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THERMODYNAMIC BEHAVIOUR OF SULPHUR AND CHLORINE AS MINOR ELEMENTS IN METALLURGICAL MELTS

by
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Abstract

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This thesis is presented on the equilibrium studies that have been carried out on a series of slags, specifically chosen to cover the range of composition and conditions appropriate to the melters of the platinum group metals (PGM) producers of South Africa. New measurements have been made on the ferric to ferrous ratio, sulphide capacity as well as the chloride capacity mainly for the PGM melter-type slags.

In South Africa, these slags are produced from the smelting of low-grade copper-nickel sulphide ores. The typical mass compositions are 5-10% Al₂O₃, 2-15% CaO, 5-30% FeO, 15-25% MgO and 40-60% SiO₂. The industrial furnaces operate at temperatures ranging from 1450°C to 1600°C under fairly reducing conditions (typically a partial pressure of oxygen (pO₂) close to 10⁻⁴ atm at 1500°C).
The gas-slag equilibrium was studied by subjecting synthetic slags to controlled atmospheres in a vertical tube-furnace using Ar-CO-CO$_2$ (SO$_2$) and Ar-H$_2$-H$_2$O-HCl gas inlet mixtures. The ratio of ferric to ferrous was determined at 1450°C for a range of oxygen activities by analyzing the quenched slags using the standard titration and X-ray Fluorescence (XRF) techniques. The measured Fe$^{3+}$/Fe$^{2+}$ ratio increased with oxygen activity and slight non-ideal iron redox behaviour was observed, as has been reported for other low alumina and low iron-containing slags. The present results are in good agreement with the trends found in the literature for similar multi-component slag systems (mostly iron bath smelter slags).

Sulphide capacity was measured for a set of slags with varying iron content. The sulphur levels in the quenched slags were analysed with a Leco combustion technique. The expected increase in sulphide capacity with increasing temperature and basicity was observed, and at a given temperature, the sulphide capacity increased with an increase in the iron oxide content.

The chloride capacity was measured for iron-free melter-type slags, as iron reacted with the chlorine to form volatile iron chlorides. The chloride contents of the quenched slags were analyzed using an “online dialyses High Precision Liquid Chromatography” analysis. The chloride capacity of the slags studied was not sensitive for an increase in temperature, however a strong dependence was
observed with basicity: an increase in the basicity had an increasing effect on the slags' chloride capacity. Myoung, Lee and Min (2003) observed that the chlorides in the Al₂O₃-CaO-MgO-SiO₂ slag system are mainly associated with calcium. The magnesia had only a diluting effect on the lime contents and might have affected the liquidus temperature for certain magnesia contents. The observation that the chlorides are mainly associated with calcium for Al₂O₃-CaO-MgO-SiO₂ slags was confirmed. The subsequent deduced activity–composition data showed that Henrian behaviour was present for concentrations of up to 0.06 wt% CaCl₂. The infinite activity coefficient and interaction parameter of calcium chloride was determined as 0.004 and 1871.6, respectively. The liquid state of CaCl₂ was used as the standard reference state and a negative deviation from ideal behaviour was observed. Moreover, the increase in basicity, partial pressure of chlorine and decrease in partial pressure of oxygen all had a positive effect on the calcium chloride activity coefficient. In other words, the activity coefficient increased and therefore moved closer to ideal behaviour. The dependence of the activity coefficient of calcium chloride on temperature was found to vary with the expected variation for regular solution behaviour.

A matte was introduced so as to act as a high iron reservoir to supply the slag with iron so that an iron containing slag could be investigated. It was found that the chlorides tend to prefer the slag phase as the mass distribution coefficient for the chlorides \( (L_{\text{Ch}^{\text{Matte}/\text{Slag}}}^{\text{Matte}/\text{Slag}}) \) had a typical value of 0.1. Significant increases were
observed for the chloride capacity of the slags used for the matte-slag-gas equilibrations. These initial slag compositions had similar mass basicity ratios, defined as the ratio of CaO and MgO to SiO₂, compared with the initially investigated iron-free melter-type slags. Although the slag chemistry changed slightly due to the matte-slag exchange reactions and dissolution of the magnesia crucibles used, it was still observed that these slags' chloride capacity increased significantly relative to the iron-free slags. Therefore, the significant increase in chloride capacity was ascribed to the additional iron present in these slags.
DECLARATION

I, Adam Jacobus du Toit, certify that the work embodied in this document is my own independent and unaided work, both in conception and execution, and that apart from the normal guidance of my supervisors and sponsors, except where otherwise referenced or acknowledged¹. Neither the substance nor any part of this thesis has been submitted for a higher degree at any other university or institution.

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Adam Jacobus du Toit

December 2006

¹ The decorative pictures used in this thesis were taken from the Anglo Platinum website and from RT Jone's Pyrometallurgy short course presentations prepared for Murdoch University.
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To my grandparents, Adam and Liz du Toit,
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Chapter 1

INTRODUCTION

The demand for valuable metals of greater quantity, better quality and produced in a more environmentally safe manner is gaining increasing importance in today's competitive age. The thermodynamic behaviour of toxic minor elements needs to be examined in order to produce the valuable metals in a more environmental friendly manner. Amur International initiated a project (P671) to study the deposition of minor elements in smelting processes. Subsequently, three of the international platinum and copper producers and two research organizations have joined the Amur P671 project. One of the aims of the project was to enable the producers to comply with increasingly stringent restrictions on the toxic levels of effluent streams.

It was identified that the lack of experimental data and models limited the predictive capability, management and control of minor elements in smelting processes. This is a growing problem due to the depletion of ore bodies with low levels of impurities, often referred to as "clean" ore bodies, because of the intensive extraction that has taken place.
The low-level elements could be divided into three main groups:

- **Economic elements** [platinum group metals, Ag, Au, Co and Os]
- **Toxic elements** [As, Se, Te, Sb, Bi, Cr, Pb, Cl, F, S]
- **Nuisance impurities** [P, Mg, Cr]

It was also identified that standard reference materials and methods for analysing the low-level elements had to be established and explored as a secondary outcome of the P671 project. The melt chemistry research conducted for this degree benefited from the standardization and development work.

The focus of the thesis was directed at the toxic elements as increasingly stringent restrictions on the concentrations of these elements in waste and emission streams are enforced by governments. The thermodynamic behaviour of low levels of dissolved sulphur and chlorine in metallurgical melts were allocated to the student project, while the remaining minor elements were investigated by senior researchers. The available literature was surveyed, reported in Chapter 3, and the lack of knowledge of the behaviour of sulphur and chlorine in the base metal and platinum group metals (PGM) metal operations was identified. The behaviour of sulphur and chlorine was investigated by subjecting synthetic slags to controlled atmospheres. The gas-slag (matte) systems were equilibrated in a high-temperature, vertical-tube furnace fitted with water-cooled end-caps (See Chapter 4 for details). The partial pressure of sulphur or chlorine was controlled...
simultaneously with that of oxygen by controlling the gas flow rates of the various species present in the gas mixtures used (mainly SO$_2$-CO$_2$-CO-Ar and HCl-H$_2$-H$_2$O-Ar).
Chapter 2

BACKGROUND

This chapter consists of a summarised background on the generic metallurgical processes of the platinum producers in South Africa and a discussion of the basic chemistry of slags.

2.1. METALLURGICAL PROCESSES

The melting operations used in the platinum industry are very similar to those used in nickel and copper smelter operations and processes, which are discussed in detail by Biswas and Davenport (1994). Some of the South African platinum producers use six-in-line, submerged-arc furnaces to primarily treat dried Merensky concentrates. In this study, only the ores mined from the Merensky reef were investigated and discussed. It is acknowledged that the ores mined from the LG2 reef contain some chromite, which results in chromium containing systems. Pierce-Smith converters, basic metal refining and precious-metal refining are the three other generic processes used with the electric smelting of the concentrates (a general description of these processes can be found in Vermaak, 1995). Nevertheless, a brief description will follow in order to give the reader a background to PGM extraction processes in general.
The process for treating sulphide ores of copper, nickel and iron that contain trace amounts of valuable PGMs, Ag, Au, Co, Os, as well as other minor elements mentioned in the introduction is a long and intricate process that consists of five levels of treatment:

- Beneficiation (mineral liberation & separation from the silicate gangue)
- Concentrate smelting
- Matte converting
- Base-metal separation and refining
- Precious-metal separation and refining

2.1.1 Beneficiation

Two methods of beneficitation exist, be it the concentration of a valuable mineral in a process stream or concentration of a valuable element in a solution: physical (froth flotation and magnetic separation) and chemical (leaching). Mineral concentration is discussed next in more detail.

First, the mined ore is crushed and screened. The fines are then fed into a primary mill before the concentration step can take place (a few plants remove some of the platinum group elements by means of gravity separation because of their higher density, whereas the remainder is removed along with the rest of the base-metal sulphides with further downstream upgrading). The milled material is classified in a hydrocyclone. The overflow is fed into a primary flotation unit. Flotation uses differences in surface chemistry of the various components in an
separated aqueous slurry. Flotation works on a density separation principle where hydrophobic particles attached to air bubbles and enter the floated phase. The surface chemistry of components can also be manipulated by adding chemicals. The tailings of the primary flotation unit are fed into a secondary milling unit. The secondary milled material is also classified in a hydrocyclone. The overflow of the hydrocyclone is fed into a secondary flotation unit. The tailings from the secondary flotation unit are discarded, whereas the concentrate is combined with that of the primary flotation unit. The combined concentrate is then fed into a thickener before being spray or flash dried. There are two reasons for dewatering the concentrate: first, an economic reason — to reduce the energy consumption of the furnace; secondly, a safety reason — to reduce "blowback" explosions experienced with wet concentrates.

2.1.2. Concentrate Smelting

With the smelting of the dried concentrates which originates from the mined low-grade copper-nickel sulphide ores, the sulphides combine to form a dense \( (4.8-5.3 \text{ g/cm}^3) \) PGM-rich molten matte, while the silicates and oxides melt to form a less dense \( (2.7-3.3 \text{ g/cm}^3) \), immiscible slag (Merkle and McKenzie, 2002). The concentrates usually contain high concentrations of silica and magnesia that, upon smelting, produce a highly acidic slag. This acidic slag requires very high smelting temperatures (typically \( >1600^\circ\text{C} \)) to achieve the low viscosities required
for effective operation of the separation process. Therefore, the diked concentrates are fluxed with limestone, which normally lowers the liquidus temperature of a slag.

The six-in-line furnaces operate at temperatures between 1450 and 1600°C at slightly more oxidising conditions relative to the Fe/FeO (IW) redox buffer (with partial pressures of oxygen \(p_O\)) typically close to \(10^{-16}\) atm at 1500°C. Smelting of the fluxed Merensky concentrates results in an iron-copper-nickel-cobalt matte (known as green matte) enriched in PGMs, and a CaO-AlO\(_3\)-MgO-SiO\(_2\)-FeO\(_2\) slag with a typical molar basicity ratio \((\text{CaO} + \text{MgO})/\text{SiO}_2\) of 0.6 to 1.0. The furnaces are normally operated with an arc submerged beneath a “black top”, a layer of unsmelted concentrate above the slag. The thermal energy is generated by a current passing through the resistive slag layer.

The slag produced from the concentrate smelting process is usually treated in a slag cleaning furnace before disposal as some valuable metals could be physically or chemically captured within the slag. The physically captured valuables are a result of small PGM-rich matte droplets entrained within the slag, as dictated by the simplified Hadamard-Kybcznaski formulae for the gravity separation process (Wacholder and Wels, 1972). The chemically trapped valuable metals are dissolved as oxides, or it could be that the dissolved valuable metals are associated with dissolved sulphur, which is measured in the sulphide-capacity experiments (detailed in the discussion chapter).
The green matte is tapped into refractory lined ladles, which are used to transport the green matte to the converters. The furnace off-gases pass through gas-cleaning systems such as ceramic filters, electrostatic precipitators and acid plants before being discharged to the atmosphere through a tall stack.

2.1.3. Matte Converting

Air is blown through the molten matte in the converting process to remove most of the iron and sulphur as iron oxide and sulphur dioxide. The platinum producers in South Africa use Pierce-Smith (P-S) converters, except for one producer which has commissioned a bath converter, a process based on Sintermet technology. The thermal energy for the converter is supplied by the exothermic reaction of oxygen with the iron sulphide. The heat generated by the exothermic reaction is enough to maintain the vessel temperature at 1250°C, (Jones, 1999). Cold feed and revert materials (collected spillages and wastes) are added to control temperature. The atmospheric condition within the converter is more oxidising relative to the smelters. The converter operates close to the quartz-fayalite-magnetite (QFM) redox buffer (Nell, 2004). The green matte in the ladles is fed into the mouth of the semi-batch P-S converters. Silica is added as a fluxing agent to react with the iron oxide formed and produce a liquid fayalitic (Fe₂SiO₄) slag containing some dissolved magnetite. Therefore, air or an oxygen-enriched gas is injected through tuyeres. The fayalitic slag is skimmed off
regularly until the white matte (matte of copper, nickel and cobalt containing some copper-nickel alloy) has reached a matte grade sufficient for slow-cooled casting or granulation. Only one South African producer uses the slow-cooled casting technique in order to enable separation of the PGMs by magnetic separators. Other producers granulate the molten matte in a water jet.

Most of the sulphur leaves the process as sulphur dioxide, which is sent to a sulphuric acid plant. The converter slag, which contains some dissolved or entrained valuable metals, is usually returned to the concentrate smelting furnace, or it is granulated, milled and treated by flotation to recover the valuable metals in a concentrate. Some of the producers do not return the slag to the furnace; rather, they treat the slag in a separate slag-cleaning furnace.

2.1.4. Base-Metal Separation and Refining

Slow-cooled white matte is crushed and milled. An iron-rich magnetic fraction is recovered in a magnetic separator. It contains most of the PGMs. The magnetic fraction is leached and the PGM-rich concentrate is sent to the precious-metals refinery. The solution from the leach is combined with the non-magnetic fraction rich in base-metals. The mixture is sent to the base-metal extraction circuit.

The flowsheets of the producers using either the granulation or the slow-cooled process overlap, where the granulated matte and the non-magnetic and leach...
solutions of the slow-cooled matte undergo further downstream upgrading at the base-metal extraction circuit and will be discussed as one process.

The extraction circuit starts with a leach. Nickel and cobalt are removed in solution as sulphates. A few of the producers treat the sulphate solutions by removing nickel as a nickel cathode in an electrowinning process or as nickel powder and briquettes in a high-pressure hydrogen reduction. The residue of the primary pressure-leach is fed into a secondary pressure-leach. The copper is removed in a solution of copper sulphate, after which some producers remove the copper from solution as a copper cathode in an electrowinning process. The residue is leached again and the subsequent solution is recycled to the primary and secondary pressure leaching operations. At the end of the extraction circuit, the PGM-rich concentrate goes to the precious-metals refinery for the granulated-matte process and for the slow-cooled-matte process the residue is sent to a smelter.

2.1.5. Precious-Metal Separation and Refining

First, the PGM-rich concentrate is leached with chlorine and hydrochloric acid. The leached product is filtered and the residue is smelted. The PGM-rich solution is treated in a series of operations—solvent extraction, ion exchange, selective precipitation and distillation—to recover the valuable metals. Gold, palladium,
platinum, ruthenium, rhodium and iridium are removed and purified sequentially. Gold is extracted using a solvent extraction or ion exchange process. Palladium is removed using solvent extraction or molecular recognition technology. Thereafter, platinum is extracted in a solvent extraction process or as an ammonium chloride complex in a precipitation process. Ruthenium is separated using distillation and rhodium and iridium are isolated sequentially using solvent extraction or an ion exchange process. Final purification steps for each separated, isolated or removed valuable metal ensures a metal product with a high purity.

2.2. SLAG CHEMISTRY

Two theories were developed to describe the chemistry of slags; one treats the species in slags as molecules, the other, as ions. Both these theories made a significant contribution to the understanding of the chemistry of slags as it currently exists.

The molecular theory considers a liquid slag to consist of individual molecules (FeO, CaO, MnO, SiO₂, P₂O₅, Fe₃O₄, FeS, MnS, CaF₂, etc.). Two or more of these molecules combine to form a more complex molecule (Ca₂SiO₄, Ca₂Fe₂O₇, Fe₃SiO₄, etc.), which is in dissociated equilibrium with the corresponding constituent molecules. The molecular theory is good for describing phases and a number of properties of slags. However, one of the shortcomings of the theory is
that it does not take into account the nature of silicate ions, and so it fails to explain electrical conductivity, slag electrolysis and viscosity.

The ionic theory is the more generally accepted of the two theories. Observations of electrical conductivity, slag electrolysis and viscosity suggested that slags consist of cations and anions. Hennymenke (1938) was the first to describe slags in terms of ionic structures. He divided them into three categories:

- Freely mobile cations: Ca\(^{2+}\), Fe\(^{2+}\), Fe\(^{3+}\), Mg\(^{2+}\), Mn\(^{2+}\), etc.
- Non-metallic anions: S\(^{2-}\), Cl\(^{-}\), O\(^{2-}\), F\(^{-}\)
- Anion complexes: SiO\(^{4-}\), PO\(^{4-}\), AlO\(^{3-}\), FeO\(_{2}^{-}\), Fe\(_{2}O_{3}^{-}\), etc.

Silica can be present in a silicate melt in five structural forms which are illustrated in Figure 2.1 (Masson, 1984).

\[ \text{Silica network: } \text{CaSiO}_3, \text{FeSiO}_3, \text{MgSiO}_3, \text{MnSiO}_3, \text{etc.} \]

**Figure 2.1** Structural forms of silica possibly present in a silicate melt (Masson, 1984).

The network structure of a silicon ion can be compared with that of carbon, which forms the backbone structure of polymers. The silica structure(s) determines how densely this network will pack. A dense structure or network can be altered by the addition of the following network breakers or modifiers: Na\(_2\)O,
K₂O, BaO, PbO, CaO, Fe₂O₃, CoO, ZnO, NiO and MgO. If oxides of iron, phosphorus and aluminium are added, they might increase the network density and strength; they are considered to be network-forming oxides. The influence of various metal oxides on silicate melts will be discussed next in the context of acid-base reactions.

Terkin (1945) introduced the concept of ideal ionic solutions. He defined the activity of an anion or cation as the number of moles of ions divided by the count of the anions or cations respectively. The acid-base concept of slags consists of two main ionic reactions as presented next:

- Oxygen ion producing dissociation (basic reactions)
  
  \[ \text{FeO} \rightarrow \text{Fe}^{2+} + \text{O}^2^- \]
  \[ \text{CaO} \rightarrow \text{Ca}^{2+} + \text{O}^2^- \]
  \[ \text{MgO} \rightarrow \text{Mg}^{2+} + \text{O}^2^- \]
  \[ \text{MnO} \rightarrow \text{Mn}^{2+} + \text{O}^2^- \]

- Oxygen ion consuming reactions (acidic reactions)
  
  \[ \text{SiO}_2 + 2\text{O}^2^- = \text{SiO}_4^{4-} \]
  \[ \text{P}_2\text{O}_5 + 3\text{O}^2^- = 2\text{PO}_4^{2-} \]
  \[ \text{Al}_2\text{O}_3 + 3\text{O}^2^- = 2\text{AlO}_4^{3-} \]
  \[ \text{Fe}_2\text{O}_3 + \text{O}^2^- = 2\text{FeO}_4^{2-} \]
  \[ \text{Fe}_2\text{O}_3 + 2\text{O}^2^- = \text{Fe}_3\text{O}_4^{3-} \]

The addition of a basic oxide (divalent or monoalkaline) will break (or depolymerise) the silica network as shown in the acid-base reactions (2.1) and
(2.2), and is shown schematically in Figure 2.2.

\[
\begin{align*}
\left(:\text{Si}-\text{O}-\text{Si}\right) + \text{Me}O &= 2\left(:\text{Si}-\text{O}^-\right) + \text{Me}^{\text{tr}} \quad (2.1) \\
\left(:\text{Si}-\text{O}-\text{Si}\right) + \text{Me}_2\text{O} &= 2\left(:\text{Si}-\text{O}^-\right) + 2\text{Me}^{\text{tr}} \quad (2.2)
\end{align*}
\]

where Me denotes the metallic ions or atoms

![Diagram showing the network structure of silicate melts.](image)

**Figure 2.2** The dense silica network breaks up with an increase in the free oxygen and cations. (Richardson, 1974a)

Three types (states) of oxygen can exist in silicate melts as seen in acid-base reactions (Slag Atlas, 1981):

- Oxygen bonded to two silicon atoms (called a “bridging oxygen”: twin bonded or denoted as O\textsuperscript{t})
• Oxygen bonded to one silicon atom in the company of metal atoms (called a “non-bridging oxygen”, single bonded or denoted as O)

• Oxygen related to metal atoms only (“free oxygen” or denoted as O³⁻)

The basic metal oxides break the silicate network to form non-bridging oxygen groups, which become silicate ions. This acid-base reaction can repeat itself until all the silicate ions are present in the SiO₂⁺ form. The extent to which this reaction takes place is governed by the equilibrium of the acid-base reaction. Therefore, an increase in the concentration of base-metal oxides will accelerate the disruption of the silica network, and simultaneously form more free oxygen ions. The addition of a base-metal oxide to silica changes the silica structure; it is described in the Slag Atlas (1981) as follows:

<table>
<thead>
<tr>
<th>MeO (Weight %)</th>
<th>Silica forms</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 10 or 20%</td>
<td>3D network, partially distorted</td>
</tr>
<tr>
<td>12 - 33%</td>
<td>Spatial anion complex (Si₃O₆+₃)⁶⁺ or (Si₆O₂₄−₄)⁶⁻</td>
</tr>
<tr>
<td>33 - 50%</td>
<td>Spatial and ring anion complexes (Si₄O₁₀)²⁻</td>
</tr>
<tr>
<td>50 - 67%</td>
<td>Simple anion rings and chains (Si₃O₆)³⁻</td>
</tr>
<tr>
<td>67 - 100%</td>
<td>Simple chains &amp; SiO₂⁺ tetrahedra</td>
</tr>
</tbody>
</table>
Different structures can be expressed in terms of dissociation equilibria:

\[ 2\text{SiO}_4^2- \quad \rightarrow \quad \text{Si}_4\text{O}_{10}^6- + 2\text{O}^2- \]

- Tetrahedral
- Chains

\[ 2\text{SiO}_4^2- + \text{SiO}_4^2- \quad \rightarrow \quad \text{Si}_4\text{O}_{10}^6- + 2\text{O}^2- \]

- Tetrahedral
- Chains

\[ \text{Si}_4\text{O}_{10}^6- \quad \rightarrow \quad \text{Si}_2\text{O}_6^4- + 2\text{O}^2- \]

- Rings

\[ \text{Si}_2\text{O}_6^4- + \text{SiO}_4^2- \quad \rightarrow \quad \text{Si}_4\text{O}_{10}^6- + 2\text{O}^2- \]

- Tetrahedral
- Rings

Heraeymenko (1938) observed that molten silica had the highest viscosity of all the anion complexes (or network-forming oxides). P₂O₅ and Al₂O₃ have a lower network-forming ability compared with the three-dimensional tetrahedral network of silica. This is because the structures of PO₄³⁻ and AlO₄³⁻ are limited to less than four spatial bonding directions as seen in Figure 2.3. This explains the more dense silicate melts and subsequently the higher viscosity observed for molten silica compared with melts of other oxides and oxide mixtures.

