant of the reaction (5.8). The available reaction area in cm$^2$ is represented by $A$. Assuming steady state conditions i.e. $r = \dot{n}_{CO} = \dot{n}_{CO_2}$, the mathematical procedure given in Section 6.1.2.2 can be repeated to eliminate the interfacial concentrations to arrive at the following expression

$$\frac{r}{A_o} = \frac{1}{k_s K^* a_{Fe_2O_3}} \left( \frac{C_{CO}^b - \frac{C_{CO_2}^b a_{Fe_3O_4}^2}{K^* a_{Fe_2O_3}}}{} \right) \text{ moles/cm}^2\cdot\text{s}$$

where $A/A_o$ is the fraction covered by the ferric oxide species. The first term represents the overall rate constant and the term in the bracket is reaction driving force.
Equation (6.40) can be rewritten in the practical form as

\[
\frac{r}{A_o} = \frac{1}{a^2_{FeO}} \left( P^b_{CO} \frac{P^b_{CO} a_{FeO}^2}{K^* a_{FeO}} \right) \frac{g}{cm^2.s}
\]  

(6.41)

in which all terms except intrinsic rate constant, \( k^* \), are known. Therefore, by choosing appropriate values for the \( k^* \) term predicted rates could be matched to the observed data.

### 6.2.1.1.2 Rate-time behaviour

The weight loss data revealed that after about 60-90 minutes into the reduction period the reaction rates slowed down with time. This fact suggested that the resistance offered by the liquid phase had to be accommodated in the rate expression during the latter stages of the reduction period. To enable this the following equations were written

\[
\dot{n}_{Fe_2O_3} = k_L A_o \left( C^b_{Fe_2O_3} - f \cdot C^{*}_{Fe_2O_3} \right)
\]

(6.42)

and

\[
r = k^* A \left( f \cdot \gamma^b \cdot C^{*}_{Fe_2O_3} \cdot C^{*}_{CO} - \frac{C^{*}_{CO} a_{FeO}^2}{K^*} \right)
\]

(6.43)

Explanation on some of the new terms in the above two equations is necessary before proceeding further. Superscripts * and b represent interfacial and bulk concentrations of the species and the activity coefficient is indicated by \( \gamma \). Ferric oxide species is chosen as a convenient way to represent oxygen anion transport. The parameter \( f \) is the ratio of ferric oxide activity coefficients for the surface and bulk regions i.e.

\[
f = \frac{\gamma}{\gamma^b}
\]

(6.44)

At equilibrium the activity of ferric oxide is same for the entire melt and the variations in concentrations between the surface and bulk regions lead to different activity coefficient values.
for these regions. The ratio is $< 1$ because the concentration of ferric oxide at the surface is higher than the bulk due to its surface active nature. [102,103,107,108] Therefore, in the equation (6.43) the term in the bracket represents the activity driving force of the ferric-to-ferrous reaction.

In the derivation of an earlier gas + reaction model the liquid phase contribution was ignored and therefore equation (6.42) was excluded from the mathematical scheme. Also, it can be easily proved that the equation (6.43) readily converts to equation (6.39) when the $f_r^\phi C_{FeO3}^*$ term in the former is replaced by $a_{FeO3}$. The above facts suggest that the only difference between the gas + reaction model and the gas + liquid + reaction model lies in the inclusion of liquid phase resistance in the latter. The direct consequence of this results in the modification of equation (6.39) and the addition of equation (6.42) to the mathematical scheme.

By combining equations (6.42) and (6.43) with the three previous equations (equations 6.2, 6.3 and 6.5) i.e.

$$\dot{n}_{CO} = A_o k_s (C'^b_{CO} - C'^*_B)$$  \hspace{1cm} (6.2)

$$\dot{n}_{CO_2} = A_o k_s (C'^b_{CO_2} - C'^*_B)$$  \hspace{1cm} (6.3)

$$r = \dot{n}_{CO} = \dot{n}_{CO_2}$$  \hspace{1cm} (6.5)

the interfacial concentration terms were eliminated and the rate expression for the gas + liquid + reaction model was developed. The assumptions in the model formulation were same as those mentioned for the gas + reaction model. The procedure is briefly described below.

From equations 6.2, 6.3 and 6.5 we can get

$$C'^*_B = C^b_{CO} + C^b_{CO_2} - C'^*_B$$  \hspace{1cm} (6.45)

Also by equating equations (6.3) and (6.43) we get

$$k_s A_o C'^b_{CO} - k_s A_o C'^*_B = k_g A^\phi C_{FeO3}^* C_{CO} - \frac{k_g A C_{CO_2}^* a_{FeO3}^2}{K^*}$$  \hspace{1cm} (6.46)

Upon substitution of equation (6.45) in equation (6.46) the interfacial concentration of CO can be eliminated as per the following

$$k_s A_o C'^b_{CO} - k_s A_o (C'^b_{CO} + C^b_{CO_2} - C'^*_B) = k_g A^\phi C_{FeO3}^* C_{CO} + C^b_{CO_2} - C'^*_B - \frac{k_g A C_{CO_2}^* a_{FeO3}^2}{K^*}$$  \hspace{1cm} (6.47)
By equating (6.3) and (6.42) after rearrangement yields

\[
C_{CO_2}^* = \frac{k_L \cdot C_{FeO_3}^b}{k_g} \cdot \frac{k_L \cdot f \cdot C_{FeO_3}^b}{k_g} + C_{CO_2}^b
\]  

(6.48)

After combining equations (6.47) and (6.48) the interfacial concentration for the $CO_2, C_{CO_2}^*$ was eliminated and a final equation with one unknown was obtained. This was a quadratic equation in terms of $C_{FeO_3}^b$. Further calculations showed that a positive root should be used for expressing interfacial concentration of ferric oxide species (in terms of all the other parameters).

The final equation by following this procedure is given below

\[
r = \dot{n}_{FeO_3} = k_L \cdot A_o \cdot \left( C_{FeO_3}^b - \left[ \frac{-b + \sqrt{b^2 - 4 \cdot a \cdot c}}{2a} \right] \right)
\]  

(6.49)

where \[ a = \frac{k_c \cdot \frac{A}{A_o} \cdot f^b \cdot \gamma^b \cdot k_L}{k_g} \]

(6.50)

\[ b = \left[ k_c \cdot \frac{A}{A_o} \cdot f \cdot \gamma^b \cdot C_{CO}^b - \frac{k_c \cdot \frac{A}{A_o} \cdot f \cdot \gamma^b \cdot k_L \cdot C_{FeO_3}^b}{k_g} + \frac{k_c \cdot \frac{A}{A_o} \cdot a_{FeO}^2 \cdot f \cdot k_L}{k_g \cdot K^*} + f \cdot k_L \right] \]

(6.51)

and \[ c = \left[ \frac{k_c \cdot \frac{A}{A_o} \cdot a_{FeO}^2 \cdot k_L \cdot C_{FeO_3}^b}{k_g \cdot K^*} + \frac{k_c \cdot \frac{A}{A_o} \cdot a_{CO_2}^2 \cdot C_{CO_2}^b}{k_g \cdot K^*} + k_L \cdot C_{FeO_3}^b \right] \]

(6.52)

Acknowledging that

\[
\Delta w_n = \int_{t_{n-1}}^{t_n} (rate) \cdot dt + \Delta w_{n-1} \sim (rate)_{n-1} \cdot (t_n - t_{n-1}) + \Delta w_{n-1}
\]

(6.53)

and the rate is given by the expression (6.49) a technique was developed to perform the requisite calculations. Based on the Euler method an equation was derived to predict the weight loss data for any time interval $\Delta t$ and the same is given below

\[
\Delta w_n = (rate)_{n-1} \cdot \Delta t + \Delta w_{n-1}
\]

(6.54)

Of the various parameters in equation (6.49), only $C_{FeO_3}^b$ varies with time because the ferric oxide species is depleted due to the reduction reaction. Its highest value at $t = 0$ was first calculated
from a knowledge of the melt composition and the volume of the melt and in turn this was utilized in equation (6.54) to arrive at the weight loss after any fixed time interval \( \Delta t \). Using this weight loss value it was possible to calculate the new \( C_{F_aO_2}^b \) value assuming negligible changes in the melt volume during the time interval \( \Delta t \). By repeating these calculations in the program the weight loss at the end of the reduction period could be determined.

In the rate expression all the parameters except \( k_c^* \) and \( k_L \) are known and therefore with the knowledge of these two parameters the rate calculations could be performed. For all the melts studied the intrinsic rate constant value was obtained first using gas + reaction model and later this value was employed in the gas + liquid + reaction model. After fixing the \( k_c^* \) value, \( k_L \) was used as a fitting parameter to predict the weight loss data for studying rate-time behaviour in all the melts. A computer program was written for this purpose.

6.2.1.2 Application

6.2.1.2.1 Calculation of \( k_c^* \)

By using \( k_c^* \) as a fitting parameter in equation (6.41) the predicted rates were matched to the measured data. The results obtained thus for all the melt compositions are listed in Tables 6.11-6.14. Additional information on reaction resistances, overall rate constants, fractional coverage parameters and activity data for the individual melts is also provided in these tables. Table 6.11 shows the comparison of predicted and measured rate data at three reaction temperatures in lime-free melts (\( \text{Fe}_2\text{O}_3-\text{SiO}_2-\text{Al}_2\text{O}_3 \) system). The information reveals that the fitted \( k_c^* \) values range between 0.025 and 0.035 \( g/cm^2 \cdot s \cdot atm \) for a reaction temperature of 1400 °C whereas the equivalent values for the melts at 1300 °C and 1200 °C are 0.005 and 0.001 respectively. Since only limited data was obtained at lower temperatures the resultant values of the intrinsic rate constants may not be very accurate. However, these do show the expected trend of decreasing values with decreasing temperature.
Table 6.11 Fitted intrinsic rate constant values for the lime-free melts.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>Overall rate constant</th>
<th>D.F.</th>
<th>Predicted rate</th>
<th>Measured rate</th>
<th>$\frac{a_{F_{2}O}}{A_{eq}}$</th>
<th>$\frac{A}{A_{eq}}$</th>
<th>Fitted $k'$</th>
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<td>94</td>
<td>3777</td>
<td>5720</td>
<td>18433</td>
<td>3.58 x 10⁻³</td>
<td>0.013</td>
<td>4.7 x 10⁻³</td>
<td>4.6 x 10⁻⁷</td>
<td>0.73</td>
<td>0.01</td>
<td>0.217</td>
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<td>3.58 x 10⁻³</td>
<td>0.013</td>
<td>4.7 x 10⁻³</td>
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<td>0.01</td>
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<td>0.196</td>
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<td>0.011</td>
<td>4.5 x 10⁻³</td>
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<td>0.190</td>
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<td>0.184</td>
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<td>1.3 x 10⁻³</td>
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<td>0.017</td>
<td>0.184</td>
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<td>586</td>
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<td>7.89 x 10⁻³</td>
<td>0.005</td>
<td>3.9 x 10⁻³</td>
<td>4.1 x 10⁻⁷</td>
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<td>0.024</td>
<td>0.248</td>
</tr>
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<td>0.005</td>
<td>3.9 x 10⁻³</td>
<td>4.0 x 10⁻⁷</td>
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<td>6720</td>
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<td>0.001</td>
<td>0.8 x 10⁻³</td>
<td>1.0 x 10⁻⁷</td>
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<td>0.024</td>
<td>0.248</td>
</tr>
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<td>137'</td>
<td>402</td>
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<td>3.51 x 10⁻³</td>
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<td>3.9 x 10⁻³</td>
<td>4.4 x 10⁻⁷</td>
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<td>0.030</td>
<td>0.277</td>
</tr>
<tr>
<td>138'</td>
<td>402</td>
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<td>21879</td>
<td>3.51 x 10⁻³</td>
<td>0.011</td>
<td>3.9 x 10⁻³</td>
<td>4.0 x 10⁻⁷</td>
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<td>0.030</td>
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</tr>
<tr>
<td>141''</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.017</td>
<td>-</td>
<td>1.5 x 10⁻⁷</td>
<td>0.40</td>
<td>0.040</td>
<td>0.406</td>
</tr>
<tr>
<td>142''</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.017</td>
<td>-</td>
<td>1.2 x 10⁻⁷</td>
<td>0.40</td>
<td>0.040</td>
<td>0.406</td>
</tr>
</tbody>
</table>

