MICROELEMENT DISTRIBUTION DURING MATTE SMELTING

By

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Dissertation submitted in fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering

School of Civil & Chemical Engineering

RMIT University
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Dedicated to my parents Siaw Boon and Adeline as well as my brother Tak Siang
.......for their unyielding love and relentless encouragement.
DECLARATION

I hereby certify that this dissertation is my own original work, except where specifically acknowledged in the text. Neither the present dissertation nor any part thereof has been submitted previously at any other university. The content of this dissertation is the result of the work which has been conducted since the commencement of the approved research program in February 2003.

__________________________

Tak Seng Kho
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<td>( )</td>
<td>Reference to slag phase.</td>
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<tr>
<td>{ }</td>
<td>Reference to matte phase.</td>
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<td>[ ]</td>
<td>Reference to metal phase.</td>
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<tr>
<td>ΔG°</td>
<td>Standard Gibbs free energy change at defined temperature.</td>
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<td>γ&lt;sub&gt;M&lt;/sub&gt;</td>
<td>Activity coefficient of species M.</td>
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<tr>
<td>α&lt;sub&gt;M&lt;/sub&gt;</td>
<td>Activity of species M.</td>
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<td>K</td>
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<td>M°</td>
<td>Species M in the metallic form.</td>
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<tr>
<td>M&lt;sub&gt;O&lt;/sub&gt;</td>
<td>Species M in the oxidic form.</td>
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<td>M&lt;sub&gt;S&lt;/sub&gt;</td>
<td>Species M in the sulfidic form.</td>
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<tr>
<td>M&lt;sub&gt;M&lt;/sub&gt;</td>
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<tr>
<td>n&lt;sub&gt;T&lt;/sub&gt;</td>
<td>Total moles of constituents in 100 g of a molten phase.</td>
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ABSTRACT

Element distribution studies provide part of the necessary framework for improving the sustainability of base metal production by opening future opportunities for profitable recovery or by anticipating future legislative restrictions that impact on profitability. Determining the distribution of microelements between the phases present during copper smelting by classical methods is often very difficult, and because there are potentially so many of them, very time-consuming and expensive. The main focus of the present study was to develop a generic model to predict the distribution behavior of minor and microelements and then to validate it.

The distribution of elements between matte & slag was examined thermodynamically to develop the generic model. The procedure involved predicting the likely form of the species present in matte and slag, determining the equilibrium constant for the interaction between those species, making an assumption about the value of the activity coefficient ratio for them and then calculating the distribution ratio. When activity coefficient data was available in the literature it was used, otherwise they were assumed to be unity. The model was first validated against published distribution data available and the agreement found was generally satisfactory.

Since distribution data is only available for a limited range of elements, experiments were performed to obtain the necessary data for other elements. The distribution of microelements was studied at 1523 K using industrial matte and slag as well as with matte and slag samples synthesized from laboratory reagents. The industrial matte and slag samples provided the distribution behavior of many microelements naturally present, whereas the synthetic phases were used to determine the distribution behavior of two selected elements, cobalt and tungsten. The predicted distribution coefficients again compared very well with the experimental data derived from this study.

Two cases were identified where the generic model predicted the distribution behavior poorly, with failure in both cases being due to difficulties with activity coefficient data. Group I and II elements in the Periodic Table form very basic oxides which interact very strongly with oxides in typically acidic copper smelting slags. Their activity coefficients are very much smaller than unity. Metals which can be present as neutral atoms in slag and/or matte also behave very non-ideally, and there is almost no published data on their activity coefficients. That which is available indicates activity coefficient values much greater than unity.
In general, the results documented in this study shows that the generic model developed can be used as a reliable predictive tool when experimentation is inconvenient or inadvisable.
CHAPTER 1: INTRODUCTION

Moving towards operating in a sustainable manner is now an obligation on all companies processing raw materials. Sustainable development involves the simultaneous pursuit and integration of economic prosperity, environmental integrity, and social equity. All industry sectors perform against this triple bottom line as the framework for decision making and for identifying best practices. The presence of many minor elements within a base metal production circuit provides opportunities for increased revenue via by-product production but may also induce extra cost for impurity management. Understanding and controlling the behavior of minor elements has always been an important feature of copper smelting. Nowadays it is becoming necessary to extend this understanding to the behavior of elements which are present at the parts-per-million level, the so-called ‘microelements’, especially if they become the focus of environmental interest. Determining the distribution of such elements between the phases present during copper smelting by classical methods is often very difficult, and because there are potentially so many of them, very resource intensive.

The thermodynamics of metal-slag equilibria has been well documented in literature. Yazawa (1994) described oxidic dissolution of metal in slag in an essentially simple manner; i.e. in terms of the equilibrium constant for the metal oxidation reaction, oxygen potential and the activity coefficients of the species in solution. Using available thermodynamic data, Yazawa (1994) analyzed the oxidic dissolution loss of common metals in slag and concluded that the results obtained are in agreement with experimental results. The matte-slag system can be analyzed in a similar manner, however the system is far more complicated due to the added presence of sulfur. By developing the Yazawa approach further and examining the features of the matte-slag system, a predictive tool can potentially be established as the next best alternative to experimental distribution data. While always to be preferred, experimental determinations of distribution data are not always possible, or financially justified. Some microelements are very dangerous to human health, while some are present in concentrations that are beyond the detection limit of usual analytical techniques. In many situations, all that is required is a good estimate of the distribution ratio of a minor element.

The primary focus of this study is to create a predictive tool to determine the distribution behavior of microelements between copper matte and silica-saturated iron silicate slag under matte smelting conditions. The merits and limitations of the thermodynamic model are first examined using existing distribution data for elements between matte and slag available from literature. However, such data are limited in scope to only a few minor elements. Further validation will come from experimental data produced in this study.
from experiments using both industrial samples and synthetic phases. The industrial samples permit the estimation of the distribution ratio of many microelements naturally present in industrial matte and slag as a result of their presence in the raw materials. The experiments using synthetic matte and slag enable the distributions of a few minor elements to be determined rigorously and to a greater precision than available in the literature.

The validated distribution model can be used to quickly and inexpensively estimate the distribution behavior of many minor and microelements so that opportunities for the recovery of values can be assessed or the risks of environmental harm similarly assessed.
This section covers the fundamentals of copper production by examining the aims of each unit operation involved, as well as the issues associated with achieving those aims. Figure 2-1.1 shows the principal processes involved in extracting copper from sulfide ores.

**Figure 2-1.1:** Principal processes for extracting copper from sulfide ores (Biswas & Davenport, 1994).
The diagram starts from the liberation of copper mineral grains from the sulfide ore in order to produce concentrates more suitable for pyrometallurgical processes. The concentrate is fed into one of the alternative pyrometallurgical processes available to ultimately produce blister copper. The blister copper is refined through a number of subsequent processes including anode refining and casting followed by electrorefining to produce the final copper product containing less than 20 ppm of impurities. The following sections look into each step in detail and identify the key aims and issues involved.

2-1.1 RAW MATERIALS

The three primary sources for copper are copper sulfide minerals, oxidized minerals, and recycled scrap copper. The most common form of sulfide ore is the mineral chalcopyrite, CuFeS₂. The copper content of ores is low, in the range of 0.5% to 2.0% Cu and would constitute excessive waste of furnace capacity and energy by heating and melting large quantities of waste rock if directly fed into any pyrometallurgical process. An effective way of concentrating the minerals before being smelted is a physical operation known as froth flotation.

The copper ore needs to undergo the process of comminution in the form of crushing and grinding before being fed into a froth flotation circuit. The aim of comminution is to liberate the copper mineral grains from non-copper mineral grains. Greater liberation of chalcopyrite is achieved by having a finer grind; however this is accompanied by higher energy costs as well as flotation difficulties. There is an optimum particle size for reducing the loss of copper minerals into the tailings. This optimum is governed by the fact that overly large particles prevent flotation whereas undersized particles cause a slime formation, which coats the copper minerals and prevents flotation. The ground ore is then sent on to flotation.

Copper froth flotation entails conditioning a water-ore mixture to make the copper minerals water repellent (hydrophobic) and leaving the non-copper minerals hydrophilic while passing a dispersed stream of air bubbles up through the aqueous pulp. This causes the copper mineral particles to become selectively attached to the rising bubbles and rise to the surface of the flotation cell. The copper mineral froth overflows the flotation cell into a trough to become a concentrate bearing between 20-30% copper.
2-1.2 MATTE SMELTING

Copper ores are mostly available in the form of chalcopyrite and hence the ultimate aim of copper production is to separate copper from iron and sulfur. This separation is achieved in a series of steps, the first stage being the pyrometallurgical process of matte smelting. Matte smelting is aimed at oxidizing, heating and melting the Cu-Fe-S flotation concentrates in order to oxidize some of the iron and sulfur and as little copper as possible from the concentrate in order to produce a molten sulfide phase richer in copper than the original chalcopyrite concentrate. The process takes place in a furnace heated to approximately 1523 K. Figure 2-1.2 shows the matte smelting flowsheet.

Figure 2-1.2: Matte smelting flowsheet (Biswas & Davenport, 1994).

The products of matte smelting are a molten sulfide matte containing 45-75% copper, a molten oxide slag phase and sulfur dioxide bearing off-gas. Mattes and slags have a significant difference in density, thus forming two separate molten phases which are tapped from the furnace through high and low tap-holes. The matte is sent forward to a converting furnace to form impure copper whereas the slag is discarded, usually after a copper recovery stage. The sulfur dioxide bearing off-gas is cleaned by dust removal and subsequent purification processes before being converted into sulfuric acid.

The matte smelting reaction for a chalcopyrite ore is detailed below:
Chapter 2: Literature Review

4CuFeS\(_2\) + 5O\(_2\) + SiO\(_2\) = 2(Cu\(_2\)SFeS\(_2\)) + 4SO\(_2\) + (2FeO.SiO\(_2\)) + Heat \[2-1.1\]

The amount of O\(_2\) provided for these reactions is controlled to obtain the desired amount of iron and sulfur oxidation. The heat evolved goes to heating and melting the furnace products thus minimizing the amount of fossil fuel which must be burnt in the furnace. Copper which is inadvertently oxidized is resulfidized by reactions like:

\[\text{Cu}_2\text{O}(l) + \text{FeS}(l) = \text{Cu}_2\text{S}(l) + \text{FeO}(s)\] \[2-1.2\]

This reaction has a Gibbs free energy change of -121.04 kJ at 1523 K, indicating that Cu\(_2\)O is almost completely sulfidized by FeS at smelting temperatures.

Various matte smelting technologies exist depending on the needs of the smelter and environmental regulations. Industrial smelting furnaces can be categorized into flash and bath smelters and will be discussed in Section 2-3 Copper Production Technology.

2-1.3 CONVERTING

Converting is the process of air oxidation of the molten matte product obtained from smelting. The aim of converting is to essentially remove all the remaining iron and sulfur from the matte to produce crude molten metallic copper which is sent for further refining downstream. Converting is mostly carried out in the Peirce-Smith converters although other technologies exist as will be discussed in Section 2-3.

Converting takes place in two sequential stages, the first being the slag forming stage, where all FeS reacts with oxygen to form FeO, white metal (Cu\(_2\)S) and SO\(_2\) gas. The second stage is the blister copper forming stage, where the white metal is oxidized into liquid copper. Copper making does not occur until the matte contains less than approximately 1% iron, so that most of the iron can be removed from the converter before copper production begins. Significant oxidation of copper does not occur until the sulfur content of the copper falls below approximately 0.02% (Biswas & Davenport, 1994). This point will be more clearly illustrated when the competing reactions are compared in Section 2-2. The converting process is terminated when copper oxide formation is apparent in samples of the molten copper.

Stepwise charging is practiced to better utilize the limited capacity of the converter. As the matte is gradually oxidized into slag and removed, the remaining volume of matte in the converter is decreased hence more matte is added. This results in gradual
accumulation of white metal (Cu$_2$S) in the converter in preparation for the final ‘coppermaking’ blow (Biswas & Davenport, 1994). Converter conditions are strongly oxidizing; hence inevitably the slag will contain two to eight percent copper. Converter slags are usually recycled to the matte smelting furnace for copper recovery.

### 2-1.4 Electrorefining

The blister copper produced is electrochemically refined to high purity cathode copper containing less than 20 ppm impurities (Biswas & Davenport, 2002). The anodes required in electrorefining are produced by fire-refining molten blister copper to remove sulfur and oxygen and by casting the resultant copper in open, anode shaped molds (Biswas & Davenport, 2002). These anodes are then interleaved with cathode copper in the refining cell.

Copper electrorefining involves electrochemically dissolving copper from the impure anodes into CuSO$_4$-H$_2$SO$_4$-H$_2$O electrolyte and then electrochemically plating pure copper from the electrolyte onto copper or stainless steel cathodes (Biswas & Davenport, 2002).

The electrolyte is an aqueous solution of H$_2$SO$_4$ and CuSO$_4$ in addition to trace amounts of chlorine and other impurities. Many anode impurities are insoluble in this electrolyte and do not interfere with the electrolysis (Biswas & Davenport, 2002). They are collected as ‘slimes’ and sent to a byproduct recovery plant. Arsenic, antimony, bismuth, iron, and nickel are partially or fully soluble in the electrolyte. Although they do not electrochemically deposit with the copper at the low voltages used in the electrorefining cell (~0.3V), they must be kept to low levels in the electrolyte to avoid contamination of the cathode (Biswas & Davenport, 2002). This is done by continuously bleeding part of the electrolyte through a purification circuit (Biswas & Davenport, 2002).
The previous sections described briefly the unit operations involved in copper production circuits as well as the aims of each operation. This section takes a thermodynamic approach towards the important operations of matte smelting and converting. The issues of copper loss to slag and magnetite formation are also thermodynamically explained. The final aim of this section is to introduce Yazawa’s chemical potential diagram, which has been shown to be the best way to illustrate a number of important aspects of smelting and converting simultaneously.

2-2.1 PROCESS THERMODYNAMICS

As discussed in Section 2-1.2, the purpose of smelting is to oxidize the sulfide concentrates to form matte and slag. The initial reactions that occur when chalcopyrite is heated are represented by the following oxidation reactions:

\[
4\text{CuFeS}_2(s) = 2\text{Cu}_2\text{S}(l) + 4\text{FeS}(l) + S_2(g) \quad [2-2.1]
\]

\[
S_2(g) + 2O_2(g) = 2\text{SO}_2(g) \quad [2-2.2]
\]

The first reaction shows the melting of the concentrate into matte containing copper sulfide and iron sulfide while liberating sulfur gas. The liberated sulfur gas is then oxidized into sulfur dioxide, leaving the furnace as an off-gas.

The standard Gibb’s free energy change for the formation of the sulfides at 1523 K shows the stability of copper sulfide and iron sulfide are relatively similar.

\[
4\text{Cu}(l) + S_2(g) = 2\text{Cu}_2\text{S}(l) \quad \Delta G^o = -160.3 \text{ kJ} \quad [2-2.3]
\]

\[
2\text{Fe}(s) + S_2(g) = 2\text{FeS}(l) \quad \Delta G^o = -135.8 \text{ kJ} \quad [2-2.4]
\]

The formation of oxides can be observed in a similar fashion. The standard Gibb’s free energy change for the formation of copper oxide and iron oxide is shown in reactions [2-2.5] and [2-2.6].

\[
4\text{Cu}(l) + O_2(g) = 2\text{Cu}_2\text{O}(l) \quad \Delta G^o = -111.3 \text{ kJ} \quad [2-2.5]
\]
2\text{Fe}(s) + \text{O}_2(g) = 2\text{FeO}(l) \quad \Delta G^o = -328.9 \text{ kJ} \quad [2-2.6]

The standard Gibb’s free energy change for the formation of the oxides is much more negative for the iron oxide meaning that iron oxide is much more stable than copper oxide. This means that when the matte is oxidized during matte smelting, iron sulfide is preferentially oxidized into iron oxide while the copper remains in the sulfide form in the matte as expected.

One problem with the above analysis is that it assumes unit activity of all species, whereas in reality most of the species are in slag. Another problem is that iron oxide is soluble in the matte forming a single phased oxysulfide liquid. Figure 2-2.1 represents a partial phase diagram for the FeS-FeO-SiO$_2$ ternary system. The shaded region of the diagram represents a solution consisting only of FeO and FeS. This region of the diagram demonstrates the solubility of FeO in FeS and how a single oxysulfide liquid is formed. The diagram also illustrates how a miscibility gap appears when silica is added.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{phase_diagram.png}
\caption{Partial phase diagram for the FeO-FeS-SiO$_2$ system showing slag matte immiscibility caused by SiO$_2$ (Biswas & Davenport, 2002).}
\end{figure}

The addition of silica into the furnace will cause iron oxide to react with the silica to create an iron silicate slag. As more silica is added, the slag and matte become more immiscible as observed by the increase in the region of the miscibility gap from ‘line-a’ to
‘line-d’ (silica saturated) in Figure 2-2.1. This immiscibility allows for the removal of most of the iron oxide from the matte phase thus increasing the concentration of copper in the matte.

The oxidation of copper sulfide to form copper oxide is a concern because copper oxide can dissolve into the slag thereby leading to reduced recovery of copper in the matte phase. As mentioned in Section 2-1, the presence of iron sulfide in the matte resulfidizes copper oxide into copper sulfide based on reaction [2-1.2]. At equilibrium:

\[
a_{\text{Cu}_2\text{O}} = \frac{a_{\text{FeO}} a_{\text{CuS}}}{K a_{\text{FeS}}}
\]  

Equation [2-2.7] shows that by increasing the matte grade; thereby increasing the activity of copper sulfide in the matte (and simultaneously decreasing the activity of FeS in matte), there will be greater losses of copper to the slag in the form of copper oxide. Depending on economic factors, smelters have the choice of producing a lower matte grade to prevent loss of copper to the slag phase or produce a higher matte grade followed by a slag cleaning process to recover copper. In the slag forming stage of converting where most of the iron sulfide has been oxidized to form white metal (molten Cu2S), copper loss to slag is unavoidable. This is the reason for recycling converting slags back into matte smelters for copper recovery.

Magnetite formation is another major concern because it is not very soluble in slag and so separates into fine crystals which will raise the viscosity of the slag. The more viscous slag causes matte droplets to become more easily entrained in the slag, thereby increasing copper losses to slag. In addition to this, magnetite formation gradually builds up on the furnace floor and reduces the capacity of the furnace and may block tapping and charging holes.

Generally, any slag containing FeO in contact with oxygen can undergo reaction [2-2.8] to form magnetite. This is especially so in the later stages of smelting where the partial pressure of oxygen is high.

\[
6\text{FeO}(l) + \text{O}_2(g) = 2\text{Fe}_3\text{O}_4(s) \\
K = \frac{(a_{\text{Fe}_3\text{O}_4})^2}{(a_{\text{FeO}})^6 p_{\text{O}_2}}
\]  

\[2-2.8\] 

\[2-2.9\]
From equation [2-2.10], the activity of magnetite is directly proportional to the third power of the activity of FeO and the partial pressure of oxygen. The activity of magnetite (relative to pure solid magnetite) at saturation is 1, so at a given temperature, there is a value of $P_{O_2}$ for a given $a_{FeO}$ which gives magnetite saturation. In order to keep magnetite in solution in the slag, the activity of magnetite must be kept below 1, relative to pure solid magnetite.

As mentioned earlier, having the slag silica saturated is advantageous because this increases the immiscibility between matte and slag. In addition to this, it has the added benefit of lowering the activity of iron oxide and thereby lowering the activity of magnetite; ideally keeping it below unity and thus preventing magnetite saturation. Alternatively the oxygen partial pressure can be lowered (but target matte grade will not be achieved) or the operating temperature can be raised. Increasing the temperature decreases the value of the equilibrium constant, and so at constant $a_{FeO}$ and $P_{O_2}$, the higher the temperature the lower the activity of magnetite. Increasing the operating temperature does however increase costs associated with replacing refractories (due to increased attack) as well as fuel costs.

The thermodynamic discussions thus far relate to both matte smelting and the slag forming stage of converting. As previously mentioned in Section 2-1, the products from the first stage of converting are iron silicate slag and white metal. In the coppermaking stage of converting, the white metal is further oxidized. There are two competing reactions as shown by reactions [2-2.11] and [2-2.12].

$$\frac{2}{3}Cu_2S(l) + O_2(g) = \frac{2}{3}Cu_2O(l) + \frac{2}{3}SO_2(g) \quad \Delta G^{0}_{1523K} = -151.1 \text{ kJ} \quad [2-2.11]$$

$$Cu_2S(l) + O_2(g) = 2Cu(l) + SO_2(g) \quad \Delta G^{0}_{1523K} = -171.0 \text{ kJ} \quad [2-2.12]$$

From the Gibb’s free energy values for reactions [2-2.11] and [2-2.12] it is apparent that reaction [2-2.12] is the favored reaction. This means that at converting temperatures, copper sulfide oxidizes to become copper metal. Figure 2-2.2 shows the Cu-S equilibrium phase diagram showing the coppermaking reaction path.
When the sulfur content in the molten white metal reaches approximately 19.6% (point b), a metallic copper phase with approximately 1% sulfur (point c) is formed. The sulfur bearing copper forms because the melt composition enters a liquid-liquid immiscibility region. This miscibility gap results in the activities of copper and copper sulfide (relative to the respective pure liquids) remaining close to constant at a value of approximately 1 during sulfur removal. Further blowing therefore removes sulfur from the system and changes the proportions of the two melts but their compositions will remain the same. Eventually the white metal becomes so sulfur deficient that the sulfide phase disappears leaving behind molten copper with 1% sulfur. Further blowing removes most of the remaining sulfur although great care must be taken not to over-oxidize the copper to copper oxide.

2-2.2 Yazawa Chemical Potential Diagram

Section 2-2.1 examined the various reactions taking place in matte smelting and converting. Yazawa (1974) showed that the thermodynamics of the copper smelting system can best be illustrated by a chemical potential diagram in which sulfur and oxygen potentials at a given temperature are taken as the axes. Figure 2-2.3 represents the chemical potential diagram for a temperature of 1573 K. The chemical potential diagram shows the relationship between possible species of an element, whether as metal, oxide or sulfide and specifies the conditions under which they are stable at the specified temperature. The later part of this section will show how the chemical potential diagram provides an easy method of defining the conditions within various stages of smelting.
The Gibb’s phase rule is applied to the five component smelting system of Cu-Fe-S-O-SiO$_2$ to determine the number of variables that need to be fixed in order to define the system. According to the phase rule:

$$C = P + F - 2$$ \tag{2-2.13}$$

Where,

- $C$ = Number of components
- $P$ = Number of phases
- $F$ = Degrees of freedom

The minimum number of phases coexisting in the system is 3, i.e. matte (or copper), slag and gas. By having the oxygen potential and sulfur potential as the variables for the diagram; the phase rule shows that there are two more degrees of freedom. Yazawa chose to have the system isothermal, setting the temperature to 1573 K for Figure 2-2.3.

Figure 2-2.3: Sulfur-oxygen chemical potential diagram for the Cu-Fe-S-O-SiO$_2$ system at 1573 K (Yazawa, 1974).
One more variable still remains to be defined. Slag has been assumed to be present in all regions of the potential diagram with the exception of the region marked Fe in the lower left hand corner (where it breaks down into Fe and SiO$_2$) and at any P$_{O_2}$ above line s-t (where it gradually breaks down into Fe$_3$O$_4$ and SiO$_2$). As discussed in the previous section and illustrated in Figure 2-2.1, in order to obtain the maximum immiscibility between slag and matte, the slag needs to be silica saturated. Yazawa thus chose to fix the activity of iron oxide, a$_{FeO}$ at the value corresponding to a slag saturated with silica.

The region bounded by the points p-q-r-s-t-p in Figure 2-2.3 represents the region of matte stability, where two liquid phases, the matte and slag, are in equilibrium with a gas phase. The stability region of a matte, consisting of Cu$_2$S and FeS, logically is located between the stability regions of Cu$_2$S and FeS.

The lower limit of the matte stability region (line p-q) is represented by the reaction:

\[ 2\text{FeS}(l) + O_2(g) = 2\text{FeO}(l) + \text{S}_2(g) \]  

[2-2.14]

The equilibrium expression can be written:

\[ K = \frac{a_{FeO}^2 p_{S_2}}{a_{FeS}^2 p_{O_2}} \]  

[2-2.15]

By rearranging the equation and taking logarithms on both sides:

\[ \log p_{O_2} = 2\log a_{FeO} - 2\log a_{FeS} + \log p_{S_2} - \log K \]  

[2-2.16]

K is the equilibrium constant at 1573 K. Figure 2-2.4 shows the activity of iron oxide in FeO-Fe$_2$O$_3$-SiO$_2$ melts at 1623 K. From the figure, it is observed that the activity of FeO (relative to pure liquid FeO) in silica saturated slags varies from 0.3 at magnetite saturation to 0.4 at iron saturation. Yazawa (1974) chose to fix a$_{FeO(l)}$ at a value of 0.3 when constructing the chemical potential diagram. Figure 2-2.5 represents the activity diagram for the Cu$_2$S-FeS-FeO system at 1473 K.
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Figure 2-2.4: Activity of iron oxide in FeO-Fe$_2$O$_3$-SiO$_2$ melts at 1623 K (Schumann, 1955).

Figure 2-2.5: Activity diagram for the Cu$_2$S-FeS-FeO system at 1473 K (Yazawa, 1974).

The activity of iron oxide in the matte is the same as that of the activity of iron oxide in the slag because they are both in contact and at equilibrium. A copper free matte is represented by point Q in Figure 2-2.5. Thus for a copper free matte in equilibrium with silica saturated slag the value of activity for iron sulfide is 0.66 from Figure 2-2.5. Substituting these values into equation [2-2.16] will give the line p-q.

Similarly, the equation can be used to calculate for any line with constant copper content in matte. Referring back to Figure 2-2.5, for any value of $a_{\text{Cu}_2\text{S}}$, there is a particular value for $a_{\text{FeS}}$ if the $a_{\text{FeO}}$ is fixed at 0.3. By reading off values for $a_{\text{FeS}}$ for chosen values of mol% Cu$_2$S (from which wt% Cu can be calculated) and substituting these values into equation [2-2.16], any line of constant copper content in matte can be plotted on the
chemical potential diagram. These lines are located in the matte stability region and are parallel to line p-q.

The issue of magnetite saturation has been discussed in the previous section and has been identified as a problem for furnace operations. Its importance is recognized and the conditions for magnetite saturation, \( \alpha_{Fe_3O_4} \) (relative to pure solid magnetite) = 1, has been included on the chemical potential diagram. The reaction for magnetite formation is given by equation [2-2.8]. From equation [2-2.8]:

\[
\log p_{O_2} = -6\log a_{FeO} - \log K
\]  

[2-2.17]

Noting that for a silica saturated slag, \( a_{FeO} = 0.3 \), so equation [2-2.17] translates into a horizontal line on the chemical potential diagram corresponding to the line s-t.

Another issue as discussed in the previous section is copper oxide loss to slag. Equal copper oxide activity lines are drawn onto the chemical potential diagram to show the activities of copper oxide in the slag within the region of matte stability.

\[
2\text{Cu}_2\text{S}(l) + \text{O}_2(g) = 2\text{Cu}_2\text{O}(l) + \text{S}_2(g)
\]  

[2-2.18]

\[
\log p_{O_2} = 2\log a_{\text{Cu}_2\text{O}} - 2\log a_{\text{Cu}_2\text{S}} - \log K + \log p_{\text{S}_2}
\]  

[2-2.19]

The value of \( a_{\text{Cu}_2\text{S}} \) in equation [2-2.19] is fixed as unity which corresponds to high grade mattes where copper losses are high. Lines of \( a_{\text{Cu}_2\text{O}} \) with values of 0.1, 0.01 and 0.001 are shown on the chemical potential diagram of Figure 2-2.3. From the diagram it can be observed that the activity of copper oxide becomes more significant at higher matte grades i.e. when the oxygen potentials are high.

The upper limit of the matte stability region corresponds to the diagonal line of \( p_{\text{SO}_2} = 1 \) atm. The relationship between the partial pressures of oxygen, sulfur and sulfur dioxide is expressed by the reaction:

\[
\frac{1}{2}\text{S}_2(g) + \text{O}_2(g) = \text{SO}_2(g)
\]  

[2-2.20]

The upper limit line p-t corresponding to \( p_{\text{SO}_2} = 1 \) atm only holds true for copper smelting conditions where pure oxygen is injected into the furnace. For processes where air is used,
the value of $p_{SO_2}$ is approximately 0.1 atm. Lines of varying $p_{SO_2}$ can be plotted based on the following equation:

$$\log p_{O_2} = \log p_{SO_2} - \log K - \frac{1}{2} \log p_{S_2}$$ \hspace{1cm} [2-2.21]

In order to illustrate how convenient the chemical potential diagram is to describe the smelting and converting processes, the next part of this section analyzes these processes with reference to the diagram. The pathway for oxidative smelting where air is used approximately follows the line of $p_{SO_2} = 0.1$ atm. The usual copper concentrate has between 20-30% copper and is represented by point A in Figure 2-2.3. As smelting proceeds the matte grade rises to about 70% copper. At this point the copper oxide activity is still not significant. It is due to this reason that most slags are not treated for copper recovery and are discarded. The activity of magnetite is still below unity and so magnetite precipitation is not an issue at this point as well.

An alternative to oxidative matte smelting is reductive matte smelting. It is similarly illustrated on the chemical potential diagram as oxidative smelting with the exception of the process operating at a much lower $p_{SO_2}$ line. Reductive matte smelting usually takes place below the $p_{SO_2} = 10^{-5}$ atm line.

The slag forming stage of converting begins at point B and proceeds along the line of $p_{SO_2} = 0.1$ atm to point C. There is a larger rise in oxygen potential from point B to point C. This rise in oxygen potential corresponds to a significant increase in the activity of copper oxide in the slag. The slag contains a significant amount of dissolved copper and is recycled to the matte smelting furnace to reduce loss of copper. Magnetite activity rises rapidly towards unity at the end of converting indicating that magnetite crystals will precipitate in the slag.

The coppermaking stage starts at point C and ends close to point D on the chemical potential diagram. In this stage white metal is oxidized into blister copper. Although the oxygen potential during coppermaking is close to the magnetite saturation line, the iron content in white metal is very little; therefore the amount of magnetite formed will be minute. The absence of slag during this stage also means that the activity of copper oxide is no longer an issue.
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2-3 COPER PRODUCTION TECHNOLOGY

The fundamental concepts of matte smelting and converting have been discussed in the previous sections. This section examines the different technologies available to achieve the aims of matte smelting and converting. The more important issue with regards to this section is to become familiar with the varying conditions that are employed in different technologies to achieve the same aims. Knowledge of the different conditions becomes important in later sections when trying to correlate published data for minor element distribution which are quoted for varying processes.

2-3.1 MATTE SMELTING

a. FLASH SMELTING

Flash smelting is a widely used technology accounting for over 50% of copper matte smelting. The feed into flash smelting furnaces includes dried chalcopyrite concentrate, oxygen, air, flux and recycled materials. The feed is fed into a furnace at 1523 K where the sulfide particles react rapidly with the oxygen blast in the reaction shaft resulting in controlled oxidation of iron and sulfur from the concentrate, evolution of heat and melting of the solids. Flash smelting is a continuous and largely autothermal operation when enriched oxygen is employed. There are two processes associated with flash smelting technology, namely the Outokumpu process and the Inco flash smelting process.

Figure 2-3.1 shows a schematic of the Outokumpu flash furnace. The furnace consists of concentrate burners, a reaction shaft, a settler, water-cooled tapholes for removing matte and slag and an uptake for removal of the off-gas.
The core of the Outokumpu flash furnace is the central jet distributor concentrate burner. It is important in flash smelting operations to have a uniform distribution of blast and solid feed throughout the reaction shaft. The concentrate burner’s main goal is to achieve this uniform concentrate-blast suspension. The use of such a concentrate burner requires the feed to consist mainly of dry chalcopyrite concentrate and silica flux. The oxygen blast is introduced into the furnace through a distributor cone at the tip of the concentrate burner as shown in Figure 2-3.2. The Outokumpu process uses heated oxygen enriched air (50-80% oxygen).

Figure 2-3.1: Schematic diagram of the Outokumpu Flash Furnace (RHI Refractories, www.rhi-ag.com).
The Outokumpu process produces a copper matte containing approximately 65% copper in matte.

The Inco flash smelting process similarly takes in dried chalcopyrite concentrate, silica flux and recycled material as feed into a furnace operating at 1523 K. Instead of using oxygen enriched air as the Outokumpu process uses, the Inco process employs industrial oxygen (~95% oxygen). Figure 2-3.3 represents a schematic of the Inco flash furnace.

In addition to the use of industrial oxygen instead of oxygen enriched air, the Inco process employs a different concentrate burner as shown in Figure 2-3.4. The Inco concentrate
burners have dry feed dropping in from an angled tube. Industrial oxygen is blown in horizontally at high velocity, reacting with the concentrate and creating a concentrate/oxygen flame that reaches the central uptake.

**Figure 2-3.4**: Inco concentrate burner (Biswas & Davenport, 2002).

The Inco process produces a matte containing 55-60% copper. The molten matte is removed through tapholes located along the sidewall of the furnace, whereas slag is tapped from a taphole at the endwall of the furnace. Off-gas leaves through the central uptake.

b. **Bath Smelting**

In bath smelting the concentrate reacts in the molten layers of matte and slag to form more matte and slag. There are a number of processes which employ the concept of bath smelting including the Noranda process, Ausmelt process, and the older electric and reverberatory smelters.

Figure 2-3.5 shows the Noranda smelting furnace. The Noranda process is a continuous process.
Concentrate, flux, scrap and coal or coke is flung into the furnace through the endwall into the bath using a slinger and is quickly absorbed and melted in the bath. Oxygen enriched air (30-50% O₂) is fed through tuyeres into the molten matte layer in the furnace. Matte and slag is tapped from the tapholes on the sidewall and endwall of the furnace respectively. The offgas is collected through a hood on the top of the furnace.

The Ausmelt process is a vertical cylindrical furnace. Solid feed is dropped into the furnace while oxygen enriched air (50-60% O₂) is blown through a vertical lance into the molten bath. The Ausmelt process differs from other smelting processes in that the furnace does not directly incorporate a settler in which matte and slag can be separately tapped. Instead, a matte slag mixture is tapped out of the furnace periodically into a secondary fuel-fired or electric settling furnace for separation. The settled matte has a grade of approximately 60% copper.
The reverberatory and electric smelting furnaces are no longer widely employed technologies. Reverberatory smelters are continuous smelters in which concentrate and flux are fed through feedholes along the sides of the furnace roof. The feed reacts with hot combustion gas and air in the furnace to generate molten slag, matte and offgas. Matte and slag are tapped intermittently through separate tapholes. The use of hydrocarbon combustion gases which contain little oxygen results in the production of low grade mattes between 40-50% copper. The rate of concentrate oxidation is also much slower compared to that of flash smelting because the mixing of concentrate and air is not great.

Electric smelting furnaces are similar to reverberatory furnaces but use electricity as the energy source instead of hydrocarbons. Electric smelters produce mattes containing 50-60% copper and are very good for processing a mix of roasted concentrates and various secondary recycle materials. The electric furnace finds most of its use in the present day for recovering copper from molten slags as well as in cases where the reducing environment is advantageous for element distribution. Figure 2-3.7 is a schematic of the electric matte smelting furnace.
2-3.2 CONVERTING

a. FLASH CONVERTING

Flash converting uses a smaller version of the Outokumpu flash furnace to convert solidified matte to molten metallic copper. The matte tapped from a smelting furnace is granulated, crushed to 50 μm granules and dried before being fed continuously to the flash converter. This process employs lime in place of silica as flux and produces basic calcium ferrite slag in the system FeO-Fe₂O₃-CaO. The lime flux and oxygen enriched air (80% O₂) are also fed into the furnace together with the feed. The process produces molten blister copper and molten calcium ferrite slag which is tapped periodically from tapholes. The molten copper contains 0.2% S and 0.3% O and is sent forward for further refining. The calcium ferrite slag contains approximately 20% copper and is water granulated and recycled to the smelting furnace for copper recovery.

b. BATH CONVERTING

One of the more popular converters is the Peirce-Smith converter shown in Figure 2-3.8.
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Figure 2-3.8: Peirce-Smith Converter (Boldt & Queneau, 1967).

The Peirce-Smith converter is a batch converter. Molten matte from the smelting process is fed into the converter together with silica flux, air and industrial oxygen (enriched up to 29% O₂) to produce molten blister copper which is sent for further refining and molten iron silicate slag which is sent for copper recovery then discarded. The oxygen enriched air is introduced into the converter through submerged tuyeres directly into the molten matte. The molten blister copper contains about 0.02% sulfur and 0.6% oxygen. There is approximately 4 to 8% dissolved copper in the iron silicate slag which warrants a copper recovery operation, usually by recycle to the matte smelting furnace or by milling and flotation.