![Figure 2.3](image-url)
Richardson (1974a) reported that $\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ are amphoteric — i.e., they can act as network formers or as network modifiers. The amphoteric behaviour of alumina was observed by Richardson when it behaved as a "basic" component in acidic slags, while alumina also contributes to the formation of complex clustering silicate anions in basic melts.

The concentration of free oxygen is a minimum in highly siliceous melts and, conversely, in very basic melts there would be low concentrations of bridging oxygen. The basicity of a melt can be described as a measure of the electron donor power of the oxygen ions within the slag and will vary with the different states of oxygen as defined earlier. Basicity is also considered as the activity of the free oxygen in a melt. The first measure of basicity was defined as the concentration ratio of lime to silica. Subsequently, this ratio was expanded to the concentration ratio of the base to the acidic oxides within the melt. Although good for characterising various slags and quantifying some properties, this concentration ratio was limited in its application as the user had to decide if the amphoteric components would behave in a basic or acidic manner. It was also assumed that all the basic or acidic components were equally basic or acidic respectively. This concept was initially introduced to attempt to quantify the reactivity of various components in a slag for various industrial applications and is usually constrained to a small composition range.
Duffy and Ingram (1971) proposed to quantify the electron donor power by measuring the expansion of orbitals (nephelauxetic effect) of the coordination bonds for different elements with ultraviolet spectroscopic studies, from which the optical basicity concept was developed. The optical basicity is calculated as the product of a molar fraction of a component and the respective index of that component (see the optical basicity equations 2.3 and 2.4).

\[ B_{opt} = \sum_{i=1}^{n} X_i \times A_i \]  

(2.3)

\[ X_i = \frac{N_i \times Q_{\text{oxygen atoms in } m_j}}{\sum_{i=1}^{m} N_j \times Q_{\text{oxygen atoms in } m_i}} \]  

(2.4)

where \( A \) denotes the index and \( N \) the molar fraction of the species and \( Q \) the number of oxygen atoms present in the same species.

The optical basicity has been used successfully in the clear glass industry; however, the inability to measure and determine indices for opaque glasses and transitional metal oxides limited the application of optical basicity.

Duffy and Ingram found that the optical basicity of an oxide was related to the Pauling electronegativity, and therefore the theoretical optical basicity could be quantified for components for which indices could not be measured directly. Again, the inability of the Pauling electronegativity to differentiate between the various transitional metal oxides, limited this application.
Nalamuma et al. (1986) proposed the use of average electron density as an alternative scale for optical basicity in order to try and overcome the transitional metal-oxide dilemma.

Sommerville and Sosinski (1984) have noticed an effect regarding specific chemical reactions in slags and defined the effective optical basicity of a transitional metal oxide. The effective optical basicity was determined by varying the slag composition, while investigating the effect of the change in composition on a slag property, which was used to deduce optical basicity indices. The sulphide capacity of slags was a typical slag property used for these deductions. This deductive approach included a number of assumptions and flaws, which will be explained and discussed in the literature chapter after the concept of sulphide capacity has been introduced.

A number of basicity indices exist in the literature for various components. Therefore, it should be clearly stated which indices were used, particularly for the transitional metal oxides, whenever the optical basicity concept is used.
Chapter 3

LITERATURE REVIEW

A review of the available literature on low levels of sulphur and chlorine in slags follows. As this is a thermodynamic study, it is a prerequisite to confirm that equilibrium has been reached. Therefore, the iron redox equilibria literature will be reviewed and included in these next sections. Moreover, as possible kinetic limitations could govern the redox states at a steady state instead of equilibrium as experienced with the current work's preliminary experiments, the redox states will also be reviewed.

3.1. IRON REDOX EQUILIBRIA (CO, CO or H₂O-H₂ gas mixtures)

The redox reaction of an iron-containing slag could be represented by iron oxides reacting with CO and CO₂ as described in reaction (3.1).

\[(\text{FeO}) + \frac{1}{2}\text{CO}_2 \leftrightarrow (\text{FeO}_1) + \frac{1}{2}\text{CO}\]  \hspace{1cm} (3.1)

where the brackets denote the slag phase.

The redox state could be reported as the ratio of FeO₁/FeO, which may be expressed as the ratio of ferric to ferrous (Fe⁺³/Fe⁺²). This ratio could either be on a weight or a molar basis, as the atomic weight of ferrous iron and ferric iron is the same, and the molar ratio of Fe⁺³/Fe⁺² is the same as that of FeO₁/FeO. This ratio can also be expressed as a function of the ratio of the partial pressures.
of CO₂ to CO by rewriting the equilibrium constant of reaction (3.1) for a constant slag composition and temperature as shown in equation (3.2).

\[
\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} = K_{eq} \left( \frac{\gamma_{\text{FeO}}}{\gamma_{\text{FeO}_2}} \right) \left( \frac{p\text{CO}_2}{p\text{CO}} \right)^\gamma
\]

where \( K_{eq} \) denotes the equilibrium constant of reaction (3.1) and \( \gamma_{\text{FeO}}/\gamma_{\text{FeO}_2} \) the ratio of the activity coefficients of FeO and FeO₂. The \( p\text{CO}_2/p\text{CO} \) ratio may be considered as the oxygen activity.

Equation (3.2) is the standard way of representing the iron redox states as a function of the oxygen activity. At a constant slag composition and temperature, the equilibrium constant and ratio of the activity coefficients remains constant if a slag behaves ideally, and the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratio is a power function of the \( p\text{CO}_2/p\text{CO} \) ratio with an exponent of \( \gamma/2 \). However, ideal behaviour is not expected for all slag types and compositions, as a dependence of the activity coefficient ratios on oxygen activity could exist and the exponent could deviate from the ideal value of \( 1/2 \). Note that the word "ideal" used in this regard differs from the classic definition of ideal behaviour in thermodynamics and refers to an iron redox ratio dependent only on the oxygen activity — i.e., the activity coefficient ratio is not dependent on the oxygen activity.

Extensive literature on the iron redox equilibria of slags exists, and this will be summarised in the following sections, in order to identify whether iron redox equilibria of the slags of the platinum producers had previously been investigated and quantified.

> 22
Takeda et al. (1980) studied the oxygen isobars and liquidus isothersms for the FeO$_x$-CaO system at 1200 and 1300°C. Takeda and co-workers incorporated the data of Timucin and Morris (1970), Larson and Chipman (1953) and Dukken and Garry (1946) into their data in order to represent the Fe$^{2+}$/Fe$^{3+}$ ratio as a function of slag composition (0–40 wt% CaO), P$_O$, and temperature (1200–1600°C). This calcium ferrite data is in accord with more recent measurements by Sun et al. (1988), Sayadyaghoubi et al. (1994) and Tran (1997). The behaviour observed for lime-saturated calcium ferrite slags was close to ideal, while a significant dependence of the activity coefficient on oxygen activity was observed for slags with given Ca/Fe ratios. Tran (1997) and Sun (1988) observed exponents of 0.38 and 0.36 respectively for a 20–80 wt% CaO–FeO$_x$ slag composition that deviates significantly from the ideal 0.5 value.

The iron redox equilibria in the CaO–FeO$_x$–SiO$_2$ system were investigated by Timucin and Morris (1970) for various levels of silica (0–30 wt%), whereas Larson and Chipman (1953) had studied the same slag system previously by changing the CaO/SiO$_2$ molar ratios (from 0.54 to 2.24). Larson and Chipman found that the CaO/SiO$_2$ ratio had a strong effect on the Fe$^{3+}$/Fe$^{2+}$ ratio, which doubled over the same composition range investigated at a fixed oxygen partial pressure.
Jahanshahi and Wright (1993) determined the $\gamma_{Fe}^+/\gamma_{Fe}^{0}$ ratios for Al$_2$O$_3$-CaO-FeO$_2$-SiO$_2$ slags and found that the ratio changed significantly as the total iron content of the slag was increased from 0.75 to about 2 wt%, but remained virtually constant from 6 to 24 wt% total iron. The apparent increase in the $\gamma_{Fe^{3+}}^+/\gamma_{Fe^{2+}}^{0}$ ratio with iron content over the low range was thought to be due to the inaccuracies associated with the analysis used (Mossbauer spectroscopy and iteration) at these low total-iron levels.

![Figure 3.1 $\gamma_{Fe}^+/\gamma_{Fe}^{0}$ ratios for slags with a similar basicity and various levels of iron plotted as a function of oxygen activity. The insensitivity of the iron redox equilibrium relative to the iron content can be observed. Adapted from Sun & Jahanshahi (2000) and original research papers and thesis as listed in the legend.](image-url)
Xie (1992) investigated the iron redox equilibria for a 41:38:21 wt% CaO:SiO₂:Al₂O₃ slag containing total iron levels from 6 wt% to as low as 0.7 wt% and confirmed the insignificant effect of the total iron content on the redox equilibria (see Figure 3.1). The iron redox equilibria of this slag departed slightly from ideal behaviour and Xie reported a slope of 0.45. Although the redox states were similar for H₂O-H₂ and CO₂-CO equilibrations, he reported that the rates of H₂O-H₂ reactions were considerably faster than those of CO₂-CO reactions for the iron-containing calcium aluminosilicate slags. This is discussed further in 3.2.

Multi-component CaO-FeOₓ-SiO₂-MgO-(Al₂O₃) slag systems were investigated by Mysen et al. (1985), Tran (1997) and Yang and Belton (1998). Yang (1994) determined the redox equilibria for CaO-SiO₂-Al₂O₃ and CaO-SiO₂-Al₂O₃-MgO slag systems containing low levels of iron (2–10 wt%) and concluded that the exponents for these slags ranged from 0.40 to 0.47 for slags containing about 20 wt% Al₂O₃. However, a more significant departure was observed for slags enriched with Al₂O₃, and Yang reported that the exponents ranged from 0.36 to 0.39, concluding that Al₂O₃ is amphoteric for additions of 10 to 15 mol%. She observed that ratios of the iron redox equilibrium increased with increasing slag basicity and with additions of 5–9 wt% MgO at constant CaO/SiO₂ ratios. It was reported furthermore that iron redox equilibria were independent of temperature in the range 1350–1600°C. This insensitivity to temperature is expected when the Fe³⁺/Fe²⁺ ratio is expressed as a function of the CO₂/CO ratio, because of the
small entropy change of reaction (3.1) in this temperature range. Yang and Belton (1998) and Tran (1997) correlated log(Fe$^{3+}$/Fe$^{2+}$) as a function of the log(pCO$_2$/pCO) and the molar or mass ratio of (CaO + MgO)/SiO$_2$ for iron–bath–smelter type slags. The correlations developed for these CaO-Al$_2$O$_3$-MgO-SiO$_2$-FeO$_x$ multi-component slags could be used to predict the equilibrium iron redox state of various slags. However, melter-type slags are more acidic than modelled iron bath smelter slags and significant extrapolations would be required. Owing to the lack of published equilibrium data on the oxidation state of iron in melter-type slags, some iron redox equilibria experiments will be conducted for validation of the existing thermodynamic models available.

The review paper by Sun and Jahanshahi (2000) concluded that the redox–equilibria for transition metals (Fe, Mn, Ti and V) of calcium silicate-based melts showed close-to-ideal behaviour relative to oxygen activity. However, a more substantial departure could be observed for multi-component slag systems containing high levels of alumina or titania. The magnitude of the Fe$^{3+}$/Fe$^{2+}$ ratio depended strongly on slag basicity, while the transition–metal content had an insignificant effect, unless complex species were formed with other slag constituents at high concentrations.

After reviewing the redox-equilibria literature, it was identified that an experimental study was required for melter-type slag's iron redox-equilibria in order to determine if the behaviour of this multi-component slag deviates
significantly from ideal behaviour. The generated data will also be used to validate existing thermodynamic models.

3.2. IRON REDOX STEADY STATE (Influences of interfacial gas-slag kinetics)

Belton (1984) highlighted the need for understanding the relative rates of iron redox reactions with gases containing water vapour. He reported that the relative rates of iron redox reactions of CO-CO\textsubscript{2} and H\textsubscript{2}O-H\textsubscript{2} gas mixtures with liquid silicate melts had been investigated thoroughly, but at that stage there were no measurements available of the rate of dissociation of water vapour at the surface of a slag. This initiated a PhD study undertaken by Yang (1994). She used typical bath smelter slags (calcium aluminosilicates), which contain 5 to 10 wt\% FeO\textsubscript{2}. In general, the same iron redox result was obtained when CO\textsubscript{2}-CO and H\textsubscript{2}O-H\textsubscript{2} gas mixtures, with an equivalent oxygen partial pressure calculated at equilibrium, were reacted individually over a liquid silicate slag containing iron. However, not only has Xie (1992) reported that rates of reaction are faster for H\textsubscript{2}O-H\textsubscript{2} reductions than for CO\textsubscript{2}-CO reductions, but Yang (1994) used H\textsubscript{2}O-H\textsubscript{2} kinetic data reported by Glaws and Belton (1990), which had been converted to a function of CO\textsubscript{2}/CO ratio in equilibrium with the melt, and found that the rate of dissociation of H\textsubscript{2}O is faster than that of CO\textsubscript{2} for silica-saturated iron silicates at 1400\textdegree{}C at given oxygen activities.
A steady-state oxygen activity can therefore be measured at the surface of a slag when the rate of oxygen donated is equal to the rate of oxygen removed from the slag.

### 3.2.1. Interfacial Gas and Molten Silicate Slag Kinetic Influences

Belton (1984) studied the interfacial kinetics between CO₂-H₂ gas mixtures and silicate slags or liquid copper. He took special care to ensure that the water-gas shift reaction did not influence the CO₂/H₂ ratio at the inlet and in the reaction zone. Sasaki and Belton (1983) measured the oxygen activity of a slag with a solid electrolyte cell, which was inserted into a pool of liquid silver placed beneath the slag for a similar interfacial kinetic study (a CO₂-H₂ gas mixture reacted with a molten silicate slag). Both studies measured a steady state oxygen activity of the melts that was lower than the expected redox equilibria.

Subsequently, Yang and Belton (1997) investigated the redox equilibria and relative rates of reaction of H₂O and CO₂ from 1300 to 1500°C by reacting H₂O-CO gas mixtures and calcium aluminosilicate slags, which contained 5 to 10 wt% FeO. The calcium aluminosilicate slags had molar CaO/SiO₂ ratios of 0.45, 1.09 and 1.52. They found that steady state was reached when the rate of oxygen removed by CO was equal to the rate of oxygen addition by H₂O dissociation at the gas-slag interface. It was noted that interfacial kinetic limitations between H₂O-CO gas mixtures and molten silicate slags were responsible for measuring oxygen activities in the slag that were higher than those of the expected redox equilibria.
equilibria. Moreover, Yang (1994) noted that deviations from the redox equilibria were dependent on the slag chemistry. The steady state deviations increased with increasing ratios of CaO/SiO₂. The observation that slags in contact with H₂O-CO gas mixtures are more oxidised than the iron redox equilibrium stands in contrast to more reduced redox states in silicate slags in contact with CO₂-H₂ gas mixtures.

3.3. SLAG CAPACITY AND GAS SOLUBILITY

The solubility of certain chemical species in slags is considered to be important for the metal processing industry. This is evident when reviewing the ability to manage various species by stabilizing them in a final solid-waste slag phase, which can be easily handled and treated. The role of liquid slags in high temperature unit operations is to absorb impurities, such as sulphur, phosphorus and arsenic, and to stabilize them for convenient disposal. A well-known example is the impurity–removal ability of slags used in the steelmaking industry. The demand for higher purity metals and metal–alloys in the iron and steelmaking industry has increased as maximum allowable impurity levels have come down so that manufacturers can produce materials with properties that meet stringent specifications. “Clean” steels with very low levels of sulphur and phosphorus are in demand. Certain grades of free-cutting steels require some sulphur, which weakens the steel for
specific applications. Other industries use slags, which can be in equilibrium or contact with another phase, to absorb or remove the impurities. A directly applicable example is the converting process of the PGM industry, where slags are used to absorb and remove the iron as a fayalitic slag in order to produce a final high-grade matte.

3.3.1. Sulphur Capacity of Slags (Sulphate-Sulphide Capacities)

Sulphur distribution was initially determined by means of slag-metal equilibrations. Bardenheuer and Geller (1934) and Grant and Chipman (1946) explained and quantified the desulphurizing ability of the slags in terms of the transfer of sulphur from the metal to the slag and simultaneous transfer of oxygen from the slag to the metal phase. This slag-metal transfer reaction is described by equation (3.3). Gas-metal equilibrations limited the possibility of studying the individual effects of slag composition and oxygen potential on sulphur partitioning. Fincham and Richardson (1954) overcame this limitation by introducing a gas-slag equilibration technique; they subsequently defined the sulphur capacity of slags. They found that sulphur from the gas phase dissolved into calcium aluminosilicate slags as a sulphate under oxidising conditions ($pO_2 > 10^{-4}$ atm) and as a sulphide under reducing conditions ($pO_2 < 10^{-4}$ atm). The relationship between sulphate and sulphide capacities is illustrated as a function of oxygen potential in Figure 3.2, which was extracted from the Slag Atlas (1981).
$\text{(O}^3\text{)} + S \leftrightarrow (S^2\text{)} + Q \quad (3.3)$

where the brackets denote the slag phase and the underlined symbols the metal phase.

Figure 3.2 The sulphide-sulphate relationship as a function of the logarithm of the oxygen potential. Adapted from Slob Atlas (1981).

The various sulphur capacities can be derived mathematically from their individual gas-slag exchange reactions.

Richardson and Fincham (1954), St. Pierre and Chipman (1956), and Turkdogan and Darken (1961) re-wrote the sulphur distribution reaction for reducing conditions. The gas-slag sulphide exchange reaction can be represented as follows:
\[(O^{3-}) + \frac{1}{2} S_2 \Leftrightarrow (S^{2-}) + \frac{1}{2} O_2\]  
(3.4)

where the brackets denote the slag phase.

The equation for the equilibrium constant of reaction (3.4) can be rewritten by substituting the sulphide content for the sulphide activity (multiplied by the sulphide activity coefficient).

\[Cs^{2-} = \text{wt\% S} \left(\frac{pO_2}{pS_2}\right)^{\frac{1}{2}} = K_{s4} \left(\frac{ao^{2-}/\gamma s^{2-}}{\gamma s^{2-}}\right)\]  
(3.5)

\(K_{s4}\) is the equilibrium constant of reaction (3.4), \(\gamma s^{2-}\) the activity coefficient of the sulphide, and \(ao^{2-}\) the activity of the oxide ion.

According to equation (3.5), sulphide capacity is a function of temperature and slag composition \((ao^{2-}/\gamma s^{2-})\). Therefore, the sulphide capacity at constant slag composition is a function of temperature alone, as we see in equations (3.6) and (3.7).

\[Cs^{2-} = K_s (ao^{2-}/\gamma s^{2-}) = \exp(-\Delta G/RT) \times D = \exp(-a/RT - bR) \times D\]  
(3.6)

where \(\Delta G\) is the Gibbs free energy (a linear function of temperature with constants \(a\) and \(b\)), \(R\) the gas constant, \(T\) the temperature, and \(D\) the grouped constant value of \(ao^{2-}/\gamma s^{2-}\) (for a constant slag composition).

Equation (3.6) can be expressed in the natural logarithm form as

\[\ln(Cs^{2-}) = -E/T + F\]  
(3.7)

where \(E\) and \(F\) denote the grouped constants. The equation of the logarithm of sulphide capacity as a linear function of temperature.
Equation (3.5) defines the sulphide capacity of a slag; however, there exists a sulphate capacity—see equation (3.9)—that can be derived from the gas-slag sulphate exchange reaction (3.8) in a manner similar to that of the sulphide capacity.

\[(O^{2-}) + \frac{1}{3}S_2 + \frac{2}{3}O_2 \Leftrightarrow (SO_4^{2-})\]  
\((3.8)\)

where the brackets denote the slag phase.

\[C_{SO_4^{2-}} = \frac{(\text{wt}\%\ S)}{(pO_2)^{\frac{1}{2}} \times pS_2^{\frac{3}{2}}} = K_s (\alpha_{SO_4^{2-}}/\gamma_{SO_4^{2-}})\]  
\((3.9)\)

where \(K_s\) is a combination of the equilibrium constant of reaction (3.8) and a proportionality constant, which converts the sulphate ion concentration to a sulphur concentration; \(\gamma_{SO_4^{2-}}\) is the activity coefficient of the sulphate and \(\alpha_{SO_4^{2-}}\) the activity of the oxide ion.

Although a sulphate capacity exists, only the sulphide capacity will be investigated, as copper-nickel and PGM melters operate under reducing atmospheres (typically \(pO_2 < 10^{-4}\) atm)—see the Background chapter.

Compilations of sulphide capacity data from binary to multi-component slag systems at various temperatures and compositions are available in the literature.

Nzotta (1999) gives a list of sulphide capacity data for many slag systems over a wide range of temperatures.

Several attempts have been made to model and predict the sulphide capacity of slags. Sosinsky and Sommerville (1986) correlated the sulphide capacity of slags to temperature and optical basicity (introduced in the background chapter).
Subsequently, Young et al. (1992) indicated that the equation of Sonsinsky and Sommerville is valid for concentrations at which the optical basicity is 0.8, a figure that corresponds to an ortho-silicate composition. They determined the "best fit" relationships for concentrations at which the optical basicity was lower than, equal to, and greater than 0.8. Although optical basicity predicts sulphide capacity of complex slags accurately, the approach has its weaknesses: it does not account for interactions between cations and sulphide ions. Concerns arose when sulphide capacity was used as a measure of basicity, and the effect of the addition of a metal oxide to a system was ascribed entirely to the addition of the free oxygen. Many studies used this approach to derive optical basicity indices for components, in instances where these indices could not be measured directly.