Note:  
1. Melts * and ** are at 1300 °C and 1200 °C respectively. All other data is for 1400 °C.  
2. Overall rate constant = $\frac{1}{(1/R₁ + 1/R₂ + 1/R₃)}$  
3. Reaction driving force, D.F. = $P_{CO} \frac{A_{eq}a_{F_{2}O}}{k'_{eq}A_{eq}a_{F_{2}O}^2}$
Table 6.12  Fitted intrinsic rate constant values for the lime-containing melts at 1400 °C.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>Overall rate constant</th>
<th>D.F.</th>
<th>Predicted rate</th>
<th>Measured rate</th>
<th>a_FeO</th>
<th>a_Fe₂O₃</th>
<th>A/A₀</th>
<th>Fitted k'</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>1346</td>
<td>5363</td>
<td>44092</td>
<td>1.97 x 10⁻⁵</td>
<td>0.014</td>
<td>2.8 x 10⁻⁷</td>
<td>3.0 x 10⁻⁷</td>
<td>0.45</td>
<td>0.009</td>
<td>0.126</td>
<td>0.020</td>
</tr>
<tr>
<td>42</td>
<td>1435</td>
<td>5720</td>
<td>48991</td>
<td>1.78 x 10⁻⁵</td>
<td>0.013</td>
<td>2.8 x 10⁻⁷</td>
<td>2.8 x 10⁻⁷</td>
<td>0.45</td>
<td>0.009</td>
<td>0.126</td>
<td>0.018</td>
</tr>
<tr>
<td>46</td>
<td>1702</td>
<td>5720</td>
<td>47281</td>
<td>1.83 x 10⁻⁵</td>
<td>0.016</td>
<td>2.9 x 10⁻⁷</td>
<td>2.8 x 10⁻⁷</td>
<td>0.49</td>
<td>0.010</td>
<td>0.141</td>
<td>0.015</td>
</tr>
<tr>
<td>47</td>
<td>1596</td>
<td>5363</td>
<td>47281</td>
<td>1.84 x 10⁻⁵</td>
<td>0.016</td>
<td>2.9 x 10⁻⁷</td>
<td>2.4 x 10⁻⁷</td>
<td>0.49</td>
<td>0.010</td>
<td>0.141</td>
<td>0.015</td>
</tr>
<tr>
<td>43</td>
<td>1914</td>
<td>5363</td>
<td>28462</td>
<td>2.19 x 10⁻⁵</td>
<td>0.016</td>
<td>3.5 x 10⁻⁷</td>
<td>3.4 x 10⁻⁷</td>
<td>0.48</td>
<td>0.008</td>
<td>0.130</td>
<td>0.025</td>
</tr>
<tr>
<td>48</td>
<td>2041</td>
<td>5720</td>
<td>38462</td>
<td>2.16 x 10⁻⁵</td>
<td>0.017</td>
<td>3.7 x 10⁻⁷</td>
<td>3.8 x 10⁻⁷</td>
<td>0.48</td>
<td>0.008</td>
<td>0.130</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Note:  
(1) Overall rate constant = \( \frac{1}{(1/R₁ + 1/R₂ + 1/R₃)} \) and \( K^* = 80.7 \) at 1400 °C.  

\[
R₁ = \frac{kₙ K^* a_{Fe₂O₃}}{a_{FeO}^2} \quad \quad R₂ = \frac{1}{k₂} \quad \quad R₃ = \frac{1}{kₙ K^* A/A₀ a_{Fe₂O₃}}
\]

(3) Reaction driving force, D.F. = \( P_{CO} \frac{a_{FeO}^2}{K^* a_{Fe₂O₃}} \)
Table 6.13 Fitted intrinsic rate constant values for the lime-containing melts at 1300 °C.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>R_1</th>
<th>R_2</th>
<th>R_3</th>
<th>Overall rate constant</th>
<th>D.F.</th>
<th>Predicted rate</th>
<th>Measured rate</th>
<th>( a_{FeO} )</th>
<th>( a_{Fe_2O_3} )</th>
<th>( \frac{A}{A_o} )</th>
<th>Fitted ( k' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td></td>
<td></td>
<td></td>
<td>g/cm².s.atm</td>
<td>atm.</td>
<td>g/cm².s</td>
<td>g/cm².s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>1376</td>
<td>5763</td>
<td>58072</td>
<td>1.53 x 10⁻⁴</td>
<td>0.025</td>
<td>3.8 x 10⁻⁷</td>
<td>3.8 x 10⁻⁷</td>
<td>0.51</td>
<td>0.012</td>
<td>0.205</td>
<td>0.007</td>
</tr>
<tr>
<td>70</td>
<td>1376</td>
<td>5763</td>
<td>50813</td>
<td>1.73 x 10⁻⁵</td>
<td>0.011</td>
<td>1.9 x 10⁻⁷</td>
<td>2.1 x 10⁻⁷</td>
<td>0.51</td>
<td>0.012</td>
<td>0.205</td>
<td>0.008</td>
</tr>
<tr>
<td>67</td>
<td>1376</td>
<td>5763</td>
<td>45167</td>
<td>1.91 x 10⁻⁴</td>
<td>0.018</td>
<td>3.4 x 10⁻⁷</td>
<td>4.0 x 10⁻⁷</td>
<td>0.51</td>
<td>0.012</td>
<td>0.205</td>
<td>0.009</td>
</tr>
<tr>
<td>65</td>
<td>1320</td>
<td>5763</td>
<td>50524</td>
<td>1.74 x 10⁻⁵</td>
<td>0.019</td>
<td>3.3 x 10⁻⁷</td>
<td>3.5 x 10⁻⁷</td>
<td>0.52</td>
<td>0.013</td>
<td>0.203</td>
<td>0.0075</td>
</tr>
<tr>
<td>68</td>
<td>1320</td>
<td>5763</td>
<td>50524</td>
<td>1.74 x 10⁻⁵</td>
<td>0.019</td>
<td>3.3 x 10⁻⁷</td>
<td>3.2 x 10⁻⁷</td>
<td>0.52</td>
<td>0.013</td>
<td>0.203</td>
<td>0.0075</td>
</tr>
<tr>
<td>139</td>
<td>731</td>
<td>5763</td>
<td>31526</td>
<td>2.63 x 10⁻⁵</td>
<td>0.020</td>
<td>5.3 x 10⁻⁷</td>
<td>5.1 x 10⁻⁷</td>
<td>0.48</td>
<td>0.020</td>
<td>0.244</td>
<td>0.0065</td>
</tr>
</tbody>
</table>

Note:  
1. Equilibrium constant, \( K^e = 90.8 \) at 1300 °C.  
2. Reaction driving force, D.F. = \( P_{CO} = \frac{P_{CO_2} a_{FeO}^2}{K^e a_{Fe_2O_3}} \)  
3. \( k_g \) (cm/s) = 8067.5 x (\( k_g \) in g/cm².s.atm)
Table 6.14 Fitted intrinsic rate constant values for the lime-containing melts at 1200 °C.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>Overall rate constant</th>
<th>D.F.</th>
<th>Predicted rate</th>
<th>Measured rate</th>
<th>$a_{FeO}$</th>
<th>$a_{Fe_2O_3}$</th>
<th>$A/A_s$</th>
<th>Fitted $k_i^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td></td>
<td></td>
<td></td>
<td>g/cm².s.atm</td>
<td>atm.</td>
<td>g/cm².s</td>
<td>g/cm².s</td>
<td></td>
<td></td>
<td></td>
<td>g/cm².s.atm</td>
</tr>
<tr>
<td>54</td>
<td>1031</td>
<td>6296</td>
<td>68376</td>
<td>$1.32 \times 10^{-3}$</td>
<td>0.010</td>
<td>$1.3 \times 10^{-7}$</td>
<td>$1.7 \times 10^{-7}$</td>
<td>0.42</td>
<td>0.013</td>
<td>0.225</td>
<td>0.005</td>
</tr>
<tr>
<td>108</td>
<td>1031</td>
<td>6296</td>
<td>68376</td>
<td>$1.32 \times 10^{-3}$</td>
<td>0.012</td>
<td>$1.6 \times 10^{-7}$</td>
<td>$2.0 \times 10^{-7}$</td>
<td>0.42</td>
<td>0.013</td>
<td>0.225</td>
<td>0.005</td>
</tr>
<tr>
<td>52A</td>
<td>1031</td>
<td>6296</td>
<td>85470</td>
<td>$1.08 \times 10^{-3}$</td>
<td>0.023</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$2.5 \times 10^{-7}$</td>
<td>0.42</td>
<td>0.013</td>
<td>0.225</td>
<td>0.004</td>
</tr>
<tr>
<td>63</td>
<td>1031</td>
<td>6296</td>
<td>85470</td>
<td>$1.08 \times 10^{-3}$</td>
<td>0.034</td>
<td>$3.7 \times 10^{-7}$</td>
<td>$3.5 \times 10^{-7}$</td>
<td>0.42</td>
<td>0.013</td>
<td>0.225</td>
<td>0.004</td>
</tr>
<tr>
<td>53</td>
<td>1031</td>
<td>6296</td>
<td>68376</td>
<td>$1.32 \times 10^{-3}$</td>
<td>0.018</td>
<td>$2.4 \times 10^{-7}$</td>
<td>$2.2 \times 10^{-7}$</td>
<td>0.42</td>
<td>0.013</td>
<td>0.225</td>
<td>0.005</td>
</tr>
<tr>
<td>55</td>
<td>1549</td>
<td>6296</td>
<td>78709</td>
<td>$1.16 \times 10^{-3}$</td>
<td>0.018</td>
<td>$2.1 \times 10^{-7}$</td>
<td>$2.1 \times 10^{-7}$</td>
<td>0.53</td>
<td>0.011</td>
<td>0.231</td>
<td>0.005</td>
</tr>
<tr>
<td>105</td>
<td>1549</td>
<td>6296</td>
<td>78709</td>
<td>$1.16 \times 10^{-3}$</td>
<td>0.016</td>
<td>$1.8 \times 10^{-7}$</td>
<td>$2.1 \times 10^{-7}$</td>
<td>0.53</td>
<td>0.011</td>
<td>0.231</td>
<td>0.005</td>
</tr>
<tr>
<td>56</td>
<td>1549</td>
<td>6296</td>
<td>78709</td>
<td>$1.16 \times 10^{-3}$</td>
<td>0.025</td>
<td>$2.9 \times 10^{-7}$</td>
<td>$2.8 \times 10^{-7}$</td>
<td>0.53</td>
<td>0.011</td>
<td>0.231</td>
<td>0.005</td>
</tr>
<tr>
<td>57</td>
<td>1120</td>
<td>6296</td>
<td>78174</td>
<td>$1.17 \times 10^{-3}$</td>
<td>0.021</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$2.3 \times 10^{-7}$</td>
<td>0.49</td>
<td>0.013</td>
<td>0.246</td>
<td>0.004</td>
</tr>
<tr>
<td>58</td>
<td>1120</td>
<td>6296</td>
<td>104232</td>
<td>$0.9 \times 10^{-3}$</td>
<td>0.026</td>
<td>$2.3 \times 10^{-7}$</td>
<td>$2.1 \times 10^{-7}$</td>
<td>0.49</td>
<td>0.013</td>
<td>0.246</td>
<td>0.003</td>
</tr>
<tr>
<td>107</td>
<td>1120</td>
<td>6296</td>
<td>62539</td>
<td>$1.43 \times 10^{-3}$</td>
<td>0.014</td>
<td>$2.0 \times 10^{-7}$</td>
<td>$2.0 \times 10^{-7}$</td>
<td>0.49</td>
<td>0.013</td>
<td>0.246</td>
<td>0.005</td>
</tr>
<tr>
<td>59</td>
<td>2211</td>
<td>6296</td>
<td>155473</td>
<td>$0.61 \times 10^{-3}$</td>
<td>0.022</td>
<td>$1.3 \times 10^{-7}$</td>
<td>$1.3 \times 10^{-7}$</td>
<td>0.54</td>
<td>0.008</td>
<td>0.201</td>
<td>0.004</td>
</tr>
<tr>
<td>60</td>
<td>1578</td>
<td>6296</td>
<td>170940</td>
<td>$0.56 \times 10^{-3}$</td>
<td>0.024</td>
<td>$1.3 \times 10^{-7}$</td>
<td>$1.1 \times 10^{-7}$</td>
<td>0.51</td>
<td>0.010</td>
<td>0.195</td>
<td>0.003</td>
</tr>
<tr>
<td>61</td>
<td>1578</td>
<td>6296</td>
<td>170940</td>
<td>$0.56 \times 10^{-3}$</td>
<td>0.024</td>
<td>$1.3 \times 10^{-7}$</td>
<td>$1.0 \times 10^{-7}$</td>
<td>0.51</td>
<td>0.010</td>
<td>0.195</td>
<td>0.003</td>
</tr>
<tr>
<td>143</td>
<td>611</td>
<td>6296</td>
<td>33300</td>
<td>$2.49 \times 10^{-3}$</td>
<td>0.019</td>
<td>$4.7 \times 10^{-7}$</td>
<td>$4.6 \times 10^{-7}$</td>
<td>0.46</td>
<td>0.021</td>
<td>0.286</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Note:
(1) Equilibrium constant, $K^e = 103.8$ at 1200 °C.

(2) Reaction driving force, D.F. = $P_{CO} \cdot \frac{a_{FeO}^2}{k_i^* \cdot a_{Fe_2O_3}}$

(3) $k_i$ (cm/s) = 7554.6 x ($k_i$ in g/cm².s.atm); $k_i$ in (cm/s) is derived using equation (5.5).
Tables 6.12, 6.13 and 6.14 list the data on lime-containing melts at 1400 °C, 1300 °C and 1200 °C respectively. It can be seen from the information in these tables that the fitted $k_c$ values range from 0.015 to 0.02 at 1400 °C, whereas a lower value of 0.007 represents the melts at 1300 °C. For a reaction temperature of 1200 °C the rate constant values range between 0.003 and 0.005 g/cm$^2$·s·atm. Since the ferric oxide reduction reaction is same for all the melts at three reaction temperatures, one expects a single value for the intrinsic rate constant at each temperature. Based on the measured data the reaction rate constant values of 0.025, 0.0075 and 0.004 are proposed for the 1400 °C, 1300 °C and 1200 °C temperatures respectively.

### 6.2.1.2.2 Calculation of apparent activation energy of chemical reaction

From the knowledge of intrinsic rate constants at three reaction temperatures the apparent activation energy value of about 44,500 cal/mole was derived for the ferric-to-ferrous reduction reaction. Comparison of activation energy values for the ferrous-to-iron and ferric-to-ferrous reactions reveal a relatively lower value (~ 28,000 cal/mole) for the former. This difference suggests that perhaps the reaction mechanisms involved in these two reduction reactions are different. Arrhenius plot obtained for the ferric-to-ferrous reaction is shown in Figure 6.13.