The popularity of the Peirce-Smith converter is due to its simplicity and high chemical efficiency. With all processes however, there are downsides. The Peirce-Smith converter, being a batch process, allows for leaks of sulfur dioxide bearing offgas in between batches as well as makes for uneven flow of the sulfur dioxide offgas to the sulfuric acid plant.

Alternative bath converting processes include the Mitsubishi and Noranda continuous converting processes. The Mitsubishi process employs vertical lances to blow oxygen-enriched air downwards onto the molten matte, slag and copper bath. Figure 2-3.9 shows the Mitsubishi continuous converting process.
The Mitsubishi converter is part of the Mitsubishi continuous smelting/converting system. Molten matte is fed continuously into the furnace from the electric slag-cleaning furnace which precedes the converter in the Mitsubishi continuous smelting/converting system. Oxygen enriched air, calcium carbonate flux and granulated converter slag is blown into the furnace via the vertical lances. Iron and sulfur from the matte is continuously oxidized to make molten copper which is sent for further refining. The calcium ferrite slag produced contains up to 14% copper and is granulated and recycled back to the smelting and converting furnaces for copper recovery and temperature control in the converting furnace. The main advantage of the Mitsubishi continuous smelting/converting process is the high efficiency of sulfur dioxide capture.

The Noranda continuous converter converts matte from a Noranda smelting furnace. It is a rotary furnace with a liquid feed mouth for charging molten matte and an endwall slinger for feeding silica flux, revert pieces and coke. There is a second mouth on the roof of the converter to draw offgas to the acid plant. Tuyeres are located along the base of the converter for injecting oxygen-enriched air into the molten matte. Copper and slag are tapped intermittently from separate tapholes. Slags from the Noranda continuous converter contain the lowest content of dissolved copper at approximately 10% copper.

Boliden’s Rönnskär smelter is located in northern Sweden, near the town of Skellefteå. The raw materials fed to the smelter originate from a multitude of sources. Boliden has
integrated its Rönnskär smelter with its own mines thus ensuring steady arrivals of copper and lead concentrates. External concentrates are imported from countries such as Chile, Indonesia, Argentina and Australia. In addition to concentrates, Rönnskär processes a multitude of base metals from recycled materials.

Figure 2-4.1 shows all the unit operations involved in the Rönnskär Smelter operations. This research program is directed towards the copper production circuit and hence the lead circuit will not be discussed.

![Figure 2-4.1: Rönnskär Smelter Flowsheet (New Rönnskär, 2000).](image)

As observed from Figure 2-4.1, Boliden Minerals AB operates two smelting furnaces, the electric furnace being the original of the two. The electric smelting furnace is well suited for accepting recycled materials, whereas the flash furnace is best suited to efficiently smelt copper concentrates.

The feed into the electric furnace consists of roasted primary copper concentrates and dried secondary concentrates along with calcine, dried ashes and reverts. The electric current passing through the liquid slag supplies the energy required for melting. The diversity of the feed into the electric furnace introduces other metals like zinc which reports to the slag phase. This makes it worth treating the slag for recovery of these metals. The zinc containing slag is transferred to the fuming plant for zinc recovery. The
matte, containing approximately 55% copper along with iron, zinc, lead, precious metals, nickel and selenium is transferred to the converters.

Primary copper concentrates are blended and dried prior to smelting by oxygen enriched air in the flash smelting furnace. The slag is cooled and crushed and sent to the Boliden concentrator. The matte contains approximately 70% copper, together with minor elements and precious metals and is fed to the converters.

In the fuming plant, zinc clinker (zinc oxide) is extracted from slags and steel mill dust. Zinc and lead are present in the slag as oxides. Coal injection into the furnace provides a very low oxygen potential thereby reducing the oxides to their metal form. The metals, particularly zinc are volatile at the operating temperature and enter the gas phase. In the gas phase the metals are reoxidized and recovered in the offgas. Zinc clinker, containing approximately 70-75% zinc, is exported to the Norzink zinc smelter in Norway.

Boliden operates a Peirce-Smith converter for production of blister copper from copper matte. The blister copper is cast into anode copper containing 98% copper. The anodes are then converted into copper cathodes in the electrolytic refinery. Stainless steel sheets are used as cathodes at Rönnskär. Using direct current, copper is selectively transferred by the electrolyte to the cathodes. Other chemical elements, such as precious metals, but also impurities settle as anode slimes. The slime is pumped to the precious metals plant. The cathodes are separated from the steel plates, bundled, sampled, weighed and sent to domestic customers.

Anode slimes, typically containing gold, silver, platinum, palladium and other impurities are pressure leached. Copper telluride and nickel sulfate is recovered from the solvent. The leach residues are dried and after the addition of fluxes smelted in the precious metals Kaldo. During smelting, selenium is recovered. The converted silver is cast into silver anodes. A high intensity electrolytic refining produces high purity gold and silver slimes. The gold slimes are leached and high purity gold as well as palladium and platinum sludge are precipitated. The silver is granulated and the gold is cast into 12.5 kg bars or granulated.
2-5 MINOR ELEMENT DISTRIBUTION

Nagamori and Mackey (1978) cleverly stated that where steelmaking is a technique of slag-making, in that quality steel results from good control of the slag; copper-making can be seen as a technique of minor element control, where the quality of the copper product results from a controlled elimination of minor elements in the course of smelting and electro-refining.

The processing of secondary recycled raw materials also introduces minor elements, more suitably named ‘microelements’, into the copper production circuit. The term “microelement” refers to elements present in very small amounts within the smelting circuit, amounts smaller than typical for the minor elements present in concentrates. They have generally been of little interest to smelters until recently. The renewed emphasis on minor element control and interest in microelement distribution in copper smelting is generated largely due to declining ore quality (wt% main metal in ore), increasing ore complexity (other elements present in significant amounts) and environmental protection and accountability reasons. The importance of element distribution can be viewed from three different standpoints:

- The copper product
- Commercial value of the individual elements
- Environmental protection.

Tan and Zhang (1977) summarized the deleterious effects of trace elements on copper, stating that trace materials in copper reduces ductility, electrical conductivity and thermal conductivity. In addition to this, embrittlement of copper also occurs due to impurity phases precipitating at the copper grain boundaries, diminishing not only electrical conductivity but also its workability in hot working.

Secondly, the minor elements in question may be of commercial value, and hence worth recovering. Based on the mineralogical nature of sulfide concentrates, they are often accompanied by a myriad of minor elements. Nagamori and Mackey (1978) listed gold, silver (noble metals), cobalt, nickel, platinum, palladium (Group VIII), zinc, cadmium, mercury (Group I-B), tin, lead (Group IV-A), molybdenum (Group VI-B), bismuth, arsenic, antimony (Group V-A), selenium, tellurium (chalcosens) and chlorine (halogen) as minor elements commonly associated with sulfide ores. From this list alone, a large number of the elements can be identified as having significant commercial value.
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Thirdly, environmental legislation continues to become ever more stringent with regards to industrial operations. This is no different for the copper base metal production industry, where there is essentially the presence of heavy metals which can be of a concern from an environmental standpoint. Elements such as arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, tin, vanadium and zinc are typified as the heavy metals of significant relevance in the environmental context (HeavY Metals 2001). The importance of distribution studies in this context is to ensure optimum concentration of hazardous minor elements in a waste stream within which they will have the minimum deleterious effect on the environment.

2-5.1 DISTRIBUTION THERMODYNAMICS

The previous section described the three important reasons for element distribution studies in copper production. Many studies have been conducted to determine how elements distribute between the phases present during the various operations in copper production, particularly during matte smelting and converting. Thermodynamic models have also been developed to explain and predict the distribution trends of different elements.

Yazawa (1980) classified the processes involved in copper production and the phases present in each process as in Figure 2-5.1.

![Classification of copper smelting processes](Yazawa, 1980).

The experimental portion of this study is largely concerned with the distribution of microelements in reducing matte smelting; Case No. 2 in Figure 2-5.1. The phases present in this system are gas, slag and matte. Thermodynamic analysis of element distribution
requires knowledge on the species of the element in the molten phases. It has been generally assumed that an element distributes into the matte phase as a sulfide and into the slag phase as an oxide.

Most oxides dissociate into the ionic state in molten slag; however, it is impossible to define or measure thermodynamic data for ions because a standard state for ions cannot exist. The availability of free energy data and phase diagrams for compounds leads to the convenient use of molecular expressions for thermodynamic equations. Yazawa (1994) points out that while compounds are usually expressed in multi-cation integer form such as, Fe$_3$O$_4$, Cu$_2$O etc., the mono-cation form (FeO, FeO$_{1.33}$, CuO$_{0.5}$, etc.) is more reasonable from both theoretical and practical standpoints.

The convenience of expressing compounds in the mono-cation form lies partly in the simplification of conversion from mass percent to mole fraction. Also, when all species in a phase are expressed in this form, the total number of moles in 100g of slag, matte or copper is approximately constant over a wide range of smelting conditions. This further leads to mathematical simplification. Figure 2-5.2 shows the total moles of constituents in 100 g of slag, matte and copper phases as a function of matte grade.

![Figure 2-5.2: Total moles of constituents in 100g of slag, matte and copper phases (Yazawa, 1983).](image)

Yazawa et al. (1983) give the values of $n_T$ for slag, matte and copper to be 1.48, 1.22 and 1.54 respectively. They also stated that because the variation in the composition of
mattes or slags is limited in a particular smelter, the total mole number can be taken as a constant for each smelter with a precision of 1%.

Another advantage of the mono-cation expression of compounds is that when the oxides are expressed in this manner, their activity coefficients remain almost constant over a large range of compositions. Figure 2-5.3 illustrates this point by showing that activity coefficients, when expressed in multi-cation form, vary with concentration but remain constant when expressed in the mono-cation form.

Figure 2-5.3: Activity coefficients of oxides plotted against the mole fraction of oxides in the slag at 1523 K (Yazawa, 1983).

Yazawa et al. (1983) also showed that liquid sulfide solutions, when expressed as a solution of monocation species, are nearly ideal, while when expressed in the normal integer form would exhibit significant negative deviation from ideality. This is more clearly illustrated in Figure 2-5.4, showing how the activities of the sulfide species for the Cu$_2$S-FeS system display large negative deviation from ideality whereas the activities of the monocation sulfide species are nearly ideal for the CuS$_{0.5}$-FeS system.
The following describes the development of the distribution ratio expression for the simplest case of metal-slag distribution as shown by Yazawa (1983) and will, for the purpose of this thesis, henceforth be referred to as the Yazawa thermodynamic model for element distribution between metals and slags. Oxidic dissolution of an element, $M$, from molten metal to slag can be represented by the metal-metal oxide equilibrium:

$$M + \frac{x}{2}O_2(g) = MO_x$$  \hspace{1cm} [2-5.1]

The activity of the metal oxide can be expressed as:

$$a_{Mo_x} = \left( \gamma_{Mo_x} \right) N_{Mo_x} = \left( \gamma_{Mo_x} \right) \frac{n_{Mo_x}}{n_T}$$  \hspace{1cm} [2-5.3]

When expressed in the mono-cation form, $n_{Mo_x} = n_M$;

$$\left( N_{Mo_x} \right) = \frac{n_{Mo_x}}{n_T} = \frac{n_M}{n_T}$$  \hspace{1cm} [2-5.4]
The activity of metal oxide can then be written in terms of weight percent concentrations of the element in slag:

\[
[a_{\text{MO}}] = \left(\gamma_{\text{MO}}\right)\frac{[\text{n}_{\text{M}}]}{[\text{n}_{\text{T}}]} = \left(\gamma_{\text{MO}}\right)\frac{[\% \text{M}]}{[\% \text{T}]}M_{\text{M}} \quad \text{[2-5.5]}
\]

Similarly, the activity of the metallic element can be written as:

\[
[a_{\text{M}}] = \left[\gamma_{\text{M}}\right]\frac{n_{\text{M}}}{n_{\text{T}}} = \left[\gamma_{\text{M}}\right]\frac{[\% \text{M}]}{[\% \text{T}]}M_{\text{M}} \quad \text{[2-5.6]}
\]

By substituting equations 2-5.5 and 2-5.6 into equation 2-5.2;

\[
K_{i} = \frac{[a_{\text{MO}}]}{[a_{\text{M}}][P_{\text{O}}^{2/2}]} = \frac{n_{\text{T}}}{n_{\text{T}}}\left[\gamma_{\text{MO}}\right][% \text{M}]\frac{x}{[\gamma_{\text{MO}}][n_{\text{T}}]} \quad \text{[2-5.7]}
\]

The ( ) and [ ] parentheses around each term represents the values in slag phase and in the metal phase respectively. Rearranging equation [2-5.7];

\[
L_{\text{M}}^{s/c} = \frac{[\% \text{M}]}{[\% \text{M}]} = \frac{K_{i}[\gamma_{\text{M}}][n_{\text{T}}]P_{\text{O}}^{2/2}}{[\gamma_{\text{MO}}][n_{\text{T}}]} \quad \text{[2-5.8]}
\]

The term \(L_{\text{M}}^{s/c}\) in equation [2-5.8] represents the distribution ratio of element \(M\) between slag and metal. By taking the logarithm and rearranging equation [2-5.8];

\[
\log L_{\text{M}}^{s/c} = A + \frac{x}{2}\log P_{\text{O}}^{2} \quad \text{[2-5.9]}
\]

By plotting experimental values of \(\log L_{\text{M}}^{s/c}\) against \(P_{\text{O}}^{2}\), equation [2-5.9] plots as a straight line. This only holds true provided the activity coefficients of all species are constant over the composition range of interest and this is much more likely to be true when using the mono-cation expressions. The gradient \(x/2\) gives the identity of the dissolved species in the slag, e.g. if the gradient was found to be 0.25 then the metal oxide must be \(\text{MO}_{0.5}\) and the metal must be \(\text{M}^{+}\). Figure 2-5.5 shows the distribution ratios for zinc, lead, copper and bismuth at various partial pressures of oxygen, plotted in the form of equation [2-5.9]. From the slope of each line in Figure 2-5.5, the dissolved species in the slag for each of the elements can be assumed to be \(\text{ZnO}, \text{PbO}, \text{BiO}_{1.5}\) and \(\text{CuO}_{0.5}\).
The expression for the distribution of an element $M$ between matte and metal can be developed in a similar fashion.

\[
M + \frac{V}{2} S_{2}(g) = MS_{v} \quad [2-5.10]
\]

\[
K_S = \frac{\{a_{MS_v}\}}{[a_M]p_{S_{v}^{2}}} \quad [2-5.11]
\]

The $\{ \}$ and $[ ]$ parentheses around each term this time represent values in the matte phase and in the metal phase respectively. The final expression for the distribution ratio of an element $M$ between matte and metal, $L_{m/c}$:

\[
L_{M}^{m/c} = \frac{\{\%M\}}{[\%M]} = \frac{K_S[\gamma_M][n_T]p_{S_{v}^{2}}}{\{\gamma_{MS_v}\}[n_T]} \quad [2-5.12]
\]
This study is concerned with microelement distribution in matte smelting and hence is interested in developing an expression for the distribution of M between matte and slag. Such an expression can be formulated from equations [2-5.8] and [2-5.12] as shown in equation [2-5.13]. Equation [2-5.13] also applies to the sum of equations [2-5.1] and [2-5.10] to give the oxidation of sulfide species in matte to oxide species in slag.

\[
L_M^{m/s} = L_M^{m/c} \times L_M^{c/s} = \frac{K_2(n_T)\gamma_{MO}}{K_1(n_T)\gamma_{MS}} \frac{P_{S_2}^m}{P_{O_2}^s}^{\frac{v}{x}}
\]  

[2-5.13]

For a system, where the valence of the metal in both the metal oxide and metal sulfide is \(2^+\), equation [2-5.13] can be simplified as shown in equation [2-5.14]. This is a useful simplification because many metals have a valence of \(2^+\).

\[
L_M^{m/s} = \frac{K_2(n_T)\gamma_{MO}}{K_1(n_T)\gamma_{MS}} \left( \frac{P_{S_2}}{P_{O_2}} \right)^{\frac{1}{2}}
\]  

[2-5.14]

Equation [2-5.14] shows how the distribution ratio, \(L_M^{m/s}\), is dependent upon the activity coefficients of the oxide in slag and sulfide in matte as well as the partial pressures of sulfur and oxygen and the temperature (through the value of the equilibrium constant, \(K\)). The partial pressures of sulfur and oxygen are not independent but are linked through the equilibrium between iron species in the gas/slag/matte system:

\[
FeS(l) + \frac{1}{2}O_2(g) = FeO(l) + \frac{1}{2}S_2(g)
\]  

[2-5.15]

The equilibrium expression for this reaction is:

\[
K_3 = \frac{a_{FeO} \left( \frac{P_{S_2}}{P_{O_2}} \right)^{\frac{1}{2}}}{a_{FeS}}
\]  

[2-5.16]

For silica-saturated slags, the activity of FeO at 1573 K is close to 0.3 and the activity of FeS for mattes containing between 55-60 wt% Cu at 1573 K can also be estimated to be close to 0.3 (Yazawa, 1974) so:

\[
K_3 \approx \left( \frac{P_{S_2}}{P_{O_2}} \right)^{\frac{1}{2}}
\]  

[2-5.17]
By substituting [2-5.17] into equation [2-5.14] it can be seen that for such a matte in equilibrium with silica-saturated slag;

\[
L_M^{m/s} \approx \frac{K_2 \{n_T\} \{\gamma_{MO}\} K_3}{K_1 \{n_T\} \{\gamma_{MS}\}}
\]

[2-5.18]

The simplified expression in equation [2-5.18] shows that for copper smelting operations where matte grades are typically between 55-60 wt% Cu, the distribution of a minor element between matte and slag is independent of the oxygen partial pressure i.e. whether matte smelting is carried out under oxidizing or reducing conditions. The distribution ratio is a function of the equilibrium constants, \(K_1\) & \(K_2\), of the relevant exchange reactions [2-5.1] and [2-5.10]. The independence of the distribution ratio on the oxygen partial pressure assumes that the activity coefficients of the oxide and sulfide are also independent of oxygen potential. The activity coefficient of the metal oxide and the metal sulfide can also be affected by the state of oxidation of the slag and matte in that the oxygen potential affects the oxidation state of other species in the matte and/or slag.

Copper smelting slags in actual practice are seldom silica-saturated, so the activity of iron (II) oxide, \(a_{FeO}\), will be between 0.4-0.45, so equation [2-5.16] becomes;

\[
K_3 \approx 1.5 \left( \frac{P_{Si}}{P_{O_2}} \right)^{1/2}
\]

[2-5.17a]

Equation [2-5.18] correspondingly becomes;

\[
L_M^{m/s} \approx \frac{K_2 \{n_T\} \{\gamma_{MO}\} K_3}{K_1 \{n_T\} \{\gamma_{MS}\} 1.5}
\]

[2-5.18a]

It appears from equation [2-5.18a] that the distribution coefficient decreases as the silica content in the slag decreases, hence the minor element distributing more into the slag phase. However, the activity coefficient of the minor metal oxide, \(\gamma_{MO}\), may also be a function of slag composition and this must be taken into account for each particular minor element. An example of this is given by Teague et al. (1998), who showed that the limiting activity coefficient of cobalt (II) oxide in iron silicate slag is a function of the silica content in the slag. Teague et al. (1998) showed that for silica-saturated slags, the activity coefficient of cobalt (II) oxide is close to unity; however, the value slowly rose towards 1.5 at 25 wt% SiO\(_2\). Yazawa and Hino (1993) described in their paper the use of the regular solution model to qualitatively model the activity behavior of metal oxides in the CaO-
FeO-SiO$_2$ ternary slag system as a function of slag composition. The following paragraphs describe Yazawa and Hino’s approach and their findings.

Metal oxides in slag have traditionally been classified as acidic, basic or neutral. This classification is convenient when attempting to quantify the degree of interaction expected between pairs of oxides. Similarly to aqueous solution chemistry, the underlying assumption is that acids will interact with bases while acids repel acids and bases will repel bases. The interaction between the pairs of oxides is described by the activity coefficient ($\gamma$) of the species in solution, e.g. an activity coefficient value less than one would indicate strong interactions between the two oxides such as with a strong acidic and strong basic oxide.

The regular solution model is a convenient single parameter model used to describe regular solutions; the single parameter being $\alpha$. For binary systems, the $\alpha$-function is related to the activity coefficient and mole fraction as expressed in the following equation:

$$\alpha = \frac{\ln \gamma_i}{(1 - N_i)^2} = \text{Constant} \quad [2.5.19]$$

The $\alpha$ value provides an indication of the interaction (or lack thereof) between the two components of the binary system; a large negative value e.g. -15 would indicate the tendency for compound formation whereas an $\alpha$ value greater than +2 would indicate a tendency towards phase separation corresponding to miscibility gaps. This is shown more clearly in Figure 2-5.6.

![Figure 2-5.6: Variation in binary activity curves depending on the value of $\alpha$-function (Yazawa & Hino, 1993).](image)
The regular solution model provides a good representation of binary regular solutions and thermodynamic data is certainly readily available for most binary systems, however most metallurgical processes, copper smelting included, are impossible to discuss by use of just binary data. In principle, copper smelting can be described by a ternary system. Taking advantage of accessible thermodynamic data for binary solutions, Yazawa and Hino (1993) used THERMOCALC to derive ternary equilibria based upon the thermodynamics of three binary systems.

The ternary system in Figure 2-5.7 is made up of three binaries, AO-MO, AO-BO and BO-MO; AO being a strong acidic acid i.e. silica, BO a strong basic oxide i.e. lime and MO the neutral metal oxide, FeO. The values of $\alpha$ are assumed to be -9, -1 and 0 for the binary AO-BO, BO-MO and MO-AO systems, respectively. The activity and activity coefficients for the neutral metal oxide in the ternary system are shown by the solid and dashed lines respectively. As indicated by the $\alpha$ values, the activity behavior of the AO-MO system displays strong negative deviation from ideality, indicating a strong tendency towards the formation of the intermediate compound AO.Bo. The slightly negative $\alpha$ value for the BO-MO system suggests weak interactions between BO and MO. The AO-MO binary has been assumed to be ideal.

**Figure 2-5.7**: Isobars of activity and activity coefficient of the neutral oxide, MO, in the AO-BO-MO ternary system (Yazawa and Hino, 1993).
As observed from Figure 2-5.7, both isobars of $\gamma_{MO}$ and $\gamma_{MO}$ display strong convexities on the tie line between MO and the intermediate compound AO,BO. The activity coefficient of the neutral oxide, $\gamma_{MO}$, in the ternary system is highest along the tie line between MO and AO,BO and increases with decreasing FeO content. It can be shown from equation 2-5.3 that the mole fraction of the species in slag is inversely proportional to the activity coefficient of the species. Based on this, the oxidic dissolution of neutral metal oxides in slag is expected to be minimum at maximum $\gamma_{MO}$. This is especially so for slag compositions on the tie line between MO and AO,BO. Yazawa and Hino (1993) stated that the activity behavior shown in Figure 2-5.7 is generally similar with the activity trends displayed for FeO in FeO-CaO-SiO$_2$ slag and expect similar trends to be observed when FeO is replaced by any other neutral metal oxide such as CuO$_{0.5}$, SnO and ZnO.

The same approach used above to describe the behavior of a neutral oxide in the ternary system can be applied to observe the interactions of an acidic or basic metal oxide. To explain the behavior of a basic metal oxide such as lead oxide, the $\alpha$ values for the AO-MO and BO-MO binaries are assumed to be -5 and +2, respectively, as shown in Figure 2-5.8a. The derived ternary isobars of $\alpha_{MO}$ and $\gamma_{MO}$ are considerably deformed in comparison with the isobars for the neutral metal oxide. The isobars of $\gamma_{MO}$ show strong convexity on the tie line close to the BO-MO binary. It is therefore clearly evident that the activity coefficient values for the BO-MO system are higher than for the AO-MO system, thus implying that the dissolution of lead oxide is lower in a system using basic CaO flux (calcium ferrite slag) compared to in a system using acidic SiO$_2$ flux (iron silicate slag).

Figure 2-5.8: Isobars of activity and activity coefficient of a) basic metal oxides; b) acidic metal oxides in AO-BO-MO ternary (modified from Yazawa and Hino, 1993).

If the metal oxide is an acidic metal oxide such as SbO$_{1.5}$, the $\alpha$ values for the AO-MO and BO-MO binaries would be +2 and -5, respectively, and the isobars of activity and activity
coefficient of metal oxide in Figure 2-5.8b would apply. As observed from Figure 2-5.8b, the isobars of $\gamma_{MO}$ are maximum on the tie line close to the MO-AO binary. Accordingly, the dissolution of an acidic metal oxide such as SbO$_{1.5}$ would be higher in basic slags (calcium ferrite slag) rather than in acidic slags (iron silicate slag).

2-5.2 Effect of Saturation on the Distribution Coefficient

In the previous section, thermodynamic equations were developed to express the distribution coefficient of a minor element between molten phases of matte and slag.

In performing microelement distribution studies, the solubility of microelements in the molten phases of matte and slag play an important role because it is assumed that at the concentration of microelement being discussed, the species are fully in solution. Unfortunately, solubility data for such systems are often not available. The importance of solubility data lies with the possibility that saturation of the microelement could occur in either phase during the experiment. Correct assay of the molten phases would therefore require the identification of precipitated phases which is certainly possible with SEM/EDAX analysis but not so with wet chemical analysis. In studies where wet chemical analysis is used, such as in this study, the assay will include both dissolved and undissolved element and thus cause a systematic error in the value of the distribution coefficient. A result oriented approach is therefore required to establish whether or not a system has become saturated with the element when wet chemical analysis is used.

To quantify this more clearly, generic scenarios are set up with the element introduced into either the; a) matte as a sulfide compound, or b) slag as an oxide compound. For both these cases, the effect of saturation on the distribution coefficient is observed for when:

- The matte first becomes saturated with the minor element
- The slag first becomes saturated with the minor element

It has been assumed that the element M dissolves as the metal oxide (MO) in the slag and the metal sulfide (MS) in the matte. The two compounds are related by the following equilibrium reaction:

$$M$nS$n + \frac{1}{2}O_2(g) = MO(g) + \frac{1}{2}S_2(g) \quad [2-5.20]$
It is important to note that saturation of the molten phases with element M corresponds to saturation of the respective dissolved species, i.e., MO in the slag and MS in the matte; and not the metal, M.

**a. ELEMENT DOPED INTO THE MATTE**

For this illustration, 100 grams of iron silicate slag is assumed to be equilibrated with 100 grams of copper matte under a certain set of fixed conditions. An element, M, is doped into the matte phase. Assume it has been established for the given system that saturation of M in the slag phase occurs at 3 wt%, saturation of the matte occurs at 5 wt% and that the equilibrium distribution coefficient of M between matte and slag, $L_{M}^{m/s}$, is 2. Table 2-5.1 is set up with increasing mass of element M added to the matte phase to observe the effect of saturation on the distribution coefficient. In order to differentiate between the equilibrium distribution ratio and the apparent distribution ratio, the term $L_{M}^{m/s}_{apparent}$ is used. $L_{M}^{m/s}_{apparent}$ includes both dissolved and undissolved M in the concentration terms.

**Table 2-5.1:** Effect of saturation of the matte phase on distribution ratio when M is added to the matte.

<table>
<thead>
<tr>
<th>Mass M Added (g)</th>
<th>{M} Dissolved</th>
<th>{M} Undissolved</th>
<th>{M} Total</th>
<th>(M)</th>
<th>$L_{M}^{m/s}_{apparent}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.33</td>
<td>0.00</td>
<td>1.33</td>
<td>0.67</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>2.67</td>
<td>0.00</td>
<td>2.67</td>
<td>1.33</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
<td>0.00</td>
<td>4.00</td>
<td>2.00</td>
<td>2</td>
</tr>
<tr>
<td>7.5</td>
<td>5.00</td>
<td>0.00</td>
<td>5.00</td>
<td>2.50</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>5.00</td>
<td>0.50</td>
<td>5.50</td>
<td>2.50</td>
<td>2.2</td>
</tr>
<tr>
<td>10</td>
<td>5.00</td>
<td>2.50</td>
<td>7.50</td>
<td>2.50</td>
<td>3</td>
</tr>
</tbody>
</table>

From Table 2-5.1, it can be observed that saturation of the matte phase with element M occurs when the addition of element M into the matte phase reaches 7.5 grams. At this point the activity of MS with reference to the solid standard reference state is 1.0. Only dissolved M can distribute between the molten phases and thus once the matte reaches saturation, any further addition of MS remains undissolved in the matte phase. This is the reason for the increasing value of the apparent distribution coefficient, $L_{M}^{m/s}_{apparent}$, as in Figure 2-5.9 below.
The following scenario examines the expected change in distribution ratio if the slag phase were to become saturated before the matte phase. In order for this scenario to occur, the saturation of M in the matte phase is changed to a value of 8 wt% with all other conditions remaining the same. Table 2-5.2 shows the effect of saturation of the slag phase on the distribution ratio.

Table 2-5.2: Effect of saturation of the slag phase on distribution ratio when M is added to the matte.

<table>
<thead>
<tr>
<th>Mass M Added (g)</th>
<th>{M}_Dissolved</th>
<th>{M}_Undissolved</th>
<th>{M}_Total</th>
<th>(M)</th>
<th>(L_{M}^{\text{apparent}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.00</td>
<td>0.00</td>
<td>2.00</td>
<td>1.00</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
<td>0.00</td>
<td>4.00</td>
<td>2.00</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>6.00</td>
<td>0.00</td>
<td>6.00</td>
<td>3.00</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>6.00</td>
<td>1.00</td>
<td>7.00</td>
<td>3.00</td>
<td>2.3</td>
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<tr>
<td>12</td>
<td>6.00</td>
<td>3.00</td>
<td>9.00</td>
<td>3.00</td>
<td>3</td>
</tr>
<tr>
<td>15</td>
<td>6.00</td>
<td>6.00</td>
<td>12.00</td>
<td>3.00</td>
<td>4</td>
</tr>
</tbody>
</table>

From Table 2-5.2 it is observed that saturation of the slag phase occurs when the addition of element M into the matte reaches 9.0 grams. At this point, the activity of MO in the slag with reference to the solid standard state has a value of 1.0. From equation [2-5.20]:

\[ L_{M}^{\text{apparent}} = \text{constant} \times \frac{\text{activity of } MO}{\text{activity of } MO_{\text{standard}}} \]
Equation [2-5.22] shows that under fixed conditions (temperature, partial pressures of oxygen and sulfur) when the slag phase becomes saturated with MO, the activity of MS is fixed. This would mean there is no longer any driving force for dissolution of MS into the matte and hence any further additions of M will remain undissolved in the matte and result in an increase of the apparent distribution ratio as shown in Figure 2-5.10.

![Figure 2-5.10: Distribution ratio as a function of concentration of element M with saturation occurring in the slag.](image)

As observed in both Figure 2-5.9 and Figure 2-5.10, with the element doped into the matte phase, the apparent distribution coefficient increases when saturation occurs in either the matte or slag.
b. ELEMENT DOPED INTO THE SLAG

Similarly to the previous system, 100 grams of iron silicate slag is equilibrated with 100 grams of copper matte under a fixed set of conditions. The saturation of M in the slag phase occurs at 3 wt%, saturation of the matte occurs at 5 wt% and the equilibrium distribution coefficient of M between matte and slag, \( L_{m/s} \), is 2. Element M, however, is now doped into the slag phase as MO. Table 2-5.3 is set up with increasing mass of element M added to the slag phase to observe the effect of saturation on the distribution coefficient.

<table>
<thead>
<tr>
<th>Mass M Added (g)</th>
<th>Mass M dissolved</th>
<th>Mass M Undissolved</th>
<th>Total Mass M</th>
<th>L_{m/s}^{apparent}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.33</td>
<td>0.67</td>
<td>0.67</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>2.67</td>
<td>1.33</td>
<td>1.33</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2</td>
</tr>
<tr>
<td>7.5</td>
<td>5.00</td>
<td>2.50</td>
<td>2.50</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>5.00</td>
<td>2.50</td>
<td>2.50</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>5.00</td>
<td>2.50</td>
<td>2.50</td>
<td>2</td>
</tr>
</tbody>
</table>

From Table 2-5.3, it is observed that saturation of the matte phase occurs when the addition of element M into the slag phase reaches 7.5 grams. From equation [2-5.21];

\[
\{a_{MO}\} = \{a_{MS}\} K \left( \frac{p_{O_2}}{p_{S_2}} \right)^{1/2} \quad [2-5.23]
\]

From equation [2-5.23], under fixed conditions (temperature, oxygen and sulfur partial pressure), when the matte phase is saturated with MS \( \{a_{MS}(s) = 1.0\} \) the activity of MO in slag with reference to the solid reference standard state is fixed. Any further additions of M will remain in the slag phase; as undissolved MO. The apparent distribution ratio, \( L_{m/s}^{apparent} \), is observed to decreases once saturation occurs as shown in Figure 2-5.11.
In order to facilitate the saturation of M in the slag instead of the matte, the saturation of M in the matte is changed to a value of 8 wt% with all other conditions remaining the same. Table 2-5.4 shows the effect of saturation of the slag on the distribution ratio when M is doped into the slag.

Table 2-5.4: Effect of saturation of the slag phase on distribution ratio when M is added to the slag

<table>
<thead>
<tr>
<th>Mass M Added (g)</th>
<th>M(M) Added</th>
<th>(M) Dissolved</th>
<th>(M) Undissolved</th>
<th>(M) Total</th>
<th>$L_{M}^{M/M_{apparent}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.00</td>
<td>1.00</td>
<td>0.00</td>
<td>1.00</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
<td>2.00</td>
<td>0.00</td>
<td>2.00</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>6.00</td>
<td>3.00</td>
<td>0.00</td>
<td>3.00</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>6.00</td>
<td>3.00</td>
<td>1.00</td>
<td>4.00</td>
<td>1.5</td>
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<td>12</td>
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<td>3.00</td>
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<td>1</td>
</tr>
<tr>
<td>15</td>
<td>6.00</td>
<td>3.00</td>
<td>6.00</td>
<td>9.00</td>
<td>0.67</td>
</tr>
</tbody>
</table>

From Table 2-5.4, it is observed that saturation of the slag phase occurs when 9.00 grams of M is added to the slag phase. The activity of MO with reference to the solid standard state is 1.0 and therefore any further addition of MO to the slag phase would remain undissolved. It has to be emphasized again that only dissolved M can distribute between
the molten phases and because of this the apparent distribution ratio, $L_{M/m/s\text{apparent}}$, decreases as shown in Figure 2-5.12.

Having examined the possible scenarios involving saturation of an element in molten phases, it can be concluded that:

- When doping the element into the matte, once either phase becomes saturated, any further additions will increase $L_{M/m/s\text{apparent}}$
- When doping the element into the slag, once either phase becomes saturated, any further additions will decrease $L_{M/m/s\text{apparent}}$

It must also be noted that these observations will depend on the definition of the distribution coefficient used. In this study, the distribution ratio has been defined as:

$$L_{M}^{m/s} = \frac{\text{wt}\% M}{\text{wt}\% M} \quad [2-5.24]$$

However, it has also been defined by some authors as the inverse:

$$L_{M}^{s/m} = \frac{\text{wt}\% M}{\text{wt}\% M} \quad [2-5.25]$$
If the form in equation [2-5.25] is used, the reverse would apply, i.e.:

- When doping the element into the matte, when saturation of either phase occurs, any further additions will decrease $L_{\text{M}^m/\text{M}^\text{apparent}}$.
- When doping the element into the slag, when saturation of either phase occurs, any further additions will increase $L_{\text{M}^{m}/\text{M}^\text{apparent}}$.

There are limitations to using the technique described above as an indicator of saturation. From equation [2-5.14] it can be seen that the distribution coefficient is related to the activity coefficients of the relevant species as follows:

$$L_{\text{M}^m} = \frac{\gamma_{\text{MD}}}{\gamma_{\text{MS}}} \quad [2-5.26]$$

The test for saturation described in this section therefore requires the assumption that the activity coefficients obey Henry’s Law, i.e. are constant for the concentrations of the element tested. If this assumption does not hold true for both phases, then the distribution coefficient would change without phase saturation and the test would not be an indicator of saturation as implied. It must be stated however, that the concentration of elements used in microelement distribution studies are usually less than 1 wt% and are therefore dilute solutions which are very likely to obey Henry’s Law.