Investigations in industry have shown that the empirical calculation of the indices does work for certain systems (Van der Colf, 2005). However, as the approach is theoretically incorrect, difficulties will be encountered when the model is extended to other systems. The change in sulphide capacity with the addition of metal oxides cannot be ascribed only to the increase in the basicity of the slag; certain cations may also be responsible for some of the increasing behaviour, as there exists a fairly strong interaction between some transition-metal cations and sulphide ions. The presence of cations can alter the activity coefficient of sulphides in the slags, which can bring about an increase in sulphide capacity, and it may lead to an unaccountable basicity scale—i.e., the increase in sulphide capacity cannot be ascribed solely to the addition of free oxygen ions as an
electron-neutral compound needs also to be added. Therefore, the cations added may contribute to an increase in sulphide capacity.

Reddy and Blander (1987 & 1989) developed sulphide-capacity models for binary silicate systems. Pelton et al. (1993) expanded the Reddy-Blander model to study multi-component slags produced industrially. The expansion of the Reddy-Blander model incorporated multi-component systems containing either a single basic component with two or more acidic components or vice versa. Gaye et al. (1984, 1988 and 1992) developed a statistical thermodynamic model, also called the "cell" model. It represented and predicted accurately such properties as phases and component activities of complex multi-component iron and steelmaking slags over a wide range of temperatures and compositions. The model was initially developed for complex steelmaking slags and was based on assumptions about slag structures proposed by Frohberg and Kapoor (1901). The model has since been extended to ferrous and non-ferrous multi-component slags containing up to 17 components. The main assumption is that slags consist of an unordered mixture of cells; their cell arrangement is assumed to have an anionic sub-lattice, filled with divalent oxide anions, and a cationic sub-lattice. This model predicted accurately the basicity of a slag. This statistical thermodynamic model gave good correlations for the prediction of sulphide capacity. Another sulphide capacity model (KTH) was developed by Nilsson et al. (1995). It uses the sulphide capacity of pure FeO as the standard reference.
sulphide capacity; the $ao^2/ys^2$ ratio is taken as unity. This ratio is then described as an exponential function of a model parameter that is divided by the product of the ideal gas constant and the absolute temperature. These model parameters are then calculated/modelled for various slag systems, single- and multi-component (Nzotta, 1999). After reviewing the literature on sulphide capacities, Nzotta (1999) conducted the relevant experiments to fill the gaps he identified in the literature. The experiments also helped to develop more accurate model parameters.

A summary of the sulphide capacity data available in the literature is listed in Appendix A2. As extensive data and discussions are available in the literature, only the various sulphide capacity sources are tabulated. The sources are sorted by slag system for which the measured temperatures are indicated.

In general, sulphide capacity increases with increasing temperature at constant slag chemistry. However, it was observed that the sulphide capacity increases with increasing iron content for acidic slags, such as those of iron silicate, whereas a decrease was observed for basic slags, such as those of calcium ferrite (du Toit et al., 2006).

Previously, the determination of the capacity of liquid melter-type slags to absorb sulphur was not considered as important as quantifying the desulphurisation of metal phases in converting processes and in the iron and steel industry, because
the melter slag is in contact with a high-sulphur (matte) phase. However, some base and precious metals do dissolve in the slag and subsequently associate with dissolved sulphides. Therefore, knowing the sulphide capacity aids in explaining the presence of these metals in slags. All of the sulphide capacities for slag systems of the melter-type reported in the literature were for more basic slags, that contain higher levels of CaO. More basic slags were usually investigated for blast-furnace-type slags. One of the research objectives was to quantify the sulphide capacity of melter-type slags over a wide range of temperatures and to determine whether an increase in iron content would lead to an increase in sulphide capacity, as observed for acidic slags.

3.3.2. Other Capacities of Slags

The activity of the free oxygen (O$_2^+$) in a system is a hypothetical entity; it has no real, independent existence in actual systems. First, the formation of such an ion would require complete ionic bonding, which does not occur in reality. Secondly, the activity of ions cannot be measured because of the limitation of having a reference state — i.e. it is impossible to add single ions to a solution in order to measure the corresponding activity; therefore it is required to add an electron-neutral entity for actual activity measurements. Hence, the activity of an ion is a theoretical construct. Nevertheless, the measurement (be it direct or indirect) of the activity of this oxide ion has been, and continues to be, a popular pursuit of
metallurgist for years. This interest is because metallurgists aim at identifying and quantifying the basicity of slags.

The relation between sulphide capacity of a slag and slag basicity was determined empirically by Sommerville (1984). However, the interaction between specific metal cations (especially transition-metal cations) and the sulphide ions is fairly large and can cause an unaccountable basicity scale as discussed before. Wagner (1975) suggested that the carbonate capacity — which he defined by analogy with sulphide capacity — be used as another measure of basicity. He suggested that the carbonate capacity be determined for a reference slag and the other slags be quantified as a relative carbonate capacity ratio. The use of carbonate capacity as a measure of basicity would be limited because it has been quantified for only a small number of slags.

Sommerville, McClean and Yang (1997) concluded that the use of any capacity as a measure of basicity can only be regarded as trustworthy when four limitations and laws were recognised and met. First, that a single species and its form in a solution be known over the whole composition range. Secondly, that the concentration of the solute be low enough to follow Hentian behaviour and hence have a constant activity coefficient. Thirdly, that the compound be dissolved and not precipitated at the temperature concerned. Lastly, that the slag under investigation be completely liquid at the applicable temperature(s).
Wagner (1975) also suggested determining the capacity of such components as phosphate and chromite present in a slag. The definitions for various capacities are described in the literature and are summarized in Table 3.1.

Table 3.1 Capacities available in the literature (C_X represents the concentration of species X in the slag). Extracted from Pilat (1984).

<table>
<thead>
<tr>
<th>Species, 1</th>
<th>Reaction</th>
<th>Capacity, C_X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide, ( \text{S}^{2-} )</td>
<td>( \frac{1}{2} \text{O}_2(g) + \text{S}^{2-} \rightarrow \frac{1}{2} \text{S}_2 ) + ( \text{CO} )</td>
<td>( \text{C}<em>X \times (\text{P}</em>{\text{O}<em>2}/\text{P}</em>{\text{S}_2})^{0.5} )</td>
</tr>
<tr>
<td>Pyrosulfate, ( \text{S}_2 \text{O}_7^{2-} )</td>
<td>( \text{S}_2 \text{O}_7^{2-} + 9 \text{H}_2 \text{O} \rightarrow 2 \text{SO}_4^{2-} + 7 \text{H}_2 \text{O} )</td>
<td>( \text{C}_Y/\text{C}<em>X \times \text{P}</em>{\text{H}_2 \text{O}} )</td>
</tr>
<tr>
<td>Sulfite, ( \text{SO}_3^{2-} )</td>
<td>( \frac{1}{2} \text{O}_2(g) + \text{SO}_3^{2-} + 3 \text{H}_2 \text{O} \rightarrow \frac{1}{2} \text{SO}_4^{2-} + 3 \text{H}_2 \text{O} )</td>
<td>( \text{C}<em>Z/\text{P}</em>{\text{O}<em>2} \times \text{P}</em>{\text{H}_2 \text{O}} )</td>
</tr>
<tr>
<td>Carbide, ( \text{C}_2 )</td>
<td>( \text{C}_2 + 2 \text{H}_2 \text{O} \rightarrow \text{CO}_2 )</td>
<td>( \text{C}<em>{2X} \times \text{P}</em>{\text{H}<em>2 \text{O}} / \text{P}</em>{\text{CO}_2} )</td>
</tr>
<tr>
<td>Carbonate, ( \text{CO}_3^{2-} )</td>
<td>( \text{CO}_3^{2-} + \text{H}_2 \text{O} \rightarrow \text{CO}_2 + \text{OH} )</td>
<td>( \text{C}<em>{2X} \times \text{P}</em>{\text{H}<em>2 \text{O}} / \text{P}</em>{\text{CO}_2} )</td>
</tr>
<tr>
<td>Hydroxyl, ( \text{OH}^- )</td>
<td>( \text{H}_2 \text{O}(g) + (\text{OH}^-) \rightarrow 2 \text{H}_2 \text{O} )</td>
<td>( \text{C}<em>{2X} \times \text{P}</em>{\text{H}<em>2 \text{O}} / \text{P}</em>{\text{H}_2 \text{O}} )</td>
</tr>
<tr>
<td>Nitride, ( \text{N}_2^- )</td>
<td>( \text{N}_2 + 3 \text{H}_2 \text{O} \rightarrow 2 \text{NH}_3 + 3 \text{H}_2 )</td>
<td>( \text{C}<em>Y/\text{P}</em>{\text{N}<em>2} \times \text{P}</em>{\text{H}_2 \text{O}} )</td>
</tr>
<tr>
<td>Cyanide, ( \text{CN}^- )</td>
<td>( \text{CN}^- + \text{H}_2 \text{O} \rightarrow \text{H}_2 \text{CN}^- + \text{OH} )</td>
<td>( \text{C}<em>{2X} \times \text{P}</em>{\text{H}<em>2 \text{O}} / \text{P}</em>{\text{H}_2 \text{CN}^-} )</td>
</tr>
<tr>
<td>Phosphate, ( \text{PO}_4^{3-} )</td>
<td>( \text{PO}_4^{3-} + 5 \text{H}_2 \text{O} \rightarrow 5 \text{H}_2 \text{PO}_4^- + 3 \text{OH} )</td>
<td>( \text{C}<em>{2X} \times \text{P}</em>{\text{H}<em>2 \text{O}} / \text{P}</em>{\text{H}_2 \text{PO}_4^-} )</td>
</tr>
<tr>
<td>Phosphite, ( \text{PO}_3^{2-} )</td>
<td>( \text{PO}_3^{2-} + 3 \text{H}_2 \text{O} \rightarrow 2 \text{H}_2 \text{PO}_4^- + \text{OH} )</td>
<td>( \text{C}<em>{2X} \times \text{P}</em>{\text{H}<em>2 \text{O}} / \text{P}</em>{\text{H}_2 \text{PO}_4^-} )</td>
</tr>
</tbody>
</table>

* Designates that \( \text{C}_Y \) combines with a singly-bonded oxygen, \( \text{P}_{\text{O}_2}/\text{P}_{\text{S}_2} \), or it may remain a doubly-charged free ion. * Designates that the oxygen may be singly or doubly charged, and that, respectively, the hydroxyl ion is unchanged and the other carries a single charge, or that both are singly charged.

For sulphur capacity of slags it is known that the sulphur can be dissolved in the slag as either a sulphate or a sulphide, depending on the oxygen potential. Similarly, phosphorus dissolves as a phosphite or a phosphate. These binary phenomena force one to investigate the gas-slag solubility mechanism of species as a function of oxygen potential before any experiments are conducted.
Blander (2000) reviewed the available theories and concepts underlying the thermodynamic properties of high-temperature liquid solutions and vapours. One of the theories drew on the polymer theory to predict such capacities as $\text{PO}_4^{3-}$, $\text{SO}_4^{2-}$, $\text{Cl}$, $\text{Br}$, and $\text{I}$.

### 3.3.3 Chlorine Capacity of Slags (Chloride Capacity)

The importance of understanding the dissolution mechanisms of species cannot be underestimated. When the chlorine solubility literature was initially investigated, it was thought that not only the chloride ions, but also the oxychloride ions ($\text{ClO}^-$, $\text{ClO}_3^-$, etc.) could influence the dissolution mechanism at the oxygen potential range relevant to PGM melter operations.

Hirosumi and Morita (2000) and Miwa and Morita (2002) studied the chloride capacity of calcium aluminosilicate slags in order to predict the behaviour of chlorine distribution during the incineration of plastics (PVC), which are used as an alternative source of energy in the iron and steel industry. They investigated calcium aluminosilicate slag systems similar to those in the iron and steel industry, with the exception of $\text{Na}_2\text{O}$, which was added along with $\text{FeO}$, $\text{MgO}$ and $\text{MnO}$ to the base $\text{CaO-SiO}_2-\text{Al}_2\text{O}_3$ slag. They used a gas-slag equilibration technique similar to the one Fincham and Richardson (1954) developed for the determination of sulphur capacities. The experimental conditions of these two papers differ in that Hirosumi and Morita (2000) ran their tests under reducing
conditions \( (p_{O_2} \times 10^{-16} - 10^{-19} \text{ atm}) \) at \( p_{Cl_2} \) of \( 10^{-10} - 10^{-19} \text{ atm} \) and at 1400 – 1475°C, whereas Miwa and Morita (2002) ran tests under more oxidising conditions \( (p_{O_2} \times 10^{-5} - 10^{-13} \text{ atm}) \) at \( p_{Cl_2} \) \( 10^{-7} - 10^{-10} \text{ atm} \) and at 1400°C. The initial chlorine dissolution mechanism was assumed to be the formation of chlorides as described by equation (3.10).

\[
\frac{1}{2} \text{O}_2^- + \frac{1}{2} \text{Cl}_2 \leftrightarrow (\text{Cl}) + \frac{1}{4} \text{O}_2 \quad (3.10)
\]

where the brackets denote the slag phase.

It is evident from the data presented in Miwa and Morita (2002) —see Figure 3.3— that the log([mass%Cl]/\( p_{Cl_2}^{1/4} \)) decreases linearly with increasing log[\( p_{O_2} \)] with a slope of \(-\frac{1}{4}\) log units. Therefore, the solubility of chlorine into the slag phase from the gas phase is proportional to \( p_{O_2}^{1/4} \) and \( p_{Cl_2}^{1/4} \) as expected from the assumed chloride dissolution mechanism expressed in equation (3.10). The \( p_{O_2} \) range \( (10^{-5} - 10^{-19} \text{ atm}) \) investigated in these two papers confirmed the instability of possible oxochloride dissolution under the other conditions investigated.

Thus, the chloride capacity was defined as follows:

\[
C_{Cl} = (\text{wt} \% \text{ Cl}) (p_{O_2}^{1/4}) / (p_{Cl_2}^{1/4}) = K_{410} (\text{o}_2^3) / (\text{yCl}) \quad (3.11)
\]
Myoung, Lee and Min (2003) expanded the slag system(s) investigated by Miwa and Morita (2002) to generate data for a slag system more applicable to typical blast furnace operations. Miwa and Morita found that the chloride capacity \((\text{Cl}^-)\), as defined in equation (3.11), increases with increases in \(\text{Na}_2\text{O}, \text{FeO}, \text{MgO} \) and \(\text{MnO}\). They concluded that the chloride capacity increased with additions of base metal oxides, and concluded the converse for additions of \(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\). The addition of \(\text{FeO}\) to a \(\text{CaO-SiO}_2\) slag was controlled by reacting the slag with the iron of an iron crucible. The iron content was varied by changing the oxygen partial pressure of the system. The slight increase in chloride capacity for similar mass additions of \(\text{FeO}, \text{MgO} \) and \(\text{MnO}\) compared with the considerable increase for additions of the more basic \(\text{Na}_2\text{O}\) confirmed that chloride capacity is strongly dependent on basicity.
Hirosumi and Morita (2000) determined the dependence on temperature of chloride capacity in calcium aluminosilicate slags for a range of basicity (see Figure 3.4). Chloride capacity generally increases with increasing temperature. The effect of temperature was stronger for basic slags than for acidic slags. Myoung et al. (2003) verified the experimental technique as well as the dissolution of chlorine as chlorides in a 40:20:40 wt% CaO:Al₂O₃:SiO₂ slag at 1400°C under reducing conditions similar to those investigated by Hirosumi and Morita (2000).
Although Myoung et al. (2003) obtained results that showed good correlation compared with those of Hirosumi and Morita (2000), the effect of temperature on chloride capacity contradicted expectation: whereas Hirosumi and Morita (2000) showed increasing chloride capacity with temperature, Myoung et al. (2003) found that chloride capacity decreased with increasing temperature. No explanation has been offered for this discrepancy. Therefore,
the effect of temperature on chloride capacity was identified as an area for further investigation.

Besides the effect of temperature, Myoung et al. (2003) observed the effect of lime and magnesia on chloride capacity. They concluded that chloride capacity increased with increasing CaO/SiO₂ ratio at constant MgO contents. This increase was not entirely unexpected as the basicity of these slags increased. Moreover, they found that chloride capacity increased linearly with increasing log[CaO], and suggested that the influence of MgO was insignificant, except that MgO dilutes CaO. Myoung et al. (2003) investigated the effect of increasing the MgO content (~0 – 13 wt%) for three slags with CaO/SiO₂ mass ratios of 0.75, 1.0 and 1.2, respectively. They noted that the increase in MgO did not affect the chloride capacity significantly. However, when log[Ccl⁻] was plotted as a function of the MgO mass content, a dip in log[Ccl⁻] was observed at the 5 wt% MgO mark. They argued that the decrease in liquidus temperature of the slag around the 5 wt% MgO content is responsible for this dip. They suggested that CaO has a greater influence on the chlorine dissolution reaction than MgO, which only affects the liquidus of the slag and dilutes CaO.

In summary, a review of the literature shows that the available chloride capacity data is limited, and that the effect of temperature shows inconsistencies. The solution thermodynamics of chlorine in melter-type slags has not been studied previously. There also exists a lack of knowledge on the chloride capacity of such
slags. Therefore, the current understanding of the chloride species in the melter-type slags is incomplete. The author also identified that iron redox equilibria and the sulphide capacity of melter-type slags were not quantified. Therefore, the thermodynamic behaviour of sulphur and chlorine as minor elements in melts found in the base-metal and PGM industry requires investigating. The understanding of the behaviour of these toxic minor elements will aid producers in predicting, managing and controlling these minors so as to enable them to comply with the increasingly stringent restrictions set on toxic levels in effluent streams.
3.4. HYPOTHESES

With the overall objectives of the sponsors of this research project in mind, I postulated the following hypotheses after reviewing the available literature:

- The low levels of chlorides present in metallurgical slags obey Henry’s law.

- Based on the ionic theory of slag chemistry, FeO₂ acts as a basic oxide for acidic melter-type slags and decreases the degree of polymerization in silicate melts so that more anions are dissolved in the slag. Furthermore, as iron has a strong affinity for sulphur in silicate melts, its presence contributes significantly to the Fe²⁺-S⁻ interaction and hence lowers the activity coefficient of sulphur in the slag, thus, increasing the sulphide capacity of melter-type slags by its increase.

- If the thermodynamic behaviour of low-level chlorides deviates negatively from ideal behaviour, then one can expect a decrease in pO₂ and an increase in pCl₂ and slag basicity to increase the prevailing chloride activity coefficient, thereby causing the chloride activity coefficient in slags to follow ideal behaviour more closely.

- The iron redox equilibria of melter-type slags follow closely the ideal behaviour of melts based on calcium silicate.
3.5. RESEARCH QUESTIONS

Once the literature was reviewed and the hypotheses postulated, it was possible to summarize the deliverables of this study in the form of a set of research questions:

- Do the iron redox equilibria of melter-type slags deviate significantly from ideal redox behaviour?

- Can the iron redox equilibria of melter-type slags be predicted accurately by extrapolation of the available models for iron-bath smelter slag?

- What is the holding capacity of metallurgical slags in the PGM industry at low levels of sulphides and chlorides?

- Would an increase in the iron content of melter-type slags cause an increase in sulphide capacity?

- What effect do changes in temperature, partial pressures and slag composition have on chloride capacity? In particular, what is the effect of temperature on chloride capacity — i.e. does the effect agree with the observations of Myoung et al. (2003) or of Hirosumi and Murita (2000)?

- Does the activity of chlorides in slags show negative or positive deviation from ideal behaviour?
Chapter 4

EXPERIMENTAL

The primary series of experiments conducted for this thesis was aimed at equilibrating various gas mixtures, which were predetermined to produce the desired gas compositions, with molten slags. The objective was to introduce minor elements, through the gas phase and allow enough reaction time for the gases to equilibrate with molten slags, in order to investigate the solubility and holding capacity of slags for the minor elements under investigation.

Generally, synthetic slags were prepared after which they were equilibrated with purified gases at high temperature in an appropriate vertical-tube furnace.

The materials, equipment, procedures and preliminary experiments will be discussed in this chapter.

4.1. RAW MATERIALS

In this section the quality and purity of the commercially available reagents, metal oxide powders and gases, used for the synthesizing of the slags and mixing and purification of the reaction gases are listed in Table 4.1 and Table 4.2 respectively.
The metal oxide powders were dried for at least 12 hours in a Watson Victor Ltd drying oven at about 120°C before use.

Some furnace matte samples were used as iron reservoirs where necessary. The normalized matte sample compositions used are reported in Table 4.3.
4.2. MATERIAL PREPARATION

4.2.1. Slag Making

Master slags were prepared by using pre-dried powders of laboratory reagent grade Al₂O₃, CaCO₃, Fe₂O₃, MgO and SiO₂. The required amounts were dried, weighed, mixed and then milled in a clean tungsten carbide ring mill. Thereafter, the mixture was pre-melted at 1500°C in an eggcup shaped Pt-10%Rh crucible (15 mm base ø, 50 mm high with a 40 mm top ø) using a B & L Teflon MoSi₂ muffle-furnace. The melt was poured onto a steel launder at ambient temperature to form a quenched glass. When cooled, the glass was pulverized in a ring mill and mixed to result in a fine homogeneous master slag. The average slag compositions obtained by X-Ray Fluorescence (XRF) are reported in Table 4.4 with the Basicity (B) defined as the mass ratio of CaO and MgO to SiO₂.

A well-characterized CAS (calcium aluminosilicate) slag was chosen in order to compare, correlate and confirm the current experimental techniques, procedures and analytical methods. An iron silicate slag was prepared with a similar composition to fayalitic slags found in industrial converters of the platinum producers, whereas the melter-type slags were prepared to simulate the slags obtained with the smelting of chromium-free Merensky concentrates. The melter-type slags' iron content was varied at two levels, while keeping all the other components at similar composition ratios. Multi-component iron-free CaO-Al₂O₃-MgO-SiO₂ melter-type slags were also prepared. These iron-free melter-type slags
were used where the volatilization of iron as metal chlorides has proven to be problematic and inevitable. MgO or CaO was substituted for SiO₂ so as to investigate the effect of basicity on the minor element's behaviour.