### 6.2.1.2.3 Calculation of $k_L$

In equation (6.49) all the parameters except $k_L$ are known and therefore by choosing appropriate values for this parameter the weight loss data were fitted. From this information weight-time plots were prepared for all the melts studied. As an illustration, several examples are shown in Figures 6.14 - 6.17. A trend of decreasing rate with time is evident in all these plots. The individual plots also show that for the initial reduction period (of approximately 3000 seconds) the rate does not vary much.

The fitted $k_L$ values obtained for the lime-free and lime-containing melts at three reaction temperatures are listed in Table 6.15. The data reveals the highest values of about $2 \times 10^4$ and $1 \times 10^4$ cm/s for the lime-containing and lime-free melts respectively at 1400 °C. With decreasing temperature lower values were obtained.
Figure 6.13  Arrhenius plot of $\ln k_e$ versus $1/T$ for the ferric-to-ferrous reaction.

Arrhenius plot of $\ln k_e$ versus $1/T$

Ferric-to-ferrous reaction study

Apparent activation energy of reaction 44.5 kcal/mol
Figure 6.14 Weight loss data for the ferric-to-ferrous reaction study at 1400 °C in lime-free melts (FeO-SiO2-Al2O3 system) (a) 6.5 mole% silica; (b) 16.6 mole% silica; (c) 25.7 mole% silica and (d) 31.3 mole% silica.
Figure 6.15  Weight loss data for the ferric-to-ferrous study in lime-containing melts (Fe$_2$O$_3$-SiO$_2$-CaO-Al$_2$O$_3$ system) at 1400 °C (a) molar ratio 1.5, (b) molar ratio 1.9 and (c) molar ratio 1.8.
Figure 6.16 Weight loss data for the ferric-to-ferrous study in lime-containing melts at 1300 °C (a) molar ratio 1.8, (b) molar ratio 1.9 and (c) molar ratio 1.8.
Figure 6.17 Weight loss data for the ferric-to-ferrous study in lime-containing melts $(Fe^3+/\Sigma Fe = 0.15)$ at 1200 °C (a) molar ratio 1.5, (b) molar ratio 1.9 and (c) molar ratio 1.8.
Table 6.15 Derived values of the liquid phase mass transfer coefficients and diffusivity for the melts at three temperatures.

<table>
<thead>
<tr>
<th>Melt type</th>
<th>( \frac{Fe^{3+}}{\Sigma Fe} )</th>
<th>Temp.</th>
<th>Fitted ( k_L )</th>
<th>( D_L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime-free melts</td>
<td>0.15-0.2</td>
<td>1400</td>
<td>( \sim 1 \times 10^4 )</td>
<td>( \sim 5 \times 10^6 )</td>
</tr>
<tr>
<td>Fe(_2)O-SiO(_2) -Al(_2)O(_3)</td>
<td>0.23</td>
<td>1300</td>
<td>( \sim 2 \times 10^5 )</td>
<td>( \sim 1 \times 10^6 )</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>1200</td>
<td>( \sim 2 \times 10^6 )</td>
<td>( \sim 1 \times 10^7 )</td>
</tr>
<tr>
<td>Lime-containing melts</td>
<td>0.15</td>
<td>1400</td>
<td>( \sim 2 \times 10^4 )</td>
<td>( \sim 1 \times 10^5 )</td>
</tr>
<tr>
<td>Fe(_2)O-SiO(_2) -CaO-Al(_2)O(_3)</td>
<td>0.15-0.2</td>
<td>1300</td>
<td>( \sim 7 \times 10^5 )</td>
<td>( \sim 3.5 \times 10^5 )</td>
</tr>
<tr>
<td></td>
<td>0.1-0.2</td>
<td>1200</td>
<td>( \sim 2 \times 10^5 )</td>
<td>( \sim 1 \times 10^6 )</td>
</tr>
</tbody>
</table>

Note: Diffusivity values are calculated using equation (6.1) and assuming boundary layer thickness of 500 \( \mu m \).
Another important feature emerges from the data in this table. It shows that for a fixed reaction temperature the lime-containing melts have a relatively higher $k_L$ value when compared to the lime-free melts. Further comparison reveals that this discrepancy widens at lower temperatures. The ratio of $k_L$ values (i.e. $k_L$ for lime-containing melts to the lime-free melts) at 1200 °C is 10 whereas the corresponding value for the melts at 1400 °C is about 2. The variations in $k_L$ imply that perhaps the melt diffusivity values also change in a similar manner.

6.2.1.2.4 Estimation of diffusivity data

Diffusivity values were determined using equation (6.1) i.e.

$$k_L = \frac{D_{O^{2-}}}{\delta_t}$$  \hspace{1cm} (6.1)

where $\delta_t$ is the boundary layer thickness in the melt. An estimated thickness of this layer is approximately 500 μm from the Mössbauer spectroscopic analysis of the slag melts discussed in Chapter 7. It was assumed that oxygen anions move to and away from the reaction site. The proposed diffusivity data for both the lime-free and lime-containing melts are listed in Table 6.15. A consistent trend of decreasing diffusivity values with decreasing temperatures is evident from this information. Furthermore the estimated diffusivity value of $\sim 5 \times 10^{-6}$ cm$^2$/s at 1400 °C for the lime-free melts agrees well with the value estimated using Sutherland equation (Table 6.3).

One striking feature of the diffusivity data is that the values for lime-containing melts are higher than those for lime-free melts. Such a comparison clearly highlights the effect of lime on enhancing the diffusivities of species in the melts. Sasabe and Asamura [109] have reported similar finding based on their oxygen transport study in molten slags using electrochemical technique.
With the knowledge of the melt \( k_L \) values at three temperatures activation energy plot of \( \ln D \) against reciprocal temperature was constructed for lime-containing melts and this is illustrated in Figure 6.18. A similar plot was not constructed for lime-free melts because only limited low temperature data was available for these melts. However, rough calculations showed that the apparent activation energy for diffusion in lime-free melts was \( \sim 96 \) kcal/mole. Indeed, this is not a reliable value but all the same it does show a trend in the right direction. The corresponding value for the lime-containing melts is about 53 kcal/mole. This value is in excellent agreement with that reported by Sasabe and Asamura [109]. For the diffusion of \( O^{2-} \) anions the authors report the apparent activation energy value of 56 kcal/mole.

### 6.2.2 Reaction mechanism

In the proposed scheme the ionic melt consists of silicate, aluminate, ferric and oxygen anions and ferrous (Fe\(^{2+}\)) and calcium (Ca\(^{2+}\)) cations. Due to the amphoteric nature of both ferric oxide and alumina species however, the presence of Fe\(^{3+}\) and Al\(^{3+}\) can not be ruled out. At the gas-melt interface the carbon monoxide reacts with the ferric anions to produce Fe\(^{2+}\) as per the following:

\[
FeO_3^{2-} + CO = Fe^{2+} + 2O^{2-} + CO_2 + e^- \quad (6.55)
\]

\[
FeO_3^{2-} + e^- = Fe^{2+} + 3O^{2-} \quad (6.56)
\]

The observed slowing down of the rate with time is attributed primarily to the decrease in the bulk ferric oxide concentration and the accompanying structural and compositional changes in the boundary layer (top 500 \( \mu \)m) region in the melt. In addition to above reactions the charge transfer reaction as proposed by Belton [80] will take place. However, due to the amphoteric nature of ferric oxide species and in general due to the ionic constitution of slags it is very difficult to view a reaction mechanism in a particular context and therefore the possibilities of other co-existing mechanisms cannot be ruled out.
Arrhenius plot of $\ln k_L$ versus $1/T$

**Ferric-to-ferrous reaction study**

Apparent activation energy of diffusion 53 kcal/mol

Figure 6.18 Arrhenius plot for determination of the activation energy for diffusion, $E_a$. 

$$1/T \text{ K}^{-1}$$

$$\ln k_L \text{ mole/cm}^2\text{s.atm}$$
According to the proposed scheme the ferric-to-ferrous reaction involves breakdown (or dissociation) of ferric anions but it is likely that in addition the restructuring of anions may take place as per the following:

\[ 2\text{Fe}_2\text{O}_3^{4-} + \text{CO} = 2\text{FeO}_3^{3-} + 2\text{Fe}^{2+} + 3\text{O}^{2-} + \text{CO}_2 \]  

(6.57)

Richardson [130] has suggested the following reaction in ternary silicate melts

\[ \text{Ca}_2\text{SiO}_4 + \text{Fe}_2\text{SiO}_4 = 2\text{CaSiO}_3 + 2\text{FeO} \]  

(6.58)

to explain the positive deviation of \( a_{\text{FeO}} \) in these melts. This reaction indicates the occurrence of a change in the anionic configuration of silica. Therefore, it is not unrealistic to extend the similar concept to the changes in ferric anion configuration.

Gaskell et al. [110] have proposed 'discrete ion theory' to explain their density data in silicate melts. According to the theory, in the liquid state the extent of polymerization in orthosilicate compositions is governed by the relative energetics of \( \text{M}^{2+} - \text{O}^{2-} \) and \( \text{M}^{2+} - \text{O}^{-} \) associations. Since the \( \text{O}^{2-}/\text{O}^{-} \) ratio in the iron silicates is greater than the corresponding calcium silicate, when \( \text{Fe}^{2+} \) ions are replaced by \( \text{Ca}^{2+} \) the latter cations attempt to decrease the \( \text{O}^{2-}/\text{O}^{-} \) ratio in their coordination and in so doing cause a depolymerization of silicate anions in the vicinity. According to this scheme the \( \text{Ca}^{2+} \) ions associate preferably with the silicate anions whereas the \( \text{Fe}^{2+} \) cations preferably associate with decreasing number of free oxygen ions. This preferred ionic association introduces an element of microheterogeneity in the melt structure. It is possible that the behaviour of ferric anions follows that of silicate anions as per the above scheme and therefore proposed reaction (6.57) is likely in lime-containing melts. Additional evidence in support of this finding can be obtained from the work of Chipman and Chang [111].

6.3 Comparison with previous work

In the foregoing paragraphs the data obtained in this work was critically analyzed to develop an understanding of two complex reduction reactions. In order to derive additional benefits from the generated information the data obtained is compared with the work of Nagasaka et al. [56]
Some of the common features of the two investigations are: (1) the ferrous-to-iron reaction was studied primarily at 1400 °C; (2) carbon monoxide-containing gas mixtures were employed for promoting the chemical reaction and thermogravimetry technique was used; (3) a wide range of slag compositions were chosen to identify the effects of acidic and basic oxide species; and (4) limited low temperature work was undertaken to calculate apparent activation energy of the chemical reaction. The important points that emerged from the work of Nagasaka et al. were: (1) lime addition to the FeO melts led to higher rates; (2) the ferric content of the melt exceedingly influenced the rate; (3) the values of composition-dependent apparent rate constant increased with the melt lime and ferric contents and (4) the apparent activation energy of chemical reaction is 33 kcal/mol. The present work suggests an apparent activation energy value of 28 kcal/mole and the data clearly highlights the rate enhancement due to the increased ferric proportion. Both studies showed that the silica additions lowered the rates. In terms of the lime effect however, the conclusion of the present work is at variance with that of Nagasaka et al.

It is possible to explain an important observation made by Nagasaka et al. concerning the rate enhancement due to higher ferric levels in the melts in the light of the new information generated in this work. Since the intrinsic rate constant of the ferric-to-ferrous reaction is much greater than the one for the ferrous-to-iron reaction, the variations in the apparent rate constants as observed by Nagasaka et al. can be explained by assuming the concurrent ferric-ferrous reaction. To demonstrate this the following procedure is employed:

1. apparent rate constant, \( k_a \) values for two melt compositions - one pseudo-binary (FeO-CaO) and the other pseudo-ternary (FeO-CaO-SiO\(_2\)) are obtained from the rate versus driving force plot provided by Nagasaka et al.

2. by employing gas + reaction model developed in this work and a knowledge of gas and melt compositions rates are predicted assuming the ferric-to-ferrous reaction.

3. apparent rate constant values are predicted from the above data i.e. \( k_a (predicted) = predicted \ rate / D.F. (asperNagasaka) \); and

4. the predicted \( k_a \) values are compared with those reported by Nagasaka et al.
The results obtained are listed in Table 6.16. Agreement between the two sets of apparent rate constants supports the hypothesis on the concurrent ferric-to-ferrous reaction. To further highlight the above fact and the accuracy of the gas + reaction model predictions, the predicted $k_a$ data for various melt compositions is superimposed on the $k_a$ versus ferric/ferrous relation given by Nagasaka et al. (Figure 6.19).

One important feature of the gas + reaction model proposed in this work is that it clearly identifies the components of the gas and reaction resistances. Thus, it is possible to factor out the gas phase contribution and look closely at the remaining term mentioned in equation 6.31 i.e.

$$k_a = k_c \frac{A}{A_o} \cdot a_{FeO}$$

(6.31)

which essentially describes the nature of the apparent rate constant for the ferrous oxide melts ($Fe^{3+}/\Sigma Fe < 0.05$). By mathematical manipulation one can remove the activity component from this term and incorporate the same in the driving force term. Thus the effect of melt composition on the rate can be represented by either rate constant or driving force terms. Nagasaka et al. chose the former method, however the authors account for the activity contribution by the empirical relation in terms of a complex ferric/ferrous ratio.

The concept of the apparent rate constant can be extended to include the ferric-to-ferrous reaction for which the following expression can be written in absence of gas and liquid phase resistances.

$$k_a = k_c \cdot A \cdot a_{FeO}$$

(6.59)

Confirmation on equations (6.31) and (6.59) proposed above can be obtained by comparison of $k_a$ values reported by Nagasaka et al. and those predicted using these equations. This is illustrated in Table 6.16 and Figure 6.19.
Table 6.16  Comparison of predicted and reported $k_\text{r}$ data for the pseudo-binary and pseudo-ternary melts at 1400 °C.