The effect of saturation of species on the distribution coefficient can be further complicated by the density of the added species e.g. if the species added to matte is less dense than the matte so causing it to float into the slag phase. While this is a possible scenario, if the particles of species added are very small the surface tension of the matte may help retain the particles in the matte phase. The undissolved species is then likely to accumulate at the matte-slag interface and could be an issue during sampling.

This investigation on the effect of saturation on the distribution coefficient leads to the conclusion that where solubility data is not available for species in a phase under study, the distribution ratio must be determined as a function of the amount of element added; otherwise there is no certainty that the measured distribution ratio is the true thermodynamic distribution ratio for the system.
2-5.3 Experimental Techniques

In studying the distribution behavior of impurities, the experimental technique must be well defined in order for valid comparisons to be made with other researchers (Yazawa et al., 1983). This section examines the various techniques used in element distribution experiments; first by providing a detailed summary of the methodology employed by Kaiura, Watanabe and Yazawa (1980) in their study of lead behavior in copper smelting systems. Focus was placed on Kaiura et al. (1980) due to the level of detail provided regarding the methodology employed for distribution experiments. From Kaiura et al. (1980), the main constituents of a distribution experiment are established and comparisons are made with other distribution studies. This study will adopt the best practices from the techniques available.

Kaiura et al. (1980) determined the equilibrium distribution coefficient of lead between matte, slag and metallic phases in the silica-saturated copper smelting system. They investigated a number of conditions, including low oxygen potentials associated with iron and copper saturation as well as constant sulfur dioxide partial pressure of 0.1 atm. Nitrogen was used for reducing conditions, whereas a mixture of argon-sulfur dioxide gas was used to achieve $p_{SO_2}=0.1$ atm. The matte constituents, iron (II) sulfide and copper (I) sulfide, were prepared by reacting a powdered mixture of metal and sulfur at 723 K under a controlled partial pressure of sulfur. Fayalite slag was prepared by fusing iron, iron (III) oxide and silica in an iron crucible followed by granulation in water. For experiments at metal saturation, iron sheet or copper shot was added to the crucible. The impurity element; lead, was introduced as either lead pellets or powdered lead sulfide. The purity of all reagents used in the study was 99.5% or greater.

The synthesized matte and slag, together with other reagents as detailed above were placed in a 14 mm inner diameter silica crucible. This sample was then placed in a mullite protection crucible and the assembly loaded into a silica reaction tube. Phosphorous pentoxide and calcium sulfate drying columns were used to dry each gas before entering the reaction tube. In addition to drying, argon gas was also deoxidized in a furnace charged with titanium. A typical experiment consisted of loading the sample, evacuating the reaction tube and introducing the flushing gas at a fixed flowrate. The furnace was equipped with a spiral silicon carbide element which was raised around the reaction tube. The temperature was raised to 1573 K and held for the necessary reaction time. Preliminary experiments were performed to establish equilibrium times required for the different conditions. Upon equilibration, air quenching of the sample was achieved by lowering the furnace element, thereby resulting in a temperature drop from 1573 K to 1273 K in approximately 40 seconds.
Preparation of samples for chemical analyses was considered to be a critical part of the work. Upon cooling, the various phases were separated and cleaned of all crucible debris with a wet diamond wheel. For the slag samples, low-powered microscope examinations were carried out to ensure the removal of any visibly entrained matte. In addition, slag samples showing evidence of SiO₂ precipitation at high temperature were discarded. Analyses of copper in slag and all lead contents were carried out by atomic absorption spectrometry. Oxygen content in matte was determined by a high temperature, selective hydrogen reduction-H₂O absorption technique. The remaining constituents were analyzed by wet chemical methods.

From the detailed description of the techniques employed by Kaiura et al. (1980), a distribution experiment can be divided into the following sections for closer examination:

a. Choice of conditions
b. Materials preparation
c. Equipment
d. Procedure

a. CHOICE OF CONDITIONS

Choice of conditions is dependent upon the process that is to be examined. For this it becomes necessary to understand the phase relations in the system under consideration. Yazawa et al. (1983) produced a classification of copper smelting processes, similar to that in Figure 2-5.1, to determine experimental conditions for three different processes; oxidative matte smelting, reductive matte smelting and direct copper production. From an understanding of the phase relations in the system, and applying the Gibb’s Phase Rule (equation [2-2.14]), the set of conditions required to fully define the system can be determined.

As an example, consider the low oxygen potential, iron and copper saturation condition employed by Kaiura et al. (1980). Referring to Figure 2-2.3, the sulfur-oxygen chemical potential diagram, this condition corresponds to line q-r on the diagram. For this extreme case of reducing matte smelting, the components present in the system are iron, copper, sulfur, oxygen and silica, therefore C=5; and the phases present are gas, matte, slag, silica (provided the slag is silica saturated) and iron, thus P=5. Based on this only 2 degrees of freedom remain, one being temperature and the other being a single composition parameter, for example the copper content of the matte, partial pressure of oxygen, or the partial pressure of sulfur. If the copper content of the matte is fixed, then the partial
pressures of oxygen and sulfur are constant. For melts saturated with silica and iron with a copper content in matte of approximately 50 wt% the partial pressures of oxygen and sulfur generated can be calculated using equations [2-5.27] and [2-5.28] for temperatures between 1473 K and 1573 K (Takeda, 1997).

\[
\log p_{O_2} = 3.93 - \frac{24070}{T} \quad [2-5.27]
\]

\[
\log p_{S_2} = 3.72 - \frac{15050}{T} \quad [2-5.28]
\]

The generated partial pressures of oxygen and sulfur in the equilibrium gas phase at 1523 K are $10^{-11.87}$ atm and $10^{-6.16}$ atm, respectively. These values, being so low, allow for the use of an inert gas such as nitrogen as the gas phase for equilibrium experiments (Yazawa, 1983). Precise control of the gas flow is not necessary as long as positive pressure is maintained in the furnace. Provided the gas flushing flowrate is low, the very small amounts of oxygen and sulfur lost from the condensed phases will not affect the slag and matte compositions significantly (Nagamori, 1974).

An understanding of the phase relations also assists in the matter of crucible selection. In the above case, the matte and slag coexists with solid iron. This suggests the suitability of iron crucibles for use in the experiments. Another viable option in this case would be silica crucibles, as used by Kaiura et al. (1980), as this would cause silica saturation in the slag. The issue of crucible selection is more closely examined in Section 2-5.3c.

b. MATERIALS PREPARATION

Due to the complex nature of the systems involved, all samples are prepared from synthetic pure materials to eliminate any effects caused by impurities (Yazawa & Kameda, 1953). In preparation of the matte, Kaiura et al. (1980) as well as other researchers including Johnson et al. (1982), Westland & Webster (1990), Louey (1999) and Roghani et al. (2000) first prepared iron (II) sulfide and copper (I) sulfide from their respective elements of copper, iron and elemental sulfur. Whilst some researchers simply added the appropriate amounts of iron (II) sulfide and copper (I) sulfide into the sample crucible together with the slag and other reagents, others first synthesized the matte phase. By first synthesizing a master batch of matte, errors induced due to the inconsistency of additions of the matte constituent [Cu$_2$S & FeS] to each separate experiment can be avoided. Johnson et al. (1982), Westland & Webster (1990) as well as...
Louey (1999) prepared the synthetic matte by melting an appropriate mixture of iron (II) sulfide and copper (I) sulfide at 1473 K in a carbon crucible with close fitting carbon lids. Carbon crucibles have been used in other copper smelting investigations by Yazawa & Kameda (1954) as well as Nagamori (1974) and have the benefit of reducing the oxygen partial pressure inside the crucible due to the reaction of the outer walls of the crucible with oxygen. Louey (1999) added a small layer of excess sulfur on top of the sulfide mixture to allow for oxidation of sulfur during the initial stages of melting.

In preparing iron silicate slags, Kaiura et al. (1980), Johnson et al. (1982), Westland & Webster (1990) and Louey (1999) fused high purity iron, iron (III) oxide and silica. Iron crucibles were most commonly used for synthesizing iron silicate slag. Louey (1999) however, reported that iron crucibles were difficult to support safely in the hot zone of a tube furnace and therefore used magnesia crucibles instead. The use of magnesia crucibles has the disadvantage of adding another oxide into the system due to dissolution of crucible material into the slag. The maximum solubility of magnesia in fayalite slags however, is only 4% at 1523 K as observed from Figure 2-5.13.

![FeO-MgO-SiO2 phase diagram](image)

**Figure 2-5.13:** FeO-MgO-SiO2 phase diagram indicating maximum magnesia solubility in silica saturated iron silicate slag at 1523 K.

Impurity elements are introduced into the system either into the matte as sulfides, the slag as oxides or added as pure metallic powder. Choi & Cho (1997) added selenium and tellurium as pure metallic powder charged between the matte and slag phases within the
crucible. Westland & Webster (1990) examined molybdenum distribution by doping molybdenum sulfide directly into the matte phase during matte synthesis. Louey (1999) studied the effect of tin on silver loss in copper smelting slags and added both electrolytic silver and tin foil together with copper, iron and sulfur while preparing synthetic matte. The method in which the element is introduced into the system should not affect the distribution ratio of the element and there has been no evidence to suggest otherwise.

c. EQUIPMENT

The choice of crucible for distribution experiments again varied between authors. Kaiura et al. (1980) found silica crucibles suitable for their experiments, based on their choice of conditions required. Yazawa & Kameda (1953), Choi & Cho (1997) as well as Westland & Webster (1990) also used silica crucibles in their studies to facilitate silica-saturation in the slag phase. Louey (1999) tested silica, iron, alumina and magnesia crucibles for their suitability for distribution experiments and found silica crucibles to be fragile, becoming badly attacked by slag when used at 1523 K. In addition to this, the silica reacting with the slag makes it difficult to separate the contents from the crucible for chemical analysis. Iron crucibles were found to be unsuitable because the iron in the crucible reduced the copper sulfide present in matte to copper following reaction 2-5.29:

$$\text{Cu}_2\text{S}(l) + \text{Fe}(s) = 2\text{Cu}(l) + \text{FeS}(l) \quad \Delta G^\circ = 19.797 \text{ kJ} \quad [2-5.29]$$

The system therefore could not reach equilibrium because the copper formed from the reaction was continuously absorbed into the crucible wall. Alumina and magnesia crucibles have the disadvantage of adding another oxide into the system due to dissolution of crucible material into the slag. Both alumina and magnesia crucibles did not corrode as severely as silica crucibles. Figures 2-5.13 and 2-5.14 show the maximum solubility of magnesia and alumina in fayalite slag at 1523 K to be 4% and 14%, respectively. Although alumina is the cheaper option, Louey (1999) deemed magnesia crucibles to be more suitable due to their lower reactivity with the melt, allowing for much cleaner separation of the crucible contents from the crucible. Roghani et al. (2000) also used magnesia crucibles for their distribution experiments.
Louey (1999) used a crucible assembly that included an upturned alumina crucible acting as a lid to limit the volatilization of tin oxide, as shown in Figure 2-5.15. A small magnesia crucible containing the slag and matte was placed on a bed of alumina powder held in a large shallow alumina pan. An upturned alumina crucible was then placed over the sample crucible. This technique was similarly employed in the germanium distribution work under lead smelting conditions performed by Yan & Swinbourne (2003). This crucible assembly is also useful when using an inert gas as the gas phase for equilibrium experiments. The upturned crucible minimizes the loss of sulfur and oxygen gas which gets swept out of the crucible by the inert gas and so stops the composition of the phases from slowly changing.
Figure 2-5.15: Crucible assembly to limit loss of volatile species to the gas phase (Louey, 1999).

d. **PROCEDURE**

The procedures employed for distribution experiments do not vary greatly. As described by Kaiura et al. (1980) and observed in most studies, the experiments consist of charging the sample into a furnace, introducing the flushing gas, heating the furnace to the desired temperature and holding for the necessary reaction time. At the end of the reaction time samples are quenched and the phases are carefully separated for analysis.

Although the procedures are standard, the determination of the equilibrium duration warrants some discussion. Various documented investigations show the necessary reaction time to vary greatly. The criterion for equilibrium varies for different systems as determined by the researchers, although the trend from literature is to observe constancy of the distribution of impurity element with time and/or observe constancy of the major matte and slag constituents (copper, sulfur etc.) with time.

Kaiura et al. (1980) set the criteria for equilibrium for their low oxygen potential experiments to be the independence of the copper content in slag and the lead distribution coefficient with respect to time. Yazawa & Takeda (1982) confirmed the
heating time as required for copper-calcium ferrite equilibrations by observing the copper content in slag; equilibrium being achieved when the copper content no longer changes with time, as shown in Figure 2-5.16.

**Figure 2-5.16:** Copper content in slag as a function of time (Yazawa & Takeda, 1982).

Both Choi & Cho (1995) and Louey (1999) determined the time required for the distribution of silver to reach equilibrium to be when the silver content was constant in the slag. Unlike the previous cases, Johnson et al. (1982) established equilibrium time for their distribution experiments, not by observing constancy in the concentration of impurity element, but instead by observing changes to the copper and sulfur contents of matte and slag as shown in Figure 2-5.17.

**Figure 2-5.17:** Copper and sulfur contents of matte and slag for different equilibration times (Johnson et al., 1982).
Of the techniques used to determine the equilibrium time, it is more logical to observe constancy of the impurity element with time, the reason being that the amount of impurity element added to each experiment is small, so there may be little or no change in the composition of the major matte and slag constituents. It is therefore important that the method of chemical analysis be capable of providing sufficiently accurate analysis of the impurity element.

When performing element distribution studies it is important to approach equilibrium from both directions. Experiments that do not use this technique cannot show that the system is truly at equilibrium because results showing constant distribution coefficient with time could simply mean the equilibrium reaction occurs at a very slow rate. If this scenario, approaching from both sides will clearly show this because the distribution ratios from both sets of experiments will not converge.

This section has examined the experimental techniques employed in literature for element distribution studies and found the techniques to not differ significantly between the various studies. The best practices detailed in literature were implemented in this study and detailed in Chapter 5.
2-5.4 Element Distribution Data

The previous sections provide the necessary framework towards understanding element distribution studies. This section examines matte smelting distribution data available from literature over the full range of copper smelting conditions. It will become apparent that some elements have been studied in more detail than others due mainly to the amounts in which they are present in the feed, as well as their effect on the smelting or electro-refining processes.

<table>
<thead>
<tr>
<th>Element</th>
<th>Authors</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>Yazawa (1980)</td>
<td>1573 K; constant $P_{S_2}$; $P_{O_2}$ $10^{-6}$ to $10^{-11.5}$ atm</td>
</tr>
<tr>
<td></td>
<td>Johnson et al. (1982)</td>
<td>1523 K; $P_{SO_2}$ 0.1 atm; slag additives</td>
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<tr>
<td></td>
<td>Johnson et al. (1984)</td>
<td>1523 K; $P_{SO_2}$ 0.1 atm; slag additives</td>
</tr>
<tr>
<td></td>
<td>Roghani et al. (1997)</td>
<td>1573 K; $P_{SO_2}$ 0.1, 0.5, 1.0 atm; lime addition</td>
</tr>
<tr>
<td></td>
<td>Roghani et al. (2000)</td>
<td>1573 K; $P_{SO_2}$ 0.1, 0.5, 1.0 atm</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Yazawa (1980)</td>
<td>1573 K; constant $P_{S_2}$; $P_{O_2}$ $10^{-6}$ to $10^{-11.5}$ atm</td>
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<tr>
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<td>Johnson et al. (1984)</td>
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</tr>
<tr>
<td></td>
<td>Roghani et al. (1997)</td>
<td>1573 K; $P_{SO_2}$ 0.1, 0.5, 1.0 atm; lime addition</td>
</tr>
<tr>
<td></td>
<td>Roghani et al. (2000)</td>
<td>1573 K; $P_{SO_2}$ 0.1, 0.5, 1.0 atm</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Johnson et al. (1982)</td>
<td>1523 K; $P_{SO_2}$ 0.1 atm, slag additives</td>
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<td></td>
<td>Johnson et al. (1984)</td>
<td>1523 K; $P_{SO_2}$ 0.1 atm, slag additives</td>
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<tr>
<td></td>
<td>Roghani et al. (1997)</td>
<td>1573 K; $P_{SO_2}$ 0.1, 0.5, 1.0 atm; lime addition</td>
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<tr>
<td></td>
<td>Roghani et al. (1997)</td>
<td>1573 K; $P_{SO_2}$ 0.1, 0.5, 1.0 atm</td>
</tr>
<tr>
<td></td>
<td>Mackey (1982)*</td>
<td>1503 K; $P_{SO_2}$ 0.29 atm; 65wt% Cu</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Mackey (1982)*</td>
<td>1503 K; $P_{SO_2}$ 0.29 atm; 65wt% Cu</td>
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<tr>
<td>Zinc</td>
<td>Mackey (1982)*</td>
<td>1503 K; $P_{SO_2}$ 0.29 atm; 65wt% Cu</td>
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<tr>
<td></td>
<td></td>
<td>1473 K; 21% $O_2$; 75wt% Cu</td>
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<tr>
<td>Cobalt</td>
<td>Yazawa (1980)</td>
<td>1573 K; constant $P_{S_2}$; $P_{O_2}$ $10^{-6}$ to $10^{-11.5}$ atm</td>
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<td></td>
<td>Mwema et al. (1995)</td>
<td>1623 K; $P_{O_2}$ $10^{-7}$ to $10^{-10}$ atm</td>
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<tr>
<td></td>
<td>Choi and Cho (1997)</td>
<td>1523 K; $P_{O_2}$ 6x10-8 atm, 1x10-9 atm, argon; slag additives; Cu-Ni mattes</td>
</tr>
</tbody>
</table>

*denotes distribution coefficients reported from industry.
## Chapter 2: Literature Review

<table>
<thead>
<tr>
<th>Element</th>
<th>Reference</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nickel</strong></td>
<td>Mackey (1982)*</td>
<td>1503 K; $p_{SO_2} 0.29$ atm; 65wt% Cu</td>
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<td></td>
<td>Yazawa (1980)</td>
<td>1573 K; constant $p_{SO_2}$; $p_{O_2} 10^{-4}$ to $10^{-11.5}$ atm</td>
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<td></td>
<td>Mackey (1982)*</td>
<td>1573 K; Fe &amp; Cu saturation, low $p_{O_2}$</td>
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<tr>
<td></td>
<td>Larouche (2001)*</td>
<td></td>
</tr>
<tr>
<td><strong>Lead</strong></td>
<td>Kaiura et al. (1980)</td>
<td>1573 K; $p_{SO_2} 0.1$, $0.01$ atm</td>
</tr>
<tr>
<td></td>
<td>Roghani et al. (1997)</td>
<td>1573 K; $p_{SO_2} 0.1$, $0.5$, $1.0$ atm; lime addition</td>
</tr>
<tr>
<td></td>
<td>Roghani et al. (2000)</td>
<td>1573 K; $p_{SO_2} 0.1$, $0.5$, $1.0$ atm</td>
</tr>
<tr>
<td></td>
<td>Mackey (1982)*</td>
<td>1503 K; $p_{SO_2} 0.29$ atm; 65wt% Cu</td>
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<td><strong>Tin</strong></td>
<td>Park et al. (1982)</td>
<td>1573 K, Cu saturation, low $p_{O_2}$</td>
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<td></td>
<td>1573 K, $p_{SO_2} 0.1$, $0.01$ atm</td>
</tr>
<tr>
<td></td>
<td>Koike and Yazawa (1994)</td>
<td>1523 K, $p_{SO_2} 0.05$, $0.1$, $0.2$ atm</td>
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<tr>
<td></td>
<td>Louey et al. (1999)</td>
<td>1523 K, nitrogen gas, 50wt % Cu</td>
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<td><strong>Selenium</strong></td>
<td>Johnson et al. (1982)</td>
<td>1523 K; $p_{SO_2} 0.1$ atm; slag additives</td>
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<td></td>
<td>Johnson et al. (1984)</td>
<td>1523 K; $p_{SO_2} 0.1$ atm; slag additives</td>
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<td></td>
<td>Choi and Cho (1997)</td>
<td>1523 K; $p_{O_2} 6\times10^{-8}$ atm, $1\times10^{-9}$ atm, argon; slag additives; Cu-Ni mattes</td>
</tr>
<tr>
<td></td>
<td>Mackey (1982)*</td>
<td>1503 K; $p_{SO_2} 0.29$ atm; 65wt% Cu</td>
</tr>
<tr>
<td><strong>Tellurium</strong></td>
<td>Johnson et al. (1982)</td>
<td>1523 K; $p_{SO_2} 0.1$ atm; slag additives</td>
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<td>Johnson et al. (1984)</td>
<td>1523 K; $p_{SO_2} 0.1$ atm; slag additives</td>
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<tr>
<td></td>
<td>Choi and Cho (1997)</td>
<td>1523 K; $p_{O_2} 6\times10^{-8}$ atm, $1\times10^{-9}$ atm, argon; slag additives; Cu-Ni mattes</td>
</tr>
<tr>
<td></td>
<td>Mackey (1982)*</td>
<td>1503 K; $p_{SO_2} 0.29$ atm; 65wt% Cu</td>
</tr>
<tr>
<td><strong>Molybdenum</strong></td>
<td>Westland and Webster (1990)</td>
<td>1573 K, $p_{O_2} 5\times10^{11}$ atm</td>
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<td></td>
<td>1573 K, $p_{SO_2} 0.1$, $0.01$ atm</td>
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<td></td>
<td>Park et al. (1982)</td>
<td>1573 K, Cu saturation, low $p_{O_2}$</td>
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<td></td>
<td></td>
<td>1573 K, $p_{SO_2} 0.1$, $0.01$ atm</td>
</tr>
<tr>
<td><strong>Silver</strong></td>
<td>Roghani et al. (1997)</td>
<td>1573 K; $p_{SO_2} 0.1$, $0.5$, $1.0$ atm; lime addition</td>
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<td></td>
<td>Roghani et al. (2000)</td>
<td>1573 K; $p_{SO_2} 0.1$, $0.5$, $1.0$ atm</td>
</tr>
<tr>
<td></td>
<td>Louey et al. (1999)</td>
<td>1523 K, nitrogen gas, 50wt % Cu</td>
</tr>
<tr>
<td><strong>Gold</strong></td>
<td>Henao et al. (2006)</td>
<td>1573 K, $p_{SO_2} 0.1$ atm, 40-70wt% Cu</td>
</tr>
</tbody>
</table>


\begin{table}[H]
\centering
\begin{tabular}{|l|l|l|}
\hline
Platinum & Henao et al. (2006) & 1573 K, pSO\textsubscript{2} 0.1 atm, 40-70wt\% Cu \\
\hline
Palladium & Henao et al. (2006) & 1573 K, pSO\textsubscript{2} 0.1 atm, 40-70wt\% Cu \\
\hline
Rhodium & Henao et al. (2006) & 1573 K, pSO\textsubscript{2} 0.1 atm, 40-70wt\% Cu \\
\hline
Ruthenium & Henao et al. (2006) & 1573 K, pSO\textsubscript{2} 0.1 atm, 40-70wt\% Cu \\
\hline
\end{tabular}
\caption{Summary of experimental conditions for platinum, palladium, rhodium, and ruthenium.}
\end{table}

\subsection{Antimony, Arsenic & Bismuth}

Distribution experiments for the minor elements antimony, arsenic and bismuth were performed by Yazawa (1980), Johnson et al. (1982), Johnson et al. (1984), Roghani et al. (1997) and Roghani et al. (2000). The conditions at which these authors performed their experiments are detailed in the following paragraphs as well as highlighted in the Yazawa chemical potential diagram in Figure 2-5.18.

Yazawa (1980) examined the distribution behavior of various elements between liquid copper, matte and slag using experimental results together with thermodynamic discussion. Experimental studies were carried out for the gas-slag-matte-metal system for matte grades greater than 50 wt\% Cu, represented on the chemical potential diagram by line rC' in Figure 2-5.18 below. Increasing oxygen potential along line C'C results in increasing matte grades to reach the gas-slag-matte-copper system.

The distribution thermodynamics for the metal-slag and the metal-matte systems were discussed using the following reaction equations respectively:

\begin{equation}
X + \frac{V}{2}O_2 = XO_V \tag{2-5.30}
\end{equation}

\begin{equation}
X + y CuS = XS_y + 2y Cu \tag{2-5.31}
\end{equation}

Equation [2-5.24] assumes that the sulfidic form, XS\textsubscript{y}, is the prevailing form of species in the matte. While this may be true for some elements, it has been suggested that elements such as arsenic and antimony may be present in the metallic state (Roghani et al., 2000). Kashima et al. (1978) showed the distribution ratios of arsenic and antimony between copper and matte to heavily favor the copper phase and believes this may be a strong indication of the formation of metallic form for these elements in the melts.

From equations [2-5.30] and [2-5.31], the distribution ratios were derived as follows:
The distribution ratio for the matte-slag system was then derived from equations [2-5.32] and [2-5.33] as shown:

\[
L_{\text{c/s}} = \frac{\%X_{\text{metal}}}{\%X_{\text{slag}}} = \frac{K' \gamma_{XO_2}}{p_{O_2}^{1/2} \gamma_X}
\]  

\[
L_{\text{c/m}} = \frac{\%X_{\text{metal}}}{\%X_{\text{matte}}} = \frac{K' \gamma_{XS}}{\gamma_X}
\]  

Johnson et al. (1982) examined the distribution of antimony between matte and silica-saturated iron silicate slag at 1523 K, as well as the effects of slag additives on the distribution behavior. Their experiments concerned the five component system Cu, Fe, S, O, and SiO\(_2\) with the phases gas, matte and slag. Using the phase rule, fixing the temperature and having the slag silica-saturated leaves two degrees of freedom. The authors thus fixed the partial pressure of sulfur dioxide at 0.1 atm and used a mixture of CO-CO\(_2\) gas to control the partial pressure of oxygen to obtain various matte grades. The time required to establish equilibrium was determined by equilibrating fayalite slag and matte at 1523 K in a silica crucible at oxygen and sulfur potentials of 1x10\(^{-8}\) atm and 5.1x10\(^{-4}\) atm, respectively, for up to 64 hours. They concluded from the copper and sulfur contents of the matte and slag that 24 hours was sufficient to achieve equilibrium, as shown earlier in Figure 2-5.16.

Johnson et al. (1982) performed distribution experiments with five minor elements (arsenic, antimony, bismuth, selenium, and tellurium) present simultaneously in the matte-slag system. Johnson et al. (1984) followed up that previous study by investigating the possibility of interactions among the minor elements. It was suggested that the distribution coefficients may vary according to the presence of other minor elements in the system. Any inter-element effect is likely to be the result of other elements affecting the activity coefficients of either the oxide or sulfide species of the target element. The authors thus performed distribution experiments using the same five minor elements, with each element individually doped into the matte-slag system.

Roghani et al. (1997) performed distribution experiments for arsenic, antimony and bismuth between copper matte and slag containing various amounts of lime. The amount of lime in the slag was defined by the term, \(Q=\%CaO/(\%CaO+\%SiO_2)\). The authors performed experiments for Q of 0 (FeO\(_x\)-SiO\(_2\)), 0.35 (CaO-FeO\(_x\)-SiO\(_2\)) and 1 (CaO-FeO\(_x\)).
The results for slag system Q=1 are not relevant for this study and will not be reported. The results reported for Q=0 are the same data used in Roghani et al. (2000) and thus will not be repeated. Results for Q=0.35 will be used to show the effect of lime addition on the distribution coefficient. The authors investigated slag-matte equilibrium ranging from air-blowing conditions ($p_{O_2}=10.1$ kPa) to oxygen-smelting conditions at much higher oxygen potentials. A mixture of Ar-SO$_2$-$S_2$ gas was used to control the partial pressure of sulfur dioxide and sulfur in order to define the oxygen partial pressure in the system.

Roghani et al. (2000) performed distribution studies with copper matte and silica-saturated iron silicate slag containing 5 to 10 wt% magnesia under high partial pressures of sulfur dioxide at 1573 K. In order to fully define the system, the authors controlled the partial pressures of sulfur dioxide and sulfur using a mixture of Ar-SO$_2$-$S_2$ gas. Experiments were performed at different $p_{SO_2}$ values of 10.1, 50.7 and 101.3 kPa. The magnesia content in the slag was reported to be higher than that of industrial slags, but this is only because magnesia crucibles were used in the study.

![Figure 2-5.18: Chemical potential diagram at 1573 K highlighting regions of element distribution studies.](image-url)
Antimony

Figure 2-5.19 shows antimony distribution data for experiments conducted between mattes of various grades and silica-saturated iron silicate slag in silica crucibles. The filled data points represent experiments conducted using nitrogen to generate low oxygen potentials. The unfilled data points were from experiments performed under varying sulfur dioxide pressures, corresponding to varying oxygen potentials as shown in the figure.

It is observed from Figure 2-5.19 that at low oxygen potentials (between $\log P_{O_2} = -11.5$ to $-10$) the distribution ratio appears to be constant with a value of approximately 50, although there is some scatter in the data. It is also apparent that the distribution coefficient ($L_{X/m/s}$) of antimony decreases with increasing matte grade. This is expected as an increase in oxygen partial pressure both raises the matte grade through iron (II) sulfide oxidation and lowers the antimony content of the matte, also through oxidation.

![Figure 2-5.19](image)

**Figure 2-5.19**: Distribution ratio of antimony between matte and slag plotted against oxygen potential at 1573 K (Yazawa, 1980).

There is an obvious difference in the slopes of the trend line at low oxygen potentials compared to that at higher oxygen potentials. The presence of the two regions indicates that antimony is present in the slag in two oxidation states:
• Neutral antimony atoms in the low oxygen partial pressure region, where the slope is near zero,
• Neutral antimony atoms and a cationic form at high oxygen partial pressures.

Dissolution of an element as neutral atoms is independent of $pO_2$, thus the same concentration of Sb° will be present at all $pO_2$. At low $pO_2$ almost all antimony is present as Sb°, but as the $pO_2$ rises the concentration of Sb in the slag rises and the proportion that is ionic in form rapidly rises and predominates at high $pO_2$. The slope of the line at the highest $pO_2$ will provide the best indication of the ionic charge, but only if the Sb° is present is insignificant in amount compared to the ionic state.

The slope of the line at high oxygen partial pressures is approximately 0.5, suggesting that antimony is dissolved in the slag as SbO. The Gibbs free energy of formation for various antimony oxide compounds, from the HSC Chemistry v5.1 database, however, shows that antimony only exists in the SbO state as a gas and is otherwise most stable as SbO$_{1.5}$ i.e. as Sb$_{3+}$.

\[
\frac{4}{3} \text{Sb}(l) + \text{O}_2(g) = \frac{4}{3} \text{SbO}_{1.5}(l) \quad \Delta G^\circ_{1573 K} = -225.150 \text{ kJ} \quad [2-5.35]
\]

\[
\text{Sb}(l) + \text{O}_2(g) = \text{SbO}_2(s) \quad \Delta G^\circ_{1573 K} = -156.441 \text{ kJ} \quad [2-5.36]
\]

\[
\frac{4}{5} \text{Sb}(l) + \text{O}_2(g) = \frac{4}{5} \text{SbO}_{2.5}(s) \quad \Delta G^\circ_{1573 K} = -73.008 \text{ kJ} \quad [2-5.37]
\]

In order to justify the observations above, Yazawa (1980) suggested that at higher oxygen potentials, antimony is dissolved in both metallic and oxidic states; the SbO$_{1.5}$ form becoming predominant at higher oxygen potentials. This suggestion has been similarly used by Swinbourne and You (1999) in their examination of silver solubility in sodium silicate slags. Swinbourne and You (1999) showed that at high oxygen potential, silver is present in the slag in both the neutral and cationic form. The authors showed that if the element dissolves in more than one oxidation state, then the slope of log $L_{Ag}$ vs log $pO_2$ will not correspond to the expected cation species. The slope corresponding to the correct ionic species can be determined by subtracting the concentration of silver present in the neutral state from the analyzed total. It is therefore highly likely that the slope at high oxygen potentials observed by Yazawa (1980) in Figure 2-5.19 is a result of a combination of Sb° and Sb$_{3+}$ oxidation states.
Johnson et al. (1982) examined the effect of doping level on the distribution of antimony between matte and slag to investigate the possibility of antimony species saturation in either phase. Figure 2-5.20 shows the concentration of antimony in matte (60 wt% Cu) and slag as a function of the concentration of elemental antimony added to the charge (up to 0.25 wt% Sb). The authors stated, based on Figure 2-5.20, that saturation with an antimony species did not occur in either the slag or matte.

![Figure 2-5.20: Effect of doping level on the distribution of antimony between matte and slag at 1523 K and \( P_{O_2} = 1 \times 10^{-8} \) atm (Johnson et al., 1982).]

A disadvantage of using a diagram such as in Figure 2-5.20 is that although it shows neither phase is saturated, it does not confirm whether the system has actually reached equilibrium. A more useful diagram would be a plot of the distribution of antimony against the concentration of antimony added to the charge; showing constant distribution ratio for an equilibrated system when neither phase is saturated. Table 2-5.6 shows the distribution ratios calculated for the data given in Figure 2-5.20.

**Table 2-5.6** Distribution ratio of antimony as a function of antimony concentration in the charge.

<table>
<thead>
<tr>
<th>Wt% Addition</th>
<th>%Sb in Matte</th>
<th>%Sb in Slag</th>
<th>( L_{Sb^{m/s}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>0.006</td>
<td>0.025</td>
<td>0.24</td>
</tr>
<tr>
<td>0.18</td>
<td>0.053</td>
<td>0.077</td>
<td>0.69</td>
</tr>
<tr>
<td>0.27</td>
<td>0.068</td>
<td>0.108</td>
<td>0.63</td>
</tr>
</tbody>
</table>

The initial addition of elemental antimony to the charge should result in the element entering the matte phase. Referring to Section 2-5.2, when doping the element into the
Chapter 2: Literature Review

matte; if either phase becomes saturated, any further additions will increase $L_{Sb}^{m/s}$. From the data in Table 2-5.5, there is an increase in the distribution ratio from 0.03 wt% addition to 0.18 wt% addition, however the distribution ratios are nearly constant for 0.18 wt% and 0.27 wt% additions. If saturation were to have occurred, the distribution ratio would continue to increase with increasing antimony additions. It is likely that the result for 0.03 wt% addition of antimony is suspect. This highlights the disadvantage of presenting the data in the form used in Figure 2-5.20. It is possible that equilibrium was not achieved for that experiment or that the small amount of antimony in the matte phase has had an effect on the accuracy of chemical analysis.

Figure 2-5.21 shows the distribution of antimony between matte and slag at 1523 K as a function of matte grade.

![Figure 2-5.21: The distribution of antimony as a function of matte grade at 1523 K (Johnson et al., 1982).](image)

The distribution coefficients, $L_{Sb}^{m/s}$, reported by Yazawa (1980) for mattes containing 40-70 wt% Cu are much higher in comparison to the data by Johnson et al. (1982). It is expected that the conditions employed by the different authors is the cause for the above discrepancy, with Johnson et al. (1982) using much higher oxygen potentials compared to Yazawa (1980). The use of higher oxygen potentials would push antimony to the slag phase through oxidation and thus decrease the distribution ratio of antimony. It is important to note that while a plot of $\log L_{Sb}^{m/s}$-$\log P_O^2$ for Yazawa's work can provide data about the state of antimony in the slag (because the sulfur partial pressure is
constant), a similar plot for Johnson’s work will not provide any useful information because both the oxygen and sulfur partial pressures vary.

Johnson et al. (1982) also studied the effects of slag additives on the distribution of antimony between slag and matte, the results of which are shown in Figure 2-5.22.

![Figure 2-5.22: Effect of slag additives on the distribution of antimony between matte and slag as a function of matte grade (Johnson et al. 1982).](image)

From the data, the authors came to the following conclusions:

- Addition of lime (2.4 wt% to 9.1 wt%) decreases the distribution ratio of antimony at all matte grades.
- Addition of alumina (2.4 wt% to 9.1 wt%) also pushes antimony towards the slag phase.
- Magnesia additions were done at considerably lower additions (0.7 wt% to 2.4 wt%), most likely because the maximum solubility of magnesia in fayalite slag at 1523 K is 4% as shown in Figure 2-5.13 earlier. The addition of magnesia to the slag also decreases the distribution ratio of antimony.

Careful examination of the data in Figure 2-5.22 undermines the conclusions suggested by Johnson et al. (1982). The data points are scattered around the trend line for experiments with ‘no additives’. There does not appear to be any correlation between the amount of additive added and the change in the distribution ratio, suggesting that the observed effect of additives on the distribution ratio could simply be attributed to experimental error. Either way, there is no clear evidence to suggest that the additives have had any effect on the distribution of antimony between matte and slag.