**Table 4.1 Slag compositions analysed by XR**

<table>
<thead>
<tr>
<th>Slag Name</th>
<th>CaO (w%)</th>
<th>Al₂O₃ (w%)</th>
<th>FeO (w%)</th>
<th>MgO (w%)</th>
<th>SiO₂ (w%)</th>
<th>CaO + MgO (B)</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS</td>
<td>38.4</td>
<td>19.8</td>
<td>---</td>
<td>41.8</td>
<td>60.9</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>8S</td>
<td>60.9</td>
<td>30.1</td>
<td>---</td>
<td>64.7</td>
<td>9.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT1-A</td>
<td>9.4</td>
<td>9.1</td>
<td>26.9</td>
<td>54.7</td>
<td>9.66</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>MT1-B</td>
<td>9.3</td>
<td>9.1</td>
<td>19.8</td>
<td>61.8</td>
<td>9.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT1-C</td>
<td>16.8</td>
<td>9.1</td>
<td>19.7</td>
<td>54.5</td>
<td>9.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT1-D</td>
<td>21.3</td>
<td>9.1</td>
<td>19.5</td>
<td>50.6</td>
<td>9.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT1-E</td>
<td>28.7</td>
<td>8.9</td>
<td>19.7</td>
<td>42.2</td>
<td>8.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT1-F</td>
<td>20.4</td>
<td>9.0</td>
<td>20.0</td>
<td>51.6</td>
<td>9.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT1-G</td>
<td>20.0</td>
<td>9.1</td>
<td>9.1</td>
<td>61.8</td>
<td>9.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT2-A</td>
<td>7.0</td>
<td>7.2</td>
<td>20.1</td>
<td>43.2</td>
<td>9.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT2-B</td>
<td>8.3</td>
<td>8.5</td>
<td>10.3</td>
<td>45.7</td>
<td>9.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT3-A</td>
<td>8.2</td>
<td>7.9</td>
<td>40.1</td>
<td>37.1</td>
<td>9.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The iron containing slags were pre-reduced in order to minimize the equilibration time, see section 4.5, by reacting the powdered slag in a small Ceramic Engineering furnace capable of heating up to 1000°C. The fine slag powder was placed on porous alumina blocks in a removable quartz reaction tube and reacted at 600°C in a reducing atmosphere. This technique was employed as the rate of reduction increases, with an increase in the gas-solid contact area per unit volume. This increase in the rate of reduction resulted in significant decreases in pre-reduction times, relative to conventional high temperature pre-reduction.

---

*CAS: Calcium aluminate 8S: Iron silicate MT: Molybdenum FeO: reported as Fe₂O₃*
methods. For example, reagent-grade hematite powder was reduced to wustite (analysed using X-Ray Diffractometry) by reacting hematite with a 1:1 \( pCO:CO_2 \) atmosphere at 800°C and a total flow rate of 500 cm\(^3\)/min (NTP) for 1.5 hours.

4.2.2. Gas Cleaning

The gases listed in Table 4.2 were purified by passing them through a gas-cleaning train before introducing them into the reaction riga. The arrangement of the train is illustrated in Figure 4.1. Water was removed by passing the gases through magnesium perchlorate and or silica gel.

![Figure 4.1 Schematic of the gas-cleaning train](image)

The low levels of oxygen were then extracted by passing the gas over pre-heated copper chips at 500°C. The desired gas flows were mixed using a 50 mm \( \theta \times 15\)
cm long tube packed with 5 mm φ quartz beads. The purification train also allowed the purified gases to be used individually.

4.3. EQUIPMENT AND EXPERIMENTAL TECHNIQUES

The uncertainties and errors present in the experimental results originate largely from uncertainties associated with the measurement of temperature, the monitoring of gas flow rates, and the analysis of chemical composition of the generated samples. The calibration of the thermocouple and mass-flow controllers are discussed here; the analytical techniques and methods are discussed briefly in the section on sample analysis.

An overview of calibration techniques and selected results are presented here; some details are reported in the Appendix.

4.3.1. Calibrations

An ASTM R type (Pt/Pt-13% Rh) thermocouple was used to measure and monitor the temperature at the hot zone in the furnace. The position of the thermocouple in the furnace is illustrated in Figure 4.3. The ceramic platform was replaced by a graphite crucible filled with high-purity copper-chips for the calibration of the thermocouple. The whole unit was slowly inserted from the bottom of the furnace while the furnace was set at a predetermined temperature. The furnace was purged with clean Ar at a flow rate of 1000 cm³/min (STP) for an hour. This hour ensured that the copper was fully molten and that the
temperature measured by the thermocouple to be calibrated had stabilized (above the freezing point of copper). Air was introduced to minimize any infiltration of air. A graphite crucible was used to generate and maintain a reducing atmosphere at the measuring point specifically to prevent the copper from being oxidised, thereby changing the overall melting/freezing point measured.

The furnace was allowed to cool slowly. The measured temperatures stabilized for about 4.5 minutes at 1082 and 1081°C, which indicate the transition from liquid to solid copper (the measured freezing point is shown in Figure 4.2). These temperatures compare within 2°C of the melting point of copper (1083°C), reported by Turkdogan (1980).

MKS mass-flow controllers were used to control the various gas flow-rates required to maintain the desired atmospheric conditions within the reaction-tube. Different sizes of mass-flow controllers were used, depending on the magnitude of the gas flows required. Typical sizes of controllers used, ranged from the standard reported maximum nitrogen flows of 50 to 5000 cm³/min (STP). These mass-flow controllers use the principle of measuring a differential heat transfer between two sensing elements for a laminar flow of the gas in order to deduce the prevailing flow-rate. The 1179A MKS flow controllers with metal seals were used for all the gases, except for the corrosive gases, where those controllers were replaced by controllers containing elastomer seals.
Figure 4.2 The calibration of an ASTM type R thermocouple against the melting/freezing point of copper.

The gas flow-rates were calibrated using an MKS mass-flow meter with a range of 1 to 6000 cm³/min or a soap-bubble moving through a burette/bubble-tower technique. The latter technique was used to measure the flow of corrosive gases. The calibrations were done for each gas at various set-points equally distributed between 10 and 90%. The controller accuracy decreases sharply below a set-point of 10% or above 90%, and is therefore considered to be out of the range of the controller.
4.3.2. **Vertical Tube Furnace**

A high-temperature, vertical-tube furnace fitted with U-shaped MoSi2 resistive-heating elements was used for the equilibration experiments. The temperature was controlled using ASTM R-type thermocouples. A recrystallized alumina and several fused mullite (Pythagoras) reaction tubes with a 60 mm outer diameter served as work-tubes. Water-cooled end caps fitted with the appropriate O-rings maintained the desired atmospheric conditions within the reaction tube. Two gas bubblers were installed in series (front-to-back) in the exhaust line of the furnace to prevent the backflow of air through the exhaust line. One of the bubblers contained di-o-butyl phthalate, which was replaced regularly and imparted a slight positive pressure in the work-tube.

There were two variations of the experimental rig used and these will be discussed in turn.

Initially, the gases were introduced at the bottom of the furnace as shown in Figure 4.3 to allow the gases to heat up before reaching the gas-slag reaction zone. The various crucible set-ups were suspended from an alumina lance, which could be adjusted to various depths while still maintaining a gas seal. The crucibles were held securely connected to the alumina lance with a ceramic thermocouple-spline, fitted with safety Pt wires. Gases left the system through
The exhaust gases were vented through the standard laboratory gas extraction and cleaning systems, before being released to atmosphere.

![Diagram of a furnace with labeled parts](image)

**Figure 4.3** Sketch of the vertical tube furnace fitted with a lance-suspended crucible set-up.

The suspended crucible was loaded into the work tube. The preheated furnace was flushed with Ar at a flow-rate of 1000 cm³/min (STP) for half an hour before lowering the crucibles into the hot zone. The desired gas mixtures were then introduced. The hot zone of the furnace was determined as the hottest part of the tube. After the crucible had been placed in the hot zone and the desired reaction time had been reached, the samples were quenched by submerging the crucible in...
pure water. The samples were removed from the crucibles and prepared for analysis.

Figure 4.4 Sketch of the (a) Pt – 10% Rh and (b) MgO Crucible Set ups

Two crucible arrangements were used and are shown in Figure 4.4. The first setup shown consists of two Pt/Pt-10% Rh vessels and a ceramic heat shield. The heat shield was fused mullite (Pythagoras), cut into a circular disc. The larger Pt
alloy crucible was used to suspend the smaller Pt-alloy boat (approximately 1 cm × 1 cm × 2.5 cm) loaded with 2 g of the fine and homogeneous powder reagents.

The other crucible set-up, (Figure 4.4), was used whenever a matte was introduced simultaneously with a slag. This set-up consisted of a dense magnesia eggcup-shaped crucible and a similar ceramic heat-shield.

MgO crucibles were used for reacting matte-containing samples because matte attacks Pt-alloy crucibles. However, the MgO crucibles will develop a growing solid-solution region that will change the composition of the reagents towards magnesia saturation as magnesia from the crucible dissolves in the molten material.

The other variation in experimental set-up was the introduction of water vapour into the reaction tube. The apparatus was modified to produce superheated water vapour, which would deliver the required water vapour fraction to the reaction zone. Liquid water was introduced into an overheated unit by a Mettler 718 STAT Titriso automatic dosing unit. The overheated chamber was flushed with cleaned Ar, which was used as the carrier-gas (see Figure 4.5 for more graphical details). However, problems may arise if the water vapour composition at the top end-cap were to reach the dewpoint temperature. Some of the water would condense and trickle down the wall of the reaction tube, thereby causing severe thermal shock, which could crack the tube. Therefore, the flow of water in the top water-cooled end-cap was controlled to maintain a temperature of 50°C or
higher. This temperature limits the highest fraction of water vapour that may be introduced with the carrier gas. A special Viton O-ring, which has a higher operating temperature than a standard O-ring, was used. The variation of the experimental rig is shown schematically in Figure 4.5. The hot zone remained the same for both experimental set-ups.

Figure 4.5 Sketch of the of the vertical tube furnace fitted with a Pt/Pt-13% Rh wire suspended crucible. This set-up was used for tests introducing water vapour into the experimental rig.
The set-up shown in Figure 4.5 used the same experimental procedure as described previously. However, the crucible was suspended using a long Pt/Pt-13% Rh wire and was raised into the hot zone from the bottom of the furnace. The gases were introduced through the lance and removed at the bottom of the furnace. The flow rates used were low enough to allow preheating of the reaction gases, thereby preventing quenching of the slag at the gas-slag interface. The off-gases passed through a condenser to remove any water before the gases reached the bubblers (water in the gases would change the density of di-n-butyl phthalate).

4.4. SAMPLE ANALYSIS

The various analytical techniques are discussed briefly, while the detailed procedures and variations from standard methods are described in Appendix A.1.

All the samples were analysed by the analytical services department of CSIRO Minerals. The melt chemistry research conducted for this study benefited from the analytical developments of the management of minor elements program of AMIRA that ran in parallel with the current investigation.

The quenched samples were dried at 120°C overnight, and were either ground with a mortar and pestle or pulverized in a tungsten carbide ring mill before being analysed. However, small pieces of the dried samples were chipped off from the products of the matte-slag-gas equilibriations to see if any minor elements
(specifically dissolved chlorides) and their associated phases could be detected by scanning electron microscopy (SEM).

The analytical methods most frequently used for measuring major components included XRF for the metal oxide content, ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) for the oxide-containing samples, and wet-chemistry titrations for the ferrous analyses. The analytical techniques used for measuring minor components included LECO CS-600 carbon/sulphur analyser (internal combustion spectrometer) for low levels of sulphur and HPLC (High Precision Liquid Chromatography) with an online dialysis unit (developed by the analytical team at CSIRO Minerals) for measuring low levels of chlorides.

The relative errors associated with sample analysis are discussed in the Discussion chapter, whereas Appendix A.I details the analytical techniques and developments.

4.5. TIME TO APPROACH EQUILIBRIUM

It is necessary to verify the reaction status with respect to time in order to confirm equilibrium for any thermodynamic study. Moreover, it is important to bear in mind that steady state may be reached, which differs from the equilibrium value because of kinetic influences as discussed in the Literature Review chapter.
It is therefore crucial to determine whether steady state rather than equilibrium has been reached.

Preliminary experiments were conducted for the various systems to determine the reaction time needed to reach equilibrium. Other checks were included to confirm equilibrium.

Gas-slag equilibrations are reported first. These are followed by some gas-slag-matte equilibrations. The matte was introduced to act as an iron reservoir to counter the volatilization of iron as a chloride. This technique is not the most desirable, however, as it consumes MgO crucibles. (The use of these crucibles changes the slag chemistry in the MgO-saturated direction.) It was observed from some preliminary gas-slag experiments that kinetic limitations mimicked equilibrium, while, in fact, a steady state had been reached. This observation will be explained in more detail in the Discussion chapter.

The appropriate combination of inlet gas flow rates was determined by calculating the inlet gas fractions at ambient conditions necessary to produce the desired gas composition at the reaction zone. In some cases the Gibbs free energy data were used to determine the required compositions. In other cases, when there were a large number of gases intersecting, the Thermochemistry program of CSIRO Minerals (named Chemix) was used (Tumble and Wadsley, 1988).
4.5.1. Gas-Slag Equilibration

**Sulphur Equilibrations**

The time required by the well-characterized calcium aluminosilicate slag to reach equilibrium in a gas atmosphere of partial pressures of sulphur and oxygen of $10^{-12}$ and $10^{-62}$ atm respectively, was initially determined at a temperature of 1400°C. Sulphur was introduced into the system as an Ar-SO$_3$ pre-mixture. The minimum equilibrium time was determined through a series of tests in which the reaction time was varied until the sulphur content of the slag stabilized. The conditions chosen were those producing the slowest kinetics. For example, the lowest temperature investigated for the particular slag, reaction times of 2, 4, 6 and 16 hours were tested and the results are shown in Figure 4.6. This slag was reacted from both the low and high sulphur side by dosing the slag with small amounts of calcium sulphide to ensure that the equilibrium was reached, as the possibility existed that a steady state, other than the equilibrium value, could have been reached due to interfacial gas-molten slag kinetic limitations. The additional sulphur was added as CaS, because elemental sulphur would have volatilized. It was also assumed that the Ca added to the slag with the small addition of CaS does not significantly affect the basicity of the slag. However, if a large amount of CaS had been required, the basicity could have been corrected for by adding more of the acidic components.
The sulphur content took up to 8 hours to stabilize from the low sulphur side. Subsequently, a 16 hour reaction period was used to ensure that more than enough time was allowed for equilibration.

The initial iron-containing synthetic slags were prepared with additions of waste, prepared by pre-reducing solid hematite powder at 800°C using a CO-CO₂ gas mixture. However, it was still necessary to monitor the iron redox states for equilibrium. It was found that they reached equilibrium within 3 to 8 hours.
depending on the pre-reduced state of the slag. The equilibration of the iron silicate and a melter-type slag are shown in Figure 4.7 and Figure 4.8 respectively.

Figure 4.7 Variation of the sulphide content and \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio for a \( \text{FeO} - \text{SiO}_2 \) slag (W) with time. The reducing gases were CO, CO\(_2\), SO\(_2\), and Ar.

The reaction time was set at 16 hours for all the sulphur equilibration experiments as the conditions of the slag had stabilized by then.
Figure 4.8 Equilibration of the melt-type (M12-3) \( \text{Al}_2\text{O}_3, \text{CaO-FeO, MgO-SiO}_2 \) slag. The inlet gases were \( \text{CO, CO}_2, \text{SO}_2 \) and \( \text{Ar} \).

Chlorine Equilibrations

The chlorine was introduced into the gas system as a premixed \( \text{Ar} \) and \( \text{HCl} \) mixture (from a gas cylinder). As it was expected that the iron-containing slags might have some difficulty in reaching equilibrium, the iron-free melt-type slags were reacted first. The multi-component \( \text{CaO-MgO-MgO-SiO}_2 \) slag, which was used in determinations of the time required to reach equilibrium, was synthesized so that the mass-basicity ratio of \( \text{MgO} \) and \( \text{CaO} \) to \( \text{SiO}_2 \) fell within the range for those of the iron-containing melt-type slags.
Figure 4.9 Variation of the chloride content for an iron-free matte-type (MT/-A) AlF₃-CaO-MgO-SiO₂ slag with reaction period. The inert gases were H₂, H₂O, HCl and Ar.

The slag was reacted at 1450°C (above the liquidus) with a gas atmosphere fixed at a pO₂ and pCl₂ of 10⁻³⁰ and 10⁻²⁴ atm respectively. The time required to reach equilibrium was found to be 8 hours, and was determined in the same way as that of the sulphur equilibrations (see Figure 4.9). The slag was dosed with predicted calcium chloride to determine whether equilibrium was obtained from low and high chloride concentrations. If different values had been obtained for the same
experimental conditions, then it would indicate that a steady state had been reached.

The iron-containing slags proved to be problematic, as iron was lost from the slag as gaseous iron chloride. The total iron content for slag MT2-A dropped from 15.6 to 1.32 wt% in the 20 hours of the attempted equilibration. The chloride content and iron redox ratio are plotted with reaction time in Figure 4.10. The plots show irregular behaviour.

![Graph showing the attempted equilibration of an iron-containing slag MT2-A Al2O3-CaO-FeO-MgO-SiO2. The inset gases were H2, H2O, Cl, and Ar.](image)

Figure 4.10 The attempted equilibration of an iron-containing slag (MT2-A) Al2O3-CaO-FeO-MgO-SiO2. The inset gases were H2, H2O, Cl, and Ar.
4.5.2. Gas-Slag-Matte Equilibration

As a result of our inability to equilibrate the iron-containing melt-type slag with the initially attempted gas-slag equilibration tests, a matte of low grade was introduced to act as an iron reservoir for the slag phase. CSIRO's MPE (Multi Phase Equilibrium – see Zhang et al., 2002) package was used to determine the composition of melt-type slags that would be in equilibrium with mattes of low grade at similar atmospheric conditions. It was determined that slag MT3-A would be close to equilibrium if reacted with the mattes reported in Table 4.3 at a $pO_2$ and $PS_2$ of $10^{-6}$ and $10^{-3}$ atm respectively at 1450°C. A magnesia crucible would be used as the matte would attack the Pt alloy crucibles, which renders them unsuitable. One of the disadvantages of using a MgO crucible is that the slag composition will change towards MgO saturation at the reacting temperature.

A CO-CO$_2$-H$_2$-HCl-SO$_2$-Ar gas mixture was used to simultaneously fix the partial pressures in the reaction zone, that is, $pO_2$, $PS_2$, and $pCl_2$ at $10^{-6}$, $10^{-3}$ and $10^{-7}$ atm, respectively.

The combined slag gas and matte phases were reacted for durations of 4, 6 and 9 hours. Figure 4.11 shows compositions of the slag and matte as functions of reaction time.
The constant value of MgO, which dissolves from the crucible into the slag after 4 hours of reaction time, indicates that the slag phase has reached a saturation of MgO containing phases. The constant Fe$^{3+}$/Fe$^{2+}$ ratio after 4 hours indicates that the gas-slag system has reached equilibrium, while the constant distribution of iron between matte and slag indicates matte-slag equilibrium. It is evident from Figure 4.11 that the matte-slag-gas system has reached equilibrium after 4 hours of reaction. Subsequently, all the three-phase equilibrations were reacted for 9 hours to ensure that all the variables had stabilized.
4.5.3. Gas-Slag Steady State Observations

This section describes the possibility of reaching a steady state that mimics equilibrium but is not in fact. The melt-type gas-slag system in Figure 4.12 appears to have reached equilibrium conditions in the slag are more or less constant after 4 hours. A closer look, however, shows the stabilized iron redox ratio to be more oxidized than the expected equilibrium value, which was determined experimentally and reported in the results section.

![Diagram showing FeOx, Fe, and Cr concentrations over reaction time](image)

**Figure 4.12** Variation of Cr, FeOx, and Fe²⁺/Fe³⁺ ratio with reaction time noted with a CO₂/H₂/HCl gas mixture. Steady state expected.
Subsequent tests on this system yielded unpredictable results and behaviour. Further investigation showed that interfacial gas-molten slag kinetic limitations were behind this phenomenon. For gas mixtures of CO, CO₂, H₂ it was expected that the oxidation state of the slag, obtained from preliminary experiments, be more reduced than oxidized relative to the equilibrium value. It was therefore hypothesized that the reaction gas mixture reacts and the water-gas shift reaction reached equilibrium while preheating before reaching the reaction zone. Thereafter, interfacial kinetics between the gas and the molten slag starts to play an important role as the formed H₂O dissociates faster than CO₂ as reported by Yang (1994). The rate of oxygen donated exceeds the rate of oxygen removed from the slag, resulting in a more oxidized slag at steady state instead of equilibrium. The reviewed literature on the interfacial kinetics between various gas mixtures and slags supports this hypothesis and a more elaborate discussion will be given after the ensuing Experimental Results chapter.
In summary, this chapter details the experimental aspects of this project and gives the reader some preliminary experimental results. It was found that a reaction time of 16 hours was more than enough for the sulphur equilibration experiments, whereas a 9 hour reaction time proved to be long enough to reach equilibrium for the chlorine equilibrations and matte-slag-gas reactions. It was also observed from the preliminary experiments that certain gases could produce a non-equilibrium steady state, an outcome due to influences of interfacial rates of reactions between gases and molten slags.
Chapter 5

EXPERIMENTAL RESULTS

The preliminary experiments were discussed in the previous chapter. The various reaction times required to reach equilibrium have been determined and it was therefore possible to conduct the necessary experiments to confirm or disprove the hypotheses and answer the research questions.

In this chapter, the iron redox equilibria results are presented first. The experiments were necessary to determine whether equilibrium has been reached. The redox results are followed by equilibrium gas-stag results for sulphide and chloride experiments. Thereafter, some gas-stag-matte results follow.

All the steady-state results (accumulated during the experimental period), —tests in which the kinetics were limited by reaction— are presented at the end of this chapter.

In order to evaluate the repeatability of the various experiments, selected experiments were duplicated throughout the experimental program. More will be said in the discussion chapter about reproducibilities and errors.
5.1. IRON REDOX-EQUILIBRIA RESULTS

The equilibrium $\text{Fe}^{2+}/\text{Fe}^{3+}$ values determined for slag MT2-A, equilibrated using a CO$_2$-CO-Ar gas system, reacted above the liquidus of the slag, at a reaction temperature of 1450°C, are shown in Table 5.1.