<table>
<thead>
<tr>
<th>Melt composition, wt%</th>
<th>Gas composition, atm</th>
<th>D.F.*</th>
<th>Apparent rate constant, $k_\text{r}$, g/cm².s.atm</th>
<th>Reduction rate, g/cm².s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{CO}$</td>
<td>$P_{CO_2}$</td>
<td>atm.</td>
<td>Nagasaka</td>
</tr>
<tr>
<td>FeO Fe₂O₃ CaO SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67.8 10.2 22.0 -</td>
<td>0.168</td>
<td>0.04</td>
<td>0.0027</td>
<td>$10 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.294</td>
<td>0.07</td>
<td>0.005</td>
<td>$8.0 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.336</td>
<td>0.08</td>
<td>0.006</td>
<td>$8.3 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.461</td>
<td>0.11</td>
<td>0.007</td>
<td>$9.3 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.798</td>
<td>0.19</td>
<td>0.013</td>
<td>$10 \times 10^{-4}$</td>
</tr>
<tr>
<td>58.0 20.5 14.0 7.5</td>
<td>0.0073</td>
<td>0.0015</td>
<td>0.0011</td>
<td>$3.6 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.011</td>
<td>0.0022</td>
<td>0.002</td>
<td>$3.5 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.0347</td>
<td>0.007</td>
<td>0.0058</td>
<td>$3.4 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
<td>$3.3 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.106</td>
<td>0.02</td>
<td>0.023</td>
<td>$2.7 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.257</td>
<td>0.05</td>
<td>0.05</td>
<td>$3.0 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Note:  
(1) * Nagasaka et al. define reaction driving force, D.F. and $k_\text{r}$ as follows  
\[ D.F. = P_{CO} \frac{r_{CO_2}}{0_{342}} \text{ and } k_\text{r} = \frac{\text{observed rate}}{D.F.}. \]  
(2) Rate data is predicted using gas + reaction model and assuming concurrent ferric-to-ferrous reaction.  
(3) $k_\text{r}$ (predicted) = predicted rate/D.F.
Figure 6.19 Empirical relationship between $k_a$ and ferric content for various melts (as per Nagasaka et al. 56). Predicted $k_a$ values using the model in this work are shown in the figure for comparison.
Rahaiby et al. [34] introduced \( k_0^o \) as a temperature dependent constant to explain the observed variations in \( k_\alpha \) and developed an expression relating the two constants. (equation 2.15) The authors noted that \( k_0^o \) values decreased with increasing additions of silica and to accommodate such behaviour they provide 4 separate equations relating \( k_0^o \) and temperature for four melt compositions (with varying silica). Sasaki et al. [68] have extended a similar concept to the lime ferrite melts and derived different relation between \( k_0^o \) and temperature. However, according to the authors the equation is based on an overall scatter of about ± 60 pct. It would appear that so far there has been no successful attempt made to explain the fundamental reasons for the observed variations in the apparent rate constant. With the help of the proposed relations (equations 6.31 and 6.59) between \( k_\alpha \) and other parameters like intrinsic rate constant (\( k_c \) and \( k_\alpha^c \)), fractional coverage parameter (A/A_\alpha) and the activity of the reactant component in the liquid phase it is easier to appreciate the basis for the observed trends in the \( k_\alpha \) values.

Belton [80] reproduced the \( k_\alpha \) versus ferric/ferrous plot reported by Nagasaka et al. (i.e. Figure 6.19) wherein the author has shown the location of Fe_2O-P_2O_5 melts relative to the line. All the points representing these melts lie considerably below the regression line and this fact clearly implied that the points did not conform to the empirical relation proposed by Nagasaka et al. Belton agrees that the behaviour is explicable in terms of a surface coverage model similar to that proposed in the present work. However, the author has proposed an alternate model as an explanation for the observed phenomenon. Pal et al. [101] also noted that additions of P_2O_5 to lead silicate melts caused a significant decrease in the rate of reduction by H_2. The depression of the rate was attributed to surface active phosphate groups. It is an accepted fact that silica is surface active in ferrous oxide melts and therefore the surface coverage explanation can be advanced for the results obtained by Nagasaka et al.

Based on the knowledge gained in the present work it is suggested that the lower \( k_\alpha \) values result from the lower activity and A/A_\alpha values. (equations 6.31 and 6.59) In this context, it is particularly interesting to examine critically the relative location of all the data points on the
regression line in Figure 6.19. The data points for the pseudo-binary Fe₂O-CaO melts are clearly above the line indicating high kₙ values for these melts. Thus the trend is obvious - basic melts lie above the line and the acidic melts (containing surface active species) below the line. It is not unrealistic to extend the analogy to characterize the location of the melts containing higher lime-to-silica ratio with respect to those containing lower ratios. Although, the distinction is not as obvious as previous two cases (i.e CaO and P₂O₅ containing melts) one can place the relatively basic melts above the line and the others below the line without much ambiguity. What this analysis implies is that the composition-dependent apparent rate constant is sensitive to the relative proportions of acidic and basic oxides in the melts and this observed behaviour is explicable using equations (6.31) and (6.59) proposed in this work.

Figure 6.19 shows that kₙ increases with increasing Fe³⁺/Fe²⁺ ratio. Based on the work of Nagasaka et al. alone it is very difficult to identify the role played by the individual oxide species on the apparent rate constant. For example, from the location of pseudo-binary Fe₂O-CaO melts it is not possible to confirm whether the higher kₙ values are due either to higher ferric level or higher lime content or both. However, from equations (6.31) and (6.59) one can appreciate the relative significance of individual oxide species on the values of the apparent rate constant.

Tsukihashi et al. [55] and Kato et al. [54] studied molten iron oxide (Fe₂O) reduction at 1600 °C using pure CO gas. However, both groups report substantially different values for the intrinsic rate constant, kₑ. The former group proposed a value of about 20 cm/s whereas the latter group reported the value as 1350 cm/s. Since it was observed in the present work that at 1400 °C the intrinsic rate constant value of Fe³⁺ → Fe²⁺ reaction was approximately 200 times greater than the Fe²⁺ → Fe reaction it can be inferred that perhaps Kato et al. recorded the kₑ value for the ferric-ferrous reaction (referred to in this work as kₑ). Such possibility cannot be overlooked especially if, for any reason, their melts were oxidized prior to the reduction period.

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Based on the data obtained in this work following expression can be derived for predicting the intrinsic rate constant of the ferric-to-ferrous reaction

\[ k_e^* = 933 \cdot \exp\left(-\frac{44500}{RT}\right) \quad (6.60) \]

Using equation (6.60) a \( k_e^* \) value of 920 cm/s was obtained which is somewhat closer to the value reported by Kato et al. This calculation implies that for the ferrous-to-iron reaction the \( k_e \) value reported by Tsukihashi et al. is more accurate than the value proposed by Kato et al.

While studying the ferrous-to-iron reaction in the present work a bulk of the data was obtained at 1400 °C and only a few experiments were performed at lower temperatures and therefore an expression similar to the above cannot be constructed exclusively on the generated data. However, by combining the apparent activation energy reported by Nagasaka et al. [56] and the \( k_e \) value \((6.875 \times 10^{-6} \text{ mole/cm}^2\cdot\text{s.atm})\) obtained in this work at 1400 °C it is possible to derive the value of the pre-exponential constant, \( a \), in the following

\[ k_e = a \cdot \exp\left(-\frac{33000}{RT}\right) \quad (6.61) \]

and develop another expression similar to equation (6.60). Simple calculation yields the value of \( a \) as 0.14 and in turn its substitution in equation (6.61) yields

\[ k_e = (0.14) \cdot \exp\left(-\frac{33000}{RT}\right) \quad (6.62) \]

The \( k_e \) value of about \( 2 \times 10^{-5} \) is predicted for 1600 °C melts using the above equation. This agrees reasonably well with the reported value of \( 4.2 \times 10^{-5} \) by Kim et al. [66] The predicted value converts to about 3 cm/s and this is much closer to the value of 20 cm/s proposed by Tsukihashi et al. [55] It may be recalled here that the \( k_e \) value of 1350 cm/s was reported by Kato et al. [54] at the same temperature.
An important point that emerges from the above discussion concerns the accuracy of the available data on intrinsic rate constants. Due to the nature of slag melts it is very difficult to study the ferrous-to-iron reaction in isolation by eliminating the ferric-to-ferrous reaction. To a degree the latter reaction is unavoidable in the ferrous reduction studies. Therefore, based on the knowledge gained in the present work it is proposed that the extent of the Fe$^{3+} \rightarrow$ Fe$^{2+}$ reaction would dictate the accuracy of both intrinsic rate constant and apparent rate constant values in any investigation.

Belton et al. [80,34,68] have proposed a charge transfer model for the redox reaction involving ferric and ferrous species. (equation 6.33) Upon close scrutiny of their concept concerning the negatively charged CO$_2$ molecule (CO$_2^-$) it appears that the authors are referring to a "gaseous anion species" at the interface. The dissociation of CO$_2^-$ molecule produces O$^-$ anion and CO molecule (equation 6.34) and according to the authors this is the rate determining step. As an aide to the data interpretation they introduce another temperature and composition dependent constant and propose the following empirical relation

\[
 k_a = \frac{k_a^o}{(a_o)^{-1}} \quad (6.63)
\]

where $a_o$ is the oxygen activity expressed either as $P_{CO}/P_{CO}$ or Fe$^{3+}$/Fe$^{2+}$ ratio. It is felt that in their analysis the authors are referring indirectly to some 'special' O$^-$ anions at the surface that can take part in the reaction. For example, the oxygen anions surrounding Si$^{4+}$ cannot take part in the reaction and so also those surrounding the phosphorus species (i.e. phosphate ions), if present, in the melt. In general, the acidic and surface active species do not release oxygen and this leads to lower rates. The lower $k_a^o$ reported by Belton et al. are in all probability result from the decreased availability of O$^-$ anions. By corollary, one expects higher rate due to the increased availability of reactive O$^2$. Perhaps the comments made by Nagasaka et al. concerning the influence of melt ferric level on the rates can be viewed in this perspective. The O/Fe ratio of ferric oxide is high. Moreover, the species is surface active and therefore the number of special
$O^2-$ is increased and this causes higher rates. While Belton et al. view co-existence of $O^2-$ and CO (as $CO_2^-$) species in their model, in the present work the ferric, ferrous and other cation species are assumed to co-exist with the $O^2-$ anions.

In either of the above schemes the common and perhaps the most important parameter is the number of special $O^2-$ anions at the interface. Any variation in this number would manifest either as a change in the surface electrochemical potential or a change in the fractional coverage parameter $(A/A_o)$ which essentially is a different perspective of the same phenomenon. Alternately, the changes in either the surface electrochemical potential or the fractional coverage parameters can be viewed as different consequences of the same phenomena, namely - minimization of the surface free energy. Indeed, it is a very difficult task to visualize what is going on at the gas-slag interface and perhaps there are other alternate ways to view the interfacial phenomenon.

However, with the technique of analysis proposed in this thesis it is easier to appreciate the reasons behind the observed variations in the apparent rate constants. For example, Belton et al. report several different expressions for the calculation of $k^e_a$ and additionally they note that the simple inverse relationship between $k_a$ and $k^e_a$ does not hold for various melts. The authors have reported large variations in $k^e_a$ with the slag basicity ratio and the melt ferric levels. Based on the knowledge gained in this work an explanation for such behaviour can be proposed using the following expression

$$k^e_a = k^*_e \cdot \frac{A}{A_o} \cdot (a_{FeO})^2$$

(6.64)

where $k^e_a$ is the apparent rate constant used by Belton et al. (for ferrous-to-ferric reaction) and $k^*_e$ is the intrinsic rate constant for the oxidation reaction. Due to silica additions the values of $A/A_o$ and $a_{FeO}$ will be lowered and this would result in the lower $k^e_a$ values. In the lime and silica containing melts the apparent rate constant values will be lowered for the same reason. In the lime-saturated melts the reported $k^e_a$ values are about 10 times greater than the one for pure...
ferrous oxide melt. Explanation for this behaviour is not available in the literature however, based on the proposed equation (6.64) one can speculate that the result is attributable either to the higher \( k^* \) or the higher \( A/A_c \) value or the combination of both. It can be postulated that the presence of ferric anions leads to the higher \( k^* \) or the addition of lime increases the active sites at which \( CO_2 \) can be adsorbed. The latter possibility has been postulated earlier by Strachan and Grieveson [32] and this implies increase in the \( A/A_c \) ratio in equation (6.64).

The model presented in this work is consistent with the accepted behaviour of various surface active species and it accounts for the amphoteric nature of ferric oxide species. Thus, the existence of both Fe\(^{3+}\) cations and ferric anions is favored in the slag melts in agreement with the published data [96,112,102,113]. In the reactions studied in this work the presence of charge transfer reaction cannot be denied however, the data suggests additional rate determining steps. What emerges from this study is that the behaviour of iron oxide containing melts during reduction and oxidation study is very complex and depends critically on melt composition. The interaction of surface activity effects with the transport of oxygen in the melt, as \( O^2- \) and ferric anions, can lead to quite different processes. It is quite clear that a quantitative understanding of the process must take these factors into account.

### 6.4 Consequences of the results to slag fuming kinetics

Previous work by Richards et al. [9] has shown zinc slag fuming to be kinetically controlled by two basic processes: the rate of coal entrainment in the slag and the rate of oxidation of ferrous-to-ferric iron by injected air. Based on their comprehensive in-plant measurements and subsequent mathematical analysis the authors developed a coal particle-slag reaction model and concluded that an increase in process efficiency would result from increasing the coal entrainment or reducing the oxidation of ferrous iron.