Johnson et al. (1984) concluded from their study of minor-element interactions in copper matte smelting that the distribution of antimony was the same (within experimental error)
as reported in Johnson et al. (1982) whether or not the other minor elements were present in the system.

Roghani et al. (2000) reported similar trends as Johnson et al. (1982) in that the distribution ratio of antimony decreases gradually with increasing matte grade as shown in Figure 2-5.23. However, the authors reported that the distribution ratio increased dramatically for matte grades of 75 wt% Cu and higher. One would expect the significant increase of oxygen potential above matte grades of 75 wt% Cu to further decrease the value of the distribution coefficient. The authors attributed their observation to the decrease of the value of activity coefficient of antimony, \( \gamma_{Sb} \), in the matte phase outweighing the effect of increasing oxygen partial pressure in that range. The decrease in the value of \( \gamma_{Sb} \) at higher matte grades was reported by Itagaki and Yazawa (1983).

Roghani et al. (1997) showed that the presence of lime in the slag had little effect on the distribution coefficient of antimony between matte and slag.

The data in Figure 2-5.23 shows the distribution ratio of antimony at \( P_{SO_2} \) of 0.1 atm to be approximately double that at \( P_{SO_2} \) of 1.0 atm.

![Figure 2-5.23](image)

**Figure 2-5.23:** Effect of \( P_{SO_2} \) on the distribution of antimony between matte and slag as a function of matte grade (Roghani et al., 2000).

In order to observe the effect of sulfur dioxide partial pressure on the distribution ratio of antimony, reference is made to equation [2-5.12]:

70
It can be seen that the distribution ratio is a function of the partial pressures of sulfur and oxygen (when all other values can be assumed to be constant):

\[
L_M^{m/s} = L_M^{m/c} \times L_M^{c/s} = \frac{K_2(\gamma_{Mo})p_{S_2}^\gamma}{K_1(\gamma_{Mo})p_{O_2}^\gamma}
\]  

[2-5.12]

From equation [2-5.38], note that the oxidation state for the dissolved species is required to observe the effect of \(p_{SO_2}\) on the distribution ratio.

Reiterating an earlier conclusion, a plot of \(\log L_{Sb}^{m/s} - \log p_{O_2}\) can provide data regarding the state of antimony in the slag provided that:

- At a given matte grade, the activity coefficients of minor elements in the slag and matte phases do not change with \(p_{SO_2}\)
- The form of antimony dissolution in the matte is independent of \(p_{S_2}\)

Data provided by Yazawa (1980) provided information regarding the state of antimony dissolution in slag because the author performed distribution experiments using a unique condition where the \(p_{S_2}\) is constant. Roghani et al. (2000), however, made a case that the metallic species of antimony was by far the more stable species and thus the distribution ratio would be independent of \(p_{S_2}\). The stability of the metallic species in the matte phase was predicted using equation [2-5.40] derived from equation [2-5.39]:

\[
(X) + \frac{V}{4} S_2(g) = (XS_{v/2})
\]  

[2-5.39]

\[
\frac{\{a_{XS_{v/2}}\}}{\{a_X\}} = K_{S_2}p_{S_2}^{V/4}
\]  

[2-5.40]

Roghani et al. (2000) stated that the activity ratio \(\{a_X\}/\{a_{XS_{v/2}}\}\) for antimony was much higher than unity over the entire range of matte grades up to 80 wt% Cu, suggesting that the metallic species of antimony is much more stable than the sulfidic species in the matte phase. Having established this, the distribution of minor elements between matte and slag when metallic and oxidic dissolution is taken into consideration is:
The relation between the distribution ratio and oxygen partial pressure as shown in Figure 2-5.24 will suggest the valence, v, in equation [2-5.41]. The plot of log $L_{Sb}^{s/m}$-log $p_{O_2}$ shows a slope of approximately $\frac{3}{4}$, indicating that the form of antimony dissolution in slag is $Sb^{3+}$. Yazawa (1980) showed a slope of 0.5. The slope likely decreased from $\frac{3}{4}$ due to the influence of $Sb^0$ present in the slag. The data by Roghani et al. (2000) would then indicate that under the conditions used, the presence of $Sb^0$ is insignificant compared to the ionic species.

Assuming Roghani's analysis is correct (antimony dissolves in the matte phase in the metallic form), then the change in distribution ratio with change in $p_{SO_2}$ will only be due to the change in $p_{O_2}$ and any associated change in the activity coefficients of the species involved. Referring back to the chemical potential diagram in Figure 2-5.18, the $p_{O_2}$ values can be read off for $p_{SO_2}$ of 0.1 atm and 1.0 atm, for a fixed matte grade of 50 wt% Cu. The effect of $p_{SO_2}$ on the distribution ratio of antimony can be calculated to be:

\[
\text{(X)} + \frac{v}{4}O_2 = (XO_{v/2}) \quad \quad [2-5.41]
\]

\[
L_{X}^{s/m} = \frac{K_{34}(n_t)(v X)p_{O_2}^{v/4}}{(v XO_{v/2})(n_t)} \quad \quad [2-5.42]
\]
Equation [2-5.43] shows that the distribution ratio of antimony at $p_{SO_2}$ of 0.1 atm is approximately 3.4 times larger than that at $p_{SO_2}$ of 1.0 atm. This value is larger than the experimental data in Figure 2-5.23, which shows a difference of approximately 2 times. The analysis used above to account for the difference in $L_{Sb}^{m/s}$ with changing $p_{SO_2}$ only takes into account the change in $p_{O_2}$ of the system at the two different conditions at a fixed matte grade. In addition to this, the activity coefficients of the species in slag and matte and experimental error could also be a factor in accounting for this difference.

Figure 2-5.25 compares the distribution of antimony obtained by Johnson et al. (1982) with that of Roghani et al. (2000), both under conditions of constant $p_{SO_2}$ of 0.1 atm and as a function of matte grade.

![Figure 2-5.25: Comparison of antimony distribution data at constant $p_{SO_2}$ as a function of matte grade.](image)

As seen in Figure 2-5.25, the trend showed by both data sets is almost identical; however there is a systematic difference between the two sets of data with Roghani’s data approximately two times larger than that of Johnson’s data. Comparing the operating conditions of both sets of experiments, the most notable difference would be that Johnson et al. (1982) worked at 1523 K whereas Roghani et al. (2000) worked at 1573 K.
Checking the equilibrium constant for the equilibrium reaction from the database in HSC Chemistry v5.1:

\[
\text{Sb}(l) + \frac{3}{4} \text{O}_2(g) = \text{SbO}_{1.5}(l)
\]

\[K_{1523} = 8.902 \times 10^5 \quad [2-5.44]
\]

\[K_{1573} = 4.049 \times 10^5
\]

The distribution coefficient is proportional to:

\[
L_M^{m/s} \propto \gamma_{MO_s} \frac{1}{\gamma_{MS_s}} \left( \frac{p_{S_s}}{p_{O_2}} \right) x
\]

The term K is the equilibrium constant for the reaction in equation [2-5.44]. When all other parameters are constant, the effect of temperature on the distribution ratio of antimony is observed:

\[
\frac{[L_{\text{Sb}}^{m/s}]_{1573K}}{[L_{\text{Sb}}^{m/s}]_{1523K}} \propto \frac{K_{1523K}}{K_{1573K}} = \frac{8.902 \times 10^5}{4.049 \times 10^5} \approx 2.2
\]

It can thus be concluded from equation [2-5.46] that the difference between the distribution data produced by Johnson et al. (1982) and by Roghani et al. (2000) can be attributed to the difference in operating temperature.

Summary of findings:

- Saturation of matte or slag with antimony species does not occur for charge containing up to 0.25 wt% Sb.
- \(L_{\text{Sb}}^{m/s}\) decreases with increasing matte grade, except for the region of low oxygen potentials where it is approximately constant as shown by Yazawa (1980).
- Antimony dissolution in slag is believed to be a mixture of \(\text{Sb}^0\) and \(\text{Sb}^{3+}\), with \(\text{Sb}^{3+}\) becoming predominant at higher oxygen potentials.
- Slag additives of lime, magnesia or alumina show no clear evidence of affecting the distribution coefficient of antimony.

Arsenic

Figure 2-5.26 shows the data by Yazawa (1980) for arsenic distribution between matte and slag. The filled data points represent experiments conducted at low oxygen partial...
pressures whereas the unfilled data points were from experiments performed at higher oxygen potentials.

![Figure 2-5.26: Distribution ratio of arsenic between matte and slag plotted against oxygen potential at 1573 K (Yazawa, 1980).](image)

It can be seen from Figure 2-5.26 that there is considerable scatter of data in the lower oxygen potential region with the distribution ratio of arsenic spanning across one order of magnitude ($10^3$ to $10^4$) heavily favoring the matte phase. The large amount of scatter is likely due to the very small arsenic content in the slag incurring large errors in analysis. The distribution of arsenic decreases with increasing matte grade, showing that arsenic dissolves into the slag in the oxidic state; this being shown more clearly at higher oxygen potentials. Yazawa (1980) noted however, that the slope of $\log L_{As \text{m/s}}$ versus $\log P_{O_2}$ is lower than expected (~0.6) for arsenic to dissolve purely in the $\text{AsO}_{1.5}$ state and therefore suggested that while the oxidic state is predominant at higher oxygen potentials, arsenic dissolves in both the metallic and oxidic states. However, no evidence was presented suggesting that neutral arsenic is present in the slag, i.e. the oxygen partial pressure was not low enough that the $\text{As}^\circ$ species greatly predominated. Yazawa et al. (2000) showed that the activity coefficient of arsenic in the matte, $\{\gamma_{\text{As}}\}$, decreases rapidly with increasing matte grade (especially past 70 wt% Cu). Because the interpretation of log distribution-log $P_{O_2}$ plots is dependant upon the relative constancy of the activity coefficient terms,
this change in $\gamma_{As}$ could very well affect the analysis in this case by shifting the line or the slope of the plot.

Johnson et al. (1982) reported the distribution ratio of arsenic to be approximately unity and to be roughly constant across the range of matte grades under consideration. This is shown in Figure 2-5.27. The distribution coefficients reported by Johnson et al. (1982) are very different from that of Yazawa (1980). Yazawa (1980) did show results for equilibrium experiments between matte, slag and gas containing 0.1 atm SO$_2$ (Kashima et al., 1980) and found $L_{As,m/s}$ to be constant with a value of approximately 6 for matte grades up to 60 wt% Cu. This result is in much better agreement with Johnson et al. (1980). Yazawa (1980) stated that the significant difference in distribution coefficient values under metal saturation compared to at constant $P_{SO_2}$ may be ascribed to the differences in oxygen potential and variations in activity coefficients.

![Figure 2-5.27](image)

**Figure 2-5.27**: The distribution of arsenic as a function of matte grade at 1523 K (Johnson et al., 1982).

In the same study, Johnson et al. (1982) investigated the effects of slag additives on the distribution of arsenic between matte and slag as shown in Figure 2-5.28.
From their data, the following conclusions were made:

- 9.1 wt% addition of lime increases the distribution of arsenic to the matte at all matte grades.
- Additions of alumina also push arsenic towards the matte phase. There is an observed proportional relation between the amount of alumina added and the distribution coefficient of arsenic, particularly at lower matte grades. The higher the additions of alumina (up to 9.1 wt%) the higher the distribution coefficient.
- Magnesia additions increase the distribution coefficient of arsenic at all matte grades.

While some of the conclusions above appear to be valid, the scatter in the data reduces their certainty. For low additions of lime there is no relationship between the amount of additive added and the distribution coefficient. The trend line for additions of 2.4 wt% alumina appears to have been exaggerated to show an increase in the distribution coefficient of arsenic; where in fact it should lie on or very close to the trend line for ‘no additives’. The data for magnesia additions similarly does not show any clear evidence of magnesia additions having any effect on the distribution coefficient.

Johnson et al. (1984) performed experiments to observe the possibility of inter-element effects influencing the distribution ratio of arsenic, but found no significant effect.

Roghani et al. (1997) reported that the presence of lime additions in the slag slightly decreases the distribution coefficient of arsenic, $L_{As}^{m/s}$. This is consistent with the theory of acid/base behavior of oxides in slags. Arsenic oxide is believed to behave as an acidic oxide and thus would have weak interactions with acidic silica-saturated iron silicate slag. The addition of lime would make the slag less acidic, allowing it to interact more strongly with both silica and arsenic oxide thus lowering the activity coefficient of arsenic oxide in
the slag. This will raise the mole fraction of arsenic oxide in slag and so lower the distribution ratio.

Roghani et al. (2000) observed similar trends as Johnson et al. (1982) in that the distribution coefficient of arsenic is close to unity and is independent of matte grade as shown in Figure 2-5.29.

![Effect of partial pressure of SO$_2$ on L$_{As}$](image)

**Figure 2-5.29**: Effect of partial pressure of SO$_2$ on the distribution of arsenic between matte & slag phases for varying matte grades (Roghani et al., 2000).

Similarly with antimony, the $P_{SO_2}$ dependency of the distribution coefficient clearly indicates decreasing $L_{As,m/s}$ with increasing $P_{SO_2}$. The data in Figure 2-5.29 shows the distribution ratio of arsenic at $P_{SO_2}$ of 0.1 atm to be approximately double of that at $P_{SO_2}$ of 1.0 atm. The same method of analysis as used in the antimony section is applied here to account for the difference.

Figure 2-5.30 shows the distribution of arsenic between slag and matte as a function of oxygen partial pressures.
Figure 2-5.30: Distribution of arsenic between slag and matte phases as a function of $pO_2$ at 1573 K (Roghani et al., 2000).

The plot of $\log L_{s/m} - \log pO_2$ shows a slope of approximately $\frac{3}{4}$, indicating that arsenic dissolution occurs in the As$^{3+}$ state. Similar results were shown earlier for antimony, which is expected given that both arsenic and antimony belong to the same group in the Periodic Table.

Referring back to the chemical potential diagram in Figure 2-5.18, the $pO_2$ values can be read off for $pSO_2$ of 0.1 atm and 1.0 atm, for a fixed matte grade of 50 wt% Cu. Given that the 3+ state is observed for both antimony and arsenic, the same observation made for antimony should be observed in the case of arsenic, i.e. the difference in arsenic distribution ratio at $pSO_2$ of 0.1 atm is approximately 3.4 times larger that at $pSO_2$ of 1.0 atm.

Figure 2-5.31 is a comparison of the distribution data obtained by Johnson et al. (1982) (without additives) with that of Roghani et al. (2000), both under conditions of constant $pSO_2$ of 0.1 atm.
Similarly to the comparison made for antimony in the previous section, a consistent difference is apparent between the two data sets with Roghani’s data roughly double that of Johnson’s. The equilibrium constant for the arsenic-arsenic oxide equilibrium reaction in HSC Chemistry v5.1 database is:

$$\text{As}(l) + \frac{3}{4} \text{O}_2(g) = \text{AsO}_{1.5}(l)$$

$$K_{1523 \, \text{K}} = 2.099 \times 10^5$$

$$K_{1573 \, \text{K}} = 9.506 \times 10^4$$

With all other parameters kept constant, the effect of temperature on the distribution ratio of arsenic is:

$$\frac{L_{As}^{m/s}}{L_{As}^{m/s}} \propto K_{1523 \, \text{K}} \div K_{1573 \, \text{K}} = \frac{2.099 \times 10^5}{9.506 \times 10^4} \approx 2.2$$

Equation [2-5.48] shows that the difference between the distribution data of Johnson et al. (1982) and Roghani et al. (2000) is probably due to the difference in temperature.

Summary of findings:

- There is good agreement between the data presented by Johnson et al. (1982) and Roghani et al. (2000); both showing that $L_{As}^{m/s}$ has a value of unity and is independent of matte grade up to 75 wt% Cu.
• Arsenic dissolution in slag is believed to be a combination of As° and As$^{3+}$, with As$^{3+}$ becoming predominant at higher oxygen potentials.
• Johnson’s data on the effect of slag additives on L$_{As}^{m/s}$ were unconvincing due to the amount of scatter present.
• Roghani et al. (1997)’s data on the effect of lime additions shows a slight decrease in L$_{As}^{m/s}$ with increase in lime content.

Bismuth

Johnson et al. (1982) examined the effect of doping level on the distribution of bismuth between matte and slag to investigate the possibility of bismuth species saturation in either phase. Figure 2-5.32 shows the concentration of bismuth in matte and slag as a function of elemental bismuth added to the charge.

![Figure 2-5.32: Effect of doping level on the distribution of bismuth between matte and slag at 1523 K and $P_{O_2} = 1 \times 10^{-8}$ atm (Johnson et al., 1982).](image)

The authors stated, based on Figure 2-5.32, that bismuth had saturated the matte and slag for bismuth concentrations greater than 0.125 wt%. The fact that both phases saturate at the same level of addition raises some questions. If in fact both phases are saturated with a bismuth species and the bismuth content in both phases remain constant past the saturation point, where then does the additional bismuth in the system go at higher levels of doping? While the authors observed precipitation of elemental bismuth via microprobe studies, it still does not explain how the authors excluded the undissolved bismuth from their analysis by flame absorption spectrophotometry.
Table 2-5.7 shows the distribution ratios calculated for the data given in Figure 2-5.32.

### Table 2-5.7: Distribution ratio of antimony as a function of antimony concentration in the charge.

<table>
<thead>
<tr>
<th>Wt% Addition</th>
<th>%Bi in Matte</th>
<th>%Bi in Slag</th>
<th>L&lt;sub&gt;Bi&lt;/sub&gt;&lt;sup&gt;m/s&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.169</td>
<td>0.008</td>
<td>21</td>
</tr>
<tr>
<td>0.125</td>
<td>0.356</td>
<td>0.014</td>
<td>25</td>
</tr>
<tr>
<td>0.25</td>
<td>0.356</td>
<td>0.014</td>
<td>25</td>
</tr>
</tbody>
</table>

The addition of elemental bismuth to the charge should portray behavior similar to doping the element into the matte phase. In this case, with reference to Section 2-5.2, if either phase becomes saturated with bismuth, any further additions will increase L<sub>Bi</sub><sup>m/s</sup>. As observed in Table 2-5.6, there is indeed an increase in the distribution ratio from 0.10 wt% additions to 0.125 wt% additions, which would be in agreement with the conclusion made by Johnson et al (1982). The data for 0.25 wt% addition of bismuth is suspect as it would appear not to include the presence of undissolved bismuth as explained in the previous paragraph. If the data included undissolved bismuth and if the assumption of undissolved bismuth being present in the matte phase is correct; then the distribution ratio would be expected to increase further from the present value of 25.

As it stands the equilibrium distribution ratio of bismuth between matte and slag under the conditions employed by Johnson et al. (1982) could be 21, however without any data at bismuth concentrations lower than 0.10 wt% or at concentrations between 0.10 wt% and 0.125 wt% to validate this, it is difficult to show any confidence in this value. Alternatively, taking into consideration the estimated error of ±3% of the amount of bismuth present in each phase, it could also be argued that a distribution ratio value of 21 is not significantly different from a value of 25. This would suggest the experiments with 0.125 wt% and 0.25 wt% additions may not be saturated after all.

As Johnson et al. (1982) suspected there may be saturation of bismuth species in both phases, they did not proceed to obtain distribution data.

Roghani et al. (2000) noted that although bismuth is in the same group (Vb) in the Periodic Table as antimony and arsenic, its distribution behavior is quite different. As observed in Figure 2-5.33, the distribution of bismuth increases with increasing matte grade. Above a matte grade of about 75 wt% Cu, the distribution of bismuth decreases abruptly. This is contrary to the trends set by antimony and arsenic. The authors explained this by stating that where the activity coefficients of arsenic and antimony in the matte decrease remarkably, the activity coefficient of bismuth in matte remains fairly constant.
in the range of high matte grade (Itagaki and Yazawa, 1983). The increase of oxygen potential at high matte grades is therefore dominant so bismuth distributes more preferentially into the slag.

![Figure 2-5.33: Effect of $P_{SO_2}$ on the distribution ratio of bismuth between matte and slag as a function of matte grade (Roghani et al., 2000).](image)

Figure 2-5.33 also shows that the distribution of bismuth increasingly favors the slag phase with increasing sulfur dioxide partial pressure. The distribution ratio for $P_{SO_2}$ of 0.1 atm is approximately double that at $P_{SO_2}$ of 1.0 atm.

Figure 2-5.34 shows the distribution of bismuth between slag and matte as a function of oxygen partial pressure.
Roghani et al. (2000) states that the slope of \( \log L_{\text{Bi}}^{s/m} - \log p_{O_2} \) is approximately \( \frac{3}{4} \), however upon closer inspection the slope has a value of approximately 0.4. This raises two possible conclusions regarding the state of bismuth dissolution in slag:

- Taking into account experimental errors, the slope being close to \( \frac{1}{2} \) suggests that bismuth dissolves in the slag as BiO
- The slope of 0.4 is a result of bismuth dissolving in both the metallic (Bi\(^0\)) and oxidic state (BiO or BiO\(_{1.5}\))

The Gibbs free energy of formation for various bismuth oxide compounds, from the HSC Chemistry v5.1 database shows that bismuth oxide does exist in both 2+ and 3+ states at 1573 K, but is slightly more stable in the 3+ state. This would suggest the latter conclusion is more likely to be correct, i.e. with the oxide present in the 3+ state.

\[
\frac{4}{3} \text{Bi}^{(l)} + O_2(g) = \frac{4}{3} \text{BiO}_{1.5}^{(l)} \quad \Delta G_{1573 \text{ K}}^{\circ} = -111.320 \text{ kJ} \quad [2-5.49]
\]

\[
2\text{Bi}^{(l)} + O_2(g) = 2\text{BiO}^{(s)} \quad \Delta G_{1573 \text{ K}}^{\circ} = -102.892 \text{ kJ} \quad [2-5.50]
\]

Mackey (1982) reported the distribution of bismuth under matte making conditions of 1503 K, \( p_{SO_2} \) of 0.29 atm and matte grade of 65 wt\% Cu as having a value of 4.5. The effect of temperature on the distribution ratio is investigated to validate the value reported by Mackey (1982).
With all other parameters kept constant, the effect of temperature on the distribution ratio of bismuth is found to be:

\[
\frac{L_{Bi}^{m/s}\text{(1573 K)}}{L_{Bi}^{m/s}\text{(1503 K)}} \approx \frac{K_{1503K}}{K_{1573K}} = \frac{7.033 \times 10^6}{2.560 \times 10^6} \approx 2.8
\]  

[2-5.52]

Considering the data provided by Roghani et al. (2000) in Figure 2-5.33, by approximation, the distribution coefficient of bismuth at \(p_{SO_2}\) of 0.1 atm is approximately 1.2 times that at \(p_{SO_2}\) of 0.3 atm.

The distribution coefficient, \(L_{Bi}^{m/s}\), for the value reported by Mackey (1982) adjusted for conditions of 1573 K and \(p_{SO_2}\) of 0.1 atm was found to be ~15. The distribution ratio of bismuth by Roghani et al. (2000) for a matte grade of 65 wt% Cu under the same conditions is approximately 3.5. There is a significant difference between these two values. Considering Mackey’s reported value is from industry, approach to equilibrium and the entrainment of one phase in the other can cause discrepancies.

Summary of findings:

- There is very limited data available for bismuth distribution between matte and slag.
- There is no evidence to support the saturation of matte and slag with bismuth species.
- Available distribution data shows that \(L_{Bi}^{m/s}\) increases with increasing matte grade.
- Evidence suggests that bismuth dissolves in the slag phase in both the metallic and oxidic states (\(Bi^{3+}\)).

b. **Cadmium & Zinc**

Cadmium

To date there has not been any research work directly targeted at the distribution behavior of cadmium in copper base metal production circuits. Mackey (1982) in his
review paper however, did list the observed distribution coefficient for cadmium for the Outokumpu flash furnace under matte making conditions of 1503 K, $p_{SO_2}$ of 0.29 atm, and 65 wt% Cu in matte. The author quotes $L_{Cd^{m/s}}$ as having a value of 3.4; distributing preferentially into the matte phase. The author lists his source of data as coming from a private communication with Mäkinen J. from Outokumpu Oy in 1980.

Observing the Gibbs free energy for the cadmium sulfide-cadmium oxide equilibrium reaction from HSC 5.1:

$$\text{CdS(s)} + \frac{1}{2}\text{O}_2(g) = \text{CdO(s)} + \frac{1}{2}\text{S}_2(g) \quad \Delta G^{\circ}_{\text{1503 K}} = -35.731 \text{ kJ} \quad [2-5.53]$$

The Gibbs free energy suggests that cadmium is slightly more stable in the oxide form, contrary to the suggestion that cadmium distributes preferentially into the matte phase. The activity coefficients of species in matte and slag, however, can greatly influence the distribution coefficient.

It is also important to note that cadmium is a very volatile metal and so the majority would be expected to be present in the gas phase. The Gibbs free energy data from HSC Chemistry for the formation of cadmium vapor emphasizes this fact:

$$\text{Cd(l)} = \text{Cd(g)} \quad \Delta G^{\circ}_{\text{1573 K}} = -50.234 \text{ kJ} \quad [2-5.54]$$

$$K_{1573 K} = 4.657 \times 10^1$$

Summary of findings:

- The distribution of cadmium in copper smelting is not very well known, with existing distribution coefficient values based on data from industrial operations.
- Existing data shows cadmium favors the matte phase.
- The volatility of cadmium leads to the belief that it is present largely in the gas phase.

Zinc

The distribution of zinc in matte making operations has also not been the subject of distribution experiments. The data quoted regarding zinc distribution are industrial values. Mackey (1982) quotes zinc distribution in matte making conditions (1503 K, $p_{SO_2} = 0.29$ atm, 65 % Cu in matte) within the Outokumpu flash furnace as having a value of 0.3.
distributing preferentially into the slag phase. The preferential distribution of zinc into the slag phase is even more apparent in matte making conditions for the Noranda Process (1473 K, tuyeres air 21% O\textsubscript{2}, 75% Cu in matte). The author quotes $L_{\text{Zn}}^{m/s}$ under these conditions as having a value of 0.08. This is almost 4 times smaller than that for the Outokumpu flash furnace i.e. a much larger proportion of the zinc in the furnace reports to the slag.

The equilibrium constant for the zinc sulfide-zinc oxide equilibrium reaction from HSC 5.1 is:

$$\text{ZnS(s)} + \frac{1}{2} \text{O}_2(g) = \text{ZnO(s)} + \frac{1}{2} \text{S}_2(g) \quad K_{1503 \text{ K}} = 4.183 \times 10^2$$  \hspace{1cm} [2-5.55]

$$K_{1473 \text{ K}} = 4.799 \times 10^2$$

The Gibbs free energy for the equilibrium reaction in equation [2-5.55] at 1503 K is -75.432 kJ, showing that the oxide form is more stable and thus that zinc favors the slag phase.

Comparing the data provided for the Outokumpu flash furnace and the Noranda process on the basis of temperature difference:

$$\frac{L_{\text{Zn}}^{m/s}}{L_{\text{Zn}}^{m/s}} = \frac{K_{1473 \text{ K}}}{K_{1503 \text{ K}}} \approx 1.2$$  \hspace{1cm} [2-5.56]

There is also a difference in the partial pressures of sulfur and oxygen for the distribution coefficients reported. The sulfur and oxygen partial pressures can be read off the chemical potential diagram for the Outokumpu (65 wt% Cu, $p_{\text{SO}_2} = 0.3$ atm) and Noranda (75 wt% Cu, $p_{\text{SO}_2} = 0.2$ atm) conditions.

$$\frac{L_{\text{Zn}}^{m/s}}{L_{\text{Zn}}^{m/s}} = \left( \frac{p_{\text{S}_2}}{p_{\text{O}_2}} \right)_{\text{Outokumpu}}^{1/2} = \frac{501.2}{89.1} \approx 5.6$$  \hspace{1cm} [2-5.57]

Taking both factors into account, the distribution ratio for the Outokumpu flash furnace is approximately 6.5 times larger than for the Noranda process. This is a considerably larger difference compared to that which was reported by Mackey (1982).
Similarly to cadmium, zinc is a volatile metal and is likely to be present largely in the gas phase. The Gibbs free energy data for the formation of zinc vapor shows that it is slightly less volatile than cadmium at 1573 K:

\[ \Delta G^\circ \text{Zn} (g) = -38.021 \text{ kJ} \]  

[2-5.58]

Summary of findings:

- The distribution of zinc in copper smelting is not very well known. Existing distribution coefficient values are reported from industrial operations.
- Existing data shows zinc favors the slag phase.
- The volatility of zinc leads to the belief that it is present largely in the gas phase.

c. COBALT & NICKEL

Cobalt

Yazawa (1980) performed cobalt distribution experiments for the gas-slag-matte-copper system as previously discussed in Section 2-5.4a.

Figure 2-5.35 shows the cobalt distribution data between matte and slag. The filled data points represent experiments conducted using nitrogen to generate low oxygen potentials whereas the unfilled data points were from experiments performed under varying sulfur dioxide partial pressures, corresponding to varying oxygen potentials.
Figure 2-5.35: Distribution ratio of cobalt between matte and slag plotted against oxygen potential at 1573 K (Yazawa, 1980).

As observed from Figure 2-5.35, the distribution coefficient of cobalt decreases with increasing oxygen potential; which is expected as an increase in the oxygen partial pressure will lower the cobalt content in the matte via oxidation. It is also apparent that the trend line fits both the data at low oxygen potential as well as at high oxygen potential. This indicates that cobalt is dissolved in the slag in a single oxidation state over the whole range of oxygen partial pressures. The plot of $\log L_{Co^{m/s}}-\log p_{O_2}$ in Figure 2-5.35 shows a slope of 0.5, indicating that the form of cobalt dissolution is $Co^{2+}$.

Mwema et al. (1995) performed distribution studies for cobalt in copper smelting processes. Their research was concentrated on metal-slag equilibrium; however they did model the behavior of cobalt under matte smelting conditions using the data collected from their metal-slag experiments. From their model they deduced the distribution coefficient of cobalt between matte and slag as shown in Figure 2-5.36.
Chapter 2: Literature Review

While it is not clear what prevailing oxygen partial pressure was assumed by Mwema et al. (1995), their distribution data are largely in agreement with that of Yazawa (1980) in that the distribution ratio values are similar in magnitude and show the same relationship with varying matte grades.

Choi and Cho (1997) examined the distribution behavior of cobalt between nickel-copper-iron matte and silica-saturated iron silicate slag as a function of temperature, matte grade and oxygen partial pressure. The weight ratio of nickel to copper in the matte had a fixed value of 2. It is believed that because nickel sulfide and copper sulfide are chemically similar, direct comparison of distribution data between copper matte and copper-nickel matte should be reasonable. Figure 2-5.37 shows the distribution of cobalt between matte and slag at 1523 K as a function of matte grade.

Figure 2-5.36: Distribution ratio of cobalt between matte and slag as a function of matte grade at 1623 K (Mwema et al., 1995).

![Figure 2-5.36: Distribution ratio of cobalt between matte and slag as a function of matte grade at 1623 K (Mwema et al., 1995).](image_url)
Choi and Cho (1997) observed that the distribution of cobalt is greatly dependant on matte grade, decreasing linearly with increasing matte grade. This trend is similarly observed by Mwema et al. (1995) and Yazawa (1980). The authors also studied the effect of slag additives on the distribution of cobalt between matte and slag, the results of which are shown in Figure 2-5.38.

From the data, Choi and Cho (1997) concluded that addition of lime, alumina or magnesia increases the distribution ratio of cobalt, \( L_{Co}^{m/s} \). An increase in \( L_{Co}^{m/s} \) due to additions in the slag phase must be caused by a decrease in cobalt content in the slag. Considering the activity of cobalt oxide in slag is fixed by the prevailing oxygen potential...
and temperature, a decrease in cobalt content in slag translates to an increase in activity coefficient of cobalt oxide in the slag. Teague (1999) showed that CoO reacts with SiO₂ to form Co₂SiO₄. Lime, magnesia and (to a lesser extent) alumina would react more strongly with SiO₂ compared to cobalt, and thus lead to an increase in the activity coefficient of cobalt oxide in slag.

Choi and Cho (1997) examined the effect of temperature on the distribution ratio of cobalt. Comparisons were made for slags containing 8 wt% of lime at 1523 K and 1573 K. The results are shown in Figure 2-5.39 below.

![Figure 2-5.39: Effect of temperature on the distribution coefficient of cobalt (Choi and Cho, 1997).](image)

The authors concluded that the distribution ratio of cobalt increases with increasing temperature. Checking the equilibrium constant for the cobalt sulfide-cobalt oxide equilibrium reaction in HSC Chemistry v5.1:

\[
\text{CoS(l)} + \frac{1}{2}\text{O}_2(g) = \text{CoO(s)} + \frac{1}{2}\text{S}_2(g) \quad K_{1523 \text{K}} = 8.342 \times 10^2 \quad \text{(2-5.59)}
\]

The distribution coefficient is proportional to:
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The term $K$ is the equilibrium constant for the reaction in equation [2-5.59]. When all other parameters are constant, the effect of temperature on the distribution ratio of cobalt is observed:

$$
\frac{L_{Co}^{m/s}}{K_{573K}} \propto \frac{1}{K} \left( \frac{P_{SO_2}}{P_{O_2}} \right) \gamma_{Co} \gamma_{M} \gamma_{S} \gamma_{M} \gamma_{S} \gamma_{M} \gamma_{S}
$$

[2-5.60]

The data from Figure 2-5.39 shows that the distribution ratio at 1573 K is on average 1.1 times larger than that at 1523 K. Equation [2-5.61] shows a difference of approximately 1.3, confirming the conclusion made by Choi and Cho (1997) regarding the effect of temperature on the distribution coefficient of cobalt.

Mackey (1982) reported the distribution coefficient of cobalt under matte making conditions of 1503 K, $P_{SO_2}$ of 0.29 atm and 65 wt% Cu in matte as having a value of unity.

Summary of findings:

- There is good agreement between cobalt distribution data available in literature.
- The distribution ratio of cobalt, $L_{Co}^{m/s}$, decreases with increasing matte grade.
- Cobalt dissolved in the slag in the $Co^{2+}$ state.
- Slag additives of lime, magnesia and alumina slightly increases $L_{Co}^{m/s}$.
- $L_{Co}^{m/s}$ is approximately 5 for a matte grade of 50 wt% Cu.

Nickel

Yazawa (1980) examined the distribution ratio of nickel between matte and slag by performing nickel distribution experiments for the gas-slag-matte-copper system as described previously. The experimental data are shown in Figure 2-5.40. The filled data points represent experiments conducted using nitrogen to generate low oxygen potentials. The unfilled data points were from experiments performed under varying sulfur dioxide partial pressures, corresponding to varying oxygen potentials as shown in the figure.
Figure 2-5.40: Distribution ratio of nickel between matte and slag plotted against oxygen potential at 1573 K (Yazawa, 1980).

Figure 2-5.40 shows that the distribution of nickel decreases linearly with increasing matte grade. The trend line for the plot of log \( \ln^{\text{m/s}} \)-log \( P_{O_2} \) shows a slope of approximately 0.5, indicating the Ni\(^{2+} \) state for nickel dissolution in slag.

Nickel and cobalt are chemically very similar metals, yet the distribution ratio of nickel (Figure 2-5.40) is approximately 15 times higher than that of cobalt (Figure 2-5.35) under the same conditions. In order to account for this difference, the equilibrium constants for the distribution equations for the two elements are compared. The equilibrium constant for the nickel sulfide-nickel oxide equilibrium reaction from HSC Chemistry v5.1:

\[
\text{NiS}(l) + \frac{1}{2} \text{O}_2(g) = \text{NiO}(s) + \frac{1}{2} \text{S}_2(g) \quad K_{1573 \text{ K}} = 1.428 \times 10^2 \quad [2-5.62]
\]

The equilibrium constant for the cobalt sulfide-cobalt oxide equilibrium reaction is given in equation [2-5.59]. The distribution coefficient, \( L_{\text{m/s}} \), is inversely proportional to the equilibrium constant as shown in equation [2-5.60], thus:
From equation [2-5.63], the distribution coefficient of nickel is approximately 5.3 times larger than that of cobalt based on the difference in equilibrium constants for the distribution reactions of the two elements. This factor is not enough to explain the large difference between the distribution ratios of nickel and cobalt under the same conditions.


Table 2-5.8: Observed distribution coefficients for nickel between matte and slag from industry (*Mackey, 1982; +Larouche, 2001).