<table>
<thead>
<tr>
<th>CO$_2$/CO Ratio</th>
<th>$\rhoO_2$ atm</th>
<th>Fe$^{2+}$/Fe$^{3+}$ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>$9.5 \times 10^{-7}$</td>
<td>0.03</td>
</tr>
<tr>
<td>0.28</td>
<td>$6.2 \times 10^{-6}$</td>
<td>0.04</td>
</tr>
<tr>
<td>1.75</td>
<td>$2.4 \times 10^{-3}$</td>
<td>0.13</td>
</tr>
<tr>
<td>0.28</td>
<td>$6.2 \times 10^{-6}$</td>
<td>0.05</td>
</tr>
<tr>
<td>1.75</td>
<td>$2.4 \times 10^{-3}$</td>
<td>0.11</td>
</tr>
</tbody>
</table>

The iron redox equilibria results for a meter-type slag, determined experimentally as a function of oxygen activity at 1450°C and with a mass basicity ($B$) of 0.69, show an increase with increasing oxygen activity, as expected from literature. Several experiments conducted at a CO$_2$/CO ratio of 0.11 failed, as the platinum boat used became brittle and broke because of the possible attack of the platinum boats by iron. The value obtained at CO$_2$/CO of 0.11 could be explained by the iron saturation reached in one of the platinum boats.

5.2. SULPHIDE CAPACITY RESULTS

The sulphide capacity of a well-characterized calcium aluminosilicate slag system was determined at several temperatures to confirm the experimental method,
which was done by comparing the experimental data with those available in the literature. An aim of determining the sulphide capacity for this well-characterized slag was to broaden the range of temperatures available in the literature before determining the sulphide capacity of melt-type slags. The calcium-alumino-silicate slag (Slag CAS in Table 4.4) was equilibrated at temperatures ranging from 1400°C to 1575°C by means of CO₂-CO-SO₂-Ar gas mixtures.

**Table 5.2 Sulphide capacity determined by reacting slag CAS at several temperatures in CO₂-CO-SO₂-Ar gas slag system**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>S (wt%)</th>
<th>ρO₂ (atm)</th>
<th>ρS₂ (atm)</th>
<th>Ca²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1450</td>
<td>0.038</td>
<td>7.9×10⁻³</td>
<td>6.5×10⁻¹</td>
<td>4.2×10⁻⁴</td>
</tr>
<tr>
<td>1400</td>
<td>0.041</td>
<td>7.9×10⁻³</td>
<td>6.5×10⁻¹</td>
<td>4.5×10⁻⁴</td>
</tr>
<tr>
<td>1450</td>
<td>0.132</td>
<td>4.9×10⁻³</td>
<td>9.6×10⁻¹</td>
<td>9.4×10⁻⁴</td>
</tr>
<tr>
<td>1525</td>
<td>0.705</td>
<td>3.3×10⁻³</td>
<td>1.4×10⁻¹</td>
<td>1.1×10⁻⁴</td>
</tr>
<tr>
<td>1575</td>
<td>0.844</td>
<td>4.3×10⁻³</td>
<td>5.3×10⁻¹</td>
<td>2.4×10⁻⁴</td>
</tr>
</tbody>
</table>

From Table 5.2 one can see that the increase in sulphide capacity with temperature is in accord with what is expected from theory.

Furthermore, it is evident from the data in Table 5.3 and Table 5.4 that, not only does an increase in temperature cause an increase in sulphide capacity as expected from theory, but an increase in sulphide capacity is also observed for an increase in total iron content from 8.2 to 15.6 wt%, a change from slag MT2-B to slag MT2-A.
5.3. CHLORIDE CAPACITY RESULTS

The solubility of chlorine in molten slags was measured by using a similar gas-slag equilibration technique developed by Pincham and Richardson (1954) and used more recently by Hirosumi and Morita (2000), Mwa and Morita (2002), and Myung et al. (2003). Before any thermodynamic experiments can be conducted, the gas-slag dissolution mechanism needs to be confirmed, as discussed in the literature review. At first, experiments were conducted on iron-free molten slag systems, as we expected the volatilization of iron as gaseous metal chlorides to reach equilibrium with difficulty. The time required to reach equilibrium was determined and is shown in Figure 4.9 (of the previous chapter).
The aforementioned authors determined the dissolution mechanism of chlorine as chlorides from the gas phase into a 40:20:40 wt% CaO-Al₂O₃-SiO₂ slag. However, we decided not only to confirm the dissolution mechanism, but also to identify the mechanism for a CaO-Al₂O₃-SiO₂-MgO slag system instead of the usual calcium-alumino-silicate slag. Our choice was influenced by the increase observed in the chloride contents of the preliminary investigations for oxygen-containing melt-type slags with increasing oxygen partial pressure that suggested possible dissolution of oxychlorides. To explain, if we assume the dissolution mechanism to be that of chlorides, then we can expect the chloride capacity of a slag with a certain chemistry to remain constant for a specific temperature. Therefore, for the chloride capacity to remain constant as expected at these conditions, an increase in oxygen potential should result in decreasing chloride contents, see equation (5.1).

\[
\text{Ccl}^- = \left(\text{wt\% Cl}^-\right) \left(\frac{pO_{2\text{v}}}{}\right) \left(\frac{pCl_{2\text{v}}}{}\right) = K_{\text{eq}} \left(\frac{ao^{2-}}{}\right) \left(\frac{\gamma Cl^-}{}\right) \tag{5.1}
\]

We then confirmed the dissolution mechanism for the CaO-Al₂O₃-SiO₂-MgO slag system as chlorides. There are two possible explanations for our observations in the preliminary experiments. One is that there could have been kinetic limitations at the gas-molten slag interface, which would produce steady state results; the other is that oxychlorides are stabilized in the slag, thereby changing the dissolution mechanism of chlorine.
The equilibrium iron-redox values for the various experiments were determined or estimated from the trend in the data reported in Table 5.1. We found that interfacial gas-melted slag kinetic limitations resulted in steady state data, which differed from the final expected equilibrium values. The steady state results obtained are reported later in this chapter.

The dissolution mechanism was determined for slag MT1A by reacting the slag, at a fixed partial pressure of chlorine of $4.0 \times 10^{-15}$ atm and a temperature of 1450°C, under varying oxygen partial pressures. H$_2$O-H$_2$HCl-Ar gas mixtures were employed and the results are reported in Table 5.5.

**Table 5.5** Relationship between $pO_2$ and chloride contents in slag MT1-A at 1450°C and a $pCl_2$ of $4.0 \times 10^{-15}$ atm, while varying the $pO_2$. H$_2$O-H$_2$HCl-Ar gas mixtures were used.

<table>
<thead>
<tr>
<th>$pO_2$ (atm)</th>
<th>Cl wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$9.9 \times 10^{-11}$</td>
<td>0.019</td>
</tr>
<tr>
<td>$3.1 \times 10^{-12}$</td>
<td>0.012</td>
</tr>
<tr>
<td>$1.0 \times 10^{-12}$</td>
<td>0.009</td>
</tr>
<tr>
<td>$3.1 \times 10^{-13}$</td>
<td>0.005</td>
</tr>
</tbody>
</table>

It is possible not only to confirm the dissolution mechanism of chlorides in the slag by varying the partial pressure of oxygen for the system using the data in Table 5.5, but also to determine the effect of the oxygen partial pressure on the prevailing chloride activity coefficient of the melt. Both the dissolution mechanism and the effect of $pO_2$ on the chloride activity coefficient are discussed in Chapter 6.
Also, the effect of chlorine potential on chloride activity coefficient was investigated by keeping the variables constant and varying the chlorine potential.

**Table 5.6** Relationship between pCl₂ and chloride contents in slag M1-A at 1450°C and a pO₂ of 4.0 × 10⁻² atm, while varying the pCl₂. H₂O-H₂-HCl-Ar gas mixtures were used.

<table>
<thead>
<tr>
<th>pCl₂ atm</th>
<th>Cl wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0 × 10⁻⁰</td>
<td>0.009</td>
</tr>
<tr>
<td>3.9 × 10⁻¹</td>
<td>0.030</td>
</tr>
<tr>
<td>3.9 × 10⁻²</td>
<td>0.035</td>
</tr>
<tr>
<td>1.7 × 10⁻³</td>
<td>0.057</td>
</tr>
<tr>
<td>4.0 × 10⁻⁴</td>
<td>0.088</td>
</tr>
</tbody>
</table>

The relationship in Table 5.6 is in accord with what is expected for a constant slag chemistry and temperature — i.e., for the chloride capacity to remain constant, the chloride content of the slag should increase with increasing partial pressure of chlorine, as expected from the equation of the chloride capacity (5.1). The data in Table 5.6 also allow one to quantify the effect of the partial pressure of chlorine on the dissolution behaviour of chlorine.

It can be seen from Table 5.7 that the level of chlorides, which dissolve in molten melter-type slags, barely changes with temperature. As the data, especially the lower values, lie close to the detection limit of the HPLC instrument, and as the uncertainty of the analytical techniques increases with decreasing chloride concentrations, so the results are more variable.
Table 5.7 The relationship between slag MT1-B and slag MT1-E with temperature. The slags were equilibrated using H₂O-H₂-HCl-Ar gas mixtures.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$\rho_{\text{Cl}}$ atm</th>
<th>$\rho_{\text{O}_2}$ atm</th>
<th>MT1-B % Cl</th>
<th>MT1-E % Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>4.0x10^{-10}</td>
<td>9.4x10^{-8}</td>
<td>0.011</td>
<td>0.061</td>
</tr>
<tr>
<td>1450</td>
<td>4.0x10^{-10}</td>
<td>1.0x10^{-7}</td>
<td>0.009</td>
<td>0.054</td>
</tr>
<tr>
<td>1500</td>
<td>4.0x10^{-9}</td>
<td>1.0x10^{-6}</td>
<td>0.011</td>
<td>0.064</td>
</tr>
<tr>
<td>1550</td>
<td>3.9x10^{-8}</td>
<td>9.8x10^{-8}</td>
<td>0.010</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Differences in chloride contents between slag MT1-B and slag MT1-E at similar conditions are ascribed to the differences in basicity. The more basic slag MT1-E dissolves more chlorides than slag MT1-B does. Therefore, it is apparent that the effect of basicity is a strong one.

A number of experiments were conducted to validate this observation, and to explore the effects of slag chemistry within the CaO-SiO₂-Al₂O₃-MgO system on the holding capacity of the slag for chlorides. First, the lime content was increased by substituting silica for lime. Thereafter, magnesia was substituted for silica. The experimental matrix was chosen so that we could explore the effect of lime-to-magnesia ratio on chloride affinity at two levels of silica. In addition, the contribution of lime and magnesia to chloride capacity was reviewed in order to confirm the observations and suggestions made by Myoung et al. (2003). They suggested that magnesia does not contribute directly to the formation of chlorides, but rather dilutes the amount of lime, which contributes directly to the formation of chlorides.
Table 5.8 The effect of the chemistry of slags on the chloride capacity was investigated by equilibrating slags MT1-B to MT1-E at 1450°C and at partial pressures of oxygen and chlorine of $10^{-3}$ and $4 \times 10^{-6}$ atm, respectively.

<table>
<thead>
<tr>
<th>Slag Name</th>
<th>Cl Content wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT1-B</td>
<td>0.009</td>
</tr>
<tr>
<td>MT1-C</td>
<td>0.014</td>
</tr>
<tr>
<td>MT1-D</td>
<td>0.027</td>
</tr>
<tr>
<td>MT1-E</td>
<td>0.034</td>
</tr>
<tr>
<td>MT1-F</td>
<td>0.048</td>
</tr>
<tr>
<td>MT1-G</td>
<td>0.013</td>
</tr>
</tbody>
</table>

Table 5.8 shows the data collected from measuring the chloride contents of the different slags after equilibrating them under similar experimental conditions. Slags MT1-B, MT1-C, MT1-D and MT1-E show an increase in chloride content from B to E. The increase is expected as the SiO$_2$ content of the slags was substituted increasingly with CaO from B to E. This observation supports the trend for increasing basicity as reported in the literature. Other interesting observations will be discussed in Chapter 6.
Table 5.9: The chlorine distribution coefficients between slag MT3-A and matte HJM and LJM at a temperature of 1450°C and atmospheric conditions of \( p_{O_2} \), \( 10^{-5} \) atm and \( p_{S_2} \), \( 10^{-11} \) atm was determined. The \( p_{Cl_2} \) was fixed at either \( 10^{-5} \) or \( 10^{-7} \) atm.

<table>
<thead>
<tr>
<th>T (1450°C)</th>
<th>Matte</th>
<th>pCl2 ( 10^{-5} ) atm</th>
<th>pCl2 ( 10^{-7} ) atm</th>
<th>( p_{S_2} ) ( 10^{-11} ) atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matte</td>
<td>Cl</td>
<td>3.27</td>
<td>28.3</td>
<td>3.40</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>766</td>
<td>4.15</td>
<td>5.09</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>5.09</td>
<td>45.2</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>29.3</td>
<td>12.1</td>
<td>25.8</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>7.92</td>
<td>32.3</td>
<td>0.19</td>
</tr>
<tr>
<td>Slag</td>
<td>Cl</td>
<td>2.54</td>
<td>2.54</td>
<td>2.54</td>
</tr>
<tr>
<td></td>
<td>FeO</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Al2O3</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>SiO2</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>FeO/F</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>LUMC</td>
<td>Cl</td>
<td>3.10</td>
<td>3.10</td>
<td>3.10</td>
</tr>
</tbody>
</table>

Gas-slag-matte experiments were conducted in order to keep the iron content in the slag constant, despite losses to the gas phase in the form of volatile metal chlorides, by introducing mattes with high iron contents. The mattes were used as high-iron reservoirs to replace iron lost to the gas phase. This was done as it was impossible to equilibrate the iron-containing matte-type slags by means of the
usual gas-slag equilibration technique. Not only were data collected for the interacting gas-slag phases, but additional data were collected to investigate the matte-slag distribution coefficient of the dissolved chlorides. The time required to attain equilibrium for gas-slag-matte systems was determined from preliminary experiments as shown in Figure 4.11.

More detailed discussions will follow in the next chapter.

5.4. STEADY STATE RESULTS

The redox steady-state results are reported first, to be followed by the small amount of steady-state data collected from the reaction of slag MT2-A with gas mixtures of CO₂, CO, H₂, HCl-Ar. The initial aim of these experiments was to confirm the dissolution mechanism. However, a dissolution trend differing from the expected chloride dissolution was observed. After careful consideration of the experimental procedure and the generated data we concluded that steady states, not equilibrium, were reached. The process of arriving at this conclusion will be explained briefly; however, more detailed discussions will follow in Chapter 6.
Table 5.10 The measured reduc states of iron in slag M\(^{12}\) A is tabulated with the calculated theoretical gas compositions. The slag was reacted with H\(_2\)-CO\(_2\)-CO-Ar-HCl gas mixtures at 1450°C. Additional flow inert data is reported in the Appendix.

<table>
<thead>
<tr>
<th>Actual gas inlet compositions</th>
<th>Equilibrium (Theoretical) gas composition at the reaction temperature</th>
<th>Measured reduc state Fe(^{0})/Fe(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)/CO</td>
<td>CO/_H(_2)</td>
<td>H(_2)/H(_2)</td>
</tr>
<tr>
<td>0.48</td>
<td>2.81</td>
<td>0.355</td>
</tr>
<tr>
<td>0.48</td>
<td>2.81</td>
<td>0.355</td>
</tr>
<tr>
<td>0.88</td>
<td>4.84</td>
<td>0.675</td>
</tr>
<tr>
<td>1.65</td>
<td>5.37</td>
<td>1.128</td>
</tr>
<tr>
<td>3.32</td>
<td>6.55</td>
<td>2.085</td>
</tr>
</tbody>
</table>

The values presented in Table 5.10 show that steady states instead of the expected iron reduc values were reached. We observed that steady states were reached, instead of expected iron reduc values. The results seemed flawed, as reducing (hydrogen-containing) gases were used. We expected the oxidation state of the slags to be rather more reduced than the equilibrium iron reduc values, a CO\(_2\)/H\(_2\) type steady state should have been observed. However, a reassessment of the data and the experimental procedure used helped us formulate the following explanation: There is ample time for the inlet gas mixture to prevent and to shift towards equilibrium on the gaseous reactants, the reaction tube, from the bottom to the reaction zone. In the reaction zone they encountered titanium-alloy crucibles which causes the water-gas shift reaction. As the gas mixture moves towards the water-gas shift equilibrium, water vapour forms. At the gas-slag interface this water causes a rate limiting step to set in, because the H\(_2\)O at the interface dissociates much faster than the interfacial dissociation of CO, (see Xi, 1992 and Young, 1991). This rate limiting step produces more oxidized slags by the reaction of CO.
CO-H₂Ar (H₂O) gas mixtures with silicate slags. The degree to which slags are more oxidized depends on both gas and slag compositions at individual gas-slag interfaces.

Table 5.11: The increasing effect of the chloride contents is shown with increasing partial pressure of oxygen. Slag MT2-A was treated with H₂CO-NO-HCl Ar gas mixtures at 1450°C and a pCl₂ of 4.0×10⁻² atm. The theoretical pO₂/r and prevailing iron reduc states are also listed.

<table>
<thead>
<tr>
<th>wt% Cl</th>
<th>Fe⁺⁺/Fe⁺⁺⁺</th>
<th>log[wτ% Cl]/log[pO₂]</th>
<th>log[pO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.027</td>
<td>0.135</td>
<td>3.131</td>
<td>-2.9</td>
</tr>
<tr>
<td>0.039</td>
<td>0.262</td>
<td>3.291</td>
<td>-8.5</td>
</tr>
<tr>
<td>0.065</td>
<td>0.192</td>
<td>3.513</td>
<td>-8.0</td>
</tr>
<tr>
<td>0.093</td>
<td>0.319</td>
<td>3.668</td>
<td>-7.5</td>
</tr>
</tbody>
</table>

Summarized in Table 5.11 are the initial unexpected results obtained from experiments conducted to confirm the dissolution of chlorine in molten slags. The unexpected increase of the chloride contents with increasing partial pressure of oxygen can be noted from these results, note that the oxygen partial pressures reported were calculated for equilibrium conditions. These oxygen activities were never experimentally attained as steady states and not equilibrium were reached. Steady state conditions were a result of interfacial gas-slag kinetic limitations.

This chapter presented the results of the various experiments conducted to answer the research questions and to address the hypotheses reported at the end of Chapter 3.
Chapter 6

DISCUSSION

In this chapter, the data presented in previous chapters will be analysed, discussed and interpreted with the aim of answering the research questions and to address the hypothesis reported at the end of Chapter 3.

6.1. IRON REDOX-EQUILIBRIA

The $\text{Fe}^{3+}/\text{Fe}^{2+}$ results for the melter-type slags, determined empirically as a function of oxygen activity at 1450°C and a mass $(\text{CaO} + \text{MgO})/(\text{SiO}_2)$ ratio of 0.69, did not depart significantly from ideal behaviour (a slope of $1/2$) as shown in Figure 6.1. The data point generated by Hundermark (2003) for a melter-type slag with a mass ratio of 0.48 at a CO$_2$/CO ratio of 10 (see Figure 6.2), is consistent with the trends in the current study, and the slight non-ideal behaviour correlates with other low iron- and low alumina-containing slags by Yang (1994). The dependence of the equilibrium redox states on the basicity (chemistry) of a slag can be noted from Figure 6.2: the higher the basicity, the higher the measured equilibrium iron redox value for a given oxygen activity.
Figure 6.1 Variation of Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio with CO\textsubscript{2}/CO ratio for slag MT2-A at 1450°C Al\textsubscript{2}O\textsubscript{3}, CaO, FeO, MgO, S\textsubscript{2}O\textsubscript{3} (7.2, 7.3, 20.1, 22.5, 43.2 wt%).

Figure 6.2 Variation of [Fe\textsuperscript{3+}]/[Fe\textsuperscript{2+}] ratio with CO\textsubscript{2}/CO.
In the absence of enough experimentally measured iron-redox equilibria for molten slags, other multi-component data, trends and correlations published in the literature could be used to predict molten slag iron-redox equilibria. The low \( \text{Al}_2\text{O}_3 \) correlation derived by Yang and Belton (1998) and the \( \text{CaO-SiO}_2-\text{MgO} \) correlation determined by Tian (1997) were used to estimate redox conditions in the slag tested in this study.

![Diagram](image)

**Figure 6.3** Variation of \( \frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} \) ratio with \( \frac{\text{CO}_2}{\text{CO}} \) ratio. Data used were extracted from Yang (1994) and combined with the present work. Yang and Belton (1998) low \( \text{Al}_2\text{O}_3 \) and Tian (1997) \( \text{CaO-SiO}_2-\text{MgO} \) correlations were used to estimate the \( \frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} \) of a slag with a mass ratio of B as 0.69.
Figure 6.3 represents graphically the correlations for a slag with a mass basicity B of 0.59 together with the data in Figure 6.2. One can see that the extrapolated trends of these correlations at a mass basicity of 0.65 are consistent with the measured data from the present. The Fe\(^{2+}/Fe^{3+}\) ratio in the melter type slag at a partial pressure of oxygen of 10\(^{-6}\) atm is less than 0.1, which is in accord with the expected value from studies on low iron slags with similar basicity.

6.2. SULPHIDE CAPACITY

The sulphide capacity of a well-characterised calcium-aluminosilicate slag system (slag CAS) was determined at various temperatures to confirm the experimental method used in determining sulphide capacity. The aim of measuring the sulphide capacity of this slag was also to broaden the temperature range of the published data. The present data correlate well with those in the literature as the relationship of \(\log(CS)\) to temperature shown in Figure 6.4.

Not only does this trend follow behaviour expected from Equation 3.6, but the measurements made in the present work on CaO-SiO\(_2\)-Al\(_2\)O\(_3\) slags at the same compositions as those measured by several other investigators are consistent with those results.
Figure 6.4 Temperature dependence of sulphide capacity of slag C-A-S. The line shown is the least squares fit to all the data excluding those of Kalyanram et al. (1960).

The sulphide capacity of melter-type slags with 10 and 20 wt% FeO, was quantified for a range of temperatures, and it was observed that the sulphide capacity increased with an increasing iron content as shown in Figure 6.5. This increase is to be expected as melter-type slags are acidic and the increase of the iron content increases the amount of free oxygen donated. From the ionic theory of slag chemistry, FeO acts as a basic oxide for the acidic slag and decreases the degree of polymerisation in the silicate melt so that more sulphides can be dissolved in the slag. Furthermore, as iron has a strong affinity for sulphur, its presence in slags makes a significant contribution to the cation-anion (Fe" + S"\(^{2-}\))
interaction and hence lowers the activity coefficient of sulphur in slags. This interaction effect also increases the sulphide capacity of the slag with increasing iron content, as shown in Figure 6.5.