In the subsequent trials Cockroft et al. [114] observed that using a high-pressure pneumatic delivery system the coal entrainment can be increased and the phenomenon led to higher fuming rates. To accommodate this change a new parameter, \( F_{HPCE} \), the fraction of high pressure coal
entrained in the slag, was added to the kinetic model of Richards et al. [9] Moreover, to obtain best agreement between the measured and predicted data the 'slag circulation velocity', $V_{slag}$, was increased 3-fold from the original value of 1 m/s.

Based on the present thesis further modifications to the kinetic model are suggested. Since the experimental work has clearly identified the role of surface blockage by the non-reactant species, it is important to account for this effect in the model. In addition, in view of the derived oxygen anion diffusivity data changes in the "ferric oxide" diffusivity values are proposed in the original model. The effect of both these factors, especially the latter is to substantially change the nature of the coal particle-slag reaction. As a result, the present work has prompted reassessment of three important parameters in the kinetic model, namely - fraction of oxygen oxidizing ferrous-to-ferric iron, $F_{oc}$ (i.e. oxygen utilization), fraction of coal combusted in the tuyere zone, $Y$ and slag circulation velocity, $V_{slag}$. 
Chapter 7
Mössbauer spectroscopy

7.1 Introduction

Mössbauer spectroscopy is a well known technique for studying the structure of disordered materials. Since 1962, chemists have made use of this technique in their study of chemical bonding, crystal structure, electron density, ionic states and magnetic properties. Metallurgists, however, have only recently appreciated the potential importance of this technique and as a result very limited data is available on the Mössbauer analysis of slags. [98-99]

Previous Mössbauer studies have focussed primarily on the bulk properties of the material, and questions such as how the coordination and oxidation state of the iron may vary spatially within a sample have not been addressed. The present research was initiated to look at the spatial variation of Mössbauer spectral parameters under conditions in which differences between the surface and bulk melt compositions are expected. A technique was developed to study ferric and ferrous cation distribution across the melt depth with a spatial resolution of approximately 500 μm.

7.1.1 Sampling of high temperature phases

Mössbauer spectroscopy works the same no matter if the phase is glassy or crystalline and therefore it serves as a means of identifying coordination of iron cations in either cases. R.D. Jones [115] in his review paper mentions several publications that have employed this technique to identify various phases in the iron-carbon alloys. However because the measurements are done on solid samples the information obtained this way is only useful if it is assumed that the high temperature melt structure is preserved during quenching. The validity of this assumption is normally tested by characterizing crystallization in the individual samples using techniques like XRD, optical microscopy and TEM. In the present work two former methods were employed and the results obtained implied that there was minimal crystallization or segregation occuring during quenching process.
The fact that in four out of eight samples a crystalline phase (iron or magnetite) was present as a result of reaction under study prevented a firm conclusion from being drawn regarding crystallization during quenching. However we believe that our assumption of minimum crystallization during quenching is valid because of the shallow melt depths (3 - 4 mm) and a short quench time not exceeding 15 seconds. Of the 4 remaining samples (experiments away from Fe and Fe$_3$O$_4$ saturation) in 3 the XRD patterns did not reveal any crystalline phases whereas in one sample in the same series of experiments (in the Fe$_x$O-SiO$_2$-Al$_2$O$_3$ system) only a minor proportion of FeO was identified. It is believed that precipitation of FeO during quenching in this case may not have caused substantial variation in the ferric-to-ferrous ratio of the slag and therefore the Mössbauer data would still be of use.

Bukrey et al. [116] have correlated the appearance of hfs (hyperfine splittings) with the method of quenching. The authors report the absence of hfs at fast cooling rate. Mössbauer spectra obtained in this work showed no hfs with the exception of two samples and in both these the result was attributed to the presence of iron and magnetite which resulted from prevailing experimental conditions. It is appreciated that these results provide only indirect evidence of a successful quenching procedure. However in this regard additional work is highly recommended.

7.1.2 Limitations of present Mössbauer analysis

It is to be appreciated that the Mössbauer analysis was initiated only to supplement the findings of the kinetic data and the mathematical modelling work. Furthermore only a few slag samples are analysed and the data comparison with equilibrium melts is lacking. In general, this being a new technique it has yet to fulfill the promise of being a reliable and reproducible analytical tool. In spite of these impeding difficulties an attempt is made to relate the Mössbauer data to the slag structure and develop some understanding of their interdependency.

7.2 Mössbauer technique

A typical Mössbauer spectrometer consists of a source of gamma rays, an absorber (the sample being studied) and a means of recording the amount of radiation passing through the
absorber. The source is moved relative to the absorber, shifting the energy spectrum of the source due to the Doppler effect. A gamma ray emitted from the source is absorbed by a nucleus in the sample if resonance occurs, that is, if the energy of the gamma ray is identical to the difference between the ground and excited energy states of the nucleus. If a gamma ray is absorbed, it is effectively removed from the flux seen by the detector and a "hole" in the energy spectrum results. The base line of the resulting spectrum therefore contains the maximum number of counts and resonance lines occur at minima. Mössbauer spectra are commonly plotted with % absorption on the y axis and velocity (energy) on the x axis.

7.2.1 Slag preparation:

For the Mössbauer analysis quenched slag samples were chosen from both simple and complex melts in the Fe$_x$O-SiO$_2$-CaO-Al$_2$O$_3$ system. Wet chemical analysis and the experimental details of the slags are listed in Table 7.1.

Two sections were cut from each quenched slag sample, one parallel to the slag surface (for surface analysis of the top 10 µm) and one perpendicular to the slag surface (for depth analysis). The sections were cold mounted in a 31 mm diameter mould using a self setting resin, and ground to a thickness of approximately 10 µm using an additional resin ring to support the thin disk. The samples were numbered in pairs corresponding to the slag that they were quenched from; for example #2 and #3 represent the surface and depth samples from different parts of the same quenched slag.

7.2.2 Generation of Mössbauer spectra:

Schematic of the sample holder is shown in Figure 7.1. The sample was mounted on a two-axis travelling stage that controlled the position of the sample with respect to the collimated gamma ray beam.
Table 7.1  Chemical composition and experimental parameters of slag samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slag Composition (wt%)*</th>
<th>Fe$^{3+}$/ΣFe*</th>
<th>Gas Mixture $P_{O_2}$ (atm)</th>
<th>Main Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>17,18</td>
<td>92 FeO, 2 Fe$_2$O$_3$, 0 SiO$_2$, 0 CaO, 6 Al$_2$O$_3$</td>
<td>0.019</td>
<td>5x10$^{-11}$</td>
<td>Fe$^{3+}<em>{\text{slag}}$ → Fe$</em>\text{(solid)}$</td>
</tr>
<tr>
<td>19,20</td>
<td>58 FeO, 2 Fe$_2$O$_3$, 0 SiO$_2$, 22 CaO, 18 Al$_2$O$_3$</td>
<td>0.030</td>
<td>1x10$^{-12}$</td>
<td>Fe$^{2+}<em>{\text{slag}}$ → Fe$</em>\text{(solid)}$</td>
</tr>
<tr>
<td>2,3</td>
<td>61 FeO, 2 Fe$_2$O$_3$, 21 SiO$_2$, 0 CaO, 16 Al$_2$O$_3$</td>
<td>0.029</td>
<td>1x10$^{-13}$</td>
<td>At Fe saturation</td>
</tr>
<tr>
<td>9,11</td>
<td>34 FeO, 6 Fe$_2$O$_3$, 22 SiO$_2$, 14 CaO, 24 Al$_2$O$_3$</td>
<td>0.137</td>
<td>3x10$^{-10}$</td>
<td>Fe$^{3+}<em>{\text{slag}}$ → Fe$^{2+}</em>{\text{slag}}$</td>
</tr>
<tr>
<td>5,6</td>
<td>29 FeO, 7 Fe$_2$O$_3$, 26 SiO$_2$, 14 CaO, 24 Al$_2$O$_3$</td>
<td>0.178</td>
<td>7x10$^{-9}$</td>
<td>Near Fe saturation</td>
</tr>
<tr>
<td>15,16</td>
<td>36 FeO, 3 Fe$_2$O$_3$, 14 SiO$_2$, 11.5 CaO, 23 Al$_2$O$_3$</td>
<td>0.152</td>
<td>2x10$^{-9}$</td>
<td>Fe$^{3+}<em>{\text{slag}}$ → Fe$^{2+}</em>{\text{slag}}$</td>
</tr>
<tr>
<td>7,8</td>
<td>70 FeO, 14 Fe$_2$O$_3$, 22.5 SiO$_2$, 0 CaO, 13 Al$_2$O$_3$</td>
<td>0.149</td>
<td>7x10$^{-10}$</td>
<td>Away from Fe saturation</td>
</tr>
<tr>
<td>12,14</td>
<td>30 FeO, 14 Fe$_2$O$_3$, 22 SiO$_2$, 14 CaO, 20 Al$_2$O$_3$</td>
<td>0.296</td>
<td>4x10$^{-8}$</td>
<td>Fe$^{2+}<em>{\text{slag}}$ → Fe$^{3+}</em>{\text{slag}}$</td>
</tr>
</tbody>
</table>

Note: * Assays determined by wet chemical analysis.
Figure 7.1 Schematic diagram of the sample holder assembly.
The tip of the source was mounted within 2 mm of the hole in the lead shielding, resulting in a very small source-to-sample distance. The position of the hole in the lead shielding was controlled with respect to the source using four thumb screws. To align the source directly behind the hole these screws were adjusted until the maximum count rate of gamma rays was recorded by the detector. Additional details are provided in our previous publication [117].

Mössbauer spectra were recorded for two different configurations of the quenched slag. The first, surface analysis, represents the top, approximately 10 μm, layer and the other, depth analysis, represents two depths within the quenched slag: 500 μm layers centred at depths of 250 μm and 1.0 mm. In the depth analysis configuration the surface of the slag was first located by moving the y axis (depth) of the sample stage and noting the position of the drop in count rate at the sample-resin boundary. Using this reference point the y axis of the stage was then moved to the appropriate depth and the Mössbauer spectrum recorded. The depths could be measured to ±50 μm, and the horizontal displacement (direction parallel to the slag surface) remained constant.

The complete set of Mössbauer spectra recorded of all eight slag samples is shown in Figure 7.2. The shapes of the spectral envelopes vary dramatically with composition, and in common with most glass spectra, they are poorly resolved with respect to individual Fe\(^{2+}\) and Fe\(^{3+}\) sites. The challenge therefore is to select a fitting model that enables a comparison of Mössbauer parameters between different spectra in order to elucidate the variation of Fe\(^{3+}\) and Fe\(^{2+}\) populations. A fitting model was chosen which used three Fe\(^{2+}\) doublets and one Fe\(^{3+}\) doublet where the line widths of all doublets were constrained to 0.5 mm/s. Each doublet corresponds to a specific ion site. The spectra were fit using a nonlinear least-squares fitting method developed by the CERN Computer Centre Program Library. [118] Further details are provided in our previous publication. [117]
Figure 7.2 Complete set of Mössbauer spectra recorded at all depths for eight slag compositions.
7.3 Results:

7.3.1 Spectral parameters:

To facilitate interpretation and comparison of the Mössbauer data for each set of quenched slag samples, several quantities were calculated as a function of depth within the slag. These quantities, namely: quadrupole splitting (QS), isomer shift (IS) and relative area (area) are frequently used in any Mössbauer spectroscopy work and additional information on these is readily available in any textbook on this subject. The individual values of QS, IS and area obtained in this work are listed in Table 7.2.

A critical look at the data in Table 7.2 highlights distinct differences in the values of the spectral parameters with depth. This fact is evident in the reported slag spectra in the Figure 7.2 as well. Since the relative differences in the spectral values are caused largely by the ferric and ferrous cation gradients across the melt depth it was believed that the Mössbauer data could be used in the estimation of the liquid phase boundary layer thicknesses. On this basis a boundary layer thickness value of roughly 500 µm is estimated. The prediction is based on the fact that generally the relative difference between 'top' and 'surface' spectral parameters for an individual slag sample was smaller in comparison with an equivalent difference between 'surface' and 'bulk' parameters.