<table>
<thead>
<tr>
<th>Furnace Type</th>
<th>Matte Grade (%Cu)</th>
<th>%O₂</th>
<th>( L_{\text{Ni}}^{\text{m/s}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Noranda</td>
<td>75</td>
<td>21</td>
<td>1.0</td>
</tr>
<tr>
<td>+Noranda</td>
<td>70</td>
<td>45</td>
<td>4.5</td>
</tr>
<tr>
<td>+ISA</td>
<td>56.9</td>
<td>45</td>
<td>14.6</td>
</tr>
<tr>
<td>+Reverberatory</td>
<td>52</td>
<td>21</td>
<td>8.9</td>
</tr>
<tr>
<td>+Reverberatory</td>
<td>41</td>
<td>21</td>
<td>2.6</td>
</tr>
</tbody>
</table>

The data compiled are for industrial smelting systems and are very unlikely to be under equilibrium conditions.

Summary of findings:

- The distribution coefficient of nickel, \( L_{\text{Ni}}^{\text{m/s}} \), decreases with increasing matte grade.
- The form of nickel dissolution in slag is the Ni\(^{2+}\) state.
- The difference in nickel and cobalt distribution can be accounted for by the difference in the equilibrium constants of their respective distribution reactions.

d. **LEAD & TIN**

Figure 2-5.41 shows the sulfur-oxygen potential diagram for the silica-saturated Cu-Fe-S-O system at 1573 K with shaded zones designating areas investigated by Kaiura et al. (1980), Mackey (1982) and Roghani et al. (2000).
Kaiura et al. (1980) determined the equilibrium distribution coefficient of lead between the matte, slag and metallic phases in the silica-saturated, copper smelting system. The experiments were carried out by simultaneously equilibrating the various phases in silica crucibles at 1573 K. The conditions investigated include iron and copper alloy saturation at low oxygen potentials as well as constant sulfur dioxide partial pressures of 0.01 and 0.1 atm for matte grades up to 75 wt% Cu.

Figure 2-5.42 shows the results for experiments performed at low oxygen potentials.
The distribution coefficient of lead between matte and slag at metal saturation showed a maximum at a matte grade of 45 wt% Cu, heavily favoring the matte phase. Under the conditions used for these experiments, Kaiura et al. (1980) stated that a matte grade of 45 wt% Cu corresponds quite closely to the composition at which iron and copper alloy coexist, i.e. point r on the chemical potential diagram (Figure 2-5.41). Kaiura et al. (1980) adopted oxidic (PbO) and sulfidic (PbS) dissolution of lead in slag to explain the maximum in the plot of L_{Pb}^{m/s} versus matte grade. This twin species dissolution mechanism in slag was previously proposed by Nagamori (1974) to explain copper losses to fayalite slag from low grade matte. Nagamori (1974) observed that copper losses to slag were considerably greater than that attributed to oxidic dissolution of copper and also that the solubility of copper in slag was related to the presence of sulfur in the slag. From these observations, Nagamori (1974) developed the concept of sulfidic dissolution. Figure 2-5.43 shows the oxidic, sulfidic and total dissolved copper content in slag as modeled by Nagamori (1974).
It is evident from Figure 2-5.43 that sulfidic dissolution of copper in slag is predominant for matte grades up to 50 wt% Cu while oxidic dissolution is the significant mechanism for copper solubility at higher matte grades. A similar mechanism was suggested for lead dissolution in slag by Nagamori and Mackey (1978).

In the matte phase, Kaiura et al. (1980) suggested the presence of both sulfidic and metallic dissolution of lead. Kaiura et al. (1980) suggested this because while the lead content in matte was high, the activity of the sulfide species, PbS, in matte was relatively low, thus suggesting the presence of another dissolved species; most likely metallic lead. Based on this, the proposed species of lead existing in the system are as follows:

- \([\text{Pb}^0]\) in the metal phase
- \(\{\text{Pb}^0\}\) and \(\{\text{PbS}\}\) in the matte phase
- \(\{\text{PbO}\}\) and \(\{\text{PbS}\}\) in the slag phase

Kaiura et al. (1980) modeled the distribution of metallic and sulfidic lead in matte as a function of matte grade and concluded that a large part of lead dissolved in matte in
the metallic form. The metallic fraction of lead in matte was also observed to increase with increasing matte grade as shown in Figure 2-5.44.

Figure 2-5.44: Distribution of metallic and sulfidic lead in matte as a function of matte grade (Kaiura et al., 1980).

The authors also modeled the oxidic and sulfidic fractions of lead in slag and showed that the sulfidic contribution decreased with increasing matte grade (Figure 2-5.45). Examination of the chemical potential diagram will show that this trend is related to the decrease in \( p_{S_2} \) and increase in \( p_{O_2} \) associated with increasing matte grade at constant \( p_{SO_2} \).

Figure 2-5.45: Fractional distribution of lead dissolved in slag in sulfidic and oxidic forms (Kaiura et al., 1980).
Based on their model, Kaiura et al. (1980) concluded that:

- The increasing trend in $L_{Pb}^{m/s}$ for matte grades below 45 wt% Cu was attributed to a decrease in sulfidic dissolution in slag.
- The decreasing trend in $L_{Pb}^{m/s}$ between matte grades of 45-80 wt% Cu was due to an increase in oxidic dissolution.

Kaiura et al. (1980) also performed distribution experiments at higher oxygen potentials, using the $SO_2-CO_2-H_2-Ar$ gas mixture. Figure 2-5.46 shows the distribution data at constant sulfur dioxide partial pressures of 0.01 atm and 0.1 atm.

Comparing distribution ratio values from Figures 2-5.42 and 2-5.46 for matte grades of 45 wt% Cu or greater, it can be seen that the values at constant sulfur dioxide partial pressures are approximately half of those at metal saturation. This is expected as the higher oxygen potentials associated with increasing sulfur dioxide partial pressure would increase the activity of PbO thus increasing the lead content in slag and ultimately reducing the distribution ratio of lead between matte and slag. The scatter present in the data in Figure 2-5.46 makes it difficult to differentiate between the experiments conducted at constant $p_{SO_2}$ of 0.01 atm and 0.1 atm.

Figure 2-5.46: Distribution coefficient of lead as a function of matte grade at higher oxygen potentials (Kaiura et al., 1980).
Roghani et al. (2000) performed distribution experiments with copper matte and silica-saturated iron silicate slag containing 5 to 10 wt% magnesia under high partial pressures of sulfur dioxide at 1573 K. The authors controlled the partial pressures of sulfur dioxide and sulfur using a mixture of Ar-SO$_2$-S$_2$ gas. The results of their experiments are shown in Figure 2-5.47.

![Figure 2-5.47: Effect of sulfur dioxide partial pressure on the distribution ratio of lead between matte and slag for varying matte grades (Roghani et al., 2000).](image_url)

From Figure 2-5.47 it can be seen that the value of $L_{Pb}^{m/s}$ increases with increasing matte grade. This contradicts the earlier trend for the data by Kaiura et al. (1980) in Figure 2-5.46 which showed decreasing $L_{Pb}^{m/s}$ with increasing matte grade. While these two trends contradict, taking into account the scatter present in the data and possible errors, both data sets could show $L_{Pb}^{m/s}$ to be almost independent of matte grade. This could imply that there is a compensating change in the activity coefficients of PbS and PbO to cause the constancy.

Roghani et al. (2000) also shows in Figure 2-5.47 that the value of $L_{Pb}^{m/s}$ for a given matte grade decreases with increasing $P_{SO_2}$. This further emphasizes the amount of scatter present in the data by Kaiura et al. (1980) in Figure 2-5.46.

Figure 2-5.48 shows the distribution of lead between slag and matte as a function of oxygen partial pressure.
A plot of $\log L_{Pb}^{m/s}$ vs $\log pO_2$ can provide data regarding the state of lead in the slag provided that:

- At a given matte grade, the activity coefficients of lead in the slag and matte phases do not change with $pSO_2$
- The form of lead dissolution in the matte is independent of $pS_2$

Roghani’s analysis assumes that lead is present in the matte largely as neutral atoms, and thus is independent of $pS_2$. Roghani reported that the activity ratio, $\{a_{Pb}\}/\{a_{PbS}\}$, is not large enough for metallic dissolution to be predominant in the matte phase. The distribution coefficient of lead would therefore not be independent of $pS_2$ and therefore the plot of $\log L_{Pb}^{m/s}$ vs $\log P_{O_2}$ would not provide information regarding the state of lead dissolution in slag.

Mackey (1982) quotes $L_{Pb}^{m/s}$ under matte making conditions (1503 K, $pSO_2 = 0.29$ atm, 65 %Cu in matte) within the Outokumpu flash furnace as having a value of 2.1. In order to compare the value quoted by Mackey (1982) with that of Kaiura et al. (1980) or Roghani et al. (2000), the distribution ratio must be adjusted for temperature and $pSO_2$ so that the conditions are similar. The equilibrium constant for the lead sulfide-lead oxide equilibrium reaction from HSC Chemistry v5.1:

$$\text{PbS(l)} + \frac{1}{2}\text{O}_2(g) = \text{PbO(l)} + \frac{1}{2}\text{S}_2(g) \quad K_{1503\,K} = 3.872 \times 10^1 \quad [2.5.64]$$
Values of $P_{S_2}$ and $P_{O_2}$ can be read off the chemical potential diagram for $P_{SO_2}$ of 0.1 and 0.29 atm, for a fixed matte grade of 65 wt% Cu to account for the difference in sulfur dioxide oxygen potential.

\[
K_{1573K} = 3.294 \times 10^1
\]

The adjusted distribution ratio (1573 K, $P_{SO_2} = 0.1$ atm, 65 %Cu in matte) has a value of ~2.4. This value is in close agreement with Kaiura et al. (1980) which shows a value of ~2.5 for a matte grade of 65 wt% Cu.

Summary of findings:

- Kaiura's and Roghani's data for lead distribution at constant $P_{SO_2}$ show similar values and taking into account the scatter present in the data could show independence of $L_{Pb}^{m/s}$ with matte grade.
- Lead is believed to exist in matte in the metallic and sulfidic form and in the slag in the sulfidic and oxidic form. The predominant species in each phase is dependent upon the conditions under consideration.
- For mattes containing 50 wt% Cu, $L_{Pb}^{m/s}$ was reported to be ~13 for reducing conditions and ~5 for more oxidizing conditions.

Tin

Park, Nakazawa and Yazawa (1982) examined the distribution behavior of tin between copper, matte and slag at 1573 K. The experiments were conducted under oxidizing smelting and reducing smelting conditions. For oxidizing conditions the slag and matte were equilibrated under constant sulfur dioxide partial pressure of either 0.1 atm or 0.01 atm. For reducing conditions, slag and matte were equilibrated with liquid copper using a $SO_2$-Ar gas mixture. The shaded zones in Figure 2-5.49 designate the regions with existing tin distribution ratio data.
Figure 2-5.49: Chemical potential diagram highlighting regions of existing tin distribution ratio data.

Figure 2-5.50 shows the distribution data compiled by Park et al. (1982) under reducing conditions. While there is quite a lot of scatter present in the data, it is apparent that the distribution ratio of tin decreases with increasing matte grade.
Figure 2-5.50: Distribution ratio of tin between matte and slag under coexistence of liquid copper (Park et al., 1982).

Figure 2-5.51 shows the data results by Park et al. (1982) under oxidizing conditions. The authors showed that at constant sulfur dioxide partial pressure, the distribution ratio of tin decreases with increasing matte grade. Park et al. (1982) also showed that increasing the partial pressure of sulfur dioxide decreases $L_{Sn^{m/s}}$ at all matte grades.

Figure 2-5.51: Distribution ratio of tin between matte and slag as a function of matte grade at 1573 K (Park et al., 1982).
Koike and Yazawa (1994) observed the distribution ratio of tin between matte and slag as a function of sulfur dioxide partial pressure at 1523 K. Experiments were performed under sulfur dioxide partial pressures of 0.05, 0.1 and 0.2 atm. Figure 2-5.52 shows the results of experiments performed by Koike and Yazawa (1994).

![Figure 2-5.52: Distribution ratio of tin between matte and slag as a function of matte grade at 1523 K (Koike and Yazawa, 1994).](image)

The data are in agreement with the trend observed by Park et al. (1982) in that the distribution ratio of tin is a decreasing function of matte grade. While the influence of $p_{SO_2}$ on $L_{Sn/m/s}$ is not very distinct for 0.05 and 0.1 atm, the data set at 0.2 atm is notably lower overall. This is also in agreement with the trend observed by Park et al. (1982) in that increasing $p_{SO_2}$ decreases $L_{Sn/m/s}$ at all matte grades.

Figure 2-5.53 compares the data from Koike and Yazawa (1994) and Park et al. (1982) for experiments performed at constant $p_{SO_2}$ of 0.1 atm. The filled data points are from Koike and Yazawa (1994) and the unfilled data points are from Park et al. (1982).
Figure 2-5.53: Distribution ratio of tin between matte and slag at constant $p_{\text{SO}_2}$ of 0.1 atm.

Figure 2-5.53 shows that the data are in very good agreement with both sets showing the same trend as a function of matte grade. The only observable difference would be that the data sets for Park et al. (1982) are on average ~1.3 times larger than that of Koike and Yazawa (1994). This difference is likely due to the different operating temperatures used by the two authors. In order to investigate this, equilibrium constant data for the tin oxide-tin sulfide equilibrium reaction was obtained from HSC v5.1:

\[
\text{SnS}(l) + \frac{1}{2} \text{O}_2(g) = \text{SnO}(l) + \frac{1}{2} \text{S}_2(g) \quad K_{1523 \text{K}} = 1.010 \times 10^3 \quad [2-5.66]
\]

\[
K_{1573 \text{K}} = 7.535 \times 10^2
\]

The effect of temperature on the distribution ratio of tin is observed:

\[
\frac{(L_{\text{Sn}^{\text{m/s}}})_{1573 \text{K}}}{(L_{\text{sn}^{\text{m/s}}})_{1523 \text{K}}} \propto \frac{K_{1523 \text{K}}}{K_{1573 \text{K}}} = \frac{1.010 \times 10^3}{7.535 \times 10^2} \approx 1.34 \quad [2-5.67]
\]

Equation 2-5.67 shows that the difference between the two data sets can be attributed to the difference in operating temperature.

Louey et al. (1999) studied the distribution of tin between copper matte and fayalite slag under reducing conditions at 1523 K. The experiments were performed under deoxidized
nitrogen gas for mattes containing 50 wt% Cu. Figure 2-5.54 shows the tin content in matte against the tin content in slag.

![Figure 2-5.54](image.png)

**Figure 2-5.54:** The equilibrium tin contents in fayalite slag and copper matte containing 50 wt% Cu at 1523 K (Louey et al. 1999).

The slope of the trend line for the data given in Figure 2-5.54 is the distribution ratio, $L_{Sn^{m/s}}$, and is quoted by Louey et al. (1999) as having a value of 2.8 ± 0.3. The prevailing oxygen partial pressure for Louey’s experiments is unknown; however the trend observed from the work of Koike and Yazawa (1994) indicates that tin increasingly favors the matte phase with decreasing oxygen partial pressure, i.e. $L_{Sn^{m/s}}$ increases with decreasing $pO_2$. Koike and Yazawa (1994) reported a tin distribution value of approximately 1.5 for matte containing 50 wt% Cu at 1523 K. The distribution coefficient reported by Louey et al. (1999) is approximately double that of Koike and Yazawa (1994) at the same temperature and matte grade and appears therefore to be reasonable since this conforms to the aforementioned trend.

Summary of findings:

- There is very good agreement between tin distribution data available in literature.
- The distribution ratio of tin between matte and slag decreases with increasing matte grade.
- For mattes containing 50 wt% Cu, $L_{Sn^{m/s}}$ was reported to be ~3 under reducing conditions and ~1.5 under oxidizing conditions.
e. **Selenium & Tellurium**

Selenium

Johnson et al. (1982) examined the distribution of selenium between matte and iron silicate slag at 1523 K, as well as the effect of slag additives on the distribution behavior. The authors fixed the partial pressure of sulfur dioxide at 0.1 atm and used a mixture of CO-CO$_2$ gas to control the partial pressure of oxygen to obtain various matte grades.

Figure 2-5.55 shows the concentration of selenium in matte and slag as a function of the concentration of elemental selenium added to the charge (0.5 to 0.75 wt% Se). The data are for distribution experiments between matte and slag at 1523 K and P$_{O_2}$ of $1 \times 10^{-8}$ atm, which corresponds to a matte grade of 60 wt% Cu.

![Figure 2-5.55: Effect of doping level on the distribution of selenium between matte and slag at 1523 K and P$_{O_2} = 1 \times 10^{-8}$ atm (Johnson et al., 1982).](image)

The authors concluded from Figure 2-5.55 that neither the matte nor slag was saturated with a selenium species at the doping levels used in their study. Table 2-5.9 shows the distribution ratios calculated for the data given in Figure 2-5.55.
Table 2-5.9: Distribution ratio of selenium as a function of selenium concentration in the charge.

<table>
<thead>
<tr>
<th>wt% Addition</th>
<th>%Se in Matte</th>
<th>%Se in Slag</th>
<th>$L_{Se}^{m/s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.58</td>
<td>0.007</td>
<td>83</td>
</tr>
<tr>
<td>0.75</td>
<td>1.44</td>
<td>0.016</td>
<td>90</td>
</tr>
<tr>
<td>0.75</td>
<td>1.53</td>
<td>0.019</td>
<td>81</td>
</tr>
</tbody>
</table>

As seen from Table 2-5.9, taking into account experimental errors, the distribution ratio values are not too different from each other. This supports the conclusion made by Johnson et al. (1982) that neither phase was saturated with a selenium species for the doping levels used.

Figure 2-5.56 shows the distribution of selenium between matte and slag at 1523 K as a function of matte grade.

![Figure 2-5.56: The distribution ratio of selenium between matte and slag as a function of matte grade at 1523 K (Johnson et al., 1982).](image)

It is apparent that selenium favors the matte phase, as would be expected considering selenium belongs in the same group as sulfur in the periodic table and both elements are chemically very similar. The trendline in Figure 2-5.56 shows that the distribution coefficient of selenium increases with increasing matte grade. The great amount of scatter evident at 60 wt% Cu in matte, however, presents some uncertainty to the actual relationship between distribution coefficient and matte grade. It could be argued that the two high value points at 60 wt% Cu are a result of some systematic error, which could lead to the conclusion that the distribution ratio of selenium is independent of matte grade.
Johnson et al. (1982) also studied the effects of slag additives on the distribution of selenium between slag and matte, the results of which are shown in Figure 2-5.57.

![Figure 2-5.57](image)

**Figure 2-5.57:** Effect of slag additives on the distribution ratio of selenium between matte and slag as a function of matte grade (Johnson et al., 1982).

Reiterating an earlier point, while Johnson et al. (1982) have decided to show an increase in selenium distribution coefficient with increasing matte grade for the line of ‘no additives’, the distribution coefficient of selenium could just as easily be shown to be independent of matte grade. The amount of uncertainty in the data presented by Johnson et al. (1982) really makes this point inconclusive.

From the data in Figure 2-5.57, Johnson et al. (1982) concluded that:

- Addition of lime (2.4 wt% to 9.1 wt%) doubles the distribution ratio of selenium at all matte grades.
- Addition of alumina (2.4 wt% to 9.1 wt%) increases the distribution ratio of selenium at all matte grades also by a factor of ~2.
- Addition of magnesia (0.7 wt% to 2.4 wt%) appeared to have no significant effect on the distribution ratio of selenium.

The authors’ conclusion for lime appears to be valid; however the data for lower additions of lime is very scattered. It is presumed that there should be a relationship between the distribution ratio of selenium and the amount of lime present; however this is not apparent in the data provided. There is also too much scatter in the data for the authors’ to arrive at their conclusion for the alumina and magnesia data sets. While a majority of data points do lie above the ‘no additives’ trend line, it is difficult to gauge the actual incremental effect of alumina additions on the distribution ratio of selenium between matte and slag. The data for magnesia shows scatter of data points above and below
the ‘no additives’ trend line making it impossible to agree with the conclusion made by Johnson et al. (1982).

Choi and Cho (1997) examined the distribution behavior of selenium between nickel-copper-iron matte and silica-saturated iron silicate slag as a function of temperature, matte grade and oxygen potential. The majority of their experiments were performed using argon gas. Additional experiments were performed using various CO-CO₂ gas mixtures to control the oxygen potential in the system. Selenium was added as powder at concentrations between 0.1 to 0.5 %. The different amounts of selenium added to the system were used to show selenium saturation did not occur in either of the molten phases. The weight ratio of nickel to copper in the matte was fixed at 2. Figure 2-5.58 shows the distribution of selenium between matte and slag as a function of matte grade at 1523 K.

![Figure 2-5.58](image)

**Figure 2-5.58**: Distribution coefficient of selenium as a function of matte grade (nickel + copper) at 1523 K (Choi and Cho, 1997).

It is seen from Figure 2-5.58 that L₆ₑ₅₉ increases with increasing matte grade, which would be in agreement with the conclusion presented by Johnson et al. (1982). The magnitude of the distribution coefficient between the two authors however is very different; with Johnson et al. (1982) reporting values much higher than Choi and Cho (1997). It is believed that because nickel sulfide and copper sulfide are chemically similar, direct comparison of distribution data between copper matte and copper-nickel matte should be reasonable.
The mechanism of dissolution of selenium in slag has been suggested by Nagamori et al. (1977) to be either monatomic (Se⁰) or molecular dissolution (FeSe). Nagamori et al. (1977) showed for the copper-fayalite slag system that the distribution ratio of selenium between slag and copper, $L_{Se^{0}/C}$, is proportional to $pO_2^{-1/2}$ for the range between $1 \times 10^{-10}$ atm to $3.6 \times 10^{-7}$ atm. This is shown in Figure 2-5.59, which also shows that the form of selenium dissolution is a combination of molecular and monatomic dissolution for oxygen pressures below $4 \times 10^{-8}$ atm. The monatomic form is predominant for oxygen potentials higher than $4 \times 10^{-8}$ atm.

**Figure 2-5.59:** Distribution coefficient of selenium between metallic copper and fayalite slag as a function of oxygen partial pressure (Nagamori et al., 1977).

It has been reported by Nagamori et al. (1975) that in the copper-white metal system, selenium is more stable in the sulfide phase. This is expected considering the chemical similarity between selenium and sulfur. The mechanism of selenium dissolution in the matte phase, however, remains unknown. This lack of knowledge makes it difficult to ascertain whether or not the data provided by Johnson et al. (1982) and Choi and Cho (1997) is valid.
Figure 2-5.60: Effect of oxygen partial pressure on the distribution coefficient of selenium at 1523 K (Choi and Cho, 1997).

Figure 2-5.60 confirms that the distribution coefficient of selenium between matte and slag, $L_{Se}^{m/s}$, increases slightly with increasing partial pressure of oxygen.

Choi and Cho (1997) also examined the effect of slag additives on the distribution coefficient of selenium between matte and slag, the results of which are shown in Figure 2-5.61.

![Figure 2-5.61: Effect of slag additives on the distribution of selenium between matte and slag as a function of matte grade at 1523 K (Choi and Cho, 1997).](image-url)
Chapter 2: Literature Review

From the data, Choi and Cho (1997) concluded that the presence of slag additives resulted in higher distribution coefficients of selenium at all matte grades; this observation being more distinct for lime additions and less so for magnesia. This observation compares well with the data by Johnson et al (1982). While the data for magnesia additions by Johnson et al. (1982) was inconclusive, Choi and Cho (1997) showed the addition of magnesia clearly increases the distribution coefficient of selenium, albeit not by much. It is odd that while both lime and magnesia are basic oxides (lime being more basic), lime shows significantly more profound effects on $L_{Se}^{m/s}$ whereas magnesia shows little to no effect. This was similarly observed in Johnson’s data, however their additions of magnesia (2.4 wt%) were much less compared to lime (9 wt%).

Choi & Cho (1997) also studied the effect of temperature on the distribution ratio of selenium by comparing results for slags containing 8 wt% of lime at 1523 K and 1573 K. The results are shown in Figure 2-5.62.

![Figure 2-5.62: Effect of temperature on the distribution coefficient of selenium (Choi and Cho, 1997).](image)

The authors concluded that the distribution ratio of selenium increases with increasing temperature. From the data, the distribution ratio at 1573 K is approximately 1.2 times that at 1523 K.
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Mackey (1982) reported the distribution ratio of selenium under matte making conditions of 1503 K, \( p_{SO_2} \) of 0.29 atm and matte grade of 65 wt% Cu as having a value of 28, which appear to be more supportive of Johnson’s findings.

Summary of findings:

- Selenium dissolution in slag is shown to be a combination of the anionic form, \( Se^{2-} \), and the monatomic form, \( Se^0 \). At oxygen partial pressures higher than \( 4 \times 10^{-8} \) atm, the monatomic form is predominant.
- The form of selenium dissolution in the matte is likely to be \( Se^{2-} \) by analogy with sulfur.
- The distribution data available in literature is not substantial enough to be conclusive but in general selenium was found to favor the matte phase.

Tellurium

Johnson et al. (1982) performed distribution studies for tellurium between matte and silica-saturated iron silicate slag. The authors doped between 0.1 to 0.75 wt% of elemental tellurium into the charge. Figure 2-5.63 shows the effect of doping level on the distribution of tellurium between matte and slag. The data are for distribution experiments between matte and slag at 1523 K and \( p_{O_2} \) of \( 1 \times 10^{-8} \) atm, which corresponds to a matte grade of 60 wt% Cu.

![Figure 2-5.63: Effect of doping level on the distribution of tellurium between matte and slag (Johnson et al., 1982).](image)
Johnson et al. (1982) concluded that saturation of the slag with a tellurium species occurs at very low levels. The data for the matte phase showed erratic nature; with 4 data points showing tellurium in matte as being independent of the amount of tellurium in the charge whereas the other points suggest increasing amount of tellurium in the matte phase with increasing tellurium in the charge. The authors suggested that the matte could be saturated with a tellurium species and that the inconsistent data for tellurium in the matte phase is caused by non-homogeneity of tellurium in the mattes. It must be noted that the trendline shown for tellurium content in the slag phase could just as easily be presented in other forms, for example a line of best fit for all the data points. There is simply not enough data to make a solid conclusion from the data provided.

Due to tellurium saturation in the phases and the inconsistency of the data, Johnson et al. (1982) did not further investigate the distribution of tellurium between matte and slag. The only conclusion that they reached is that tellurium heavily favors the matte phase, which is to be expected considering the chemical similarities between tellurium and sulfur.

Choi and Cho (1997) studied the distribution behavior of tellurium between nickel-copper-iron matte and silica-saturated iron silicate slag. The authors doped tellurium (0.1 to 0.5 %) into the charge in the form of pure metallic powder. The different amounts of tellurium doped into the system were used to show that tellurium saturation did not occur in the molten phases, contradicting the results reported by Johnson et al. (1982). Investigations were performed for the effect of temperature, slag additives and oxygen potential on the distribution coefficient of tellurium between matte and slag. Figure 2-5.64 shows the distribution of tellurium between matte and slag as a function of matte grade at 1523 K.

![Figure 2-5.64: Distribution coefficient of tellurium as a function of matte grade (nickel + copper) at 1523 K (Choi and Cho, 1997).](image)
From Figure 2-5.64, it can be seen that the distribution coefficient of tellurium between matte and slag increases with increasing matte grade, favoring the matte phase.

Similarly to selenium, Nagamori et al. (1977) reported the dissolution of tellurium in slag to be either monatomic (Te⁰) or molecular dissolution (FeTe). Nagamori et al. (1977) showed for the copper-fayalite slag system that the distribution ratio of tellurium between slag and copper, $L_{Te}^{s/c}$, is proportional to $p_{O_2}^{-1/2}$ for the range between $1 \times 10^{-10}$ atm to $3.6 \times 10^{-7}$ atm. This is shown in Figure 2-5.65, which also shows that the form of tellurium dissolution is a combination of molecular and monatomic dissolution for oxygen potentials below $1 \times 10^{-8}$ atm. The monatomic form is predominant for oxygen potentials higher than $1 \times 10^{-8}$ atm. Choi and Cho (1997) agreed that the dissolution of tellurium in the slag can be explained by either monatomic or molecular dissolution.

Similarly to selenium, the form of tellurium dissolution in the matte phase is unknown; however it is believed that the Te²⁻ form is likeliest.

Choi and Cho (1997) showed that the distribution coefficient of tellurium between matte and slag is a function of oxygen potential (Figure 2-5.66) and concluded that molecular dissolution occurs in the slag at the oxygen potentials used in their experiments.
Figure 2-5.66: Effect of oxygen partial pressure on the distribution coefficient of tellurium at 1523 K (Choi and Cho, 1997).

Figure 2-5.67 shows the effect of temperature on the distribution coefficient of tellurium between matte and slag.

Figure 2-5.67: Effect of temperature on the distribution coefficient of tellurium (Choi and Cho, 1997).
From Figure 2-5.67, it is observed that the distribution coefficient increases with increasing temperature, with the value of $L_{Te}^{m/s}$ at 1573 K approximately 1.25 times larger than that at 1523 K.

Choi and Cho (1997) also examined the effects of slag additives on the distribution coefficient of tellurium. Figure 2-5.68 shows the authors’ findings.

Choi and Cho (1997) concluded that the presence of slag additives clearly resulted in higher distribution coefficients of tellurium at all matte grades.

Mackey (1982) reported the distribution ratio of tellurium under conditions of 1473 K, 21% $O_2$ in tuyeres air and matte grade of 75 wt% Cu as having a value of 13 which compares rather well with the data presented by Choi and Cho (1997).

Summary of findings:

- Tellurium dissolution in slag is shown to be a combination of the anionic form, $Te^{2-}$, and the monatomic form, $Te^0$. At oxygen partial pressures higher than $1x10^{-8}$ atm, the monatomic form is predominant.
- The form of tellurium dissolution in the matte is likely to be $Se^{2-}$ by analogy with sulfur.
- There is not enough data available to validate the results presented by Choi and Cho (1997).
- In general tellurium distributes preferentially into the matte phase.
Park, Nakazawa and Yazawa (1982) determined the distribution ratios of molybdenum between slag, matte and copper in the silica-saturated copper smelting system at 1573 K under reducing and oxidizing conditions. For reducing conditions, slag and matte were equilibrated with liquid copper. For oxidizing conditions, slag and matte were equilibrated under constant sulfur dioxide partial pressure of 0.1 or 0.01 atm. Figure 2-5.69 shows the distribution data under reducing condition. It is observed that the distribution ratio of molybdenum, \( L_{Mo}^{m/s} \), is approximately 0.14 for matte containing 60 wt% Cu. Molybdenum distributes more preferentially into the slag phase as the matte grade increases.

![Figure 2-5.69: Distribution ratio of molybdenum between slag and matte under coexistence of liquid copper at 1573 K (Park et al., 1982).]

Figure 2-5.70 shows the results for molybdenum distribution experiments conducted at constant sulfur dioxide partial pressures of 0.01 and 0.1 atm. It is noted that the distribution coefficient does not change considerably between the two data sets at different \( P_{SO_2} \)'s. For a matte containing 60 wt% Cu, the distribution ratio of molybdenum, \( L_{Mo}^{m/s} \), was found to be 0.11 for experiments under \( P_{SO_2}=0.01 \) atm and 0.09 for experiments under \( P_{SO_2}=0.1 \) atm. The results show that the distribution ratio of molybdenum, \( L_{Mo}^{m/s} \), decreases with increasing oxygen potential. Park et al. (1982) stated that this is due to molybdenum having a high affinity towards oxygen.
Westland and Webster (1989) performed distribution studies on molybdenum between slag and copper matte at 1573 K. The authors determined the distribution coefficient for molybdenum as a function of matte grade under a controlled atmosphere of $P_{O_2}=5\times10^{-11}$ atm. They also performed experiments at constant sulfur dioxide partial pressures of 0.1 and 0.01 atm. Westland and Webster concluded from the experimental data under reducing conditions (Figure 2-5.71) that the distribution coefficient of molybdenum, $L_{Mo}^{m/s}$, decreases with increasing matte grade, which is in agreement with the findings of Park et al. (1982). It is also noted from Figure 2-5.71 that the distribution coefficient of molybdenum for matte containing 40 wt% Cu is approximately 1. This would mean that molybdenum distribution favors the matte phase for low grade mattes (<40 wt% Cu).
Figure 2-5.71: Distribution of molybdenum between fayalite slag and matte as a function of matte grade under reducing conditions of log $P_{O_2} = -10.3$ at 1573 K (Westland and Webster, 1989).

Figure 2-5.72 shows Westland and Webster’s results for experiments performed at $P_{SO_2} = 0.01$ atm and 0.1 atm. Similarly to the data presented by Park et al. (1982), there is very little difference between the distribution coefficients at 0.01 and 0.1 atm; with the distribution coefficient of molybdenum for mattes containing 60 wt% Cu being 0.08 for experiments at $P_{SO_2} = 0.01$ atm and 0.11 for experiments at $P_{SO_2} = 0.1$ atm. There is a slight discrepancy between the data presented by the two authors. Park et al. (1982) found the distribution data at 0.01 atm to be slightly higher than that at 0.1 atm, however Westland and Webster’s data shows the reverse. While a valid explanation for the opposing trends is reported, the difference between distribution data at 0.1 atm and 0.01 atm is small so it is fair to say that the data by both authors are still in good agreement.
Effect of $P_{SO_2}$ on $L_{Mo}^{m/s}$

\[ \times 0.1 \text{ atm } 1300^\circ C \\
\triangle 0.01 \text{ atm } 1300^\circ C \]

**Figure 2-5.72**: Effects of $P_{SO_2}$ on the distribution of molybdenum between matte & slag phases for varying matte grades (Westland and Webster, 1989).

Summary of findings:

- There is good agreement between molybdenum distribution data available in literature.
- The distribution ratio of molybdenum, $L_{Mo}^{m/s}$, decreases with increasing matte grade.
- $L_{Mo}^{m/s}$ is approximately 0.1 for a matte grade of 60 wt% Cu.

g. **SILVER & GOLD**

Silver

Takeda and Roghani (1993) performed distribution experiments to examine the distribution equilibrium of silver between copper matte and silica-saturated iron silicate slag under a flow of 10% sulfur dioxide at 1573 K. Figure 2-5.73 shows the results of their experiments. The distribution ratio of silver between slag and matte was shown to decrease with increasing matte grade up to 65 wt% Cu. Takeda and Roghani attributed this to sulfide dissolution of silver in slag decreasing due to decreasing sulfur content in the slag (Figure 2-5.74) with increasing matte grade. This appears to be a valid observation as the trendlines in both Figures 2-5.73 and 2-5.74 are very similar up to 65 wt% Cu. Above 65 wt% Cu, the distribution ratio of silver, $L_{Ag}^{m/s}$, increases sharply.
Roghani et al. (2000) performed distribution studies for silver between matte and slag at 1573 K under constant sulfur dioxide partial pressures of 0.1, 0.5 or 1.0 atm. Figure 2-5.75 illustrates the author’s findings.
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The data in Figure 2-5.75 clearly illustrates that silver distributes highly preferentially into the matte phase. The distribution of silver increases preferentially into the matte phase with increasing matte grade up to approximately 65 wt% Cu in matte and then sharply increases at higher matte grades. The data by Roghani et al. (2000) are in excellent agreement with the study by Takeda and Roghani (1993). Roghani et al. (2000) also examined the distribution of silver at sulfur dioxide partial pressures of 0.5 and 1.0 atm and found that the dependency of $L_{Ag}^{m/s}$ on $P_{SO_2}$ is insignificant.

Summary of findings:

- There is good agreement between published distribution data for silver.
- Silver distributes heavily into the matte phase, the distribution coefficient of silver, $L_{Ag}^{m/s}$, for mattes containing 50 wt % Cu is approximately 100.

Gold

Henao, Yamaguchi and Ueda (2006) examined the distribution behavior of gold between copper matte and iron silicate slag at 1573 K. The experiments were performed under a fixed sulfur dioxide partial pressure of 0.1 atm for matte grades between 40 and 70 wt% Cu. Figure 2-5.76 shows the gold distribution data. Gold was found to heavily favor the matte phase. The distribution coefficient of gold, $L_{Au}^{m/s}$, was reported to be roughly constant at a value of 1000 for matte grades up to 60 wt% Cu.
Summary of findings:

- Gold distribution heavily favors the matte phase with a distribution coefficient, $L_{Au^{m/s}}$, of 1000 for matte grades up to 60 wt% Cu.

h. PALLADIUM, PLATINUM, RHODIUM & RUTHENIUM

Henao et al. (2006) examined the distribution behavior of precious metals including platinum, palladium, rhodium and ruthenium between copper matte and iron silicate slag at 1573 K. The experiments were performed in magnesia crucibles under a fixed sulfur dioxide partial pressure of 0.1 atm for matte grades between 40 and 70 wt% Cu. Figure 2-5.77 shows the distribution ratios of platinum and palladium as a function of matte grade. Both palladium and platinum are seen to heavily favor the matte phase. The distribution coefficient for palladium, $L_{Pd^{m/s}}$, has a constant value of approximately 800 for mattes containing 40 to 60 wt% Cu. The distribution coefficient for platinum, $L_{Pt^{m/s}}$, is also constant for matte grades between 40 and 60 wt% Cu and has a value of 700.
**Figure 2-5.77:** Distribution ratio of palladium and platinum between slag and matte phases as a function of matte grade under $p_{SO_2}$ of 0.1 atm and at 1573 K (Henao et al., 2006).