![Graph showing temperature dependence of sulphide capacity with varying iron oxide content.]

*Figure 6.5* Temperature dependence of the sulphide capacity of mullite-type slags. The iron content was held at 10.5 w/o and at 20.1 w/o FeO, while temperature was varied.

Again, the relationship between sulphide capacity and temperature followed expectations and accord with sulphide capacity trends in theory.

In the absence of reported sulphide capacities for multi-component mullite-type slags, the effects of additions of various metal oxides to the binary and ternary
slags that represent the major components of the melt-type slags were compared. Slags in the molar concentration range 40 to 50 mol% silica were used to allow comparisons of these slags at similar initial silicate structures. A magnesia silicate slag with equimolar contents of the constituents served as the baseline (see Figure 6.6).

![Figure 6.6](image)

*Figure 6.6* The sulphide capacity of silicate based slags is represented as a function of the temperature. The magnesia silicate data were extracted from Ngutt A (1999).

The following two graphs show the effect of the additions of CaO and FeO to a magnesia silicate slag with a final SiO2 content of between 40 to 50 mol%. These
additions show what effect the various metal oxides have on the sulphide capacity of a slag with a specific silicate content and initial structure.

![Graph](image)

**Figure 6.7** The sulphide capacity of silicate based slags is represented as a function of the temperature. The introduction of time causes the sulphide capacity to increase as indicated by the arrows. The solid symbols represent the present work, the other symbols, data from Nigetta (1999).

The addition of CaO increases the sulphide capacity as indicated by the arrows in Figure 6.7. Note that the silica content of the various slags is within the range 40-50 mol%. The additional base metal oxides have a depolymerizing effect on the
silicate network and therefore one can note a higher sulphide capacity with additions of base metal oxides to silicate slags.

![Graph showing sulphide capacity vs. temperature](image)

**Figure 6.8** The sulphide capacity of silicate based slags is represented as a function of the temperature. The introduction of iron causes the sulphide capacity to increase more substantially and is indicated by the arrows. The solid symbols represent the present data while the remainder were extracted from Nigatta (1999).

The effect is similar for additions of FeO, to the magnesia silicate slag. The increase in sulphide capacity, however, is much greater. This observation suggests that not only does FeO have a depolymerising effect on the silicate structure, but as iron has a stronger affinity for sulphur, it will make a significant contribution to the cation–anion (Fe\(^{2+}\), S\(^{2-}\)) interaction, thereby also have an increasing effect
on the sulphide capacity. The significant contribution to the cation–anion interaction will lower the activity coefficient of sulphur in the slag, which results in an increased sulphide capacity (see Equation (6.1)).

$$C_s^3 = (\text{wt}\% \text{S}) \left( \frac{\rho_{O_2}}{\rho_{S_2}} \right)^3 = K \left( \frac{\rho_s^2}{\rho_s^2} \right)$$  \hspace{1cm} (6.1)

with $K$ the equilibrium constant and $\rho_s^2$ the activity coefficient of the sulphide and $\rho_o^2$ the activity of the oxide ion.

If the data from the present work on a slag with 20 wt\% (15.9 mol\%) FeO, are extrapolated to 1600°C, the sulphide capacity appears lower than that measured by Nzuta (1999) for a FeO–MgO–SiO$_2$ slag, which has higher MgO/Al$_2$O$_3$ and FeO/MgO ratios (see Figure 6.9). Although the slag from this study contains some alumina, which would decrease its sulphide capacity, it also contains some lime which leads to increase sulphide capacity. Considering all these factors one can note that the present results are in broad agreement with published data at 1600°C.
Figure 6.9 The sulphide capacity of dolomite-based slags is represented as a function of the temperature. The multi-component melter-type slag's sulphide capacity has been compared with binary and ternary slags containing the major components of the melter-type. The open symbols are the data extracted from Nagva (1992).

The sulphide capacity data for blast-furnace- (or more specifically Corex-) type slags investigated by Seo and Kim (1999) with 9.2 and 13.3 wt% additions of FeO, show an increase in sulphide capacity with increasing iron content. The Corex slags have a slightly higher sulphide capacity compared with the present melter-type slags, because Corex-type slags contain higher levels of lime and have a higher basicity ratio.
We may conclude that the magnitude of the measured molar-type sulphide capacity is consistent with extrapolations of lower order slag systems.

It follows from the foregoing discussion that the use of molar concentrations and ratios of components in multi-component slags may not be a good measure of sulphide capacity, but only a rough guide for comparison of slags of very different composition. An alternative to this would be the use of the optical basicity of oxides and slags as proposed by Sosinsky and Sommerville (1980). Although good for complex slags, it has weaknesses, as mentioned in the sulphide capacity section of the Literature Review chapter (Section 3.3). The use of optical basicity to deduce basicity indices does not account for the interaction between cations and sulphide ions and hence can lead to an unaccountable basicity scale for multivalent cations in transitional metal oxides. Perhaps a more fruitful approach would be to use structurally related thermodynamic models such as the cell model (Gaye et al., 1992), which do account for interactions between all cations and anions. This approach has been successfully employed by some research groups and excellent agreement between calculated and measured values of sulphide capacities of simple and multi-component slags over broad ranges of temperature and composition were obtained.
6.3. CHLORIDE CAPACITY

The solubility of chlorine gas as chlorides in iron-free meltore type slags was determined by means of $H_2-H_2O-HCl-Ar$ gas mixtures. The time required to reach equilibrium was measured (see Chapter 4).

Even though Myoung et al. (2003) had also determined the dissolution of chlorine gas as chlorides in a calcium-alumino-silicate slag, the chlorine dissolution into a CaO-MgO-SiO$_2$-Al$_2$O$_3$ system required confirmation. A broader discussion on the steady states reached will follow after the equilibrium work has been discussed.

Figure 6.10 shows the variation of chlorine solubility (wt. % Cl in slag / $p_{Cl}$) with the oxygen partial pressure ($p_{O_2}$). It can be noted that the chloride solubility decreases with increasing oxygen partial pressure. Furthermore, the dependence on the oxygen partial pressure is in accord with the following equation (also Equation 3.9) as the slope of the graph is close to $\frac{1}{2}$:

$$\frac{1}{2} (O^+) + \frac{1}{2} Cl^- \rightarrow (Cl) + \frac{1}{4} O_2,$$

(6.1)

where the brackets indicate the slag phase.
Figure 6.10 Variation of the activity of chlorine in slag (wt% Cl / pCl⁻) with oxygen partial pressure (pO₂) in slag MT1-Α reacted at 1450°C. Error bars represent the analytical standard deviation.

The most stable species of chlorine in these slags is expected to be that of chlorides, rather than oxy-chlorides, over the entire range of oxygen potential investigated. The chloride capacity of this slag can be represented by the following equation (also equation 3.10):

\[ C_{Cl} = \frac{[\text{wt} \%, \text{Cl}]}{[\text{pO}_2]} = K_{Cl} \frac{[\text{O}^{2-}]}{[\text{Cl}]} \]  

(6.2)

The relatively small analytical standard deviations (Figure 6.10) indicate good precision. However, the accuracy of the results cannot be confirmed because the
true values of the individual samples are not known. At best we can only use the calibration curves determined for this technique to assume that the measured values could be close to the true values. The analytical instrument was calibrated with four calibration standards (10.0, 4.00, 2.00 and 1.00 ppm) and a blank. A calibration curve was determined by a linear regression on the EPR peak area as a function of concentration. A regression coefficient (R) of more than 0.999 was obtained.

After the chloride solubility mechanism had been confirmed, it was possible to investigate the effect of that a number of variables have had on the chloride capacity.

One of the most investigated variables is temperature. Hirosumi and Morita (2000) found chloride capacity to increase with increasing temperature; Myoung et al. (2003) observed the opposite. Hirosumi and Miwa (2000) found that chloride capacity is strongly dependent on basicity of a slag: the higher the basicity, the higher the chloride capacity and the higher the temperature dependence.
The effect of temperature on the chloride capacity of slags MT1-B and MT1-E was determined by equilibrating the slags individually at a $p_{O_2}$ of 10.6 atm and $p_{Cl_2}$ of 10$^{-31}$ atm for temperatures in the range 1400°C to 1550°C (see Figure 6.11). Chloride capacity appears to be insensitive to temperature. This was expected for an acidic slag (MT1-B)—as Hirose and Miwa (2000) found. However, the temperature insensitive trend observed for the basic slag (MT1-E) does not agree with either the observations of Hirose and Miwa (2000) or Myoung et al. (2003). It is suggested that the effect of temperature on the chloride capacity for basic slags be investigated more thoroughly.
Another one of the most frequently investigated variables in metallurgical slags is chemical composition, in particular basicity. The data presented in Figure 6.11 suggests that there could be a strong relationship between basicity and chloride capacity. The effect of basicity on chloride capacity was investigated by increasingly substituting the SiO₂ in slag MT1-B with CaO (Slag MT1-B, MT1-C, MT1-D and MT1-E), and equilibrating the slags individually at similar experimental conditions (see Figure 6.12).

The data show one standard deviation about each point of the "HPLC" chloride analytical data in Figure 6.12. The standard deviations were determined from 10 measurements of 6 metallurgical samples. The standard deviations were included in Figure 6.12 so as to confirm the precision of the data points at the lower concentration levels, as the rest of the results appeared to have increased linearly with increasing basicity. As the standard deviations are relatively small, they do not support the possibility that the data could behave linearly within the analytical uncertainty.
Figure: 8.12 Variation of the chloride capacity with slag composition at 1450°C. Error bars representing one analytical standard deviation at the 95% confidence level.

Therefore, we may safely conclude that the analytical uncertainties are relatively small compared with the experimental uncertainty. The reproducibility of these results will be discussed at the end of this section.

A range of experiments and investigations has been carried out to determine the effect of slag composition (basicity) on chloride capacity.
Figure 6.13 Effect of the CaO/MgO ratio on the chloride capacity for two levels of silica.

Myoung et al. (2003) concluded that the chloride capacity increased with increasing CaO/SiO$_2$ ratio at constant MgO content. This observation was expected as the basicity of the slag increased. Moreover, Myoung and co-workers found that the chloride capacity increased linearly with increasing log[$\text{CaO}$] and suggested that the influence of the MgO content was insignificant, except for slight changes in the liquidus temperature and diluting the CaO content. Therefore, the effect of substituting CaO for MgO, while keeping the SiO$_2$ and AlO$_3$ concentrations constant (slags MT1-A, MT1-C, MT1-F, MT1-H and MT1-G were used) was examined. As shown in Figure 6.13, substitution of CaO for MgO increases the chloride capacity of these slags. This behaviour is also in
accord with theory as CaO is more basic than MgO—in other words, CaO donates its O\(^{2-}\) ion more readily than MgO does. This effect appears to be stronger at lower levels of silica.

\[
\ln[C_{\text{CaO}}] = \ln[\text{wt\% CaO}] + \frac{1}{2}\ln[\text{O}_2\text{]} - \frac{1}{2}\ln[\text{Cl}_2\text{]} - \ln[\text{O}] \ln[\text{Cl}] \tag{6.3}
\]

Figure 6.14 The relationship for the natural logarithm of acidum chloride as a function of the natural logarithm of the estimated activity of lime gives a slope of approximately \(\frac{1}{2}\), which shows that most of the free oxygen originates from the lime as shown from equation (6.3).

A plot of the natural logarithm of chloride capacity vs. the natural logarithm of the lime activity should yield a slope of \(\frac{1}{2}\) if most of the free oxygen originates from lime (See Equation 6.3). The data of Myoung and co-workers and estimates
of the activities of the oxides for the present data from MPE are presented in Figure 6.14.

The relative magnitudes of the corresponding activities for calcium chloride and magnesium chloride could also give an indication of whether the formation of calcium chloride would lead mostly to the formation of magnesium chloride.

\[
\text{CaO} + \text{Cl}_2 \rightleftharpoons \text{CaCl}_2 + \frac{1}{2} \text{O}_2 \quad (6.4)
\]

\[
\text{MgO} + \text{Cl}_2 \rightleftharpoons \text{MgCl}_2 + \frac{1}{2} \text{O}_2 \quad (6.5)
\]

The equilibrium constants for reactions (6.4) and (6.5) at 1450°C were calculated to be 34.04 and 1, respectively. Even though the reaction constant for calcium chloride formation is three orders of magnitude greater than that for magnesium chloride formation, differences in concentration and activity coefficients between magnesia and lime can play a significant role in the formation of either magnesium or calcium chloride. Therefore, various activities of magnesium and calcium chloride had to be determined to inform our understanding of chloride formation in the present work. The activities of calcium chloride and the corresponding activities of magnesium chloride for some of these slags and their conditions are reported in Table 6.1.

The relationship of the natural logarithm of the chloride capacity to the corresponding natural logarithm of the activity for lime indicates that all the
chlorides in these slags could be present as calcium chloride. The possibility that all the chlorides could be present as calcium chloride is confirmed by the low activities of magnesium chloride, which are typically one to two orders of magnitude smaller than those of calcium chloride. One can therefore assume that at these low levels of chlorides, almost all the chlorides are present in the form of calcium chloride.

<table>
<thead>
<tr>
<th>aCaCl$_2$ (s)</th>
<th>aMgCl$_2$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.69 x 10$^{-6}$</td>
<td>2.30 x 10$^{-7}$</td>
</tr>
<tr>
<td>3.66 x 10$^{-6}$</td>
<td>5.16 x 10$^{-7}$</td>
</tr>
<tr>
<td>1.58 x 10$^{-5}$</td>
<td>6.88 x 10$^{-4}$</td>
</tr>
<tr>
<td>3.18 x 10$^{-5}$</td>
<td>8.41 x 10$^{-4}$</td>
</tr>
<tr>
<td>1.12 x 10$^{-4}$</td>
<td>1.30 x 10$^{-3}$</td>
</tr>
<tr>
<td>1.12 x 10$^{-4}$</td>
<td>5.94 x 10$^{-3}$</td>
</tr>
<tr>
<td>1.47 x 10$^{-4}$</td>
<td>2.85 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

After describing the effects of composition on chloride capacity and concluding that most of the chlorides in these slags are present as calcium chloride, we investigate the solution behaviour of the calcium chlorides. A discussion on the solution thermodynamic behaviour of the calcium chlorides follows the discussion on chloride capacity.

In slags to which iron has been added by means of a matte, which acts as an iron reservoir, chlorides partition in favour of the slag phase (See Figure 6.15).
We attempted to detect the chloride-containing phases in the samples by means of a microprobe, besides using the FTPLC analytical technique to measure the low-level chlorides. Unfortunately it was found that the chloride levels were too low for detection with the microprobe.

The composition of slag M13-A changed because the slag equilibrated with the matte and because the slag became saturated with magnesia originating from the magnesia crucible used. The conditions were 1450°C, $p_{O_2}$ of $10^{-20}$ atm, $p_{S_2}$ of $10^{-33}$ atm and $p_{Cl}$ of $10^{-15}$ atm. The average chloride capacity obtained for these slags was calculated to be 10.2 from the data reported in Table 5.9.
Figure 6.16 Average chloride capacities, with units of [wt\% Cl / atm 1/2], at 1450°C and on the 10wt\% Al2O3-CaO-MgO-SiO2 phase diagram.

The chloride capacities obtained from the present experiments and those published by Myoung et al. (2003) can be represented spatially as a function of slag composition (see Figure 6.16). The average chloride capacity determined from the matte-slag equilibrations is denoted by a green shaded box (containing 27 wt\% FeO), the iron-free data are represented by the blue shaded box, and some of the data generated by Myoung et al. (2003) are represented by the oval data points. The strong effect of slag chemistry is apparent. Slags with lower silica and higher lime contents have the highest chloride capacities. The exception to
this pattern is the slag containing 27 wt% FeO. This slag shows a higher chloride capacity which is a consequence of the dual role that iron oxide plays through cation-anion interactions in these slags. In other words, apart from donating oxygen ions, the ferrous ions tend to interact strongly with the chloride ions in the slags. This behaviour is not unique; it has been observed to have an effect on the sulphide capacity of slags.

The reproducibility of the present work was demonstrated with duplicate experiments conducted throughout the experimental program. It was noted that the experimental uncertainties encountered are larger than the analytical uncertainties, especially for the chloride experiments (see for example Figure 6.12). As chloride capacities should remain constant for a given slag composition and temperature, it was possible to compare all the data generated for slag M11-A at 1450°C so as to test this conclusion (see Figure 6.17).
Figure 6.17 Chloride capacities of slag MT4-A at 1450°C under different pO₂ and pCl₂.

The error bars represent the analytical standard deviations for each individual measurement.

The reproducibility of the results is acceptable. The deviation between the experimental data seems to be larger compared to the analytical standard deviations for each data point predicted using the 10 measurements of 6 different metallurgical samples.

It was concluded in the previous sections of this chapter that, for iron-free melter-type slags, the free oxygen originates from lime. Therefore, as all the chlorides can be associated with calcium, one should examine the solution thermodynamics of calcium chloride in these molten slags.
Figure 6.18 The activities of calcium chloride as a function of the calcium chloride mass fraction. A negative deviation from ideal behaviour is observed. The standard state is taken to be liquid calcium chloride.

The activity coefficient of calcium chloride deviates negatively from ideal behaviour, and Hernan behaviour exists only for concentrations of calcium chloride lower than 0.06 wt%; at higher concentrations the activity coefficient rises more steeply, see Figure 6.18.
Figure 6.19 The calcium chloride activity coefficient is represented as a function of the calcium chloride concentration for slag MT1-A at 1450°C, pO₂ 10⁻⁶ atm with the pCl₂ ranging from 10⁻⁴ atm to 10⁻¹ atm. The standard state is taken to be liquid calcium chloride.

The infinite dilution activity coefficient (at \( X_{\text{calc}} \to 1.0 \)) and the interaction parameter for calcium chloride in this dilute system can be determined from a linear regression of the natural logarithm of the activity coefficient as a function of mass fraction. The simplified Taylor series around a zero mass fraction for the natural logarithm of the activity coefficient in a dilute solution can be represented by equation (6.6) (from Smith, Van Ness and Abbott, 1996). The associated \( \gamma_{\text{calc}}^\circ \) and \( e_{\text{calc}} \) were determined, in a linear regression, to be 0.0058 and 1871.6 respectively (see Figure 6.19).
\[ \ln[y_{CaCl}] = \ln[y^o_{CaCl}] + \varepsilon_{CaCl} X_{CaCl} \] (6.6)

It is also possible from the generated data to determine the effect of various variables (i.e., \( \rho O_2\), \( \rho Cl_2 \) and basicity) on the activity of calcium chloride. The effect should answer two questions: (1) do increases in the value of these variables cause the deviation in the activity of the chlorides to increase, or to move closer to ideal behaviour, and (2) does the effect of temperature on the activity coefficient of calcium chloride agree with the expected variation if regular solution behaviour were being followed.

The effect of basicity on the activity coefficient of calcium chloride is shown in Figure 6.20. There is an increase in the activity coefficient with basicity. We can conclude that, the higher the basicity, the closer the behaviour moves towards ideal behaviour.

The duplicate experiments for basicity and for subsequent experiments on the partial pressure of chlorine showed the reproducibility of the experiments to be acceptable (see Figure 6.20 and Figure 6.21).
The coefficient of calcium chloride increases with an increase in the pressure of chlorine and it decreases with an increase in the pressure of oxygen (see Figure 6.22).

All these observations can be justified by the definition of the equilibrium constant of the chloride equation (3.10).

$$\frac{1}{8} (O^3) + \frac{1}{8} Cl_2 \rightleftharpoons (Cl) + \frac{1}{4} O_2 \quad (3.10)$$

where the brackets denote the slag phase.
Figure 6.21 The effect of chlorine partial pressure on the chloride activity coefficient.

Figure 6.22 The effect of oxygen partial pressure on the chloride activity coefficient.
\[ K_{3.10} = (\alpha \text{Cl}) (\rho \text{O}_2)^{\frac{1}{2}} / (\alpha \text{O}^2)^{\frac{1}{2}} (\rho \text{Cl})^{\frac{1}{2}} \]  

(6.7)

For the equilibrium constant to remain constant, therefore, the activity of the chloride ion (and therefore the activity coefficient of the chloride ion) should increase with an increase in basicity \((\alpha \text{O}^2)\) and chlorine partial pressure \((\rho \text{Cl})\), and it should decrease with an increase in oxygen partial pressure \((\rho \text{O}_2)\). However, the same equation shows the activity coefficient of the chloride ion to be less dependent on the \(\rho \text{O}_2\) as the exponent is \(\frac{1}{2}\) compared with the \(\frac{1}{2}\) of the other two variables.

The relationships in Figures 6.20 to 6.22 follow all of the expected aforementioned behaviours.

The dependence of the activity coefficient of calcium chloride on temperature can be evaluated for regular solution behaviour. The following relationship holds for a regular solution as the excess Gibbs free energies is independent of temperature (Smith et al., 1996):

\[ T_1 \ln(\gamma_{11}) = T_2 \ln(\gamma_{12}) \]  

(6.8)

The dependence of the activity coefficient of calcium chloride on temperature for iron-free slags follows the expected variation for regular solution behaviour (see Figure 6.23).
6.4. STEADY STATE OBSERVATIONS

The dissolution of chlorine as chlorides in CaO-Al₂O₃-SiO₂ slags at 1400°C, as determined by Miwa et al. (2002), is shown together with some of the present preliminary data (see Figure 6.24). It was expected from the chloride capacity equations that the chlorine solubility (wt% Cl in the slag / pCl₂) would decrease with increasing oxygen partial pressure. The preliminary data, however, behaved
unexpectedly in the opposite direction; as though an oxygen chloride dissolution were taking place.

**Figure 6.21** The chlorine activity and slag chloride concentration as a function of oxygen partial pressure for the preliminary data and those of Miao et al. (2002).

It was possible to validate the oxygen activity of the slag by comparing the iron electrode results with the expected equilibrium values (see Figure 6.25).
Figure 6.25 More oxidized slags were measured relative to the iron redox equilibrium results. The more oxidized results are due to interfacial kinetic limitation between gas and molten silicate slag. The formed water vapour dissociates faster than carbon dioxide, and is therefore responsible for the more oxidized slags observed.