The mean quadrupole splitting for Fe$^{2+}$ in each spectrum was calculated as the weighted average $[(QS_1*Area_1) + (QS_2*Area_2) + ....]/(Area_1 + Area_2 + ....)$. These values are plotted in Figure 7.3 for each set of slag samples as a function of depth. Variation of the mean quadrupole splitting with depth indicates a change in the nature of Fe$^{2+}$ sites, probably in coordination or degree of distortion. The distribution of quadrupole splitting values within a given slag sample can be seen in Figure 7.4, where the quadrupole splitting of each doublet is plotted as a function of its relative area. Figure 7.5 illustrates the variation of Fe$^{3+}$ relative area as a function of depth within the slag.
Table 7.2  Mössbauer parameters of slags quenched from 1400 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe$^{2+}_{(\text{Crystalline})}$</th>
<th>Fe$^{2+}_{(\text{glass})}$</th>
<th>Fe$^{2+}_{(\text{Crystalline})}$</th>
<th>Fe$^{2+}_{(\text{glass})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>top</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#17</td>
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<td></td>
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<tr>
<td>#18</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>surface</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>#19</td>
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<td></td>
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<tr>
<td>#20</td>
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<tr>
<td>bulk</td>
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<tr>
<td>#9</td>
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<td></td>
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<tr>
<td>#11</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>top</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>#5</td>
<td></td>
<td></td>
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<tr>
<td>#6</td>
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</tr>
<tr>
<td>surface</td>
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<tr>
<td>#15</td>
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<td>#16</td>
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</tr>
<tr>
<td>bulk</td>
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<td></td>
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<tr>
<td>#7</td>
<td></td>
<td></td>
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<tr>
<td>#8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>surface</td>
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<td></td>
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</tr>
<tr>
<td>#12</td>
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<td></td>
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<tr>
<td>#14</td>
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</tr>
<tr>
<td>bulk</td>
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<td></td>
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</tr>
<tr>
<td>#2</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>#3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: "top" refers to the top 10 μm layer.
"surface" refers to the top 500 μm layer.
"bulk" refers to a depth of 1.0 mm within the quenched slag.
Figure 7.3 Mean quadrupole splitting of Fe$^{2+}$ doublets versus depth for six slag compositions.
Figure 7.4  The relative area as a function of the ferrous QS values. The symbols are as follows: ▲ top 10 μm layer; ○ 500 μm depth; ● 1.0 mm depth, and arrows indicate the direction of increasing depth. A typical set of error bars is indicated on the sample #5, #6 dataset.
Figure 7.5  The change in Fe\textsuperscript{3+} concentration with depth. A typical set of error bars is indicated on the sample #5,#6 dataset.
In Figure 7.5 the vertical axis is calculated as \( \%\text{Fe}^{3+}(x) - \%\text{Fe}^{3+}(10\mu m) \) where \( x \) is the depth within the slag; therefore all samples plot initially at zero, and then show either an increase or a decrease with depth according to the variation of the relative amount of \( \text{Fe}^{3+} \).

**7.3.2 Spectra analysis:**

Mössbauer results are sensitive to the technique adopted for resolving a spectrum into doublets and therefore even minor variations among two different techniques may cause differences in the spectra peaks of similar slags. Because of these difficulties, conclusions on slag structure which are based on Mössbauer spectroscopy are likely to be valid only if they are reached through consideration of relative changes in the spectra of a series of slags. All the conclusions drawn in this study have been limited to those which can be so deduced.

The fitting model includes three \( \text{Fe}^{2+} \) doublets and the same cannot be correlated with specific sites on a one-to-one basis because we are approximating the site-to-site variations inherent in the disordered solid with a set of discrete Lorentzian doublets. Nevertheless, the presence of a resolved \( \text{Fe}^{2+} \) doublet at high velocity in some of the spectra (Figure 7.2) suggests that \( \text{Fe}^{2+} \) occupies at least two structurally dissimilar sites, although it is not possible to deduce the coordination of these sites. Previous investigators have concluded that \( \text{Fe}^{2+} \) occupies both tetrahedral and octahedral sites in quenched Pb-Fe-O-Si glasses on the basis of similar fits [119]; however these would be subject to the same uncertainties. \( \text{Fe}^{3+} \) has been reported to occur in both tetrahedral and octahedral coordination in quenched slags [98-119]. Due to the small amounts of \( \text{Fe}^{3+} \) in the present samples however, it is not possible to resolve different site configurations; we therefore fit only one \( \text{Fe}^{3+} \) doublet to each spectrum. The QS values (for iron cations) reported by Bowker et al. [99] and the data obtained by Hollitt et al. [119], both suggest that lower QS values correspond to higher coordination numbers and the higher QS values to lower coordination numbers. In neither case however can the absolute coordination numbers can be stated. Our Mössbauer results are consistent with this observation.
Since the specific iron cationic sites are poorly resolved the following parameters of our fitting model are of less significance: (1) the number of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} doublets required to fit the spectra; and (2) the specific values of quadrupole splitting and isomer shift of each doublet. Similarly, individual values of isomer shift and quadrupole splitting should not be used to determine the absolute coordination states (e.g. octahedral or tetrahedral) of the various sites.

However, we consider the following parameters of the fitting model to be significant: (1) weighted mean values of isomer shift and quadrupole splitting averaged over all Fe\textsuperscript{2+} doublets from each sample; (2) comparison of these values with composition or depth; and (3) comparison of relative areas of doublets between different compositions or depths.

7.3.3 Mössbauer data and wet chemical analysis:

The Mössbauer spectrum of the starting material Fe\textsubscript{2}O was recorded and using a fitting model developed by McCammon and Price [120] the value of $x$ was found to be $0.97 \pm 0.01$. X-ray diffraction results showed the presence of both iron and magnetite in the Fe\textsubscript{2}O, although detailed quantitative information was not available. Wet chemical analysis was performed to obtain total iron and ferrous iron and the ferric iron content was determined by difference. On this basis a value of $x = 0.98 \pm 0.01$ was obtained which is consistent with our Mössbauer results.

A similar comparison was made between the Fe\textsuperscript{3+}/ΣFe values determined by the Mössbauer method and those obtained by wet chemical analysis for each slag compositions. The comparison is illustrated in Figure 7.6 using the Mössbauer data taken at 1.0 mm depth. It is to be noted that an accurate ferric analysis by wet chemical methods is often difficult and agreement between two independent methods is rare.

Our Mössbauer results consistently underestimate the amount of Fe\textsuperscript{3+} relative to the wet chemical method, and the trend could be explained by our decision to fit only one Fe\textsuperscript{3+} doublet. The fact that the experimental data are linearly correlated within experimental error indicates that a systematic error may be responsible for the discrepancy. However, this discrepancy does not affect the conclusions in our study because only the variation of parameters with depth are used in the analysis.
Figure 7.6 Comparison of Fe$^{3+}$ / $\Sigma$Fe values obtained by Mössbauer spectroscopy and wet chemical analysis. The solid line indicates the 1:1 correspondence line, while the dotted line is the linear best fit.
7.3.4 Identification of crystalline phases:

According to Bukrey et al. [116] the Mössbauer technique is useful in identifying the presence and amount of crystalline phases in the quenched slag. The authors have shown that such a detection is very sensitive and moreover it can detect crystalline phases at levels which are undetected by X-ray spectroscopy. Figure 7.2 illustrates the spectrum recorded of the top 10 μm layer from sample #2, #3 where the six-line pattern corresponding to metallic iron can be clearly seen. The relative area of the iron spectrum is $7 \pm 2\%$, implying a similar amount of iron present. The XRD patterns of this sample indicated presence of iron and fayalite species. By combining both the pieces of information it is estimated that in sample #2, #3 about $7 - 11\%$ of the slag volume was occupied by the crystalline phases. Application of a similar criterion to sample #12, #14 revealed that nearly $15\%$ of the slag volume was crystalline. This composition was run within the magnetite saturation field and the presence of magnetite was confirmed by both XRD and Mössbauer techniques. It is likely that some magnetite may have formed during quenching however in the interpretation of the present data this possibility is ignored.

7.4 Discussion:

Our analysis of the weight loss/gain versus time data suggested compositional gradients as a function of depth and therefore the Mössbauer spectroscopy results are examined critically to confirm this finding.

(A) Effect of SiO₂

Iron cation distribution is normally related to the nature of the surrounding anions, and it is known that $O^{2-}$ anions prefer coordination of smaller radius cations whereas other anions (e.g. $SiO_{4}^{4-}$) coordinate larger radius cations [121,96]. Any changes in the population density of the anions should therefore result in corresponding changes to cation coordination. According to surface tension data silica is surface active in iron oxide melts [67,102,103,105]. Though it is appreciated that the excess concentration of silica is restricted only to the monolayer thicknesses at the surface which cannot be detected by Mössbauer technique alone as a first approximation.
it is assumed that the redistribution of silica is likely to cause a change in anion distribution. Because Si\textsuperscript{4+} preferentially coordinates with four easily polarizable O\textsuperscript{2-} anions, a change in iron coordination with depth is likely to occur. The Fe\textsubscript{2}O-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} slag shows a change in the distribution of quadrupole splitting values for Fe\textsuperscript{2+} as a function of depth (sample #15,#16; Figure 7.4), which is consistent with this conclusion, although it is difficult to isolate the effects due to the other components. As indicated, the proportion of the lowest quadrupole splitting Fe\textsuperscript{2+} decreases as the surface is approached. This implies a decrease in the O\textsuperscript{2-} available for coordination due to the elevated level of Si\textsuperscript{4+} at the surface (because of its surface active nature).

It is important, however, not to ignore the effect of the chemical reduction reaction taking place at the gas-slag interface. The reduction of ferric to ferrous ions, for example

\begin{align}
2\text{FeO}_3\textsuperscript{3-} + CO & = 2\text{Fe}^{2+} + 5\text{O}^{2-} + \text{CO}_2 \\
2\text{Fe}^{3+} + CO + \text{O}^{2-} & = 2\text{Fe}^{2+} + \text{CO}_2
\end{align}

(7.1a) (7.1b)

is expected to result in a gradient of ferric iron concentration decreasing towards the surface. Sample #15,#16 shows this trend (see Figure 7.5 and Table 7.2). It is interesting to note that in the absence of SiO\textsubscript{2} (sample #17,#18) the coordination of ferrous ions at the surface is greater than the bulk, indicating an abundance of O\textsuperscript{2-} ions. These may result from the release of O\textsuperscript{2-} during the reduction of ferric anions by CO (equation 7.1) or metallic iron:

\[2\text{FeO}_3\textsuperscript{3-} + Fe = 3\text{Fe}^{2+} + 6\text{O}^{2-}\] (7.2)

With the addition of silica, even in minor amounts, it is expected that the availability of O\textsuperscript{2-} relative to ferrous cations will be diminished as these anions would preferably surround Si\textsuperscript{4+} cations. In the presence of other surface active species such as ferric oxide or phosphorus pentoxide similar trends in ferrous coordination would result. Although the data is not sufficient to test this prediction rigourously, the results obtained for sample #15,#16 support the above hypothesis (see Figure 7.4).
In view of the limited data generated in this study, no firm comments can be made concerning the effect of SiO$_2$ on the Fe$^{3+}$ distribution in the melts. However the changes in the coordination of Fe$^{2+}$ cations (shown in Figure 7.4 as decrease in the proportion of lower QS Fe$^{2+}$) suggest that silica acts as a Fe$^{2+}$ stabilizer, and this behaviour is in agreement with theory [122,112].

(B) Effect of CaO

To isolate the effect of CaO it is useful to examine the results for silica-free melts. Comparison of the ferric gradient with depth within the Fe$_2$O$_3$-Al$_2$O$_3$ system (sample #17,#18) and the Fe$_2$O-CaO-Al$_2$O$_3$ system (sample #19,#20) indicates that they are opposite to one another. While the proportion of Fe$^{3+}$ in the former melt is lowest on the surface, consistent with the gradient expected due to the strong reducing atmosphere, the proportion of Fe$^{3+}$ is highest on the surface in the presence of CaO. Repetition of this trend is observed in other lime-containing melts namely-samples #9,#11 and #7,#8. (Figure 7.5)

Thermodynamic studies in the Fe$_2$O-Fe$_2$O$_3$-SiO$_2$ and Fe$_2$O-Fe$_2$O$_3$-CaO systems [36,110,121] indicate that the equilibrium Fe$^{3+}$/ΣFe ratio of the slag is much higher in the calcium ferrite system at a given temperature and oxygen potential. Moreover the ratio is increased by further additions of CaO to the slag, while it is lowered by addition of SiO$_2$. The value of the equilibrium Fe$^{3+}$/ΣFe ratio for sample #19,#20 is calculated to be approximately 0.15 (Fe$_2$O-CaO-Al$_2$O$_3$ melt). The actual value, however, is 0.03 (Table 7.1). Thus there is a large difference between the equilibrium and actual Fe$^{3+}$/ΣFe ratios which acts as a driving force for the ferrous disproportionation reaction

$$3Fe^{2+} \rightarrow 2Fe^{3+} + Fe$$

(7.3)

The newly formed ferric cations can in turn react with the O$^{2-}$ anions to produce ferric anion complexes according to neutralization reactions similar to the following:

$$2Fe^{3+} + 5O^{2-} = Fe_2O_5^{3-}$$

(7.4)

$$2Fe^{3+} + 6O^{2-} = 2FeO_3^{3-}$$

(7.5)

The possibility of reaction (7.4) in lime containing slags has been suggested earlier by Chipman and Chang [111]. The authors state that the concentration of ferrite ions (i.e. ferric anion complexes) in the slag at equilibrium with molten iron increases with increasing proportions
of either CaO or MgO with an attendant decrease in the free Fe$^{3+}$ cation concentration. It is probable that similar reactions are taking place in our melts. The consumption of O$^{2-}$ ions due to above reactions (7.4) and (7.5) should lead to a depressed coordination of Fe$^{2+}$ at the surface, consistent with our data (Figure 7.4).

Yet another important point is that like silica, ferric oxide can also behave as a surface active species in the melts and this implies that its concentration at the surface would be higher than the bulk level. Surface tension data provided by P. Kozakevitch [67,103] supports the surface active nature of ferric oxide. Additional evidence in favor of this observation is available in the literature [123,107,104,124,125]. Such similarities in the behaviour of silica and ferric oxide species imply that the latter may be present as anions. This hypothesis is also consistent with the amphoteric nature of ferric oxide.