Figure 2-5.78 shows the distribution ratios for rhodium and ruthenium between slag and matte at 1573 K. Ruthenium and rhodium both exhibit strong preferential distribution towards the matte phase. The distribution ratio of rhodium, $L_{Rh}^{m/s}$, is approximately 100 for mattes containing 40 to 60 wt% Cu. The distribution coefficient of ruthenium, $L_{Ru}^{m/s}$, is approximately 500 for matte grades between 40 to 60 wt% Cu.

**Figure 2-5.78:** Distribution ratio of rhodium and ruthenium between slag and matte as a function of matte grade under $p_{SO_2}$ of 0.1 atm at 1573 K (Henao et al., 2006).
Summary of findings:

- The distribution behaviors of palladium, platinum, rhodium and ruthenium all heavily favor the matte phase.
- The distribution coefficient for the precious metals were roughly constant for matte grades between 40 to 60 wt% Cu.
CHAPTER 3: RESEARCH QUESTIONS

The main research questions for the current study:

- How do elements present in very small amounts (i.e. microelements) distribute between molten matte and iron silicate slag under reducing conditions similar to those found in an electric smelting furnace?
- Can the distribution behavior of these microelements be predicted thermodynamically?

The questions will be addressed by answering the following questions:

- Can Yazawa’s thermodynamic model for metal/metal oxides be generalized for metal sulfides/metal oxides, i.e. distribution between matte and slag?
- Can a predictive tool be developed to predict the distribution behavior of microelements based on the generalization of Yazawa’s model?
- How well do the predicted distribution data compare to minor element distribution data from literature?
- Which microelements are present in an actual electric smelting furnace, in what concentrations and what is the distribution ratio of these microelements between matte and slag at 1523 K?
- What is the distribution ratio of cobalt and tungsten between copper matte and iron silicate slag under reducing conditions at 1523 K?
- How well do the predicted distribution data compare to the experimental data produced in this study?

The approach to answering the main research question in the current study is to first generalize Yazawa’s model for matte-slag systems in order to develop a predictive tool. The necessary thermodynamic data was compiled in order to make a prediction using the model. An extensive collection of published distribution data for the matte-slag system was compiled in the literature review in Section 2-5.4. Activity coefficient data for species in matte and species in slag are compiled in Sections 4-2 and 4-3, respectively. The model is validated against literature data and the necessary assumptions and observed limitations are reported in Chapter 4. In addition to published data, experimental data were also generated to test the model. Details of experimental methodology can be found in Chapter 5. The experimental results are reported and discussed with reference to the thermodynamic model in Chapter 6.
CHAPTER 4: THERMODYNAMIC MODEL

4-1 ELEMENT DISTRIBUTION MODEL

The previous section detailed the research questions that are to be answered in this research study. The first query that needs to be examined is whether or not Yazawa’s thermodynamic model for minor element distribution between metals and slags can be extended for the case of distribution between mattes and slags. The basis for performing the thermodynamic analysis is the formulation of a relevant descriptive reaction for the distribution. In terms of element distribution, this requires knowledge on the species of the element in the various phases. While it has been generally assumed that an element dissolves in the matte as a sulfide and into the slag phase as an oxide, the literature review (Section 2-5.4) has shown that this is not always true. The presence of the matte phase (in place of the metal phase in Yazawa’s model) introduces more possible forms of dissolution of the element in the molten phases and thereby increases the degree of complexity of any model produced.

This section provides a description of the thermodynamic model for the matte-slag system, detailing the required information at each step on the decision making tree as well as the necessary assumptions where the required data are not available. The model is not expected to provide accurate values of the distribution coefficient, but rather allow users to identify elements which heavily favor one phase over the other. This would further allow researchers to identify elements which distribute more equally between matte and slag and therefore require experimental measurements to be made of distribution equilibria.

The model can be divided into 5 major sections:

- Defining the process conditions
- Establishing the nature of the species in which the microelement exists in matte and slag
- Expressing the describing reaction and from that the equilibrium expression from which the distribution coefficient can be derived
- Acquiring the activity coefficients of the species in matte and slag
- Calculating the distribution coefficient

Figure 4-1.1 shows the decision tree for the element distribution model.
Chapter 4: Thermodynamic Model

Microelement, M

Define Process Conditions: $T, p_{O_2}$ & $p_{S_2}$

Establish nature of species in matte and slag

Check by establishing activity ratio of possible species in the single phase

Matte

Sulfide

{MSx}

Metal

{M}

Slag

Metal

{M}

Oxide

(MOx)

Express equilibrium reaction:

a. $\{M\} = (M)$

b. $\{M\} + x/2 O_2(g) = (MO_x)$

c. $(M) + x/2 S_2(g) = \{MS_x\}$

d. $\{MS_x\} + x/2 O_2(g) = (MO_x) + x/2 S_2(g)$

Calculate equilibrium constant from Gibbs free energy of reaction

Derive distribution coefficient expression from equilibrium reaction

Check for activity coefficient data for species in matte and slag

Approximate required activity coefficient data

Assume Ideality

Figure 4-1.1: Decision tree for element distribution model.
The conditions which need to be defined for use in the model include temperature and the partial pressures of oxygen and sulfur. The temperature range most conducive for matte smelting operations lies between 1523 K and 1573 K. In addition to this, the sulfur-oxygen chemical potential diagram shown in Figure 4-1.2 only applies at 1573 K. A similar diagram for 1473 K is available from Yazawa and Nakazawa (1997). The matte stability region, i.e. the region of coexistence of matte and slag, on the chemical potential diagram (p-q-r-s-t in Figure 4-1.2) provides all possible values of sulfur and oxygen partial pressures for matte smelting along constant lines of $p_{SO_2}$ as discussed in Section 2-2.2. The model is to be tested at both reducing and oxidizing conditions to observe its limitations, if any are present. It is assumed that the slag is solely silica-saturated iron silicate slag. In practice the slag can contain other oxides e.g. alumina, magnesia, lime, etc., which will change $\alpha_{FeO}$ slightly and ultimately shift the position of the lines on the chemical potential diagram.

**Figure 4-1.2:** Sulfur-oxygen chemical potential diagram for the Cu-Fe-S-O-SiO$_2$ system at 1573 K.
As emphasized earlier in this chapter, the model is based upon the formulation of a relevant equilibrium reaction to represent the distribution of an element between the molten phases. For an element distributing between matte and slag, this descriptive reaction will depend on the defined conditions, which determines the oxidation state of the element in the molten phases. The only definitive method to establish the predominant species in the molten phases is by experiment, but unlike metal-metal oxide systems, the presence of sulfide species and the dependence of the equilibrium position on sulfur partial pressure introduces added complexity. It is also possible to have more than one species present in significant amounts in either phase. While experimentation is the only way to be sure which species is predominant in the molten phases it is often not justified and thus the role of the model is to be a predictive tool used prior to experimentation or when experimentation is inconvenient for various reasons (Occupational Health and Safety issues, difficulties with chemical analysis, etc.).

A method is thus required to predict the form of dissolution of the element in molten matte and slag. The possible forms of dissolution of an element in the matte-slag system are either the metallic, oxidic or sulfidic species or combinations of these, in either phase. Sulfidic dissolution of an element in slag is limited to a few elements including copper and lead and has been shown by Kaiura et al. (1980) and Takeda (1992) to be significant only in low matte grades (<45 wt% Cu). Oxidic dissolution of an element in matte is similarly presumed to not be significant at higher matte grades. Because this study is concerned with higher matte grades (50-65 wt% Cu), sulfidic dissolution of an element in slag and oxidic dissolution of an element in matte were not considered in the model. The valence of the oxide or sulfide compound in the molten matte or slag can be established thermodynamically by comparing the Gibbs free energy of formation for available oxide and sulfide compounds of the element in a manner similar to that of the Ellingham Diagram. The valence of the element is governed by the defined conditions and therefore is assumed to be the same in both phases. Having made these assumptions, the form of dissolution of the element in slag and matte can be addressed separately. In the interest of clarity, it should be noted that equations [4-1.3] and [4-1.6] are being used here to assess the likely form of dissolution of an element within a single phase in contrast to the extensive use of similar equations to determine the distribution of an element between phases.

In the slag, the element can dissolve in the metallic form or the oxidic form and can be represented by the following equilibrium reaction:

\[ M + \frac{x}{2} O_2(g) = MO_x \]  

[4-1.1]
Chapter 4: Thermodynamic Model

Where the equilibrium constant can be expressed as:

\[ K = \frac{a_{\text{MO}}}{a_{\text{M}} p_{O_2}^{\chi/2}} \]  \hspace{1cm} [4-1.2]

Equation [4-1.2] can be rewritten as:

\[ \frac{a_{\text{MO}}}{a_{\text{M}}} = K p_{O_2}^{\chi/2} \]  \hspace{1cm} [4-1.3]

The value of the activity ratio can be calculated subjected to the availability of the equilibrium constant at the appropriate temperature. While the value of the activity ratio does not give the actual concentration of metal oxide or metallic species present in the slag (the activity coefficients for the two species are required to calculate this), it does provide an indication as to which species is predominant under a certain set of conditions. Large values of the activity ratio show predominance of the metal oxide species whereas small values indicate predominance of the metallic species.

The same approach applies for the matte, where the element can dissolve in the sulfidic or metallic form:

\[ M + \frac{x}{2} S_2(g) = MS_x \]  \hspace{1cm} [4-1.4]

The equilibrium constant is expressed as:

\[ K = \frac{a_{\text{MS}}}{a_{\text{M}} p_{S_i}^{\chi/2}} \]  \hspace{1cm} [4-1.5]

And can be rewritten as:

\[ \frac{a_{\text{MS}}}{a_{\text{M}}} = K p_{S_i}^{\chi/2} \]  \hspace{1cm} [4-1.6]

The question that needs to be raised now is what value of the activity ratio can be considered large enough to suggest the predominant species is the oxide/sulfide species and what value is considered small enough to suggest the metallic species should predominate. The bounding values of the activity ratio test should reflect the condition \( p_{O_2} \) or \( p_{S_2} \) where the minor species becomes significant enough to influence the
distribution coefficient. The approach to obtaining the bounding parameters for the activity test is to validate it against two sets of experimental data:

- Firstly, for an element that should show predominance of one species across the matte stability region on the chemical potential diagram.
- Secondly, for an element that will shift predominance from one species to the other with change in conditions.

Cobalt distribution data from Yazawa (1980) was used as the first test (refer to Figure 2-5.32). The data by Yazawa (1980) was used because the sulfur partial pressure is constant and therefore the slope of the plot of \( \log L_{Co}^{m/s} - \log P_{O_2} \) confirms that cobalt is dissolved in the slag in a single oxidation state \( (Co^{2+}) \) over the whole range of oxygen partial pressures (Section 2-5.4c).

Table 4-1.1 summarizes the conditions for the test as well as the equilibrium constants (obtained from HSC Chemistry v5.11) and the calculated activity ratio values. \( K_a \) represents the equilibrium constant for the metal-metal oxide equilibria (equation [4-1.1]) and \( K_b \) represents the equilibrium constant for the metal-metal sulfide equilibria (equation [4-1.4]) for cobalt. The activity ratio at \( P_{O_2} = 1 \times 10^{-12} \text{ atm} \) has a value of 0.0125. Yazawa’s distribution data shows that at this condition the major species in terms of concentration is the oxide of cobalt. Because the distribution coefficient is expressed in wt% terms, the activity coefficient of cobalt metal in slag would have to be very large. This test then indicates that a value of 0.01 for the lower limit is a reasonable value, so that if the activity ratio shows a value below 0.01, the metallic species would predominate. Under more oxidizing conditions, the activity ratio gives a value of ~4 confirming that the oxide species remains predominant throughout the matte stability region.

**Table 4-1.1**: Summary table showing conditions, thermodynamic data and activity ratio calculations for cobalt.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature[K]</th>
<th>( P_{O_2} \text{[atm]} )</th>
<th>( P_{S_2} \text{[atm]} )</th>
<th>( K_a )</th>
<th>( K_b )</th>
<th>( a_{MOx}/a_M )</th>
<th>( a_{MSx}/a_M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1573</td>
<td>( 1 \times 10^{-12} )</td>
<td>( 1.8 \times 10^{-6} )</td>
<td>( 1.3 \times 10^4 )</td>
<td>( 1.9 \times 10^1 )</td>
<td>0.0125</td>
<td>0.0265</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>( 1 \times 10^{-7} )</td>
<td>( 1.8 \times 10^{-6} )</td>
<td>( 1.3 \times 10^4 )</td>
<td>( 1.9 \times 10^1 )</td>
<td>3.962</td>
<td>0.0265</td>
</tr>
</tbody>
</table>

For the second test, antimony distribution data reported by Yazawa (1980) was used. Again the partial pressure of sulfur is constant for all experiments so the slope of \( \log L_{Sb}^{m/s} - \log P_{O_2} \) will give the identity of the species in slag. As discussed in Section 2-5.4a, the two distinctly different slopes shown in Figure 4-1.3 indicates that antimony dissolves in two
different oxidation states. Under reducing conditions the metallic species predominates and at oxidizing conditions it becomes a mixture of an oxidic and metallic species.

Figure 4-1.3: Distribution ratio of antimony between matte and slag plotted against oxygen potential at 1573 K (Yazawa, 1980).

The activity ratio test must show that the metallic species is predominant under reducing conditions. At a $p_{O_2}=1 \times 10^{-11}$ atm, the activity ratio is much smaller than 0.01, which confirms predominance of the metallic species. The data in Figure 4-1.3 shows that the slope begins to change at an oxygen partial pressure of approximately $1 \times 10^{-10}$ atm. Performing the test for $p_{O_2}=1 \times 10^{-10}$ atm gives an activity ratio value larger than 0.01, suggesting that the oxide species is exerting some influence on the value of the distribution coefficient. This confirms the suitability of the lower bounding value such that below an activity ratio value of 0.01, the oxide species shows no influence on the distribution coefficient.

Table 4-1.2: Summary table showing conditions, thermodynamic data and activity ratio calculations for antimony.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature [K]</th>
<th>$p_{O_2}$ [atm]</th>
<th>$p_{S_2}$ [atm]</th>
<th>$K_a$</th>
<th>$K_b$</th>
<th>$a_{MOx}/a_M$</th>
<th>$a_{MSx}/a_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>1573</td>
<td>$1 \times 10^{-11}$</td>
<td>$1.8 \times 10^{-6}$</td>
<td>$4.1 \times 10^5$</td>
<td>9.34</td>
<td>0.0023</td>
<td>0.0005</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>$1 \times 10^{-10}$</td>
<td>$1.8 \times 10^{-6}$</td>
<td>$4.1 \times 10^5$</td>
<td>9.34</td>
<td>0.0128</td>
<td>0.0005</td>
</tr>
</tbody>
</table>
It is apparent from Figure 4-1.3 that the oxide species becomes dominant above $p_{O_2}$ of $1 \times 10^{-7}$ atm. The activity ratio at this condition was calculated to be 2.277. Based on the tests conducted on the distribution data for cobalt and antimony it would seem the chosen value of 0.01 is a reasonable first assumption for the lower bounding value, whereas the upper limit has been set at a value of 3. This assumption may not hold true for all other elements and only by validating these data against experimental data can a more suitable bounding value be chosen.

The following preliminary assumptions are therefore made to facilitate the use of the model:

- If the value of the activity ratio is greater than 3, the metal oxide/sulfide species is dominant
- If the activity ratio value of the activity ratio is less than 0.01, the metallic species is dominant

Difficulty in the decision making process exists when the value of the activity ratio lies between 3 and 0.01 and is most acute when the activity ratio is close to 1. In a scenario such as this, the activity coefficients of the species in the phase under consideration would be the determining factor. For example, if deciding between the metallic and sulfide species of an element in the matte and the activity ratio is close to 1 but it is known that the activity coefficient of the metal in matte is much higher than that of the sulfide in matte, then the sulfide species is assumed to predominate.

Having made justifiable assumptions as to what the form of dissolution of the element in matte and slag are using the activity ratio method, the describing equilibrium reaction for the distribution of the element between matte and slag can be expressed. There are four possible scenarios to consider when expressing the descriptive reaction as shown in Table 4-1.3 below.

<table>
<thead>
<tr>
<th>Matte/Slag</th>
<th>M</th>
<th>MOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>${M} = {M}$</td>
<td>${M} + x/2 O_2(g) = {MO_x}$</td>
</tr>
<tr>
<td>MSx</td>
<td>${M} + x/2 S_2(g) = {MS_x}$</td>
<td>${MS_x} + x/2 O_2(g) = {MO_x} + x/2 S_2(g)$</td>
</tr>
</tbody>
</table>

Table 4-1.3: Matrix of possible equilibrium reactions for describing distribution of an element between matte and slag.
The expression for the distribution coefficient, $L_{M/m,s}$, can be derived for each of the four scenarios using the same methods as in Section 2-5.1. Table 4-1.4 summarizes the distribution coefficient expressions for each case and highlights the necessary thermodynamic data to approximate the distribution coefficient. The factor 0.82 in the distribution coefficient expression is derived from the total moles of constituents in 100g of matte divided by total moles of constituents in 100g of slag, the values of which are shown in Figure 2-5.2 to be approximately constant as a function of matte grade.

Table 4-1.4: Equilibrium reactions and their respective distribution coefficient expressions.

<table>
<thead>
<tr>
<th>Case No.</th>
<th>Equilibrium Reaction</th>
<th>Distribution Coefficient Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>${M} = {M}$</td>
<td>$L_{M/m,s}^{m/s} = \frac{0.82 \gamma_M}{K \gamma_M}$</td>
</tr>
<tr>
<td>2</td>
<td>${M} + \frac{x}{2} O_2(g) = {MO_x}$</td>
<td>$L_{M/m,s}^{m/s} = \frac{0.82 \gamma_{MO_x}}{K \gamma_M p_{O_2}^{x/2}}$</td>
</tr>
<tr>
<td>3</td>
<td>$(M) + \frac{x}{2} S_2(g) = {MS_x}$</td>
<td>$L_{M/m,s}^{m/s} = \frac{0.82 K \gamma_M p_{S_2}^{x/2}}{\gamma_{MS_x}}$</td>
</tr>
<tr>
<td>4</td>
<td>$(MS_x) + \frac{x}{2} O_2(g) = {MO_x} + \frac{x}{2} S_2(g)$</td>
<td>$L_{M/m,s}^{m/s} = \frac{0.82 \gamma_{MO_x} p_{S_2}^{x/2}}{K \gamma_{MS_x} p_{O_2}^{x/2}}$</td>
</tr>
</tbody>
</table>

The first case shows distribution of the element in the metallic form in both phases and is a unique case. It is expected to apply to elements which have positive Gibbs free energy values for the metal oxide and metal sulfide formation reactions, i.e. very stable in their metallic form, such as gold. The equilibrium constant in this case is unity and the activity coefficient ratio is the dominant influence on the distribution coefficient. The values of the activity coefficients are highly unlikely to be available or easily predictable; therefore the model cannot make a prediction.

For the other cases, the value of the equilibrium constant (probably the more dominant) and the activity coefficient values of the species in matte and slag influence the value of the distribution coefficient. Gibbs free energy data (from which the equilibrium constant can be calculated) at the required temperature are readily available from databases such as that within HSC Chemistry for Windows. Activity coefficient data for species in matte and slag are limited and a survey of the available data from literature are presented in Section 4-2 for activity coefficients of species in matte and Section 4-3 for activity coefficients of species in slag. In cases where no activity coefficient data are available, the assumption of ideality for the solution and thus that activity coefficient terms are unity would still provide a reasonable approximation of the distribution behavior of a microelement between matte and slag. Alternatively, assuming solutions are not
ideal but that the activity coefficients for the relevant species are equal is an equivalent scenario, although less justifiable.

Summary of findings:

This section has provided the foundation for the distribution model. The main issues involved in developing the model include determining the form of dissolution of the element in the molten phases as well as the availability of necessary thermodynamic data. The assumptions required when developing the model include:

- Discounting sulfide species dissolution in slag and oxide species dissolution in matte.
- The assumption is that of the available sulfide and oxide compounds, the one with the lowest standard free energy of formation is most stable and therefore most likely.
- The valence of the element is governed by the defined conditions and is assumed to be the same in both phases.
- When the activity ratio is defined as in equations [4-1.3] and [4-1.6], the activity ratio test assumes:
  - If the value is greater than 3, the sulfide/oxide form predominates.
  - If the activity ratio is less than 0.01, the metallic species predominates.
  - For activity ratio values between 0.01 and 3, a decision needs to be made based on the activity coefficients of the species in the phase under consideration.
- Assumption of ideality when activity coefficient data are not available.

The observed limitations of the model include:

- When there is more than one species present in significant amounts in either phase there will be difficulty predicting a distribution ratio which is the result of the contributions of all species.
- The model fails when metal-metal equilibrium is considered unless the activity coefficients of the relevant species are available.
4-2  **Activity Coefficients for Species in Mattes**

The previous section highlighted the need for reliable activity coefficient data for use with the generic model. This section presents a literature survey of available activity coefficient data at infinite dilution for species in matte (summarized in Table 4-2.1). From the data, periodic trends, if any, are observed for the sulfide species in mattes and for the metallic species in mattes.

**Table 4-2.1:** Summary of activity coefficients at infinite dilution for species in copper mattes.

<table>
<thead>
<tr>
<th>Species, X</th>
<th>Temp (K)</th>
<th>$\gamma^{0}_X$</th>
<th>Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS(l)</td>
<td>1473</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>As(l)</td>
<td>1373</td>
<td>1.1-22</td>
<td>$\log \gamma_{As} = -1.26 + 40N_{As}$†</td>
</tr>
<tr>
<td>CoS(l)</td>
<td>1400-1500</td>
<td>0.40</td>
<td>-</td>
</tr>
<tr>
<td>SnS(l)</td>
<td>1400-1500</td>
<td>0.028</td>
<td>$\log \gamma^{0}_{SnS} = -2100/T - 0.068$</td>
</tr>
<tr>
<td>† Sb(?)</td>
<td>1473</td>
<td>0.25</td>
<td>$\log \gamma_{Sb} = -0.596 + 43N_{Sb}$</td>
</tr>
<tr>
<td>Ag(l)</td>
<td>1473</td>
<td>10-16</td>
<td>$\ln \gamma_{Ag} = 2.29 + 2.65 \times 10^{-7}$ (wt% Fe)</td>
</tr>
<tr>
<td>† Se(?)</td>
<td>1473</td>
<td>5.5x10^{-4}</td>
<td>-</td>
</tr>
<tr>
<td>† Te(?)</td>
<td>1473</td>
<td>(7.5-11)x10^{-3}</td>
<td>$\ln \gamma_{Te} = -4.72 + 7.66 \times 10^{-5}$ (wt% Fe)</td>
</tr>
<tr>
<td>PbS(l)</td>
<td>1473</td>
<td>1.3-2.2</td>
<td>-</td>
</tr>
<tr>
<td>Ni$_2$S$_3$</td>
<td>1573</td>
<td>2.4</td>
<td>$\gamma_{Ni_{2}S_{3}} = \exp(1377/T)$</td>
</tr>
</tbody>
</table>

† Reference Standard State Not Clear.

**Zinc Sulfide**

Azuma and Goto (1968) studied the thermodynamics of copper mattes in the Cu$_2$S-ZnS system and copper saturated-mattes in the Cu$_2$S-ZnS-Cu system in the temperature range from 1423 K to 1523 K. The authors proceeded to examine the thermodynamics of FeS-ZnS and Cu$_2$S-ZnS-FeS systems between 1473 K and 1523 K (Azuma et al., 1969). In the Cu$_2$S-ZnS system, the activity coefficient of ZnS was reported to be between 1 and 6. The activity coefficient of ZnS in the FeS-ZnS system was reported to fall between 4 and 6. For the Cu$_2$S-ZnS-FeS system, Azuma et al. (1969) measured the activity of ZnS for different matte grades at 1473 K. The activity values are made with reference to the liquid standard state. The results are shown in Figure 4-2.1.
Figure 4-2.1: Zinc sulfide activity in the Cu$_2$S-FeS-ZnS system at 1473 K (Azuma et al., 1969).

The slope of the lines in Figure 4-2.1 represents the activity coefficient values for ZnS at the varying matte grades. At infinite dilution, there is little to no difference for the value of the activity coefficient between the three matte grades. The value of the activity coefficient at infinite dilution is determined to be approximately 6.

Arsenic

Itagaki et al. (1983) measured the activity of arsenic in liquid mattes using an isopiestic method over the range of 1323 to 1373 K.

The authors measured the activity of arsenic for a range of different matte compositions ranging from mattes found in oxidizing smelters (X-type) to those found in reducing smelters (Y-type). A summary of matte compositions is listed in Table 4-2.2 below.

<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-1</td>
<td>20 wt% Cu$_2$S-80 wt% FeS</td>
</tr>
<tr>
<td>X-2</td>
<td>40 wt% Cu$_2$S-60 wt% FeS</td>
</tr>
<tr>
<td>X-3</td>
<td>60 wt% Cu$_2$S-40 wt% FeS</td>
</tr>
<tr>
<td>X-4</td>
<td>75 wt% Cu$_2$S-25 wt% FeS</td>
</tr>
<tr>
<td>Y-1</td>
<td>γFe saturation at 1233 K</td>
</tr>
<tr>
<td>Y-2</td>
<td>γFe saturation at 1283 K</td>
</tr>
</tbody>
</table>
The liquid standard state was used for the activity and activity coefficient of arsenic. Figure 4-2.2 shows the activity of arsenic in the X-type mattes at 1373 K. The activity is seen to show large positive deviation from Raoultian behavior.

![Activity of arsenic in liquid mattes (X-type) at 1373 K](Itagaki et al., 1983).

The slope of the activity plots correspond to the activity coefficient at infinite dilution for arsenic. The activity coefficients are considerably different between the different matte compositions, the activity coefficient decreases in sequence from X-1 to X-4, i.e. as the matte grade increases.

Figure 4-2.3 shows the activity of arsenic in the Y-type mattes at 1323 K.
There is a very clear difference between the X-type and Y-type mattes. The activity of arsenic for Y-type mattes is much smaller compared to that in X-type mattes.

Table 4.2.3 shows the activity coefficient values for the various mattes.

Table 4.2.3: Activity coefficients of arsenic in Cu$_2$S-FeS mattes with reference to the liquid standard state.

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature (K)</th>
<th>$\gamma^o_{As(l)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-1</td>
<td>1373</td>
<td>22±2</td>
</tr>
<tr>
<td>X-2</td>
<td>1323</td>
<td>20.0±1.6</td>
</tr>
<tr>
<td>X-2</td>
<td>1373</td>
<td>15.0±1.2</td>
</tr>
<tr>
<td>X-3</td>
<td>1373</td>
<td>10.0±0.5</td>
</tr>
<tr>
<td>X-4</td>
<td>1373</td>
<td>8.8±0.4</td>
</tr>
<tr>
<td>Y-1</td>
<td>1323</td>
<td>1.4±0.1 ($N_{As}=0.01$)</td>
</tr>
<tr>
<td>Y-2</td>
<td>1323</td>
<td>1.1±0.1 ($N_{As}=0.01$)</td>
</tr>
</tbody>
</table>

Mendoza, Hino and Itagaki (2001) measured the activity of arsenic in both the metal and matte phases in the Cu-Fe-S-As system at 1473 K using the double Knudsen cell-mass spectrometric method. Figure 4.2.4 shows the activity of arsenic in the miscibility gap of the Cu-Fe-S-As quaternary system at 1473 K.
Figure 4-2.4: Activity of arsenic in the miscibility gap of the Cu-Fe-S-As quaternary system at 1473 K (Mendoza et al., 2001).

Figure 4-2.4 shows that arsenic activities in the metal show negative deviation from ideality. The activity coefficients of arsenic in the matte phase at 1473 K are shown in Figure 4-2.5.

Mendoza et al. (2001) also reported that $\log \gamma_{As}$ increases proportionally with $N_{As}$ in the matte phase and can be expressed by the following relationship:

$$\log \gamma_{As} = -1.26 + 40N_{As}$$  \[4-2.1\]
The value of the activity coefficient of arsenic in matte at infinite dilution, $\gamma_{\text{As}}^\circ$, was found to be 0.055, however the standard reference state is not known. The data reported by Mendoza et al. (2001) differs greatly with that of Itagaki et al. (1983), considering the data reported by Mendoza are a lot lower than that by Itagaki, it could be that Mendoza’s data are made with reference to the gaseous standard state. A number of differences also stand out between the two studies. Firstly, Mendoza et al. (2001) used a higher temperature; the results from Itagaki’s study between X-2 at 1323 K and X-2 at 1373 K shows that at higher temperatures the activity coefficient decreases, which could explain the lower values by Mendoza et al. (2001). In addition to this, Mendoza used mattes that were very low in iron content, as evidenced by the data in Figure 4-2.5.

**Cobalt Sulfide**

Sinha and Nagamori (1982) measured the distribution coefficient of cobalt between metallic copper and copper matte at 1400 and 1500 K. The authors calculated the activity coefficient of CoS at infinite dilution with reference to the liquid standard state using the equilibrium reaction in equation [4-2.2] and the distribution coefficient value.

\[
\text{Cu}_2\text{S}(l) + \text{Co}(s) = 2\text{Cu}(l) + \text{CoS}(l)
\]  

[4-2.2]

\[
K_{1400K} = \frac{a_{\text{Co}}^2 \cdot a_{\text{CoS}}}{a_{\text{Cu}_2\text{S}} \cdot a_{\text{Co}}} = 3.999 \times 10^{-2}
\]  

[4-2.3]

The activity of cobalt for the Cu$_2$S-saturated alloy:

\[
a_{\text{Co}} = \gamma_{\text{Co}}^\circ N_{\text{Co}} = 0.2592[C\text{o}]_{\text{Cu}}
\]  

[4-2.4]

And the activity of CoS for the matte solution at infinite dilution of CoS:

\[
a_{\text{CoS}} = \gamma_{\text{CoS}}^\circ N_{\text{CoS}} = 0.027\gamma_{\text{CoS}}^\circ [\text{Co}]_{\text{Mt}}
\]  

[4-2.5]

Inserting $a_{\text{Cu}} = 0.9783$, $a_{\text{Cu}_2\text{S}} = 1$, equation [4-2.4] and equation [4-2.5] into equation [4-2.3] yields:

\[
\gamma_{\text{CoS}}^\circ = \frac{3.999 \times 10^{-2} \cdot [\text{Co}]_{\text{Cu}}}{0.09969 \cdot [\text{Co}]_{\text{Mt}}} = 0.401 \cdot L_{\text{Co}}^{\text{Cu}/\text{Mt}}
\]  

[4-2.6]
Sinha and Nagamori (1982) found the value of the distribution coefficient of cobalt between copper and matte, $L_{Co}^{Cu/Mt}$, to be $1.010 \pm 0.015$ at 1400 K. The activity coefficient of cobalt sulfide at infinite dilution can then be calculated to be:

$$\gamma^{CoS}_{\text{liq}} = 0.405 \quad (1400 \text{ K})$$  \[4-2.7\]

Similar analysis performed at 1500 K showed very little difference and were well within experimental scatter.

Sinha and Nagamori (1982) performed similar analyses for Fe-containing mattes to which they concluded that the presence of iron in matte appears to cause a small increase in the activity coefficient of CoS, however this influence was also within experimental error.

The authors thus concluded that the results at 1400 and 1500 K for both Fe-free and Fe bearing mattes may be summarized as:

$$\gamma^{CoS}_{\text{liq}} = 0.40 \pm 0.02 \quad [4-2.8]$$

**Tin Sulfide**

Sinha, Sohn and Nagamori (1984) measured the distribution coefficient of tin between copper and high grade mattes at 1400 and 1500 K for tin concentrations in matte not exceeding 0.03 wt%. The authors then used the metal-matte equilibria as shown in equation [3-1.9] to calculate the activity coefficient of SnS in matte with reference to the liquid standard state.

$$\text{Cu}_2\text{S}(l) + \text{Sn}(l) = 2\text{Cu}(l) + \text{SnS}(l) \quad [4-2.9]$$

$$K_{1400K} = \frac{a^2_{Cu} \cdot a_{\text{SnS}}}{a_{CuS} \cdot a_{\text{Sn}}} = 0.0464 \quad [4-2.10]$$

From equation [4-2.10]:

$$\gamma_{SnS(l)}^{\text{liq}} = 0.0464 \cdot \gamma_{\text{Sn}}^{\text{liq}} \cdot L_{Sn} \frac{a_{CuS}}{(a_{Cu})^2} \frac{M_1}{M_2}$$  \[4-2.11\]
Chapter 4: Thermodynamic Model

$M_1$ and $M_2$ are the number of moles in 100 g of matte and copper phases, respectively.

Inserting $a_{Cu} = 0.964$, $a_{Cu2S} = 0.841$, $\gamma^{*}_{Sn} = 0.042$ (1400K) and $L_{Sn} = 37.2$ into equation [4-2.11] yields:

$$\gamma^{*}_{Sn(S)} = 0.028 \quad (1400 \text{ K})$$  [4-2.12]

Sinha et al. (1984) also evaluated the activity coefficient of SnS at 1500 K and for Fe-containing mattes and formulated the following equation:

$$\log \gamma^{*}_{Sn(S)} = -2100 / T - 0.068$$  [4-2.13]

Equation [3-1.13] is valid for temperatures between 1400 and 1500 K, tin content in matte below 0.03 wt% and iron content in matte below 11 wt%.

Antimony

Mendoza, Hino and Itagaki (2002) measured the activity of antimony in both the metal and matte phases for the Cu-Fe-Sb-S system at 1473 K using the double Knudsen cell-mass spectrometric method. Figure 4-2.6 shows the activity of antimony in the miscibility gap of the Cu-Fe-S-Sb quaternary system at 1473 K.

![Figure 4-2.6: Activity of antimony in the miscibility gap of the Cu-Fe-S-Sb quaternary system at 1473 K (Mendoza et al., 2002).](image-url)
Figure 4-2.6 shows that antimony activities in the matte show negative deviation from ideality. The Raoultian activity coefficients of antimony in the matte phase at 1473 K are shown in Figure 4-2.7.

![Figure 4-2.7: Activity coefficients of antimony in the matte phase at 1473 K (Mendoza et al., 2002).](image)

Mendoza et al. (2002) also reported that log $\gamma_{Sb}$ increases proportionally with $N_{Sb}$ in the matte phase and can be expressed by the following relationship:

$$\log \gamma_{Sb} = -0.596 + 43N_{Sb} \quad [4-2.14]$$

The value of the activity coefficient at infinite dilution, $\gamma^0_{Sb}$, was found to be 0.25.

Silver

Zakeri, Hino and Itagaki (2000) measured silver activity in the metal and matte phases of the Cu-Fe-S-Ag system at 1473 K using the double Knudsen cell method. The activity and activity coefficient values are made with reference to the liquid standard state. Figure 4-2.8 shows the silver activity in the matte and metal for mattes with varying iron content.
Figure 4-2.8: Silver activity in the matte and metal phases in the immiscible region of the Cu-Fe-S-Ag system at 1473 K (Zakeri et al., 2000).

Figure 4-2.8 shows that the activity of silver exhibits positive deviation from ideality in both phases with the degree of deviation in the matte phase being larger. The silver activity in the matte phase is also seen to increase with increasing iron content. Figure 4-2.9 shows the activity coefficients of silver at 1473 K.

Figure 4-2.9: Relationship between the activity coefficient of silver and silver content in the metal and matte phases at 1473 K (Zakeri et al., 2000).

The activity coefficient of silver at infinite dilution can be estimated by extrapolating the best fitted line to zero percent silver. In the matte phase, the activity coefficient of silver
at infinite dilution was found to be approximately 10 for mattes containing less than 10 wt% iron. Past 10 wt% iron in matte, the activity coefficient of silver at infinite dilution gradually increases and reaches a maximum of approximately 16 at γ-Fe saturation. This is shown more clearly in Figure 4-2.10.

**Figure 4-2.10:** Effect of matte composition on the limiting activity coefficient of minor elements in copper saturated mattes at 1473 K (Zakeri et al., 1999).