The chlorine dissolution mechanism could not be determined when the theoretically calculated oxygen activities were adjusted by using the trends of the equilibrium iron redox data. Although the newly predicted oxygen partial pressures ranged from $10^{-7}$ to $10^{-5}$ atm, this range was not significantly higher than the upper levels of $p_{O_2}$ investigated by previous researchers to justify the formation of oxychlorides. However, the possibility still exists that the higher MgO content of the present slag (MT2-A) relative to the calcium aluminosilicate system investigated by Miwa and Morita could have been responsible for a
different dissolution mechanism. Even so, the possibility also exists that other species could also have participated in the interfacial gas-molten slag kinetic limitations—for example, the dissociation of hydrochloric acid vapour at the gas-slag interface. Therefore, not only has an incorrect oxygen activity been used, but also, possibly, an incorrect chlorine activity, which could explain the strange behaviour observed for chlorine dissolution in the preliminary data. At least, the iron redox states could be used to measure and confirm the oxygen activities of the slags, but there is no method for directly measuring the chlorine activity of the slag.

This unexpected behaviour of the preliminary experiments was ascribed to the steady states reached due to interfacial kinetic limitations, and the following explanation was formulated to explain this observation and assumption:

*The inlet gas mixtures moving up the tube furnace to the reaction zone had ample time to preheat and to shift towards equilibrium. Moreover, the crucible of platinum alloy in use catalysed the gas mixtures. As the gas mixtures moved towards the water-gas shift equilibrium, water vapour formed. This vapour at the gas-slag interface caused a rate limiting step to set-in, because the H₂O at the interface dissociated much faster compared with the interfacial dissociation of CO₃, as reported by Xie (1992) and Yang (1994) and discussed in the literature review. This rate limiting step is therefore responsible for the more oxidised slags obtained with the reaction of CO₂+CO-H₂Ar (H₂O) gas mixtures with silicate slags. The degree to which*
slags will be more oxidized or reduced will depend on both gas and slag compositions at various gas-slag interfaces.

All the research questions stated at the end of the literature review have been answered and some additional views on the gas-matte-slag equilibrations and steady states obtained were discussed. The main findings, observations and recommendations will follow in the ensuing Conclusions and Recommendations chapter.
Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

This study arose from a need to understand the behaviour of minor elements in the platinum producers' smelting processes, and to enable the producers to manage and control their minor elements. It focuses on the behaviour of chlorine and sulphur as minor elements. The identified research objectives were reported at the end of the Literature Review chapter as a set of research questions. The experimental work was carried out to fulfil these objectives, even though we had to improvise in order to address a range of experimental constraints and difficulties.

7.1. CONCLUSIONS

- Iron redox equilibria in melter-type slags does not deviate significantly from ideal behaviour. In general the investigated slags follow the behaviour of calcium silicate-based slags closely, even though a slight deviation is observed for the iron redox equilibria of melter-type slags. Moreover, the iron redox equilibria of melter-type slags can be accurately predicted from extrapolations of iron-bath smelter-slag models available in the literature.
• The sulphide capacity of melter-type slags has been quantified for a range of temperatures at two iron levels. The sulphide capacity of melter-type slags is in accord with trends for lower order slag systems. The main conclusion is that iron additions have a significant effect on sulphide capacity. This is explained by the ionic theory of slag chemistry and the cation-anion interaction effect: FeO$_x$ acts as a basic oxide for acidic melter-type slags; the increase in FeO$_x$ decreases the degree of polymerization in the silicate melt so that more anions can be dissolved in the slag. This explanation also addresses the increase in sulphide capacity observed with increasing CaO content. Increasing the FeO$_x$ contents, however, increases the sulphide capacity more than a similar increase in CaO content. I conclude that iron in silicate melts has a strong affinity for sulphur, and that its presence contributes significantly to the Fe$^{2+}$-$S^2$ interaction. At increasing levels, iron lowers the activity coefficient of sulphur in the slags, thereby increasing the sulphide capacity of melter-type slags. The sulphide capacity of melter-type slags ranges from $10^{-4.3}$ to $10^{-5.7}$.

• The initial experiments on chloride capacity helped to identify several experimental difficulties and problems encountered during the study. A steady state was found to be responsible for the formation of slags that are oxidised compared to the expected equilibrium values. Also,
unforeseen results were obtained from steady states, which seemed to have had influenced the dissolution behaviour. Nevertheless, the interfacial kinetic limitation between gas and molten slag that was responsible for the steady state being reached, was identified and addressed. At first, the results were considered unacceptable, as reducing (hydrogen-containing) gases were used. Therefore, it was expected that the oxidation state of the slags would be more reducing relative to the equilibrium iron redox values, and that a "CO\textsubscript{2}/H\textsubscript{2}-silicate slag" type steady state would be reached. However, it was concluded from literature and the results that the gases change composition by means of the water-gas shift reaction, after which the water that is formed dissociates much faster than carbon dioxide at the gas-slag interface. The rate of oxygen donated exceeds the rate of oxygen removed from the slag, which results in a more oxidized slag at steady state instead of at equilibrium. The problem was solved by changing the gas inlet composition to something that contains only a single principal species, such as hydrogen or carbon, when equilibrating with silicate slags to prevent the gas-shift reaction to change the gas composition.

Once equilibrium is reached, another volatilization problem arises: iron oxide reacts with chlorine gas to form a gaseous iron chloride. At first I investigated a slag free of iron in order to generate meaningful results.
Final tests substituted the iron lost from the slag phase by the introduction of an iron-reservoir, a low-grade matte in contact with the slag. Although good at supplying the slag with iron, the matte introduced unwanted changes to the slag chemistry by means of dissolution of magnesia crucibles and matte-slag-gas exchange reactions.

The following conclusions were drawn from the chloride results:

➤ It is found that chlorine dissolves as chlorides in the slags.

➤ Chloride capacity is insensitive to temperature. This behaviour is expected of acidic slags, but not of basic slags.

➤ Chloride capacity depends strongly on slag chemistry (basicity). The more basic the slag, the higher the chloride capacity.

➤ It is found that all the chlorides in the Al₂O₃-CaO-MgO-SiO₂ slags is associated with calcium. This conclusion is justified by the observation that magnesium does not appear to have had a significant effect on the chloride capacity, except for changing the liquidus temperature and diluting the lime content.

➤ The chloride capacity of iron-free melter-type slags ranges from 4.48 to 34.0 for the experimental conditions investigated.
A limited number of gas-slag-matte experiments indicates that chlorides favour the slag phase. The mass distribution coefficient of chlorides between matte and slag \( \left( L_{\text{Matte}/\text{Slag}} \right) \) is typically 0.1.

Of all the variables, slag chemistry has the strongest effect on chloride capacity. The effect can be seen from a representation of data on the 9\%Al\(_2\)O\(_3\)-CaO-MgO-SiO\(_2\) phase diagram. Slags with the lowest silica and the highest lime contents have the highest chloride capacity. The chloride capacities of the iron-containing slags in the matte-slag-gas equilibriations were higher than expected. The effect is consistent with a dual role played by iron oxide in these slags, one of them being cation-anion interactions, and the other donation of the free oxygen. Behaviour of this sort is not uncommon; it is observed in the sulphide capacity of slags.

The activity of calcium chloride in melter-type slags deviates negatively from ideal behaviour.

The behaviour of slags with a calcium chloride concentration of lower than 0.06 wt\% follows Henry's law. At higher concentrations the chloride activity coefficient increases with increasing calcium chloride content. The infinite dilute Henrian activity coefficient and
the interaction parameter of calcium chloride are 0.0038 and 1871.6, respectively.

- Increases in basicity and in chlorine partial pressure and a decrease in oxygen partial pressure all have a positive effect on the chloride activity coefficient. They cause the behaviour to move closer to ideal behaviour as expected from the equation for the equilibrium constant.

- The dependence of the activity coefficient of calcium chloride on temperature follows closely the expected variation for regular solution behaviour.
7.2. RECOMMENDATIONS

The following are recommended for further study:

- The effect of temperature on the chloride capacity of basic slags be investigated more thoroughly.

- The chloride capacity of further iron-containing slags be examined, bearing in mind that the volatilization of iron chloride should be taken into account. It is difficult to run the experiments without changing the slag chemistry because of iron volatilization as iron chlorides. Further tests could use a Pt crucible, and react some iron oxide at a lower temperature within the same furnace in order to fix the partial pressure of the iron chlorides at the reaction zone, thereby limiting the loss of iron as volatile iron chloride.

- Most of the platinum producers are processing UG2 ores, yet the work reported in this thesis has been based mainly on Merensky-type slags. It is therefore proposed that the effect of chromium on the sulphide and chloride capacity be studied.
Chapter 8

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Grant N.J. and Chipman J., 1946. Trans. AIME, Vol. 146, 134


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APPENDICES

A.1. ANALYTICAL TECHNIQUES

The analytical techniques used for analyses of the various samples generated during the experimental period will be discussed in more detail.

A.1.1. Volumetric Determination of Iron (Ferrous Iron Titrations)

The ferrous iron was determined using a N₂ blanket technique. Initially, the sample was weighed out (approximately 100 - 150 mg) into a teflon beaker and dampened with a small amount of distilled or milli-q purified water. The system was purged with nitrogen so as to displace all the air out of the system (~5 min.). Thereafter, 20 ml of concentrated HCl and 10 ml of Hydrofluoric acid₆ was added. The reaction vessel was placed on a hot plate while the nitrogen gas was still purging. The sample was left on the hot plate for a maximum of 20 minutes at 200 °C, which is near the solution's boiling point. Then, ~ 30 ml of a cold 1% H₂BO₃ - 1% HCl solution was added, and the reaction vessel was then removed from the hot plate (the boric acid would have formed a complex with the free HF that has not evaporated). The reaction vessel was placed in a water cooled bath. 15 ml of a sulphuric / phosphoric acid mixture was added. The solution was

* Please note the safety specifications with the handling of HF containing liquids and vapour. Also remember to conduct this work under an operational fume cupboard.
titrated using a Potentiometric titrator and a Potassium Dichromate titrant so as to determine the Ferrous content.

The amount of ferric iron was calculated by subtracting the ferrous iron content from the total iron content, which was obtained from the XRF analyses.

A.1.2. Sulphur Determination

The sulphur content of the slags was determined using a LECO CS-600 Carbon/Sulphur combustion analyser. The sample was weighed and iron chip accelerators were added. The sulphur in the sample was volatilized and oxidized using a closed chamber small induction furnace. The sulphur dioxide content of the exhaust gases was analysed using an infrared detector. The sulphur content could be calculated as the concentration of SO$_2$, mass of the sample and volume of oxygen were known. The typical detection limit was $\sim 0.001$ wt% S.

A.1.3. Alkaline Na$_2$O$_2$ Fusion

0.5 g ± 0.0001 g of sample were weighed into a clean dry zirconium crucible using a 4 digit analytical balance. 2 g ± 0.01 g of sodium peroxide was added on top of the weighed sample using a top loading balance. The samples were pre-heated over a Mecker burner using a LPG gas or similar. This was done until all the sample as well as the flux has melted. The samples were cooled in air and stored in a desiccator. The crucible was then transferred into a 250 ml Teflon beaker and was covered with a watch-glass. 50 ml of milli-q purified water was added. The setup was then allowed to dissolve into the water, thereafter the
content was added to a 100 ml volumetric flask and made-up to volume. The solution was then filtered and prepared for introduction into the analytical instrument.

A.1.4. Chloride Analyses

Some developmental work was carried out at the CSIRO Minerals’ laboratory so as to determine minor element levels of chlorides in the PGM producers’ process samples.

![Diagram](image)

**Figure A.1.1 Illustration of the dialysis membrane**

The determinations of trace level halides in the alkaline solutions were measured using an Ion-Chromatography, which was coupled with an on-line membrane dialysis unit. The slag samples were prepared using the alkaline fusion (Alkaline Na₂O₃) technique. The usual acidification process used would have introduced other anion species at high concentration levels and influenced the results.
Therefore, only additional water was added to dissolve the sample. A cation-exchange membrane dialysis was identified as the best technique for pre-treating the alkaline sample, as it proved to be difficult to directly measure the low level halides using only an ion-chromatograph. The on-line membrane dialysis unit consisted of the following sections: a packed cation-exchange membrane cell, pneumatic pump for dialysis acid delivery and an auto-sampler, which was used to load the sample directly through the dialysis cell into the HPLC equipment. The usual ion-chromatographic system consisted of an anion-exchange column, conductivity meter and a computer controller with a data logger.

![Diagram](image)

*Figure A.1.2 Illustration of the Anion-cation exchange reactions*

The low level chloride data generated by the CSIRO Minerals laboratory for the AMIRA analytical round robins, which was conducted in parallel with this study, was used to determine the relationship between the standard deviation as a
function of the chloride concentration. Various samples from the platinum producer's smelting processes were used. The individual samples were analysed approximately ten times, and ranged from concentration levels of 0.0035 to 0.0470 wt%. The reported detection limit was 0.0030 wt%.
### A.2. SULPHIDE CAPACITY LITERATURE SUMMARY

**Binary Systems**

*Table A2.1 Sources of Sulphide Capacity, Binary slags and temperature ranges:*

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### Ternary Systems

#### Table A.2.2 Sources of Sulphide Capacity, Ternary slag and temperature ranges

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### Quaternary Systems

#### Table A2.3 Sources of Sulphide Cubicity. Quaternary slags and temperatures

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<tr>
<td>Nazota et al. (1998)</td>
<td>1500, 1550, 1600 &amp; 1650</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CaO-FeO&lt;sub&gt;2&lt;/sub&gt;-MgO-SiO&lt;sub&gt;2&lt;/sub&gt;</strong></td>
<td></td>
</tr>
<tr>
<td>Sr. Pierre and Chipman (1956)</td>
<td>1550 &amp; 1600</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CaO-MgO-MnO-SiO&lt;sub&gt;2&lt;/sub&gt;</strong></td>
<td></td>
</tr>
<tr>
<td>Nilsson et al. (1997)</td>
<td>1500, 1575 &amp; 1650</td>
</tr>
<tr>
<td>Nazota et al. (1997b)</td>
<td>1500, 1550, 1600 &amp; 1650</td>
</tr>
</tbody>
</table>
### Quinary Systems

**Table A2.4** Sources of Sulphide Capacity, Quinary slags and temperature ranges

<table>
<thead>
<tr>
<th>Slag Composition</th>
<th>Reference</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃·CaO·Na₂O·MgO·SiO₂</td>
<td>Karand (1981)</td>
<td>1500</td>
</tr>
<tr>
<td>Al₂O₃·CaO·K₂O·MgO·SiO₂</td>
<td>Karand (1981)</td>
<td>1500</td>
</tr>
<tr>
<td>Al₂O₃·CaO·MgO·MoO·SiO₂</td>
<td>Naraia et al. (1998)</td>
<td>1500, 1600 &amp; 1700</td>
</tr>
</tbody>
</table>

### Six Component Systems

**Table A2.5** Source of Sulphide Capacity, Six component slag and temperatures

<table>
<thead>
<tr>
<th>Slag Composition</th>
<th>Reference</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃·CaO·FeO·MgO·MnO·SiO₂</td>
<td>Naraia et al. (1998)</td>
<td>1550, 1600 &amp; 1650</td>
</tr>
</tbody>
</table>
A.3. STEADY STATE INLET FLOW CONDITIONS

The inlet flow conditions for the steady state experiments are tabulated in the following table.

Table A.2 The inlet flow conditions for the experiments that reached a steady state. The total flow rate was 1400 cc/min. The partial pressure of Ar (pAr) was 0.50, excluding the Ar introduced as Ar-10% HCl.

<table>
<thead>
<tr>
<th>Ar-10% HCl cc/min</th>
<th>CO₂/CO ratio</th>
<th>CO₂/H₂ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>61.6</td>
<td>0.48</td>
<td>2.81</td>
</tr>
<tr>
<td>52.7</td>
<td>0.88</td>
<td>4.04</td>
</tr>
<tr>
<td>42.7</td>
<td>1.65</td>
<td>5.37</td>
</tr>
<tr>
<td>33.6</td>
<td>3.32</td>
<td>6.65</td>
</tr>
</tbody>
</table>
A.4. CALIBRATIONS

A.4.1. Hot-zone of the Vertical Tube Furnace

The hot zone of the furnace was determined as the temperature region where the temperature does not deviate more than 1°C from the hottest temperature.

Table A.2.6 The temperature profile of the vertical tube furnace with the controller set at a temperature of 1470°C.

<table>
<thead>
<tr>
<th>Length (cm)</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>536</td>
</tr>
<tr>
<td>5</td>
<td>925</td>
</tr>
<tr>
<td>10</td>
<td>1172</td>
</tr>
<tr>
<td>15</td>
<td>1307</td>
</tr>
<tr>
<td>20</td>
<td>1381</td>
</tr>
<tr>
<td>25</td>
<td>1408</td>
</tr>
<tr>
<td>26</td>
<td>1411</td>
</tr>
<tr>
<td>27</td>
<td>1413</td>
</tr>
<tr>
<td>28</td>
<td>1414</td>
</tr>
<tr>
<td>29</td>
<td>1414</td>
</tr>
<tr>
<td>30</td>
<td>1415</td>
</tr>
<tr>
<td>31</td>
<td>1415</td>
</tr>
<tr>
<td>32</td>
<td>1414</td>
</tr>
<tr>
<td>33</td>
<td>1414</td>
</tr>
<tr>
<td>34</td>
<td>1414</td>
</tr>
<tr>
<td>35</td>
<td>1411</td>
</tr>
<tr>
<td>36</td>
<td>1408</td>
</tr>
<tr>
<td>40</td>
<td>1394</td>
</tr>
<tr>
<td>45</td>
<td>1347</td>
</tr>
</tbody>
</table>

The hot zone of the furnace was found to be between 28 to 34 centimetres from the top reference point. The hottest temperature measured at a controller set point was 1415°C.
A 4.2. Flow Controller Calibrations

A couple of flow controller calibrations are shown with the following graphs in this section. Various calibration curves are shown for various gases controlled with a 500 cc/min maximum N\textsubscript{2} controller. Controllers ranging from 20 to 5000 cc/min were used.

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{ar_calibration.png}
\caption{Ar Calibration 500 cc/min N\textsubscript{2}}
\end{figure}
\end{center}

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{h2_calibration.png}
\caption{H\textsubscript{2} Calibration 500 cc/min N\textsubscript{2}}
\end{figure}
\end{center}

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{controller.png}
\caption{Controller Calibration}
\end{figure}
\end{center}
CO\textsubscript{2} Calibration 500 cm\textsuperscript{3}/min N\textsubscript{2}

\begin{equation}
y = 3.600x - 0.016 \\
R^2 = 0.999
\end{equation}

Ar 10\% - HCl Calibration 500 cm\textsuperscript{3}/min N\textsubscript{2}

\begin{equation}
y = 7.6345x - 0.3005 \\
R^2 = 0.999
\end{equation}
Ar % - SO₂ Calibration 500 cc/min N₂

\[ y = 7.6305x - 4.452 \]

\[ R^2 = 0.9999 \]
A.5. CALCULATIONS

CSIRO's MPE simulation package were used for various activity predictions and calculations. The equilibrium gas compositions and inlet gas compositions were mainly calculated using CSIRO's Thermochemistry software. Some of the calculations were done from first principles. An example of the calculation of the inlet $\rho\text{SO}_2$, $\rho\text{CO}_2$ and $\rho\text{CO}$ will follow for a given $T$, $\rho\text{O}_2$ and $\rho\text{S}_2$.

$$
\text{CO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO}_2 \quad K_1 = \frac{\rho\text{CO}_2}{(\rho\text{CO} \times \rho\text{O}_2^{1/2})}
$$

$$
\Delta G^o_1 = -67878 + 21.524T - 0.10445 \times 10^3 T^2 \log T
$$

$$
\frac{1}{2} \text{S}_2 + \text{O}_2 \rightleftharpoons \text{SO}_2 \quad K_2 = \frac{\rho\text{SO}_2}{(\rho\text{O}_2 \times \rho\text{S}_2^{1/2})}
$$

$$
\Delta G^o_2 = -86620 + 17.31T
$$

$$
\frac{1}{2} \text{S}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{SO} \quad K_3 = \frac{\rho\text{SO}}{(\rho\text{S}_2^{1/2} \times \rho\text{O}_2^{1/2})}
$$

$$
\Delta G^o_3 = -15354 - 1.24T
$$

$$
\frac{1}{2} \text{S}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{SO} \quad K_3 = \frac{\rho\text{SO}}{(\rho\text{S}_2^{1/2} \times \rho\text{O}_2^{1/2})}
$$

$$
\Delta G^o_3 = -15354 - 1.24T
$$
\[ \frac{1}{2} \text{S}_2 \leftrightarrow \text{S} \quad K_4 = \frac{pS}{p\text{S}_2^{1/2}} \]

\[ \Delta G^\circ_4 = 50500 - 14.41T \]

\[ \frac{1}{2} \text{S}_2 + \text{CO} \leftrightarrow \text{COS} \quad K_5 = \frac{p\text{COS}}{p\text{CO} \times p\text{S}_2^{1/2}} \]

\[ \Delta G^\circ_5 = -22860 + 18.7T \]

Assume gases behave ideally, i.e. partial pressures = fugacity

\[ \log K_i = \frac{-\Delta G^\circ}{2.303RT} \]

\[ p\text{CO} + p\text{SO}_2 + p\text{SO} + p\text{S}_2 + pS + p\text{O}_2 + p\text{CO}_2 + p\text{COS} = 1 \]

\[ p\text{CO}_2 = K_1 \times p\text{CO} \times p\text{O}_2^{1/2} \quad \text{and} \quad p\text{COS} = K_3 \times p\text{CO} \times p\text{S}_2^{1/2} \]

**Eliminate pCO**

\[ p\text{CO} + p\text{SO}_2 + p\text{SO} + p\text{S}_2 + pS + p\text{O}_2 + K_1 \times p\text{CO} \times p\text{O}_2^{1/2} + K_3 \times p\text{CO} \times p\text{S}_2^{1/2} \]

\[ \quad = 1 \]

\[ p\text{CO} = \frac{(1 - p\text{SO}_2 - p\text{SO} - p\text{S}_2 - pS - p\text{O}_2)}{(1 + K_1 \times p\text{O}_2^{1/2} + K_3 \times p\text{S}_2^{1/2})} \]

with known:

\[ p\text{SO}_2 = K_2 \times p\text{S}_2^{1/2} \times p\text{O}_2 \]

\[ p\text{SO} = K_3 \times p\text{S}_2^{1/2} \times p\text{O}_2^{1/2} \]

\[ \triangleright 166 \]
\[ p_{CO} + p_{\text{H}_2} + p_{\text{H}_2O} = p_{\text{CO}_2} + p_{\text{H}_2O} + p_{\text{H}_2} + p_{\text{H}_2O} \]

Therefore

\[ x = \frac{p_{\text{H}_2O}}{p_{\text{H}_2}} \]
A.6. PUBLICATION

Iron redox-equilibria and sulphide capacity of PGM melter-type slags

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b CSIRO Minerals, High Temperature Processing Program, Bayview Avenue, P.O. Box 312, Clayton South, Vic. 3169, Australia
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Abstract

New measurements have been made on the ferric to ferrous ratio as well as the sulphide capacity for platinum group metals (PGM) melter-type slags. In South Africa, these slags are produced from the melting of low-grade copper–nickel sulphide ores, Nell [Nell, J., 2004. Melting of platinum group metal concentrates in South Africa. The South African institute of Mining and Metallurgy 104 (7), 423–428]. The typical mass compositions are 5–10% Al2O3, 2–15% CaO, 5–30% FeO, 15–25% MgO and 40–60% SiO2 with a molar basisity of (CaO + MgO)/SiO2 of 0.6–1. The industrial furnaces operate at temperatures ranging from 1450 to 1600 °C under fairly reducing conditions (typically a pO2 close to 10−8 atm at 1500 °C). The gas-slag equilibria was studied by subjecting a synthetic slag to controlled atmospheres in a vertical tube-furnace using Ar–CO–CO2 (±SO2) gas mixtures. The ratio of ferric to ferrous was determined at 1450 °C for oxygen activities, defined as pCO2/pCO, ranging from 0.11 to 1.75 by analysing the quenched slags using the standard titration and XRF techniques. The measured Fe3+/Fe2+ ratio increased from 0.029 to 0.110 with the increasing oxygen activity. Slight non-ideal iron redox behaviour was observed, as has been reported for low alumina and low iron-containing slags. The present results are in good agreement with the trends found in the literature for similar multicomponent slag systems (mostly iron bath melting slags). Sulphide capacity was measured at partial pressures of oxygen and sulphur of approximately 10−8 and 10−3 atm respectively, with total-iron contents of 8.2 and 15.6 wt%, and temperature ranging from 1450 to 1525 °C. The present sulphide capacity data ranged from 10−3.41 to 10−5.71. The expected increase in sulphide capacity with increasing temperature was observed, and at a given temperature, the sulphide capacity increased with an increase in iron oxide content.