Both thermodynamic and surface tension data imply that it is anions that are surface active and therefore ferric is only surface active when sufficient O$^{2-}$ is available to complex it (reactions 7.4 and 7.5). When the melt contains silica the following type of reactions

$$\text{SiO}_2 + 2\text{O}^{2-} = \text{SiO}_4^{4-}$$

readily convert all silica to SiO$_4^{4-}$ or larger polymeric anions. If there is any O$^{2-}$ left over it is only then that reactions like 7.4 and 7.5 are possible. Such behaviour is consistent with ionic slag theory and with the amphoteric characteristics of ferric oxide. In basic slags ferric oxide is expected to behave as an acidic oxide and as a glass former. The melt from sample #19,#20 consists of two basic oxides (FeO and CaO) that provide O$^{2-}$ anions and two acidic oxides (Al$_2$O$_3$ and Fe$_2$O$_3$) which form complexes by consuming O$^{2-}$ ions. Additional information concerning ferric anion complexes is given by Chipman and Chang [111], Yazawa et al. [112], Gaskell [96] and Strachan [32].
(C) Effect of CaO/SiO$_2$ ratio

We have explained the effects of a single basic or acidic oxide on the melt structure and its Mössbauer parameters in the case of simple melts. We noted that in the absence of CaO the consumption of O$^2-$ ions results in the formation of SiO$_4^-$ complexes, leaving the Fe$^{2+}$ cations with only few O$^2-$ anions to coordinate. On the other hand when CaO is present and silica is absent, there is an abundance of O$^2-$ ions and the tendency is to form ferric complexes. It is natural to expect that when both lime and silica are present in the melt the individual cations will compete for the O$^2-$ coordination and thus slag basicity would play an important role. Moreover, in the presence of lime and silica the changes in the overall physicochemical properties of the melt, especially the surface tension, will become more critical and complicate interpretation of the Mössbauer data. Our studies of complex melts in the system Fe$_x$O-CaO-SiO$_2$-Al$_2$O$_3$ are therefore best examined with respect to the CaO/SiO$_2$ ratio.

Samples #5,#6 and #9,#11 were exposed to similar reducing gas mixtures and are nearly identical in composition except that the molar ratio CaO/SiO$_2$ is approximately 16% higher in sample #9,#11. The difference is more significant when the ratio of basic oxides, CaO and FeO, to silica is considered. We observe a virtual reversal in the ferric gradient with depth in sample #5,#6 consistent with the increased amount of SiO$_2$ (Figure 7.5) which would tend to displace ferric anions from the surface. In both samples there is a tendency towards higher values for Fe$^{2+}$ quadrupole splitting near the surface, with the effect being more pronounced in sample #9,#11 (Figure 7.4).

In order to provide an additional explanation of the observed Mössbauer results we propose the following scheme. (It is to noted however, that similar explanation is applicable to several other melt systems). In the ionic double layer at the melt surface the oxygen ions preferentially occupy the positions in the top layer (Figure 6.12) and in turn these are coordinated by cations to maintain the electrical neutrality. For example, in the presence of Si$^{4+}$ the tetrahedral coordination leads to the formation of SiO$_4^{4-}$ anions. In the melts studied, we suggest the presence of both silica and ferric complexes. The ferric anions can be described by the general formula
Fe$_x$O$_y^{(2y-3z^+)}$, but the predominance of only three or four different species at most is possible [96]. However, due to the amphoteric nature of the ferric oxide species (or its lower ion-oxygen attraction value) it reacts with the reducing gas mixtures according to reactions of the form:

\[
Fe_2O_3^{4-} + CO = 2Fe^{2+} + 4O^{2-} + CO_2 \hspace{1cm} (7.7)
\]
\[
2Fe_2O_3^{4-} + CO = 2FeO_3^{-} + CO_2 + 2Fe^{2+} + 3O^{2-} \hspace{1cm} (7.8)
\]

using \(Fe_2O_3^{4-}\) as an example. Both these reactions may take place simultaneously or one may predominate over the other. In either case however, there is a net production of oxygen anions. Reaction (7.7) represents dissociation of the ferric anion species whereas reaction (7.8) leads to an increase in the Fe$^{3+}$ coordination by O$^{2-}$. According to this scheme more O$^{2-}$ anions are released at the reaction site and thus there is a net increase in the availability of O$^{2-}$ ions for coordination with the other cations such as Si$^{4+}$, Fe$^{2+}$ and Ca$^{2+}$. Potentially these excess O$^{2-}$ anions can react with the complex silicate anions of the type Si$_x$O$_y^{n-}$ and depolymerize the silicate network. It is equally probable that these will immediately coordinate with the remaining Fe$^{3+}$ species at the gas-slag interface. Although we cannot firmly resolve the possibility of silicate network depolymerization, our Mössbauer parameters for Fe$^{3+}$ for samples #7,#8 and #9,#11 (listed in Table 7.2 under QS and area) support the second possibility i.e. increase in the ferric coordination at the surface. Our data imply that when various cations (e.g. Fe$^{3+}$, Fe$^{3+}$, Si$^{4+}$) are competing for coordination with the available O$^{2-}$ ions, acidic cations will have priority for coordination and as a consequence only a small number will be available to coordinate Fe$^{3+}$. Such behaviour is in agreement with the ion-oxygen values derived using considerations based on radii and charges of various ionic species. [95] The Mössbauer data for all Fe$_x$O-CaO-SiO$_2$-Al$_2$O$_3$ slags show a tendency towards lower coordination for Fe$^{2+}$ at the surface, consistent with the suggested scheme.

The proposed reduction mechanism via reactions (7.7) and (7.8) does not exclude the possibility of the following reaction proceeding to a degree:

\[
2Fe^{3+} + O^{2-} + CO = 2Fe^{2+} + CO_2 \hspace{1cm} (7.9)
\]
The above charge transfer reaction has been suggested earlier by Turkdogan and Bills [113] and Turkdogan and Pearce [126]. Reaction (7.9) implies that once the $O^2-$ releases two electrons these in turn can reduce any two ferric ions- even those farthest from the reaction interface, because of the unrestrained velocity of the electrons. The observed ferric gradients appear to be inconsistent with the charge transfer reaction model alone and hence the possibility of all three reactions (7.7), (7.8) and (7.9) is proposed. However the Mössbauer data suggests predominance of reactions (7.7) and (7.8) over (7.9).

The variations in quadrupole splitting values of Fe$^{2+}$ can be viewed from another perspective as well. The changes in $O^2-/O^-$ ratios surrounding the Ca$^{2+}$ and Fe$^{2+}$ ions could be considered the primary cause for the variations in quadrupole splitting. According to Gaskell et al. [110] the replacement of Fe$^{2+}$ by Ca$^{2+}$ in binary silicates leads to the preferential association of Ca$^{2+}$ with the silicate anions. To accomodate this new geometry the Fe$^{2+}$ cations undergo changes; they maintain the local equilibrium $O^2-/O^-$ ratio by coordinating with decreasing numbers of $O^2-$ anions. Gaskell et al. maintain that the non-ideal behaviour of oxides in ternary silicate melts can be explained by the occurrence of preferred ionic associations according to the above scheme. Because of the decreasing availability of $O^2-$ anions, the Fe$^{2+}$ coordination changes from spherical (higher or octahedral) to tetrahedral (lower). Hollitt et al. [119] have attributed higher values of Fe$^{2+}$ quadrupole splitting to lower coordination on the assumption that higher coordination more closely approximates the spherical or undistorted site. Our Mössbauer data exhibits similar tendency towards higher values for Fe$^{3+}$ quadrupole splitting at the surface, with the exception of sample #17,#18 which contains no CaO or SiO$_2$ (Figure 7.4). The tendency is most dramatic in sample #9,#11 which has the highest CaO/SiO$_2$ ratio. Sample #12,#14 was exposed to an oxidizing gas mixture, and therefore on the basis of polymerization-depolymerization model suggested by Gaskell et al. [110], one expects the tendency to be reversed. From Table 7.1 it is evident that the data supports this (the proportion of lower quadrupole splitting Fe$^{2+}$ values is highest near the surface), although as stated previously the results from this sample must be interpreted with caution due to the presence of magnetite.
(D) Effect of Al₂O₃

In the present work although the alumina level in the slags varied between 6 to 24 wt% (Table 7.2), very little attention was focussed to identify the role of alumina on the Mössbauer parameters. Alumina was added to the melt through dissolution of the crucible and therefore it is difficult to isolate the effects of the alumina component on our Mössbauer data. However, on the basis of the consistent effects shown by other components in the presence of strong basic and/or acidic oxides, we conclude that alumina plays a relatively passive role. Our melts contain predominantly Fe²⁺ however, and we should emphasize that different results are likely in the case of Fe³⁺-rich melts. Both Al³⁺ and Fe³⁺ are amphoteric, and their interactions are likely to be complex. Yet another complication to be considered is that, in accordance with Pauling’s rules, a tetrahedrally coordinated Al³⁺ (or Fe³⁺) ion blocks not just a tetrahedral position but also nearby octahedral and tetrahedral sites [99]. We therefore feel that more data is needed to interprete the role played by Al³⁺ on the slag structure on the basis of the Mössbauer parameters.

(E) Effect of solid products

The role of solid iron is best studied in those slags run within the Fe saturation field under highly reducing conditions (samples #17,#18 and #19,#20). We confirmed the presence of metallic iron in these slags both optically and through Mössbauer spectroscopy. Mössbauer data for both of these slags indicates that there is a dramatic change in the mean Fe²⁺ quadrupole splitting values (Figure 7.3) and also a shift in the distribution of Fe²⁺ quadrupole values with depth (Figure 7.4).

An explanation for the observed Mössbauer trends can be suggested in which the O²⁻ ions surrounding Fe²⁺ are consumed according to

\[ Fe^{2+} + O^{2-} + CO = Fe + CO_2 \]  \hspace{1cm} (7.10)

Additionally some of the newly formed iron metal can react with Fe³⁺ and release extra Fe²⁺ cations which in fact is the reverse of reaction (7.3). Under these circumstances the O²⁻/Fe²⁺ ratio is expected to vary and the resultant changes in the Fe²⁺coordination are inevitable. We believe
that the opposing trends shown by Fe$^{2+}$ quadrupole splitting values (samples #17,#18 and #19,#20; Figures 7.3 and 7.4) are due largely to the changes in the O$^2-/Fe^{2+}$ ratios of two samples in the top 10 μm surface region.

In addition it was expected that the tendency of metallic iron to segregate would be influenced by the silica content of the melt via the viscosity effect. Under the circumstance movement of solid iron away from the surface would diminish in spite of the density differential. This is indicated in the Mössbauer spectra of sample #2,#3 (Figure 7.2), which shows iron peaks only in the top layer and not in the bulk slag.

In the slag exposed to oxidizing conditions (sample #12,#14) magnetite formation reaction of the type

$$2FeO_3^{3-} + Fe^{2+} = Fe_3O_4 + 2O^{2-}$$

(7.11)

is proposed to offer an explanation for the increased O$^2-$ coordination of Fe$^{2+}$ cations in the surface region. Our Mössbauer data are consistent with an increase in Fe$^{2+}$ with low quadrupole splitting at the surface of the magnetite saturated slag; this can be interpreted to indicate an increase in Fe$^{3+}$ coordination [119]. However, it should be noted that this is only a tentative conclusion because only one slag sample was analyzed.

7.5 Comments

The following important points emerge from the Mössbauer spectroscopy work:

1. Using a custom designed sample holder it is possible to probe the cross section of the quenched slag. The technique would also be applicable to identify characteristics such as the change in proportion of iron phases, changes in iron coordination, and changes in iron oxidation state.

2. In the slag systems of importance to the non-ferrous smelting industry the Mössbauer data could be fit with a model which included three doublets for Fe$^{2+}$ and one for Fe$^{3+}$. Although the absolute values of the spectral parameters obtained this way lack definite physical meaning, the relative changes with both depth and composition are significant.

3. Utility and effectiveness of this technique could be further extended by repeating similar
analyses on equilibrated slag samples. For example, if such analyses were carried out in the present study for comparative purpose then it would have been easier to confirm the effects of rate phenomena.
Chapter 8
Summary and Conclusions

The kinetic study of reduction and oxidation reactions of importance to the non-ferrous smelting industry was successfully carried out in the temperature range of 1200 and 1400 °C using unstirred melts. For the first time, a study of the ferric-to-ferrous reaction was initiated in the lime-free and lime-containing melts by employing a thermogravimetry technique. The results revealed higher rates in the lime-containing melts in comparison with the lime-free melts.

The weight loss-time curves obtained during the ferrous-to-iron reaction study revealed the highest and nearly constant slope values for the initial 10 minute period. A mathematical model was developed for estimating rate values and based on the agreement between the observed and fitted data it is proposed that in this experimental system the iron formation reaction operates under a mixed-control regime involving gas phase mass transfer and interfacial reaction. For the melts at 1400 °C an average intrinsic rate constant value of $11 \times 10^{-5}$ g/cm$^2$.s.atm was obtained this way which is consistent with the value reported by Nagasaka et al. [56]. Based on the limited data at lower temperatures an activation energy value of about 28 kcal/mole is proposed for the ferrous-to-iron reaction and this agrees well with the published values by Nagasaka et al., Kim et al. [66] and Tsukihashi et al. [55].

The results of experiments on the ferric-to-ferrous reaction were analyzed using two separate mathematical models. Based on the agreement between the predicted and actual weight loss data it is proposed that the ferric-to-ferrous reaction operated under a gas and interfacial control regime during the initial period and subsequently the rate was controlled by a combined gas and liquid mass transfer and interfacial reaction. The intrinsic rate constant value at 1400 °C is approximately 200 times greater compared to the ferrous-to-iron reaction. From the knowledge of intrinsic rate constants at three reaction temperatures the apparent activation energy value of about 44 kcal/mole was derived for the ferric-to-ferrous reaction. In the melts containing relatively higher levels of
ferric oxide the Fe$^{3+} \rightarrow$ Fe$^{2+}$ reaction occurs concurrently with the ferrous-to-iron reaction and this offers an explanation on the important observation made by Nagasaka et al. concerning the effect of Fe$^{3+}$/Fe$^{2+}$ ratio on the rate.