Selenium and Tellurium

Zakeri, Hino and Itagaki (1999) measured selenium and tellurium activity in the metal and matte phases of the Cu-Fe-S-Se and Cu-Fe-S-Te systems at 1473 K using the double Knudsen cell method. The activity and activity coefficient values are made with reference to the liquid standard state. Figure 4-2.11 shows selenium and tellurium activity in the matte and metal for mattes with varying iron content.

**Figure 4-2.11:** Activity of selenium and tellurium in the miscibility gap of the Cu-Fe-S-Me (Me = Se, Te) systems at 1473 K (Zakeri et al., 1999).
Figure 4-2.11 shows that the activity of selenium and tellurium both exhibit negative deviation from ideality. The activity selenium in the matte phase is unaffected by the composition of the matte phase. Tellurium activity in the matte phase however, increases with increasing iron content. Figure 4-2.12 shows the activity coefficients of selenium and tellurium at 1473 K.

![Figure 4-2.12: Activity coefficients of selenium and tellurium in the coexisting matte and metal phases at 1473 K (Zakeri et al., 1999).](image)

The activity coefficient of selenium and tellurium at infinite dilution can be estimated by extrapolating the best fitted line to zero percent of the minor element. In the matte phase, the activity coefficient of selenium at infinite dilution was found to be constant with a value of approximately $5.5 \times 10^{-4}$. The activity coefficient of tellurium at infinite dilution increases with iron content in the matte and has a value of approximately $7.5 \times 10^{-3}$ at low iron contents up to $11 \times 10^{-3}$ at iron saturation. This is shown more clearly in Figure 4-2.10. It is not clear what the standard states are for the work by Zakeri et al. (1999) although given the small values, it may be for the gaseous form.

Lead Sulfide

Azuma et al. (1970) studied the thermodynamics of copper mattes in the Cu$_2$S-FeS-PbS system between 1473 K and 1523 K. Azuma et al. (1970) measured the activity of PbS for different matte grades at 1473 K. The activity values are made with reference to the liquid standard state. The results are shown in Figure 4-2.13.
Figure 4-2.13: Lead sulfide activity in the Cu2S-FeS-PbS system at 1473 K (Azuma et al., 1970).

The slope of the lines in Figure 4-2.13 represents the activity coefficient values for PbS at the varying matte grades. While the activity values for mattes with \( \frac{N_{Cu2S}}{N_{FeS}} \) of 1 and 1/3 show little difference, there is a significant difference in activity values for the high grade matte \( \left( \frac{N_{Cu2S}}{N_{FeS}} = 3 \right) \). The activity coefficient at infinite dilution for the lower grade mattes is approximately 1.3, while the activity coefficient for the high grade matte is approximately 2.2.

Summary of findings:

- There is no observable trend from the available activity coefficients of sulfide species in matte.
- It is also very difficult to make a conclusion from the available activity coefficient data for metallic species in matte.
- The scarcity of the data, the scatter present in available data (As) and issues relating to the use of different reference standard states makes it difficult to arrive at any conclusion regarding possible periodic trends of activity coefficients for species in matte.
Similarly to the previous section, this section aims to compile activity coefficient data for species in iron silicate slags. Again, periodic trends, if any, are observed for the oxide species in slag or for the metallic species in slag.

Table 4-3.1: Summary of activity coefficients for species in iron silicate slags.

<table>
<thead>
<tr>
<th>Species, X</th>
<th>Temp (K)</th>
<th>$\gamma^o_x$</th>
<th>Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO(s)</td>
<td>1573</td>
<td>4.0-4.5</td>
<td>$\log \gamma^o_{NiO(s)} = 3050/T - 1.31$</td>
</tr>
<tr>
<td>ZnO(s)</td>
<td>1523</td>
<td>0.6-2.6</td>
<td>-</td>
</tr>
<tr>
<td>CoO(s)</td>
<td>1523-1623</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>SnO(l)</td>
<td>1473-1573</td>
<td>0.8-2.0</td>
<td>$\log \gamma^o_{SnO(l)} = 8800/T - 5.70$</td>
</tr>
<tr>
<td>PbO(l)</td>
<td>1473-1573</td>
<td>0.07</td>
<td>$\exp(-3926/T)$</td>
</tr>
<tr>
<td>As</td>
<td>1473-1573</td>
<td>1-10</td>
<td>-</td>
</tr>
<tr>
<td>† AsO$_{1.5}$</td>
<td>?</td>
<td>?</td>
<td>$3.828 \cdot \exp(1523/T) \cdot P_{O_2}^{0.158}$</td>
</tr>
<tr>
<td>† SbO$_{1.5}$</td>
<td>?</td>
<td>?</td>
<td>$\exp(1055.66/T)$</td>
</tr>
<tr>
<td>† BiO$_{1.5}$</td>
<td>?</td>
<td>?</td>
<td>$\exp(-1055.66/T)$</td>
</tr>
</tbody>
</table>


Nickel Oxide

Grimsey and Biswas (1976) examined the solubility of nickel in silica-saturated iron silicate slags at 1573 K. The slags were placed in silica crucibles and equilibrated with liquid Ni-Au-Fe alloys and CO-CO$_2$ gas. The gas mixture was used to set the oxygen potential at fixed values between $10^{-7}$ and $10^{-10}$ atm. From their results, the authors concluded that nickel dissolves in slag as both Ni$^{2+}$ (nickel oxide) and Ni° (nickel metal). The authors used the liquid standard state for both nickel and nickel oxide. In order to determine the activity coefficient of nickel oxide in slag, the authors calculated the solubility of Ni° in slag for the raw data and determined the value of the mole fraction term which includes only Ni$^{2+}$ in slag. The activity coefficient of nickel oxide ($\gamma^o_{NiO}$) in silica-saturated iron silicate slags was determined to be 2.6 ± 0.08. In a later paper (Grimsey and Biswas, 1977), the authors examined the solubility of nickel in iron silicate slags with lime and found the activity coefficient of nickel oxide to increase with increasing CaO/SiO$_2$ ratio in iron silicate slag.

Sahoo and Reddy (1984) determined the activity coefficient for nickel oxide (NiO) in alumina-saturated iron silicate slags at 1573 K. Activity of nickel oxide in the slag was determined by equilibrating the slag with Au-Ni alloy at 1573 K and Fe/SiO$_2$ = 1.31. A
CO/CO₂ gas mixture was used to maintain the oxygen partial pressure between 10⁻¹⁰ to 10⁻⁸ atm. The authors concluded from their study that the nickel dissolves in the slag both as Ni° and Ni²⁺ (NiO) states. The standard state of the nickel and nickel oxide are that of the pure supercooled liquid nickel and liquid nickel oxide, respectively. The activity coefficient of nickel oxide (γ°NiO) in the slag was determined to be 1.59 and is independent of the oxygen partial pressure. This value is lower than that of Grimsey and Biswas (1977) for lime-free silica saturated slag and leads to the conclusion that the presence of alumina (9 to 13%) increases the solubility of nickel in slags.

Nagamori and Mackey (1978) reported the activity coefficient of NiO (s) as:

\[
\log \gamma_{\text{NiO}}^0 = \frac{3050}{T} - 1.31
\]

The convention of chemical thermodynamics states that the appropriate standard state for a species is the form of the pure species which is stable at the temperature concerned (Hultgren et al., 1973). Based on the melting points of nickel (1726 K) and nickel oxide (2233 K), the reference state for both nickel and nickel oxide was chosen in this study to be solid. The activity coefficient reported by Grimsey and Biswas (1976) and Sahoo and Reddy (1984) would therefore need to be standardized before the activity coefficient values can be compared.

\[
\text{NiO(l)} = \text{NiO(s)}
\]

\[
K = \frac{a_{\text{NiO}}(s)}{a_{\text{NiO}}(l)}
\]

From HSC Chemistry v5.1, the value of the equilibrium constant at 1573 K was found to be 3.642. Using this value, the activity data by Grimsey and Biswas (1976) and Sahoo and Reddy (1984) were converted to the solid reference state and the activity coefficient recalculated. The average activity coefficient data for the solid reference state was found to be 9.5 for Grimsey and Biswas (1976) and 4.54 for Sahoo and Reddy (1984). The data by Sahoo and Reddy (1984) for iron silicate slags containing alumina is closer in agreement to the value obtained using Nagamori and Mackey’s reported relationship.

Zinc Oxide

Grimsey et al. (1993) published a review paper on the behavior of zinc oxide in iron silicate slag. In their paper, the authors reviewed previous studies and found conflicting
activity coefficient values presented. Previous studies employed a variety of methods to overcome experimental difficulties associated with the determination of zinc oxide activity in molten slags. These difficulties arise firstly because the vapor pressure of zinc is relatively high at smelting temperatures and secondly because the oxygen and zinc vapor pressures must be determined simultaneously. The pure solid standard state was used for the activity and activity coefficient of zinc oxide unless otherwise stated. Of the studies which measured activity coefficient of zinc oxide directly, the gas-slag equilibriums of Azuma, Goto and Ogawa (1965, 1967) and the electrochemical metal-slag equilibrations of Filipovska and Bell (1978a, 1978b, 1979) seem least likely to be affected by experimental error. Grimsey et al. (1993) also performed experiments using the electrochemical method employed by Filipovska and Bell to extend the previous measurements on the FeO\textsubscript{x}-CaO-SiO\textsubscript{2} system to include slags of significantly higher Fe/SiO\textsubscript{2} ratios and with a wider range of lime content. Figure 4-3.1 shows the results published by Grimsey et al. (1993), Filipovska and Bell (1978a, 1978b, 1979) and Azuma et al. (1965, 1967).

Figure 4-3.1: Activity coefficient of zinc oxide relative to the pure solid standard state. Figure A shows data from Grimsey et al. (1993), Figure B shows data from Filipovska and Bell (1978a, 1978b, 1979) and Figure C shows data from Azuma et al. (1965, 1967).

Figure 4-3.2 combines the data from the three authors for comparison. The data by Azuma et al. (1967) are included with the iron-saturated slag data at 1523 K on the assumption that a temperature difference of 30-50 K may be neglected and that the
additional ferric iron in the slag (compared to iron-saturated slag) does not significantly decrease the activity coefficient of zinc oxide. The iso-activity curves in Figure 4-3.2 present a reasonably consistent picture of the activity coefficient behavior of zinc oxide in liquid FeO-CaO-SiO$_2$ at 1523 K.

![Figure 4-3.2: The activity coefficient of zinc oxide relative to the pure solid state (Grimsey et al., 1993).](image)

Grimsey et al. (1993) concluded that the agreement in activity coefficient values from two different experimental techniques, namely gas-slag equilibration and electrochemical metal-slag equilibrium, provides strong evidence that the data presented are correct. Within the liquidus field of the (FeO+ZnO)-CaO-SiO$_2$ system, the activity coefficient of zinc oxide relative to the pure solid state has a value between 0.6-2.6.

**Cobalt Oxide**

Teague et al. (1998) performed a very comprehensive review of the activity coefficient of cobalt oxide in non-ferrous smelting slags. The authors reviewed previous studies for the solubility of cobalt oxide in non-ferrous smelting slags and found that comparison and evaluation of the results was hampered by variations in the choice of standard states for the species. They proceeded to recalculate the published results using a common set of standard states as summarized in Table 4-3.2 below:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Temperature (K)</th>
<th>Slag(s)</th>
<th>$\gamma_{\text{CoO}}^{\circ}$ original</th>
<th>$\gamma_{\text{CoO(s)}}^{\circ}$ standardized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reddy (1985)</td>
<td>1473</td>
<td>Alumina-</td>
<td>1.65</td>
<td>4.16</td>
</tr>
</tbody>
</table>
The data provided by Grimsey and Liu (1994) cannot be compared to that of other workers because they equilibrated iron silicate slag with a matte as well as an alloy. The presence of CoS in the matte will affect the value of $\gamma_{\text{CoO}}$ in the slag. The data by Reddy (1985) was found to be too high compared to other work. Reddy (1985) used a reaction time of two hours in his work, which is significantly less than the average of 40 hours employed by the other workers. This suggests that two hours is insufficient for the system to achieve equilibrium. Reddy’s data were therefore considered to be unreliable. The standardized activity coefficient data from the other workers were plotted against temperature as shown in Figure 4-3.3.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Temperature</th>
<th>Phase Description</th>
<th>$\gamma_{\text{FeO}}$</th>
<th>$\gamma_{\text{SiO}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grimsey and Toguri (1988)</td>
<td>1523-1623</td>
<td>Silica-saturated iron silicate</td>
<td>1.94</td>
<td>1.92</td>
</tr>
<tr>
<td>Katyal and Jeffes (1989)</td>
<td>1523-1623</td>
<td>Silica-unsaturated iron silicate</td>
<td>0.93</td>
<td>2.10</td>
</tr>
<tr>
<td>Grimsey and Liu (1991)</td>
<td>1573</td>
<td>Silica-saturated iron silicate</td>
<td>0.88</td>
<td>0.84</td>
</tr>
<tr>
<td>Grimsey and Liu (1994)</td>
<td>1573</td>
<td>Alumina-saturated iron silicate with matte</td>
<td>1.20</td>
<td>1.18</td>
</tr>
<tr>
<td>Grimsey and Liu (1995)</td>
<td>1573</td>
<td>Silica-saturated iron silicate</td>
<td>0.91</td>
<td>0.88</td>
</tr>
</tbody>
</table>
Teague et al. (1998) concluded that the value of the activity coefficient of cobalt oxide referred to the solid standard state in iron silicate slags is approximately two, for temperatures between 1523 K and 1623 K.

Nagamori and Mackey (1977) examined the distribution of tin between alumina-containing fayalite slag and metallic copper at 1473 K and 1573 K for oxygen partial pressures from $10^{-6}$ to $10^{-11}$ atm. The partial pressure of oxygen was controlled using a CO-CO$_2$ gas mixture. From the results of their distribution experiments, they deduced that tin dissolves in the slag as SnO (Sn$^{2+}$) under the conditions used. The authors then calculated the activity coefficient of SnO ($\gamma^{\circ}_{\text{SnO}}$) with reference to the liquid standard state for various slag compositions and conditions as summarized in Table 4-3.3.

Nagamori and Mackey also stated that by neglecting the effect of Fe/SiO$_2$, a simplified expression for the activity coefficient of SnO (l) can be obtained:
Nagamori et al. (1975) examined the distribution behavior of lead between metallic copper and silica-unsaturated fayalite slag containing 8wt% alumina at 1473 K and 1573 K under CO-CO₂ atmospheres with oxygen potentials in the range of $10^{-6}$ to $10^{-11}$ atm. The authors also calculated the activity coefficient of PbO with reference to the liquid standard state at varying oxygen potentials. This is shown in Figure 4-3.4.

The effect of temperature in the range of 1473 K and 1573 K was found to be small and $\gamma^\circ_{PbO}$ was found to be 0.07±0.01. The authors also noted that slags with high alumina content (24 wt%) have lower $\gamma^\circ_{PbO}$ values compared to slags with lower alumina content (8 wt%). The value of $\gamma^\circ_{PbO}$ for alumina-free fayalite slags is therefore expected to be greater than 0.07.
The values of $\gamma^{\circ}_{\text{PbO}}$ reported by Nagamori et al. (1975) are in agreement with values estimated by Kellogg (1967). Kellogg (1967) reported $\gamma^{\circ}_{\text{PbO}}$ values of 0.07 at 1473 K and 0.083 at 1573 K for slags containing lime.

Shimpo, Watanabe and Goto (1983) reported a relationship for the activity coefficient of PbO with reference to the liquid standard state as:

$$\gamma_{\text{PbO(l)}} = \exp(-3926 / T) \quad [4-3.5]$$

Arsenic

Lynch and Schwartze (1981) measured the distribution coefficient of arsenic between slag and copper and the activity of arsenic in silica-saturated FeO-Fe$_2$O$_3$-SiO$_2$ slag between 1473 K and 1536 K. The distribution experiments were conducted under a controlled CO-CO$_2$ atmosphere with an oxygen pressure of $10^{-10}$ atm. The activity of arsenic in slag was measured by equilibrating arsenic vapor with slag sealed in an evacuated tube. Lynch and Schwartze (1981) concluded that under the conditions used, arsenic dissolves in the slag as As$^\circ$.

Table 4-3.4 shows the activity data for the work by Lynch and Schwartze (1981) together with data from Nagamori et al. (1975) and Kashima et al. (1978). The results shown for Nagamori et al. (1975) and Kashima et al. (1978) are average values for their data sets. There is actually a significant amount of scatter in the original data set, especially in the case of Nagamori’s data.

**Table 4-3.4:** Activity data for As in slag (Lynch & Schwartze, 1981; Nagamori et al., 1975; Kashima et al. 1978).

<table>
<thead>
<tr>
<th>Authors</th>
<th>Temperature (K)</th>
<th>$\gamma_{\text{As}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lynch &amp; Schwartze (1981)</td>
<td>1473</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>1483</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>1536</td>
<td>4.0</td>
</tr>
<tr>
<td>Nagamori et al. (1975)</td>
<td>1473</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>7</td>
</tr>
<tr>
<td>Kashima et al. (1978)</td>
<td>1573</td>
<td>2.0</td>
</tr>
</tbody>
</table>
With the data available and the scatter associated with it, it is difficult to conclude which values are correct. Lynch and Schwartze (1981) could only conclude that the Henrian activity coefficient of As in slag falls in the range of 1 to 10.

Summary of findings:

- There simply is not enough data to discern any periodic trends relating the activity coefficients of species in slags.
- Issues relating to the use of different reference standard states further complicate the task. While an attempt has been made to convert all the data to the same reference standard state, often the required data are not available.
Chapter 4: Thermodynamic Model

4-4  MODEL VALIDATION AGAINST LITERATURE DATA

The earlier sections in this chapter provide the necessary framework for developing and using the model. This section aims to test the validity of the model against distribution data from literature, which was summarized in Section 2-5.4.

The outcomes expected for this section include:

- An assessment of how closely model predictions match literature data
- Any additional assumptions or limitations that need to be made
- What type of data are lacking and what experiments need to be performed to better validate the model?

Table 4-4.1 contains all the necessary data to make justifiable assumptions of the form of dissolution of an element in matte and slag. The table summarizes the conditions used for the test as well as the equilibrium constants (obtained from HSC Chemistry v5.11) and the calculated activity ratio values for each element. The specific conditions for each test were chosen to match conditions used in distribution experiments for the respective elements as reported in literature. Where distribution data are available under significantly different conditions, e.g. reducing and oxidizing conditions, the model is tested for numerous conditions. As detailed earlier in Section 4-1, $K_a$ represents the equilibrium constant for the metal-metal oxide equilibria (equation [4-1.1]) and $K_b$ represents the equilibrium constant for the metal-metal sulfide equilibria (equation [4-1.4]) for the respective elements. The activity ratio values in the last two columns of Table 4-1.1 are used to justify which species to use in the slag and matte.
Table 4-4.1: Summary table showing conditions, thermodynamic data and activity ratio calculations for various elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature[K]</th>
<th>pO$_2$[atm]</th>
<th>pS$_2$[atm]</th>
<th>K$_a$</th>
<th>K$_b$</th>
<th>a$_{MOx}$/a$_M$</th>
<th>a$_{MSx}$/a$_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>1573</td>
<td>1x10$^{-11}$</td>
<td>1.8x10$^{-6}$</td>
<td>4.1x10$^5$</td>
<td>9.34</td>
<td>0.0023</td>
<td>0.0005</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>1x10$^{-10}$</td>
<td>1.8x10$^{-6}$</td>
<td>4.1x10$^5$</td>
<td>9.34</td>
<td>0.0128</td>
<td>0.0005</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>4.1x10$^5$</td>
<td>9.34</td>
<td>0.4049</td>
<td>0.1576</td>
</tr>
<tr>
<td>As</td>
<td>1523</td>
<td>1x10$^{-11}$</td>
<td>1.8x10$^{-6}$</td>
<td>1.9x10$^5$</td>
<td>5.3x10$^{-1}$</td>
<td>0.0011</td>
<td>0.00002</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>8.5x10$^4$</td>
<td>3.9x10$^{-1}$</td>
<td>0.0846</td>
<td>0.0067</td>
</tr>
<tr>
<td>Bi</td>
<td>1573</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>5.9x10$^2$</td>
<td>3.7x10$^{-1}$</td>
<td>0.0066</td>
<td>0.0062</td>
</tr>
<tr>
<td>Cd</td>
<td>1503</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>4.7x10$^3$</td>
<td>2.7x10$^2$</td>
<td>0.4707</td>
<td>17.75</td>
</tr>
<tr>
<td>Zn</td>
<td>1503</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>5.4x10$^4$</td>
<td>1.3x10$^4$</td>
<td>538.1</td>
<td>846.2</td>
</tr>
<tr>
<td>Co</td>
<td>1573</td>
<td>1x10$^{-11}$</td>
<td>1.8x10$^{-4}$</td>
<td>1.3x10$^4$</td>
<td>1.9x10$^1$</td>
<td>0.0396</td>
<td>0.0265</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>1x10$^{-7}$</td>
<td>1.8x10$^{-6}$</td>
<td>1.3x10$^4$</td>
<td>1.9x10$^1$</td>
<td>3.962</td>
<td>0.0265</td>
</tr>
<tr>
<td>Ni</td>
<td>1573</td>
<td>1x10$^{-11}$</td>
<td>1.8x10$^{-6}$</td>
<td>2.0x10$^3$</td>
<td>3.4x10$^1$</td>
<td>0.0063</td>
<td>0.4106</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>1x10$^{-11}$</td>
<td>1.8x10$^{-6}$</td>
<td>2.0x10$^3$</td>
<td>3.4x10$^1$</td>
<td>0.0063</td>
<td>0.4106</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>1x10$^{-7}$</td>
<td>1.8x10$^{-6}$</td>
<td>2.0x10$^3$</td>
<td>3.4x10$^1$</td>
<td>0.6306</td>
<td>0.4106</td>
</tr>
<tr>
<td>Pb</td>
<td>1573</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>2.8x10$^2$</td>
<td>1.3x10$^1$</td>
<td>0.0284</td>
<td>0.8350</td>
</tr>
<tr>
<td>Sn</td>
<td>1573</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>2.2x10$^4$</td>
<td>2.9x10$^1$</td>
<td>2.216</td>
<td>1.935</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>2.2x10$^4$</td>
<td>2.9x10$^1$</td>
<td>2.216</td>
<td>1.935</td>
</tr>
<tr>
<td></td>
<td>1523</td>
<td>3.2x10$^{-12}$</td>
<td>3.2x10$^{-6}$</td>
<td>4.1x10$^4$</td>
<td>4.1x10$^1$</td>
<td>0.0731</td>
<td>0.0724</td>
</tr>
<tr>
<td></td>
<td>1523</td>
<td>3.2x10$^{-12}$</td>
<td>3.2x10$^{-6}$</td>
<td>4.1x10$^4$</td>
<td>4.1x10$^1$</td>
<td>0.0731</td>
<td>0.0724</td>
</tr>
<tr>
<td>Mo</td>
<td>1573</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>2.3x10$^3$</td>
<td>6.5x10$^3$</td>
<td>225</td>
<td>28.16</td>
</tr>
<tr>
<td>Ag</td>
<td>1573</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>9.9x10$^{-2}$</td>
<td>3.29</td>
<td>0.001</td>
<td>0.844</td>
</tr>
<tr>
<td>Pd</td>
<td>1573</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>3.1x10$^{-2}$</td>
<td>5.9x10$^{-1}$</td>
<td>0.0003</td>
<td>0.1508</td>
</tr>
<tr>
<td>Pt</td>
<td>1573</td>
<td>1x10$^{-8}$</td>
<td>4.3x10$^{-3}$</td>
<td>1.8x10$^{-2}$</td>
<td>3.42</td>
<td>0.0002</td>
<td>0.8765</td>
</tr>
</tbody>
</table>

Table 4-4.2 summarizes the relevant describing reactions for the distribution of each respective element between matte and slag, the relevant thermodynamic data and provides a comparison between the predicted distribution coefficients and data from literature. The activity coefficient ratios were calculated from reported activity coefficient data from literature as reported in Sections 4-2 and 4-3.
Table 4-4.2: Describing reactions, thermodynamic data and comparison between predicted distribution coefficients and data from literature.

<table>
<thead>
<tr>
<th>Element</th>
<th>Describing Reaction</th>
<th>K</th>
<th>((\gamma_a/\gamma_b))</th>
<th>(L_{\text{Model}}^{m/s})</th>
<th>(L_{\text{Literature}}^{m/s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>{Sb}=(Sb)</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sb(l)+3/4O(<em>2)(g)=SbO(</em>{1.5})(l)</td>
<td>4.1x10(^5)</td>
<td>8.0</td>
<td>512</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>SbS(_{1.5})(l)+3/4O(<em>2)(g)=SbO(</em>{1.5})(l)+3/4S(_2)(g)</td>
<td>4.34x10(^4)</td>
<td>2.0</td>
<td>0.64</td>
<td>1.6</td>
</tr>
<tr>
<td>As</td>
<td>{As}=(As)</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>As(l)+3/4O(<em>2)(g)=AsO(</em>{1.5})</td>
<td>8.46x10(^4)</td>
<td>0.19</td>
<td>1.85</td>
<td>1.5</td>
</tr>
<tr>
<td>Bi</td>
<td>{Bi}=(Bi)</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>CdS(s)+1/2O(_2)(g)=CdO(s)+1/2S(_2)(g)</td>
<td>1.75x10(^1)</td>
<td>1.0</td>
<td>30.92</td>
<td>3.4</td>
</tr>
<tr>
<td>Zn</td>
<td>ZnS(l)+1/2O(_2)(g)=ZnO(s)+1/2S(_2)(g)</td>
<td>2.72x10(^3)</td>
<td>0.43</td>
<td>0.09</td>
<td>0.3</td>
</tr>
<tr>
<td>Co</td>
<td>CoS(l)+1/2O(_2)(g)=CoO(s)+1/2S(_2)(g)</td>
<td>6.37x10(^2)</td>
<td>5.0</td>
<td>2.75</td>
<td>4.0</td>
</tr>
<tr>
<td>Co</td>
<td>CoS(l)+1/2O(_2)(g)=CoO(s)+1/2S(_2)(g)</td>
<td>6.37x10(^2)</td>
<td>5.0</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(s)+1/3S(<em>2)(g)=NiS(</em>{0.667})(l)</td>
<td>3.35x10(^1)</td>
<td>1.0</td>
<td>0.34</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>NiS(_{0.667})(l)+1/2O(_2)(g)=NiO(s)+1/3S(_2)(g)</td>
<td>5.96x10(^1)</td>
<td>1.6</td>
<td>85.4</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>NiS(_{0.667})(l)+1/2O(_2)(g)=NiO(s)+1/3S(_2)(g)</td>
<td>5.96x10(^1)</td>
<td>1.6</td>
<td>0.85</td>
<td>3.0</td>
</tr>
<tr>
<td>Pb</td>
<td>PbS(l)+1/2O(_2)(g)=PbO(l)+1/2S(_2)(g)</td>
<td>2.23x10(^1)</td>
<td>0.05</td>
<td>1.21</td>
<td>4.0</td>
</tr>
<tr>
<td>Sn</td>
<td>SnS(l)+1/2O(_2)(g)=SnO(l)+1/2S(_2)(g)</td>
<td>7.54x10(^2)</td>
<td>26.7</td>
<td>19.1</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>SnS(l)+1/2O(_2)(g)=SnO(l)+1/2S(_2)(g)</td>
<td>7.54x10(^2)</td>
<td>1.0</td>
<td>0.72</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>SnS(l)+1/2O(_2)(g)=SnO(l)+1/2S(_2)(g)</td>
<td>1.01x10(^3)</td>
<td>26.7</td>
<td>21.7</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>SnS(l)+1/2O(_2)(g)=SnO(l)+1/2S(_2)(g)</td>
<td>1.01x10(^3)</td>
<td>1.0</td>
<td>0.81</td>
<td>2.8</td>
</tr>
<tr>
<td>Mo</td>
<td>MoS(_2)(s)+O(_2)(g)=MoO(_2)(s)+S(_2)(g)</td>
<td>3.46x10(^6)</td>
<td>1.0</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag(l)+1/4S(<em>2)(g)=AgS(</em>{0.5})(l)</td>
<td>3.29</td>
<td>1.0</td>
<td>0.69</td>
<td>100</td>
</tr>
<tr>
<td>Pd</td>
<td>Pd(s)+1/2S(_2)(g)=PdS(s)</td>
<td>5.88x10(^{-1})</td>
<td>1.0</td>
<td>0.03</td>
<td>400</td>
</tr>
<tr>
<td>Pt</td>
<td>Pt(s)+1/2S(_2)(g)=PtS(s)</td>
<td>7.70x10(^{-1})</td>
<td>1.0</td>
<td>0.04</td>
<td>500</td>
</tr>
</tbody>
</table>

Figure 4-4.1 shows plots of predicted distribution ratios against published distribution ratios. A line of \(L_{\text{predicted}}=L_{\text{Literature}}\) is plotted on both graphs to show the match between the two. It is concluded from both graphs that the predicted distribution ratios are generally in good agreement with distribution data from literature. The exceptions to this case are highlighted on the graph and discussed in more detail in the following section.
Antimony

The model was first validated against data by Yazawa (1980) for antimony distribution under the condition of copper saturation of matte and slag. The condition tested was for a temperature of 1573 K, oxygen partial pressure of $1 \times 10^{-11}$ atm and sulfur partial pressure of $1.5 \times 10^{-6}$. The result of the activity ratio test showed both activity ratio values to be lower than 0.01 i.e. metal-metal equilibrium was applicable. In this case, the distribution ratio is a direct function of the activity coefficient ratio. As long as the system remains metallic dissolution in both molten phases and the activity coefficient ratio remains constant the value of the distribution coefficient should remain constant with changing oxygen partial pressure. The distribution data from Yazawa (1980) in Figure 2-5.16 confirms this in the range of oxygen partial pressure below $1 \times 10^{-10}$ atm.

From Yazawa’s data in Figure 2-5.16, at oxygen partial pressures of above $1 \times 10^{-10}$ atm the oxide form of antimony was shown to exert some influence on the distribution coefficient. This was tested using the model and the value of the metal oxide/metal activity ratio was found to be greater than 0.01, confirming the presence of the oxide species (for any value of the activity ratio below 0.01 the oxide species does not exert influence on the distribution coefficient). Assuming the influence of the oxide species is still minimal (since the value of the activity ratio is only marginally larger than 0.01), the metallic species in slag should still provide a better prediction for distribution ratio under these conditions rather than assuming oxidic dissolution. The model has only taken into account the metallic form of antimony dissolution in slag, the inclusion of oxidic antimony in the slag phase would reduce the value of $L_{Sb}^{m/s}$ and bring the predicted value closer to that reported by Yazawa (1980).
Table 4-4.3 shows distribution data from the model and literature for oxygen partial pressures $1 \times 10^{-8}$ atm and higher. The activity ratio values for determining the species in the slag are considerably larger than 0.01 at these conditions and thus oxidic dissolution of antimony into the slag is assumed. Assuming oxidic dissolution of antimony into the slag, as the system shifts from a mixture of metallic and oxidic dissolution in the slag towards fully oxidic dissolution the distribution data predicted by the model should become closer in agreement with Yazawa’s data. Table 4-4.3 shows the predicted distribution coefficient for oxygen partial pressure ranging from $1 \times 10^{-8}$ atm to $1 \times 10^{-6}$ atm. It was expected that the predicted distribution coefficients at oxygen potentials greater than $1 \times 10^{-7}$ should be in better agreement with literature data as it was evidenced in Figure 4-1.3 that the system becomes fully oxidic dissolution under the said conditions. The data in Table 4-4.3 however shows that the agreement between predicted and literature distribution coefficients is best at $1 \times 10^{-8}$ atm, although there is still a considerable amount of antimony present as metal in the slag. This discrepancy could possibly be caused by the activity coefficient ratio $\gamma_{SbO1.5}/\gamma_{Sb}$. The predicted distribution values in Table 4-4.2 assume the activity coefficient ratio, $\gamma_{SbO1.5}/\gamma_{Sb}$, is constant with changing oxygen partial pressure, but this does not appear to be the case as the predicted distribution values become smaller than the values reported in literature at higher oxygen potentials.

<table>
<thead>
<tr>
<th>$P_{O_2}$(atm)</th>
<th>$L_{M/M^s}$ Model</th>
<th>$L_{M/M^s}$ Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-8}$</td>
<td>7.3</td>
<td>10</td>
</tr>
<tr>
<td>$1 \times 10^{-7}$</td>
<td>1.3</td>
<td>5.0</td>
</tr>
<tr>
<td>$1 \times 10^{-6}$</td>
<td>0.23</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Antimony distribution was also reported by Roghani et al. (2000) under oxidizing conditions. The model was tested at 1573 K with an oxygen potential of $1 \times 10^{-8}$ atm and sulfur partial pressure of $4.3 \times 10^{-3}$ atm. These conditions allowed the observation of the effect of higher sulfur partial pressure on the predicted distribution coefficient antimony. The activity ratio test showed sulfide species dissolution in the matte and oxide species dissolution in the slag. The value of $\gamma_{SbO1.5}$ is 2, but the value of $\gamma_{SbO1.5}$ is unknown and assumed to be ideal in the calculations. The agreement between the predicted distribution coefficient of 0.64 and the value of 1.6 reported in literature is good.
Arsenic

 Arsenic distribution was similarly tested at both reducing and oxidizing conditions. Under reducing conditions with copper saturation, metallic dissolution in both phases was inferred using the activity ratio test. The distribution data presented by Yazawa (1980) (Figure 2-5.23) at low oxygen potentials showed considerable scatter and made it difficult to confirm if the distribution coefficient is constant for oxygen partial pressures lower than $2 \times 10^{-10}$ atm, where the model predicts metallic dissolution in both molten phases. Under oxidizing conditions, the value of the distribution coefficient of arsenic reported by Johnson et al. (1982) and Roghani et al. (2000) has a constant value close to unity. The model predicts metallic dissolution of arsenic into the matte phase and oxidic dissolution of arsenic into the slag phase. The value of $\gamma_{As}$ is calculated from the following expression (Tan and Zhang, 1997):

$$\{\gamma_{As}\} = 8.087 - 0.128[Cu]_{Mt} + 0.014[Cu]_{Mt} \log[Cu]_{Mt}$$

[4-4.1]

The activity coefficient of arsenic oxide in slag was approximated from the following expression (Tan and Zhang, 1997):

$$\{\gamma_{AsO(\infty)}\} = 3.828 \exp[1523/ T] p_{O_2}^{0.158}$$

[4-4.2]

The predicted arsenic distribution coefficient of 1.85 compares well with the value of 1.5 reported in literature.

Cadmium

Cadmium distribution was modeled at 1503 K with an oxygen partial pressure of $1 \times 10^{-8}$ atm and sulfur partial pressure of $4.33 \times 10^{-3}$ atm. The activity ratio test shows cadmium dissolves as a sulfide in matte and as an oxide in slag. Due to the unavailability of activity coefficient data, ideality of cadmium species in both phases was assumed. The predicted distribution coefficient of cadmium was found to be approximately 31, an order of magnitude larger than the value of 3.4 reported by Mackey (1982). Assuming cadmium is chemically similar to zinc, the activity coefficient data for zinc oxide and zinc sulfide were used in place of the assumption of ideality in predicting the distribution coefficient of cadmium. The predicted distribution coefficient of 13 is much closer to the reported value of 3.4.
Zinc distribution was modeled under the same oxidizing conditions used in cadmium distribution modeling. The activity ratio test confirms zinc dissolves as a sulfide in matte and as an oxide in slag. The activity coefficient of zinc oxide with reference to the solid standard state was reported in Section 4-3 as having a value between 0.6 and 2.6. The activity coefficient of zinc sulfide with reference to the liquid standard state was reported as having a value of 6 in Section 4-2. The HSC Chemistry 5.1 database does not have data for zinc sulfide in the liquid standard state for temperatures below 2100 K, thus extrapolation of the Gibbs free energy of formation for zinc sulfide in the liquid standard state to the required temperature was required before the activity coefficient of ZnS(l) can be used. Data for the Gibbs free energy of formation for zinc sulfide with reference to the liquid standard state were obtained using HSC Chemistry for temperatures ranging from 2100 K to 3000 K as shown in Figure 4-4.2.