Keywords: Redox reactions; Sulphide ores; Pyrometallurgy; Precious metals ores; Extractive metallurgy

1. Introduction

PGM melter slags are produced by electric smelting of dried concentrates of low-grade copper–nickel sulphide ores, which are mined from the PGM-rich Bushveld Complex in South Africa. These base metal melters operate at slightly more oxidising conditions relative to the FeO/Fe2O3 oxygen buffer at temperatures ranging from 1450 to 1600 °C (Nell, 2004). The slags contain high concentrations of silica and magnesia and are fluxed with lime, which results in a CaO–Al2O3–MgO–SiO2–FeO slag system with a typical molar basisity (B') of (CaO + MgO)/SiO2 range of 0.6–1.0.

An AMIRA project ("management of minor elements") was initiated to investigate the departure of various minor elements across the unit operations, used for the pyrometallurgical treatment of base metal ores.
The sulphide capacity of the slags had to be determined in order to quantify the thermodynamic behaviour for low levels of dissolved sulphur. Due to the lack of published equilibrium data on the oxidation state of iron in melt-type slags, some redox-equilibria measurements were made for validation of existing thermodynamic models.

1.1. Iron redox-equilibria

The redox reaction of iron-containing slags with CO and CO₂ is shown in reaction (1):

\[ \text{FeO} + \frac{1}{2}\text{CO}_2 \rightleftharpoons (\text{FeO})_3 + \frac{1}{2}\text{CO} \]  

The ratio of \( \text{FeO}_3/\text{FeO} \) may be expressed as the ratio of ferric to ferrous (\( \text{Fe}^{3+}/\text{Fe}^{2+} \)) by rewriting the equilibrium constant of reaction (1) at a constant slag composition and temperature.

\[ \text{Fe}^{3+}/\text{Fe}^{2+} = K_1(\frac{\gamma_{\text{FeO}_3}}{\gamma_{\text{FeO}}})(\rho\text{CO}_2/\rho\text{CO})^{1/2} \]  

with \( K_1 \) being an equilibrium constant of reaction 1 and \( \gamma_{\text{FeO}_3}/\gamma_{\text{FeO}} \), the ratio of the activity coefficients of FeO and FeO_3. The \( \rho\text{CO}_2/\rho\text{CO} \) ratio may be considered as the oxygen activity.

The redox behaviour of a slag is considered as "ideal" if the ratio of the activity coefficients is independent of the oxygen activity and a plot of the log(\( \text{Fe}^{3+}/\text{Fe}^{2+} \)) vs. \( \log(\rho\text{CO}_2/\rho\text{CO}) \) yields a straight line with a slope of 1/2. Ideal behaviour is not expected for all slag types and compositions, as a slight dependence of the activity coefficient ratios with different oxygen activity could exist.

There is extensive literature on the redox behaviour of iron in multi-component slags from calcium-ferrite slags to slag systems similar to that of the PGM melt-type. Takeda et al. (1980) studied the thermodynamic properties and iron redox-equilibria of the CaO–FeO system. Takeda and co-workers used their data and that of Timucin and Morris (1970), Larson and Chipman (1953) and Darken and Gurry (1946) to present the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratio as a function of \( \rho\text{O}_2 \), temperature (1200–1600 °C) and slag composition (0–40 wt% CaO). More recent measurements by Sun et al. (1988), Sayadyaghoubi et al. (1994) and Tran (1995, 1997) are in accord with Takeda and co-workers findings. The trend for the lime-saturated calcium ferrite slag was close to the ideal behaviour for iron redox-equilibria, while a dependence of the activity coefficients on the oxygen activity were observed for slags with given Ca/Fe ratios.

Larson and Chipman (1953) investigated the redox-equilibria of the CaO–FeO–SiO₂ system for various CaO/SiO₂ molar ratios, while Timucin and Morris examined the same slag system by increasing the SiO₂ contents (0–30 wt%). Multi-component CaO–SiO₂–FeO₁₋ₓ–MgO (Al₂O₃) slag system(s) were investigated by Mysen et al. (1985), Tran (1995, 1997) and Yang and Belton (1998). Yang and Belton (1998) correlated log(\( \text{Fe}^{3+}/\text{Fe}^{2+} \)) as a function of the log(\( \rho\text{CO}_2/\rho\text{CO} \)) and molar (CaO + MgO)/SiO₂ ratio and reported that the iron redox-equilibria is basically independent of temperature in the 1350–1600 °C range. This is expected when the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) is expressed as a function of CO₂/ CO due to the small entropy change of the reaction. Yang and Belton also concluded that Al₂O₃ is amphoteric for additions of 10–15 mol% and that the iron redox-equilibria deviate strongly from ideal behaviour for high alumina containing slags. Jahanshahi and Wright (1993) determined the \( \gamma_{\text{FeO}_3}/\gamma_{\text{FeO}} \) ratios for Al₂O₃-CaO–FeO₁₋ₓ–SiO₂ slags and found that the ratio changed significantly as the total iron content of the slag was increased from 0.75 to about 2 wt%, but remained virtually constant from 6 to 24 wt% total iron. The apparent increase in the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratio with iron content between 0.75 and 2 wt% is thought to be due to the inaccuracies associated with the analysing methods used (Mössbauer and titration) at these low-total-iron levels. Moreover, Xie (1992) investigated iron oxide levels as low as 0.2 wt% and confirmed the insignificant effect of the iron content. The review paper by Sun and Jahanshahi (2000) concluded that the transition metals (Fe, Mn, Ti and V) redox-equilibria for calcium silicate-based melts showed a close to ideal behaviour relative to the oxygen activity. However, a more significant departure could be observed for multi-component slag systems containing high levels of alumina or titania. The magnitude of the redox ratio depended strongly on the slag basality, while the transition metal content had an insignificant effect unless complex species were formed with other slag constituents at high concentrations. After reviewing the redox-equilibria literature, it was identified that an experimental study was required for melt-type slag's iron redox-equilibria in order to determine if this multi-component slag's behaviour deviates significantly from ideal behaviour.

1.2. Sulphide capacity

The ability of liquid slags to absorb sulphur has been studied thoroughly in steelmaking applications for many years, due to its role in desulphurisation processes. The sulphur distribution between phases at high temperature was initially determined by means of slag-metal equilibration. However, with this technique it was not possible to study the individual effects of slag composition and oxygen potential on the sulphur partitioning. Fincham and Richardson (1954) addressed this problem by using a gas–slag equilibration technique and subsequently defined the sulphur capacity of slags. They found that the sulphur from the gas phase dissolved into calcium–alumino silicate slags as a sulphate at oxidising conditions (\( \rho\text{O}_2 > 10^{-3} \text{ atm} \)) and as a sulphide at reducing
conditions \((pO_2 < 10^{-6} \text{ atm})\). Only the sulphide capacity will be investigated herein as copper–nickel and PGM melters operate under reducing atmospheres (typically \(pO_2 < 10^{-9} \text{ atm}\)). The sulphide capacity, \(C_{sp}\), may be defined through the following equations:

\[
(G^{2+}) + 1/2S_2 \rightleftharpoons (S^{2-}) + 1/2O_2
\]

(1) indicates species in the slag phase.

\[
C_{sp} = (\text{wt}%) \frac{pO_2/pS_2}{1/2} = K_3(\alphaO^{2-}/\gammaS^{2-})
\]

with \(K_3\) the equilibrium constant for reaction (3) and \(\gammaS^{2-}\) the activity coefficient of the sulphide and \(\alphaO^{2-}\) the activity of the oxide ion.

Sulphide capacity is a function of slag composition \((\alphaO^{2-}/\gammaS^{2-})\) and temperature as seen from Eq. (4), which is derived from the equilibrium constant for reaction (3). The sulphide capacity for a constant slag composition should therefore only be a function of temperature and is shown in Eqs. (5) and (6):

\[
C_{sp} = K_3(\alphaO^{2-}/\gammaS^{2-}) = \exp(\Delta G/RT) \times D
\]

(5)

with \(\Delta G\) the Gibbs free energy (a linear function of temperature with constants \(a\) and \(b\)), \(R\) the gas constant, \(T\) the temperature while \(D\) is the grouped constant value of \(\alphaO^{2-}/\gammaS^{2-}\) (for a constant slag composition).

Eq. (5) can be expressed in the natural logarithm form as

\[
\ln(C_{sp}) = E/T + F
\]

where \(E\) and \(F\) represent the grouped constants to indicate the linear function of the logarithm of sulphide capacity with temperature.

Compilations of sulphide capacity data are available in the literature from binary to multi-component slag systems for various temperatures. A thesis entitled “Sulphide Capacities of Multi-component Slags” by Nzotta (1999) is a comprehensive source of sulphide capacity for a large range of slag systems.

Figs. 1 and 2 show that there is an increase in sulphide capacity with an increase in temperature at a fixed slag composition. However, the effects of the slag’s iron content show opposite trends for acidic and basic type slags. From Fig. 1, the sulphide capacity decreased with an increase in the molar FeO\(_2\) content for basic calcium ferrite slags, while for acidic iron silicate slags (shown in Fig. 2), the sulphide capacity increased.

The necessity to determine and quantify the capability of liquid melter-type slags to absorb sulphur has not previously been considered as important as the desulphurisation of the metal phases in the converting processes and in the iron and steel industry, because the melter slag is in contact with a high sulphur (matte) phase. However, some base and precious metals could be dissolved within the slag, associated with the sulphides.
2. Experimental

Three synthetic slags were prepared by using predried powders of laboratory reagent grade Al$_2$O$_3$, CaCO$_3$, Fe$_2$O$_3$, MgO and SiO$_2$. The required amounts were dried, weighed, mixed and then milled in a clean tungsten carbide ring mill. Thereafter, the mixture was melted at 1500 °C in an egg-cup shaped Pt-10%Rh crucible using a MoSi$_2$ muffle-furnace. The melt was poured onto a steel launder at ambient temperature to form a quenched glass. When cooled, the glass was pulverised in a ring mill and mixed to result in a fine homogeneous master slag. The average slag compositions obtained by X-ray fluorescence (XRF) are reported in Table 1.

Equilibration time for the iron-containing slags was minimised by pre-reducing the pulverised slag in a small vertical tube furnace capable of heating up to 1000 °C. The solid slag was placed on porous alumina blocks in a removable quartz tube and reacted at 800 °C in a reducing atmosphere. This technique required shorter pre-reduction times compared with conventional high temperature pre-reduction techniques. For example, reagent-grade hematite powder was reduced to whistle (analysed using X-ray diffraction) by reacting the powder with a CO$_2$–CO atmosphere at a $p_{CO_2}/p_{CO}$ ratio of 1.0 with a total flow rate of 500 c.c./min for 1.5 h, while conventional pre-reduction techniques usually required about 24 h or longer.

Commercially available gases were purified by passing them through a gas cleaning train before introducing them into the work tube furnace. Pure CO, high purity Ar and a mixture of Ar-99.5%SO$_2$ were used. Moisture was removed by passing the gas through magnesium perchlorate and/or silica gel. Low levels of oxygen were removed by passing the gas over 500 °C pre-heated copper chips. The desired gas flow rates were controlled with calibrated mass flow controllers and were mixed in a 50 mm $\varnothing$ x 15 cm long tube packed with 5 mm $\varnothing$ quartz beads.

The equilibrium work was carried out in a vertical-tube high-temperature furnace fitted with water-cooled end-caps that maintained a controlled atmosphere within the work tube. The gas mixtures entered at the bottom of a 50 mm $\varnothing$ Al$_2$O$_3$ reaction tube and exited through an alumina lance that was suspended from the top end-cap. The crucible assembly is shown in Fig. 3: a small Pt boat was used to hold 2 g of master slag and was placed in a larger Pt crucible. The crucible was then connected by means of a ceramic spline (fitted with a safety Pt wire) to the suspended alumina tube. An ASTM type R thermocouple (Pt/Pt-13% Rh) that was calibrated against the melting point of copper was used to measure the temperature at the base of the crucible setup. The hot zone was determined as the hottest region within the tube-furnace for which the temperature deviates by not more than 1 °C. The suspended crucible was loaded into the work tube while the pre-heated furnace was flushed with Ar at a flow rate of 1000 c.c./min (STP) for half an hour. The desired CO–CO$_2$ and Ar flows were introduced in order to remove any excess oxygen while the crucible was slowly lowered into the hot zone. Thereafter, SO$_2$ was introduced, if it was desired to control the partial pressure of oxygen, as well as sulphur, simultaneously. A total gas flow rate of 500 c.c./min (STP) was used for all the experiments. When the desired reaction time had been reached, the samples were quenched by dipping the larger Pt crucible in a plastic bucket filled with milli-Q purified reagent water.

The slag was removed from the Pt boat, dried, pulverised and analysed by XRF for the metal oxide content, while the ferrous content was determined with a standard wet chemical procedure. The ferric content was calculated by subtracting the ferrous from the total-iron content. The sulphur content was analysed with an internal combustion spectrometer (LECO CS-600 Carbon/sulphur analyser using a “Low level S-HP” method).

The time required to approach equilibrium was determined through a series of experiments where the reaction time was varied until the slag's sulphur content stabilised. Reaction times of 2, 4, 6 and 16 h were investigated and the results are shown in Fig. 4. The slags were reacted from both the low as well as the high sulphur side, by dosing the slags with small amounts of calcium sulphide to ensure that equilibrium was reached, as it is possible to reach a steady state, which differs from the equilibrium state, due to interfacial gas–molten slag

Table 1

<table>
<thead>
<tr>
<th>wt%</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>19.8</td>
<td>38.4</td>
<td>–</td>
<td>–</td>
<td>41.8</td>
</tr>
<tr>
<td>B</td>
<td>8.5</td>
<td>8.3</td>
<td>10.5</td>
<td>23.1</td>
<td>49.7</td>
</tr>
<tr>
<td>C</td>
<td>7.0</td>
<td>7.2</td>
<td>20.1</td>
<td>22.5</td>
<td>43.4</td>
</tr>
</tbody>
</table>
Fig. 4. Variation of sulphur content of a CaO-Al₂O₃-SiO₂ (38.4:19.8:41.8 wt%) slag with reaction period.

Fig. 5. Variation of Fe³⁺/Fe²⁺ ratio with CO₂/CO ratio for iron slag: B (B) of 0.95, did not depart significantly from the ideal behaviour and is shown in Fig. 5. The data point generated by Hundermark (2003) for a melter-type slag with a molar ratio (B) of 0.70 at a CO₂/CO of 10 is in agreement with the trend of the present work, and the slight non-ideal behaviour correlates with the low iron and low alumina containing slags previously investigated by Yang (1994).

In the absence of measured iron redox-equilibria on the melter slags, it could be predicted from other multi-component data and correlations (mostly that of iron bath smelting slags). The Fe³⁺/Fe²⁺ ratio for a slag (with B of 0.95) was predicted from the multi-component data and correlations available in the literature, and is included in Fig. 5. The trends are in good agreement with the present data.

3.2. Sulphide capacity of a steel-making and melter-type slags

The sulphide capacity of a well-characterised calcium–aluminosilicate slag system (Slag A, Table 1) was determined at various temperatures to confirm the experimental method. The aim was also to broaden the temperature range of the experimental data for this system. The present data correlates well with those in the literature and a clear linear function of the log(C₅₀⁺) as a function of temperature is shown in Fig. 6. This linear behaviour observed for the logarithm of the sulphide capacity as a function of temperature is purely empirical, as the mathematically and thermodynamically correct representation would be as a function of the reciprocal of the temperature, as expected from Eq. (6). However, both these plots resulted in a linear

Fig. 6. Temperature dependence of sulphide capacity of CaO-Al₂O₃–SiO₂ (46:20:40 wt% approx.) slag. Present data correlates well with that found in the literature (Gornerup and Wijk (1996), Fincham and Richardson (1954)) Line shown is the least squares fit to all the data excluding that of Kalyanaram et al. (1960).
relationship due to the small temperature ranges investigated.

The sulphide capacity of melter-type slags with 10 and 20 wt% FeO, was quantified for a range of temperatures and it was observed that the sulphide capacity increased with an increase in the iron oxide content as shown in Fig. 7. This increase is to be expected as melter-type slags are fairly acidic and the increase of the iron oxide content increased the amount of free oxygen donated. From the ionic theory of slag chemistry, FeO acts as a basic oxide for the acidic slag and should decrease the degree of polymerisation for the silicate melt so that more sulphides could be dissolved within the slag. Furthermore, as iron has a strong affinity for sulphur, its presence in slags would make significant contribution to the cation-anion (Fe$^{2+} \sim S^2$) interaction and hence lower the activity coefficient of sulphur in slags. This will result in increasing the sulphide capacity of the slag.

The multi-component melter-type slag's sulphide capacity has been compared with binary and ternary slags that represents the major components of the melter-type, and is shown in Fig. 7. The silica content and FeO/MgO ratios were used to compare the slags, and the effect of the addition of various metal oxides to the binary magnesia silicate, leading to the melter-type slag chemistry. It could be noted that the introduction of lime to the MgO-SiO$_2$ slag system produced an increase in the sulphide capacity, but less than the more significant increase observed with the addition of FeO. If the data from the present work on the slag with 20 wt% FeO$_2$ are extrapolated to 1600 °C, it appears lower than that measured by Nzotta (1999) for a FeO$_2$-MgO-SiO$_2$ slag, which has a higher MgO/SiO$_2$ and FeO$_2$/MgO ratio. Although the slag from this study contains some alumina that could decrease its sulphide capacity, it also contains some lime that tends to increase the sulphide capacity.

The sulphide capacity data for blast furnace (or more specifically Corex) type slags investigated by Seo and Kim (1999) with a 9.2 and 13.3 wt% addition of FeO$_2$ show an increase in sulphide capacity with increasing iron content. The Corex slags have a slightly higher sulphide capacity compared to the present melter-type slags, which is due to the Corex-type slags containing higher amounts of lime and having a higher molar basicity ratio B$'$. The magnitude of the measured melter-type sulphide capacity is in accord with lower order slag systems. Given that the measurements made in the present work on CaO-SiO$_2$-Al$_2$O$_3$ slags at the same compositions as those measured by a number of investigators were in very good agreement, we may exclude the possibility of errors in chemical analysis or actual experimental conditions in the present work.

It follows from the foregoing discussion that the use of molar ratios of components in multi-component slags may not be a good measure and only a rough guide for comparison of slags with very different compositions. An alternative to this would be the use of optical basicity of oxides and slags as proposed by Sosinsky and Sommerville (1986). Although good for complex slags, it has weaknesses and does not account for the interactions between cations and sulphide ions and hence can lead to an unaccountable "basicity" scale for cations such as FeO, MnO etc. Perhaps a more fruitful approach would be to use structurally related thermodynamic models such as the cell model (Gaye et al., 1992), which could account for interactions between all cations and anions. This approach has been successfully employed by some research groups and excellent agreement between the calculated and measured values of sulphide capacities of simple and multi-component slags over broad ranges of temperature and composition are obtained.

4. Conclusions

Results obtained from a series of gas-slag equilibrium experiments carried out on synthetic slags to simulate PGM melter furnace-type slags indicated that:

- The Fe$^{3+}$/Fe$^{2+}$ ratios increased from 0.029 to 0.110 with an increase in oxygen activity defined as CO$_2$/CO (0.11-1.75) at 1450 °C for a molar basicity ((CaO+MgO)/SiO$_2$) of 0.95. The iron oxidation ratios followed the slight non-ideal behaviour as expected for transition-metal redox-equilibria for calcium silicate-based slags. The present data generated for synthetic melter-type slags is in good agreement with the trends of the available literature data.

![Fig. 7. Variation of the sulphide capacity with temperature for various slags. Melter-type slags containing 10 and 20 wt% iron oxide (solid: triangles and circles, respectively). The remainder of the data were extracted from Nzotta (1999). Lines shown are hand drawn to guide the eye.](image-url)
The sulphide capacity increased with an increase in temperature (1450-1525 °C) at a constant slag composition. It was also observed that the sulphide capacity, at a given temperature, increased with an increase in the iron oxide content (from 10 to 20 wt% FeO). The present sulphide capacity data ranged from $10^{-4.65}$ to $10^{-3.71}$.

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