Estimates of diffusivity values were obtained for a wide range of melt compositions using the derived liquid phase mass transfer coefficient values and the boundary layer thickness of 500 $\mu$m. The estimated $D_{o2}$ values for the lime-free and lime-containing melts were about $5 \times 10^{-6}$ and $1 \times 10^{-5}$ cm$^2$/s respectively at 1400 °C. These values are in reasonable agreement with the theoretically predicted data and an additional support for these can be obtained from the research work of Sasabe and Asamura [109]. The predicted value of the apparent activation energy for diffusion, $E_D$, for lime-containing melts is about 53 kcal/mole and this is in excellent agreement with that reported by Sasabe and Asamura.

The results obtained in both the reduction reactions revealed the significance of surface active species in the melts and accommodation of this effect in the development of the mathematical model led to accurate prediction of rate and weight loss data. In the various melts studied in this investigation silica and ferric oxide were surface active species and their individual proportions altered the available reaction area. A general expression was developed to arrive at the fractional coverage parameters for the melts at 1400 °C and the information allowed prediction of the rate data from first principles. The $A/A_o$ expressions were derived using the available surface tension data in the literature and they provided useful information concerning the actual reaction area. A similar approach was used by Kim et al. [66], however these authors limited their observations to the ferrous-to-iron reaction in complex melts at 1600 °C and accounted only for the silica coverage effect.

An important aspect of the mathematical formulation proposed in this work is that it accounts (for the first time) for the differences in apparent rate constant values for FeO, FeO-SiO$_2$, FeO-CaO and FeO-CaO-SiO$_2$ melts reported by the previous researchers. Moreover, the formulation has allowed a closer examination of the parameters, namely - intrinsic rate constants, fractional area coverage and reactant activities, that are responsible for the variation of $k_a$. It reasonable to expect
that in any heterogeneous reaction both the composition and the constitution of the melt surface would play a critical role on the rate phenomena. In this context, it makes sense to have a single \( k_a \) value for oxygen anion surfaces and a different value for ferric anion surfaces. In the \( CO_2^- \) dissociation model proposed by Belton et al. [34,80] however the melt surface is viewed only as oxygen anions and the explanation for the observed variations in \( k_a \) is sought in terms of changes in the electrochemical surface potential. It is felt that the alternate explanation proposed in this thesis for the variations in \( k_a \) in terms of \( A/A_e \) factors and \( k_a, k_e \) difference may, in a sense, be equivalent to the electrochemical surface potential theory. But until this is verified, the model proposed in this work can still be used as a means of estimating overall reduction rates of \( Fe^{2+} \rightarrow Fe \) and \( Fe \rightarrow Fe^{2+} \) reactions in a wide range of melt compositions between 1200 °C and 1400 °C.

For the first time a theoretical justification is proposed for the variations in the apparent rate constant, \( k_a \) values reported in the literature. Based on the findings of the work it is suggested that the ferric-to-ferrous reaction is intrinsically faster than the ferrous-to-iron reaction. More important though is the fact that the information contained in the thesis has identified several critical aspects of the gas-slag reactions and with the help of all the available information a coherent and comprehensive picture of the phenomena is attempted at the end. In the proposed reaction mechanisms it is suggested that in both the reduction reactions the critical step involves transfer of oxygen anions either (1) through the melt and/or (2) from or to the melt surface. The proposed scheme is applicable to the oxidation reactions as well. The feature that differentiates the above scheme from the charge transfer model is that the latter does not comment on the movement of oxygen anions in the melt but merely takes care of \( Fe^{3+} \) and \( Fe^{2+} \) balance. Moreover, the charge transfer model does not account for the presence of ferric anions, if any, in the melts. The results obtained in the present work however suggest that the role played by the ferric anion species should not be under-estimated especially when the available surface tension data has shown that ferric oxide species is surface active.
The weight loss-time curves obtained for various melts during the ferric-to-ferrous reaction study revealed decreasing rates with time. Subsequent mathematical analysis confirmed that this trend is caused by the additional contribution coming from the liquid mass transfer resistance. Such behaviour suggested compositional gradients across the melt depth and to test this a novel technique was employed. Mössbauer spectroscopic analyses were performed on a limited number of slag samples using a special sample holder and an entire cross-section of the quenched slag was probed to identify variations in iron cations with depth. The data revealed distinct differences between the values of Mössbauer parameters obtained at the surface from those in the slag bulk for an individual sample. Additional differences were noticed between the lime-containing and lime-free slags. In the case of lime-containing melts it was observed that in spite of the prevailing reducing conditions the surface concentration of ferric was higher than the bulk. This finding is consistent with the surface active nature of ferric oxide. A value of 500 μm was obtained for the melt diffusion boundary layer thickness using the Mössbauer data.

The limited data on the ferrous-to-magnetite reaction revealed that rates decreased with time in a manner similar to the reduction reactions. The weight gain-time curves for the magnetite formation reaction in both simple and complex melts indicated that solid magnetite covered the melt surface and caused reduction in the rate values. The data on the ferrous-to-ferric reaction at 1300 °C implied that the mechanisms involved were similar to the equivalent reverse reaction.

The experimental data showed that control of oxygen partial pressure during both heating and melting periods is of primary importance in the study of iron formation reaction. The results revealed that accurate and successful control is possible by using appropriate mixtures of Ar-CO-CO₂ and in the absence of such control, the ferrous oxidation reaction is unavoidable. This leads to higher Fe³⁺/Fe²⁺ ratios in the melts and results in the higher reaction rates. In a general sense the melt oxidation prior to the reduction period complicates interpretation of results and hence it is should be avoided if possible.
The following important points emerge from the results of the kinetic investigation:

(1) Although gas phase mass transfer limitations are present in the stagnant system a mathematical approach can be employed to characterize other reaction resistances and in turn the roles played by interfacial and liquid phase mass transfer effects can be identified.

(2) The values of the apparent rate constant, $k_c$, can be evaluated from the knowledge of $k_e$ (intrinsic rate constant), $A/A_o$ (available reaction sites) and the activities of reactant species.

(3) Mixed-control models can adequately explain the observed weight changes in the slag melts.

(4) Melt physicochemical properties, namely - viscosity, diffusivity, density and surface tension, play an important role in both the reduction and oxidation rate phenomena.

(5) Mössbauer spectroscopy technique can be employed to identify the distribution of iron cations with depth.

(6) The presence of ferric anions is proposed in both lime-free and lime-containing melts and in these melts the ferric-to-ferrous reaction involves either breakdown or restructuring of ferric anions.

What emerges from this study is that the behaviour of iron oxide containing melts during reduction is very complex and depends critically on melt composition. The interaction of surface activity effects with the transport of oxygen in the melt, as $O_2^-$ or ferric anions, can lead to quite different processes. It is quite clear that a quantitative understanding of the process must take these factors into account.

8.1 Recommendations for future work

The present study has highlighted the surface active nature of ferric oxide species in the various melts and it is felt that additional work is necessary to support this fact. More data is needed to obtain further confirmation on the mechanism of ferric-ferrous redox reaction and the exact role played by the melt physicochemical properties on the overall rate phenomena. More
data is needed at 1200 °C and 1300 °C temperatures to confirm the proposed fractional coverage expressions at these temperatures. Further research work is needed to confirm the oxygen anion diffusivity data proposed in this thesis.

In the present investigation, the oxygen probe data could not be used for a quantitative comparison with the thermogravimetric data because of the flow rate dependence of its output. However, a simultaneous measurement like this could be repeated in future; perhaps by keeping the probe in a separate furnace where the flow rate restrictions of the product gases may not hinder the accurate and instantaneous probe measurements. Furthermore, by employing the technique developed in this work additional Mössbauer work should be undertaken to further confirm variations of iron cations with depth.
REFERENCES


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[121] N. Sevryukov, B. Kuzmin and Y. Chelishchev, "General Metallurgy", MIR publishers, Moscow, 1967, pp 143-147


Appendix I

In the present study activity values of silica and iron oxides were derived using the mathematical model developed by Kellogg and Goel. [83,84] A few relevant details on this are provided below.

The original model [83] considered a mathematical correlation of binary and ternary slags in the systems Fe-O and Fe-O-SiO$_2$ that was capable of reproducing all the thermodynamic properties of these slags as a function of composition and temperature, within the uncertainty of the available experimental data. In the mathematical formulation the slag phase was described in terms of hypothetical solution species in equilibrium with each other, and behaving in a non-ideal manner according to the three-suffix Margules equations with zero ternary interactions in the form:

$$
\ln \gamma_i = \frac{1}{2} \sum (k_{ij} + k_x) N_j - \frac{1}{2} \sum \sum k_{ip} N_i N_p + \Sigma (k_{ij} - k_x) N_j (N_j/2 - N_i) + \sum \sum (k_{ip} - k_{pj}) N_p N_j^2
$$

(1.1)

where $k_{ij} = k_x = 0.0$, and the summations are carried out over all species. This form for the dependence of activity coefficients on composition is valuable because it yields values consistent with Gibbs-Duhem relation and which obey Raoult’s and Henry’s laws as limiting laws.

For the temperature dependence the authors employ the following equations:

$$
\ln K_i = A_i + B_i/T
$$

(1.2)

$$
k_{ij} = c_{ij}/T
$$

(1.3)

The authors quote values of formation equilibria, $\ln k_i$ and Margules parameters $c_{ij}$ for various species. The authors claim that reliable thermodynamic data was obtained for both Fe-O and Fe-O-SiO$_2$ systems. Additionally, they describe the miscibility gap between iron and oxide phases and the saturation boundary for SiO$_2$(c) for slags in the Fe-O-SiO$_2$ system. The range of validity is for temperatures between 1150 and 1600 °C and for oxygen partial pressure, from iron saturation to 1 atm. The authors claim that extrapolations a short distance outside of these ranges would yield good estimates. Based on the success in estimation of the thermodynamic data in these systems the authors have later extended the concept to the melts in the Fe-O-SiO$_2$-CaO
system. Goel and Kellogg [84] report the same range of temperature for the applicability of lime-containing melts. Additional restrictions on the validity of the model in these melts are: (1) mol% \((\text{CaO} + \text{SiO}_2) < 65\); and (2) molar \(\text{Fe}^{3+}/\Sigma\text{Fe} < 2/3\) or molar \(\text{O}/\text{Fe} < 4/3\). All the melts used in the present work satisfied the above conditions and therefore the model was considered useful.

In all the melts studied by us alumina was present. However, in their mathematical formulation Goel and Kellogg did not study the effect of this species. To resolve this it was assumed that in silica-free melts the alumina would behave as an acidic species and therefore it was treated as silica on a mole-to-mole basis. The resultant FeO activity data was then compared with the equivalent values obtained by Ban-Ya et al. [127] using thermodynamic measurements. An excellent agreement was obtained for the ferrous oxide melts containing up to 15 mol% alumina on this basis. For example, in the melt containing about 7 wt% the model predicted \(a_{\text{FeO}}\) value of 0.96 which matched with that of 0.95 reported by Ban-Ya et al.

To accommodate the behavior of alumina in the silica-containing melts a mole of alumina was replaced by a mole each of lime and silica. The scheme is not considered unreasonable in view of the amphoteric nature of this species. Also similar calculations were repeated on the assumption of a mole of alumina to be equivalent to the mole each of ferrous oxide and silica. The ferrous oxide activity values obtained thus were compared with the available data in the literature [35,52] and it was noted that the scheme involving replacement of a mole of alumina by mole each of lime and silica yielded a more accurate data and therefore these activity data were used in subsequent calculations. It should be noted that a similar idea has been used previously to describe the viscosity behavior of the complex melts containing alumina. Turkdogan and Bills [113] have proposed a parameter, \(x_a\), which they have referred to as 'silica equivalence of alumina'. Their findings suggest that the role of alumina, as either an acidic or basic species, is essentially governed by the lime-to-silica ratio of the melts consistent with its amphoteric nature. Therefore the activity values obtained using the scheme outlined above is expected to yield reasonably accurate data.
Appendix II

The analogue millivolt signals from the probe were shielded and ground appropriately to eliminate an electrical noise and then they were split. One was taken to a pH meter (via a junction box) and then stepped down with two resistors prior to its connection to a channel 3 on the EXP-16 board. The other signal (thermocouple emf) was first taken to an isolation amplifier (where the low voltage signal was smoothened and amplified) and then to a channel 2 on the EXP-16 board. In addition, both the signals were coupled to a chart recorder using parallel connections. Channel 1 on the EXP-16 board received a signal from the furnace thermocouple. All the three channels sent analogue signals to an A/D converter (DAS-8 board) located in the computer. The weights of the alumina hanger and crucible assembly were transferred through a bi-directional interface attached to the balance to the RS-232 port on the computer. Schematic diagram of the data acquisition system is shown in Figure II.1.

The software permitted simultaneous display of the various parameters that were stored on the computer hard drive. For this purpose the monitor screen was divided to accommodate four windows and the data being recorded was displayed on x-y graphs as weight/temperature/oxygen partial pressure versus time. The performance and accuracy of the data acquisition system—balance interface, DAS-8 and EXP-16 boards, computer, pH meter, chart recorder and isolation amplifier was tested by conducting several dummy experiments. The graphical display of the parameters was especially useful in verifying the occurrence of electrical interference, if any, over a long intervals of time and such a provision was found helpful in ensuring the proper electrical connections. Additional trials were conducted to optimize the gas flow rates. Higher gas velocities (> 4 cm/sec) led to the increased pendulum-like motion of the crucible and this caused wide fluctuations in the weight values. Again the display mode was very helpful, as the weight changes with respect to the gas flow rates (or gas velocities) could be observed with ease and based on this information the necessary adjustments to the flow rates were made to ensure the accurate weight measurements.
Figure II.1 Schematic diagram showing detailed electrical connections for the data acquisition system.