![Figure 4-4.2: Gibbs energy of formation of zinc sulfide with reference to the liquid standard state extrapolated to 1503 K.](image)

The extrapolation to 1503 K gave a value of -329.458 kJ/mol for the Gibbs free energy of formation of ZnS(l). The Gibbs free energy for the reaction in equation [4-4.3] is calculated using equation [4-4.4]. The Gibbs free energy of formation for oxygen gas, sulfur gas, and zinc oxide solid at 1503 K was obtained from HSC Chemistry 5.1. The Gibbs free energy for the reaction was found to be -98.827 kJ. The equilibrium constant was calculated to be 2721.
Chapter 4: Thermodynamic Model

\[ \text{ZnS}(l) + \frac{1}{2} \text{O}_2(g) = \text{ZnO}(s) = \frac{1}{2} \text{S}_2(g) \]  

\[ \Delta G_r = \Sigma \Delta G_{f,\text{products}} - \Sigma \Delta G_{f,\text{reactants}} \]  

Having expressed the reaction in the form of zinc sulfide with reference to the liquid standard state, the activity coefficient data can be used in the model. The predicted distribution coefficient value of 0.09 is in close agreement with the value of 0.3 reported by Mackey (1982) in literature.

**Nickel**

Modeling of nickel distribution was conducted at 1573 K under conditions of copper saturation (constant sulfur partial pressure) for oxygen partial pressures between 1x10^{-11} and 1x10^{-4} atm. At oxygen partial pressure of 1x10^{-11} atm, the activity ratio test shows metallic dissolution of nickel into the slag phase and sulfidic dissolution in the matte phase. The activity coefficient of nickel in slag is not (although it is likely to be larger than unity) and therefore the activity coefficient ratio has been assumed to be unity. The model predicts the nickel distribution coefficient under these conditions to be 0.32; however Yazawa (1980) reports the distribution coefficient to be approximately 100. The activity coefficient of nickel in slag would have to be unrealistically larger than 1 to narrow the difference between the predicted and reported value of the distribution coefficient.

A more plausible explanation is that the value of the activity ratio for species in the slag phase is 0.0063 and is close to the assumed threshold value of 0.01 set for the activity ratio test. Assuming that nickel dissolves as an oxide in the slag and as a sulfide in matte, the new describing reaction can be expressed as shown in equation [4-4.5].

\[ \text{NiS}_{0.667}(l) + \frac{1}{2} \text{O}_2(g) = \text{NiO}(s) + \frac{1}{3} \text{S}_2(g) \]  

The activity coefficient of nickel oxide with reference to the solid standard state is shown to be 4.0. The activity coefficient of nickel sulfide with reference to the liquid standard state is given by the following expression (Tan and Zhang, 1997):

\[ \gamma'_{\text{NiS}_{0.67}} = \exp(1377/T) \]
The predicted distribution coefficient for nickel under these conditions was found to be 80.4, which is in much better agreement with the experimental data reported by Yazawa (1980).

The results of the two predictions have highlighted the fact that the early assumptions made with regards to the activity ratio test are not definitive. It could be that nickel is a unique case or that the appointed threshold value of 0.01 is too high. The only way to arrive at a more definitive solution is to validate the model over a broader range of elements and conditions. The model was also used to test nickel distribution at higher oxygen potentials as reported by Yazawa (1980) and the predicted distribution coefficient of 0.85 compares rather well with the reported value of 3.0 from literature.

Tin

Tin distribution was investigated at both oxidizing and reducing conditions. The activity coefficient of tin oxide in iron silicate slag with reference to the liquid standard state lies between 0.8 and 2.0 (Nagamori and Mackey, 1977). The activity coefficient for tin sulfide in matte with reference to the liquid standard state is approximately 0.028 (Sinha et al., 1984). When testing under oxidizing conditions \( \left( P_{O_2} = 1 \times 10^{-8} \text{ atm}, P_{S_2} = 4.3 \times 10^{-3} \text{ atm} \right) \) the predicted distribution coefficient was found to be 19.1 which does not compare well with the reported value of 1.5. Under reducing conditions the predicted distribution coefficient of 21.7 was again much larger than the value reported by Louey et al. (1999) of 2.8. There is actually better agreement between predicted and literature distribution coefficients when the activity coefficient ratio is assumed to be unity, suggesting perhaps the activity coefficient data from literature may not be reliable.

Of the remaining tests conducted for literature data, cobalt and molybdenum showed excellent agreement with literature data. In the case of molybdenum, the activity coefficient ratio, \( \{\gamma_{MoO_2}/\gamma_{MoS_2}\} \), is assumed to be unity. Modeling of silver and the platinum group elements (palladium and platinum) under oxidizing conditions fall under Case No. 3 (Table 4-1.4) i.e. metallic dissolution in slag and sulfidic dissolution in matte. The predicted distribution coefficients in all three cases were very much smaller than the values reported in literature when assuming the activity coefficient ratio is unity. It must be noted however that the activity coefficient of the metallic element in slag is expected to have a very large value (Swinbourne and You (1999) reported the activity coefficient of metallic silver in sodium silicate slags to have a value greater than 100), which would bring the predicted and reported distribution coefficients in closer agreement.
Summary of findings:

- The model generally predicts the distribution coefficient well. Of the elements examined, many predictions of the distribution ratio are of the correct order of magnitude when compared to literature data.

- The elements that did not model well were generally within an order of magnitude larger or smaller than reported values. These are presumed to be elements where either the influence of the activity coefficient ratio on the distribution coefficient outweighs the equilibrium constant or where there are mixed states of dissolution. Errors associated with the value of the equilibrium constant also need to be considered. Typically, a 5% change in the Gibbs free energy value changes $K$ by one order of magnitude and could explain some of the discrepancies.

- There is not enough data to fully validate the activity ratio test for determining the form of dissolution of species in the molten phases. It is not known whether the failure of the test in the case of nickel is an exception to the rule or that the rule needs to be redefined.

- The data available in literature have been useful in validating the model; however it would be invaluable to have the model tested against a broader range of elements.
Chapter 5: Experimental

CHAPTER 5: EXPERIMENTAL

5-1 OPERATING CONDITIONS

The aim of this research project is to examine how selected microelements distribute between molten matte and slag under reducing matte smelting conditions as employed by Boliden Minerals AB in their electric smelting furnace at Rönnskär. The experimental conditions are set with the intention of mimicking the conditions employed in the electric smelting furnace in order to provide data relevant to their operations. The set of conditions required to fully define the reductive matte smelting system can be determined by applying the Gibb’s Phase Rule.

The components present in the system are iron, copper, sulfur, oxygen and silica (C=5). The phases present are gas, slag and matte (P=3). The composition of major components for the Rönnskär electric smelting furnace slag is shown in Table 5-1.1.

Table 5-1.1: Rönnskär electric smelting furnace slag composition.

<table>
<thead>
<tr>
<th></th>
<th>wt% SiO₂</th>
<th>wt% Fe</th>
<th>wt% MgO</th>
<th>wt% Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>28.11</td>
<td>30.39</td>
<td>0.94</td>
<td>0.35</td>
</tr>
<tr>
<td>Maximum</td>
<td>40.71</td>
<td>40.86</td>
<td>8.77</td>
<td>2.64</td>
</tr>
<tr>
<td>Average</td>
<td>36.03</td>
<td>36.49</td>
<td>1.45</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Figure 5-1.1 shows the FeO-Fe₂O₃-SiO₂ ternary system at 1523 K. The fayalite region is bounded by the tridymite, magnetite, wustite and iron saturation boundaries. The maximum solubility of silica in fayalite slag at 1523 K is shown on the diagram to be approximately 36 wt% and close to the iron saturation boundary. The Rönnskär slag therefore has a composition close to both silica and iron saturation. The number of phases present in the system is now increased to 5, accounting for the presence of solid iron and solid silica.
The operating temperature is set at 1523 K. This leaves one degree of freedom, which can be the copper content of the matte. Table 5-1.2 shows the average matte composition at the Rönnskär smelter. A matte grade of 55 wt% Cu was chosen for the experiments.

<table>
<thead>
<tr>
<th></th>
<th>wt% Cu</th>
<th>wt% Fe</th>
<th>wt% S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>43.66</td>
<td>10.92</td>
<td>16.24</td>
</tr>
<tr>
<td>Maximum</td>
<td>58.54</td>
<td>25.35</td>
<td>25.14</td>
</tr>
<tr>
<td>Average</td>
<td>52.40</td>
<td>17.05</td>
<td>22.79</td>
</tr>
</tbody>
</table>

As mentioned in Chapter 2-5.3, for a system such as this one where the slag is saturated with iron and silica and the matte grade is approximately 50 wt%; the generated partial pressures of oxygen and sulfur in the equilibrium gas phase are so low that nitrogen can be used as the gas phase for the equilibrium experiments. Precise control of nitrogen gas flowrate is not necessary provided positive pressure is maintained in the furnace. A flowrate of 300 cm³/min was used in all experiments.
5-2 MATERIAL PREPARATION

The experiments included in this research project can be categorized into ‘industrial’ and ‘synthetic’ experiments. The industrial experiments did not require much preparation and simply involved further equilibrating matte and slag samples obtained from the Rönnskär electric smelting furnace. The industrial experiments provided data on the concentrations of a broad range of microelements which were present in the Rönnskär smelting circuit.

The synthetic experiments required preparation of matte and slag from reagent grade chemicals. Microelements are selectively doped into the synthetic phases, which allows for more controlled conditions for studying element distribution behavior. This includes varying the concentration of microelement to test for possible saturation of species in the molten phases and also provides the means for establishing that equilibrium has been achieved by approaching equilibrium from both directions.

The following section provides details for the preparation of synthetic slag and matte.

5-2.1 MATTE

The appropriate proportions of reagent grade copper (I) sulfide powder, iron (II) sulfide powder and microelement (sulfide form if doping into the matte) were mixed well using a pestle and mortar. The mixture was then packed into a 10 mm blind hole drilled into a graphite block. Carbon has been used as crucible material in other copper smelting investigations (Yazawa and Kameda, 1954; Nagamori, 1974; Louey, 1999). A small layer of excess sulfur was added to the top of the mixture to allow for oxidation of sulfur during the initial stages of melting (Louey, 1999). This was followed by a thin layer of carbon powder and a close fitting carbon lid.

The outer surface of the graphite blocks disintegrate during the heating period due to reaction with oxygen, thus a minimal wall thickness of 20 mm was required. The oxidation of the graphite block with oxygen had the added benefit of reducing the oxygen partial pressure inside the crucible.

The crucible assembly was placed inside a muffle furnace and surrounded with refractory bricks. The crucible was heated to 1473 K and held for two hours. After allowing the crucible to cool, it was cracked open to recover the matte. The matte was ground into a coarse powder in a ring mill and stored in a plastic container.
Synthetic slag was made by mixing the appropriate proportions of high purity iron powder, iron (III) oxide, silica and impurity oxide (if doping into the slag phase) and packing the mixture into a magnesia crucible. The crucible was placed into a tube furnace and left for five hours at 1523 K under a nitrogen atmosphere. At the end of the heating cycle, the crucible was lowered from the hot zone and left to cool for 10 minutes under nitrogen before being removed from the furnace. The slag was recovered and ground in a ring mill.

All experiments were conducted in a vertical tube furnace made by B&L Tetlow Pty Ltd. The furnace tube was made of mullite with a total height of 1000 mm, internal diameter of 60 mm and wall thickness of 5 mm. The ends of the vertical tube furnace were closed with removable aluminium end caps sealed with O-rings and held tightly in place with bolts. Small fans were installed on the top and bottom of the furnace with the purpose of for cooling the end caps to prevent breakdown of the O-rings due to excessive heat. The furnace was fitted with a Shinko FSC23A temperature indicating controller connected to a type R (Pt/Pt13%Rh) thermocouple situated near the middle, and touching the outside of the furnace tube. An alumina stalk with a platform was supported through the bottom end cap and held in place with a machined brass fitting made gas tight with carbon fiber impregnated rope. The carbon fiber rope was used in place of O-rings because the O-rings tended to break down and melt onto the alumina stalk, causing failure of the support stalk. The position of the platform could be adjusted by loosening the brass fitting on the end cap, moving the stalk into the required position and tightening the fitting.

The crucible assembly consisted of a magnesia sample crucible, an alumina tray and an alumina crucible. The choice of crucible to hold the sample was discussed previously in Chapter 2-5.3, with magnesia deemed most suitable due to its lower solubility in the melt. Alumina crucibles were used for the lid and tray because they did not come into contact with the melts and represented the cheaper option as opposed to magnesia crucibles. Matte and slag was packed into the sample crucible. Alumina powder was placed in the alumina tray to catch any spills and prevent damage to the platform or tube furnace. The sample crucible was placed on the alumina powder and an alumina crucible was upturned and gently placed over the sample crucible. The upturned alumina crucible acts as a lid to reduce loss of species from the sample due to volatilization, while
connection to the furnace atmosphere is maintained through the porous alumina bed. This prevents the compositions of the phases from changing. The crucible assembly is shown schematically in Figure 5-3.1.

Figure 5-3.1: Schematic diagram of the tube furnace and crucible assembly (Louey, 1999).

The platinum thermocouple wires dissolving into the matte phase, the corrosive nature of copper matte and iron silicate slag towards an alumina thermocouple sheath when dipped into the melt and the inclusion of a lid on the crucible assembly all prevented the use of a thermocouple to measure the temperature of the melt. Instead, the hot zone position in the furnace and the temperature in that region were predetermined. This was done by inserting a type R thermocouple into the hollow space of the alumina support stalk as shown in Figure 5-3.1. The height of the alumina stalk and thermocouple were adjusted by 10 mm increments and the temperature change recorded. The data are shown in Figure 5-3.2.
Figure 5-3.2: Determining the hot zone of the vertical tube furnace with furnace controller set at 1573 K.

The hottest position in the furnace was found to be 575 mm above the bottom end plate with the temperature varying by no more than 2 K for a distance of 25 mm either side of the hot zone. A furnace controller temperature of 1555 K was found to produce a temperature of 1523 K at the hot zone.

5-4 Procedure

The following section describes the experimental procedure for the distribution experiments. The procedure is similar for both the industrial and synthetic experiments; however differences where applicable will be detailed.

5-4.1 Industrial Matte and Slag Experiments

The matte and slag samples were first ground into powder to allow for easier and more accurate measurement for addition into the sample crucible. 5g of matte powder was placed into the bottom of a magnesia crucible and the crucible was knocked to settle the powder and increase the packing density. 5g of slag was then added on top of the matte layer and again knocked to increase packing density. The total mass of the crucible, matte and slag was determined. This allows accounting for any material loss.
which is an indication of volatilization of species from the molten phases. The alumina tray was filled part-way with alumina powder and the sample crucible placed gently on top of the alumina powder. An inverted alumina crucible was then placed on top of the sample crucible to act as a lid. The crucible assembly was placed on the platform of the support stalk and gently raised into the vertical tube furnace. The aluminum end cap was bolted tightly into position and the platform carefully raised to the hot zone by adjusting the height of the alumina support stalk. The vertical tube furnace was sealed and purged with nitrogen gas for a few minutes. The temperature controller was set to the desired temperature and the furnace switched on. The furnace reached 1523 K approximately two hours after being switched on and the equilibrium/reaction time began at this point. The furnace was left on for the required reaction time and then switched off. The crucible and its contents were quenched by lowering the alumina support stalk tube by 100 mm, reducing the temperature from 1523 K to 1323 K in less than five minutes. While drop quenching provides a much faster cooling rate, the technique used was deemed sufficient to preserve the composition of the phases present at 1523 K. The rate of quenching was limited by thermal shock of the alumina support stalk if cooled too quickly. After allowing the furnace to cool to room temperature, the crucible assemble was removed from the tube furnace and the sample crucible weighed for mass balance purposes. The crucible was cracked open and the slag and matte phases carefully separated. The surface of the slag in contact with matte was removed to prevent entrained matte from incurring errors in analysis. After separation, the recovered matte and slag were separately crushed in a ring mill and stored in plastic sample vials. Half of the matte and slag samples recovered were sent for chemical analysis and the other half retained in case of future need i.e. re-analysis, etc.

For the industrial experiments, the matte and slag samples have already been equilibrated since they were tapped products from an electric smelting furnace. The objective of the distribution experiments then was to allow as many microelements as possible to reach a state of equilibrium. In order to achieve this, the procedure above was repeated for increasing reaction times and the samples analyzed for impurity element concentration. Analysis of the industrial experiments was performed by Becquerel Laboratories using Neutron Activation Analysis.

5-4.2 SYNTHETIC MATTE AND SLAG EXPERIMENTS

The synthetic matte and slag experiments allowed for controlled addition of a microelement into either the synthetic matte or slag phase. This is a useful tool for
determining the true equilibrium of the system as well as to test for saturation of species in either of the molten phases.

The experimental procedure is similar to that described for the industrial experiments. The only difference was varying the concentration of the impurity element doped into the synthetic matte and slag phases. The distribution behaviors of two elements were examined; cobalt and tungsten.

For cobalt, two series of experiments were conducted. Synthetic copper matte and iron silicate slag were equilibrated at 1523 K with 0.6 wt% Co added to the matte as cobalt sulfide (CoS) in one series and the same amount added to the slag as cobalt oxide (CoO) in the other series. For each series, experiments were performed with increasing reaction time. The convergence of both data sets was used to confirm the time necessary for the system to achieve true equilibrium. Analysis of the matte and slag for the cobalt experiments was performed by Spectrometer Services using Inductively Coupled Plasma Atomic Emission Spectroscopy.

The tungsten distribution experiments were complicated by the fact that the solubility of tungsten (VI) oxide in iron silicate slag and the solubility of tungsten (IV) sulfide in copper matte are not known. As discussed in Chapter 2-5.2, saturation of species in either phase will cause systematic errors in the value determined for the distribution ratio. The first series of tungsten distribution experiments was used to investigate saturation of tungsten species in molten matte and slag. This was done by observing the change to the distribution ratio with increasing concentration of tungsten (IV) sulfide doped into the matte phase (1600 ppm W, 3090 ppm W and 6490 ppm W respectively). Again, a number of experiments were performed with incremental reaction time to establish equilibrium of the system. The second series of tungsten experiments was performed by doping 3080 ppm W in the slag phase as tungsten (VI) oxide and equilibrating it with synthetic matte. Analysis of the tungsten content in the matte and slag for these experiments was performed by Becquerel Laboratories using Neutron Activation Analysis.

5.4.3 Method of Analysis

Inductively Couple Plasma – Atomic Emission Spectrometry (ICP-AES) was used to analyze for cobalt, copper, iron, silica and magnesia. The analysis was carried out by Spectrometer Services Pty Ltd, using the Jobin Yvon (JY24) inductively coupled plasma atomic emission spectrometer. Sulfur content was analyzed by Leco Combustion using the Leco CS-200. The slag and matte samples were supplied in the form of fine powders.
Copper and cobalt were digested using a mixed acid of HNO₃, HF, HClO₄ and HCl before being analyzed. Iron, silica, and magnesia were digested using a fusion technique with a mixture of lithium metaborate and lithium tetraborate fluxes prior to analysis. Sulfur content in a sample was analyzed by combustion of the sample in an atmosphere of oxygen using an induction coil followed by detection of sulfur oxide by infrared cell.

In addition to ICP-AES, neutron activation analysis (NAA) was also used for analysis of samples. NAA was used in place of ICP-AES for the industrial experiments as well as the tungsten distribution experiments. The advantage of NAA was that it could analyze for many elements within a single sample without destroying the sample, which was extremely beneficial in the case of the industrial experiments. In addition, NAA is a very sensitive technique which was convenient for analyzing elements present in very low concentrations. Table 5-4.1 gives the minimum detection limits for elements analyzed by NAA. It should be noted that the detection limits provided are approximations and can vary by an order of magnitude depending on the sample matrix. The analysis was carried out at Becquerel Laboratories, Australia, as well as at Becquerel Laboratories, Canada.

The relative error for determination by ICP-AES is quoted to be 2-3% for concentration levels above 1% and between 3-5% for concentration levels below 1%. The relative error for sulfur determination by Leco combustion was quoted to be 5%.

<table>
<thead>
<tr>
<th>Detection Limits [ppm]</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>Gold</td>
</tr>
<tr>
<td>0.02</td>
<td>Iridium</td>
</tr>
<tr>
<td>0.1</td>
<td>Cadmium, Scandium</td>
</tr>
<tr>
<td>0.2</td>
<td>Antimony, Lutetium, Samarium</td>
</tr>
<tr>
<td>0.5</td>
<td>Europium, Hafnium, Lanthanum, Thorium, Ytterbium</td>
</tr>
<tr>
<td>1.0</td>
<td>Arsenic, Bromine, Cesium, Cobalt, Indium, Tantalum</td>
</tr>
<tr>
<td>2.0</td>
<td>Cerium, Tungsten, Uranium</td>
</tr>
<tr>
<td>5.0</td>
<td>Chromium, Molybdenum, Selenium, Silver, Tellurium, Vanadium</td>
</tr>
<tr>
<td>20</td>
<td>Rubidium</td>
</tr>
<tr>
<td>100</td>
<td>Barium, Sodium, Zinc</td>
</tr>
<tr>
<td>200</td>
<td>Strontium</td>
</tr>
<tr>
<td>500</td>
<td>Iron, Tin, Zirconium</td>
</tr>
<tr>
<td>1000</td>
<td>Germanium, Titanium</td>
</tr>
</tbody>
</table>
6-1 INDUSTRIAL EXPERIMENTS

The industrial experiments were performed by equilibrating copper matte and iron silicate slag sampled from Rönnskär’s electric smelting furnace at 1523 K under reducing conditions. The use of industrial matte and slag samples containing many microelements originating from the raw materials had several benefits:

- There was no need to dope microelements into the system, thus there was no fear of OH&S issues for handling of individual compounds and chemicals.
- The samples were already partially equilibrated in the electric smelting furnace.
- The use of Neutron Activation Analysis meant that a large amount of distribution data can be obtained for each sample.

The industrial experiments were performed to:

- Give an indication of the various microelements present in a smelting circuit and at what concentrations they are present,
- Give an indication of the distribution behavior for many microelements. While a definitive equilibrium distribution coefficient may not be able to be determined for some microelements due to analytical restrictions, it is sufficient in most cases to show a microelement heavily favoring one phase or the other.
- Generate a lot of data useful for testing the thermodynamic model.

The results of these experiments can fall into one of the following categories:

- The microelement could be at equilibrium from which actual distribution coefficient values can be reported. Because industrial samples were used, no control over the amounts of element added or to which phase it was introduced could be performed. As mentioned in Section 2-5.3, without observing approach to equilibrium from both directions, it is impossible to ascertain that true equilibrium has been achieved.
- The microelement may heavily favor one phase over the other. This scenario was most easily identified when analysis reported the concentration of the microelement in one phase but not in the other because the concentration in the latter phase was below the minimum detectable limit. The value of the distribution coefficient cannot be calculated; however the distribution behavior of the
microelement can be used to validate the prediction made by the thermodynamic model.

- The microelement does not reach equilibrium. This was assumed for microelements which did not show constant concentration as a function of time or which displayed a lot of scatter/erratic distribution behavior. These results are unreliable and therefore will not be reported.
- The concentration of the microelement is below the minimum detectable limit in both phases and no data can be reported.

Elements at Equilibrium

The elements that fall into this category include gold (Au), cobalt (Co) and molybdenum (Mo). Table 6-1.1 shows the concentration of gold in matte and slag under the conditions used. There is some discrepancy in the data such that the total concentration of gold from both phases is inconsistent. This discrepancy is likely to be caused by errors associated with chemical analysis. From the calculated distribution coefficients, equilibrium seems to be achieved after 8 hours. The distribution coefficient of gold is approximately 43, heavily favoring the matte phase.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppb Au]</th>
<th>Slag [ppb Au]</th>
<th>$L_{Au}^{m/s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>16200</td>
<td>192</td>
<td>84.4</td>
</tr>
<tr>
<td>4</td>
<td>17000</td>
<td>236</td>
<td>72.0</td>
</tr>
<tr>
<td>8</td>
<td>16800</td>
<td>408</td>
<td>41.2</td>
</tr>
<tr>
<td>16</td>
<td>17300</td>
<td>379</td>
<td>45.7</td>
</tr>
</tbody>
</table>

Table 6-1.2 gives the concentration of cobalt in matte and slag under reducing conditions. Equilibrium is achieved after approximately 4 hours and the distribution coefficient, $L_{Co}^{m/s}$, was found to be approximately 1.7.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppm Co]</th>
<th>Slag [ppm Co]</th>
<th>$L_{Co}^{m/s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>268</td>
<td>203</td>
<td>1.32</td>
</tr>
<tr>
<td>4</td>
<td>276</td>
<td>169</td>
<td>1.63</td>
</tr>
<tr>
<td>8</td>
<td>287</td>
<td>165</td>
<td>1.74</td>
</tr>
<tr>
<td>16</td>
<td>294</td>
<td>160</td>
<td>1.84</td>
</tr>
</tbody>
</table>
Table 6-1.3 gives the concentration of molybdenum in matte and slag under reducing conditions. The data at 8 hours appears to be suspect because the molybdenum content in both phases seems to have increased when compared to the data at 4 hours. Taking the errors into account, the data are still deemed to be acceptable for the purpose of this study. It was concluded that equilibrium is achieved after 4 hours and the distribution coefficient, \( L_{Mo^{m/s}} \), was found to be approximately 0.09.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppm Mo]</th>
<th>Slag [ppm Mo]</th>
<th>( L_{Mo^{m/s}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>365</td>
<td>1050</td>
<td>0.348</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>1290</td>
<td>0.078</td>
</tr>
<tr>
<td>8</td>
<td>167</td>
<td>1350</td>
<td>0.124</td>
</tr>
<tr>
<td>16</td>
<td>85.2</td>
<td>1400</td>
<td>0.061</td>
</tr>
</tbody>
</table>

The distribution coefficients for gold, cobalt and molybdenum were modeled at 1523 K with an oxygen partial pressure of \( 1 \times 10^{-9} \) atm and sulfur partial pressure of \( 3.1 \times 10^{-4} \) atm corresponding to reducing conditions as used in the experimental work. The results of the modeling are summarized in Tables 6-1.4 and 6-1.5.

Table 6-1.4: Summary table showing conditions, thermodynamic data and activity ratio calculations for gold, cobalt and molybdenum.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature [K]</th>
<th>( p_{O_2} , [atm] )</th>
<th>( p_{S_2} , [atm] )</th>
<th>( K_a )</th>
<th>( K_b )</th>
<th>( a_{MoX}/a_M )</th>
<th>( a_{MSx}/a_M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1523</td>
<td>( 1 \times 10^{-9} )</td>
<td>( 3.1 \times 10^{-4} )</td>
<td>( 5.2 \times 10^{-4} )</td>
<td>( 2.8 \times 10^{-1} )</td>
<td>( 6.1 \times 10^{-16} )</td>
<td>( 6.6 \times 10^{4} )</td>
</tr>
<tr>
<td>Co</td>
<td>1523</td>
<td>( 1 \times 10^{-9} )</td>
<td>( 3.1 \times 10^{-4} )</td>
<td>( 2.3 \times 10^{-4} )</td>
<td>( 2.7 \times 10^{-1} )</td>
<td>( 0.7137 )</td>
<td>( 0.4763 )</td>
</tr>
<tr>
<td>Mo</td>
<td>1523</td>
<td>( 1 \times 10^{-9} )</td>
<td>( 3.1 \times 10^{-4} )</td>
<td>( 9.4 \times 10^{10} )</td>
<td>( 1.7 \times 10^{4} )</td>
<td>( 9.4 \times 10^{10} )</td>
<td>( 5.351 )</td>
</tr>
</tbody>
</table>

Modeling of cobalt and molybdenum under reducing conditions fall under Case No. 4 (Table 4-1.4) i.e. oxidic dissolution of the element in slag and sulfidic dissolution of the element in matte. The predicted distribution coefficient for cobalt has a value of 2.74 which compares very well with the experimental value of 1.7. Similarly, the predicted distribution coefficient of molybdenum (0.05) was found to be in very good agreement with the value of 0.09 found experimentally. Gold was modeled and found to distribute in the metallic form in both phases. The lack of activity coefficient data means that the model cannot make a prediction.

Table 6-1.5: Describing reactions, thermodynamic data and comparison between predicted distribution coefficients and data from literature.
Table 6-1.6: Cadmium content in matte and slag at 1523 K as analyzed by NAA.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppm Cd]</th>
<th>Slag [ppm Cd]</th>
<th>(L_{Cd}^m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>108</td>
<td>&lt;30</td>
<td>&gt;3.6</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>&lt;30</td>
<td>&gt;5.0</td>
</tr>
<tr>
<td>8</td>
<td>112</td>
<td>&lt;30</td>
<td>&gt;3.7</td>
</tr>
<tr>
<td>16</td>
<td>85</td>
<td>&lt;30</td>
<td>&gt;2.8</td>
</tr>
</tbody>
</table>

Table 6-1.7 shows the concentrations of iridium in matte and slag under reducing conditions. The distribution coefficient of iridium should have a value greater than 4.5.

Table 6-1.7: Iridium content in matte and slag at 1523 K as analyzed by NAA.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppm Ir]</th>
<th>Slag [ppm Ir]</th>
<th>(L_{Ir}^m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>166</td>
<td>&lt;40</td>
<td>&gt;4.2</td>
</tr>
<tr>
<td>4</td>
<td>198</td>
<td>&lt;40</td>
<td>&gt;5.0</td>
</tr>
</tbody>
</table>
Chapter 6: Results & Discussion

Tables 6-1.8 and 6-1.9 show the results of the modeling. Modeling of the distribution coefficient of cadmium shows oxidic dissolution of cadmium into the slag phase and sulfidic dissolution into the matte phase. The activity coefficient ratio has been assumed to be unity. The distribution coefficient as predicted from the model is shown to be greater than 3.8, which is in agreement with the experimental data. Iridium was shown to dissolve in the metallic form in both matte and slag and therefore without activity coefficient values the model cannot make a prediction for the distribution coefficient.

**Table 6-1.8**: Summary table showing conditions, thermodynamic data and activity ratio calculations for cadmium and iridium.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature[K]</th>
<th>$p_{O_2}$[atm]</th>
<th>$p_{S_2}$[atm]</th>
<th>$K_a$</th>
<th>$K_b$</th>
<th>$a_{MOx/a_M}$</th>
<th>$a_{MSx/a_M}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>1523</td>
<td>$1x10^{-9}$</td>
<td>$3.1x10^{-4}$</td>
<td>$3.6x10^3$</td>
<td>$2.2x10^2$</td>
<td>$1.1x10^{-1}$</td>
<td>$3.8$</td>
</tr>
<tr>
<td>Ir</td>
<td>1523</td>
<td>$1x10^{-9}$</td>
<td>$3.1x10^{-4}$</td>
<td>$3.0x10^{-2}$</td>
<td>$5.1x10^{-1}$</td>
<td>$5.4x10^{-9}$</td>
<td>$1.2x10^{-3}$</td>
</tr>
</tbody>
</table>

**Table 6-1.9**: Describing reactions, thermodynamic data and comparison between predicted distribution coefficients and data from literature.

<table>
<thead>
<tr>
<th>Element</th>
<th>Describing Reaction</th>
<th>$K$</th>
<th>$(\gamma_a)/\gamma_b$</th>
<th>$L_{MM/s}$ Model</th>
<th>$L_{MM/s}$ Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>CdS(s)+1/2O$_2$(g)=$CdO(s)+1/2S_2(g)$</td>
<td>$1.66x10^1$</td>
<td>1.0</td>
<td>27.5</td>
<td>&gt;3.8</td>
</tr>
<tr>
<td>Ir</td>
<td>{Ir}={Ir}</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>&gt;4.5</td>
</tr>
</tbody>
</table>

The elements that heavily favor the slag phase include barium, scandium, hafnium, cerium, thorium and tungsten. Tables 6-1.10 to 6-1.15 show the concentrations of the aforementioned elements in matte and slag under reducing conditions at 1523 K. As observed in each case the concentration of the element in the matte phase was found to be below the minimum detectable limit when analyzed using Neutron Activation Analysis.

**Table 6-1.10**: Barium content in matte and slag at 1523 K as analyzed by NAA.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppm Ba]</th>
<th>Slag [ppm Ba]</th>
<th>$L_{Ba/MM/s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&lt;200</td>
<td>1230</td>
<td>&lt;0.16</td>
</tr>
<tr>
<td>4</td>
<td>&lt;200</td>
<td>1230</td>
<td>&lt;0.16</td>
</tr>
<tr>
<td>8</td>
<td>&lt;200</td>
<td>1120</td>
<td>&lt;0.18</td>
</tr>
<tr>
<td>16</td>
<td>&lt;200</td>
<td>984</td>
<td>&lt;0.20</td>
</tr>
</tbody>
</table>
### Table 6-1.11: Scandium content in matte and slag at 1523 K as analyzed by NAA.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppm Sc]</th>
<th>Slag [ppm Sc]</th>
<th>Lsc m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&lt;0.2</td>
<td>1.95</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>4</td>
<td>&lt;0.2</td>
<td>1.81</td>
<td>&lt;0.11</td>
</tr>
<tr>
<td>8</td>
<td>&lt;0.2</td>
<td>1.82</td>
<td>&lt;0.11</td>
</tr>
<tr>
<td>16</td>
<td>&lt;0.2</td>
<td>1.80</td>
<td>&lt;0.11</td>
</tr>
</tbody>
</table>

### Table 6-1.12: Hafnium content in matte and slag at 1523 K as analyzed by NAA.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppm Hf]</th>
<th>Slag [ppm Hf]</th>
<th>LHf m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&lt;1.0</td>
<td>3.18</td>
<td>&lt;0.31</td>
</tr>
<tr>
<td>4</td>
<td>&lt;1.0</td>
<td>4.09</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>8</td>
<td>&lt;1.0</td>
<td>4.35</td>
<td>&lt;0.23</td>
</tr>
<tr>
<td>16</td>
<td>&lt;1.0</td>
<td>3.56</td>
<td>&lt;0.28</td>
</tr>
</tbody>
</table>

### Table 6-1.13: Cerium content in matte and slag at 1523 K as analyzed by NAA.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppm Ce]</th>
<th>Slag [ppm Ce]</th>
<th>Lce m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&lt;5.0</td>
<td>22.5</td>
<td>&lt;0.22</td>
</tr>
<tr>
<td>4</td>
<td>&lt;5.0</td>
<td>24.1</td>
<td>&lt;0.21</td>
</tr>
<tr>
<td>8</td>
<td>&lt;5.0</td>
<td>25.5</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>16</td>
<td>&lt;5.0</td>
<td>28.9</td>
<td>&lt;0.17</td>
</tr>
</tbody>
</table>

### Table 6-1.14: Thorium content in matte and slag at 1523 K as analyzed by NAA.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppm Th]</th>
<th>Slag [ppm Th]</th>
<th>Lth m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&lt;1.0</td>
<td>3.78</td>
<td>&lt;0.27</td>
</tr>
<tr>
<td>4</td>
<td>&lt;1.0</td>
<td>2.08</td>
<td>&lt;0.48</td>
</tr>
<tr>
<td>8</td>
<td>&lt;1.0</td>
<td>3.29</td>
<td>&lt;0.30</td>
</tr>
<tr>
<td>16</td>
<td>&lt;1.0</td>
<td>3.06</td>
<td>&lt;0.33</td>
</tr>
</tbody>
</table>

### Table 6-1.15: Tungsten content in matte and slag at 1523 K as analyzed by NAA.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Matte [ppm W]</th>
<th>Slag [ppm W]</th>
<th>LW m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&lt;5.0</td>
<td>55.1</td>
<td>&lt;0.09</td>
</tr>
<tr>
<td>4</td>
<td>&lt;5.0</td>
<td>60.4</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>8</td>
<td>&lt;5.0</td>
<td>64.1</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>16</td>
<td>&lt;5.0</td>
<td>62.5</td>
<td>&lt;0.08</td>
</tr>
</tbody>
</table>
Table 6.1.16 and 6.1.17 show the results of modeling the distribution coefficient for barium, scandium, hafnium, thorium and tungsten. It is to be noted that no activity coefficient data are available. Because of this the activity coefficient ratio in each case has been assumed to be unity.

In the case of barium, the activity ratio test suggests that barium dissolves in the slag in the oxidic form and in the matte in the sulfidic form. The predicted distribution coefficient was found to have a value of approximately 89, which is not in agreement with the experimental data which indicated that the distribution coefficient should be lower than 0.18. The activity coefficients of basic oxides in acidic slags typically have small values and this would certainly bring the predicted distribution coefficient value closer to what was initially expected. This also confirms that the model does not predict well for elements where the activity coefficient ratio has a greater influence on the distribution coefficient than the equilibrium constant as was shown to be the case for the majority of other elements.

For the other elements, the model predicted values that were in agreement with the experimental data, in a sense that the predicted values confirmed that the elements heavily favored the slag phase. It must be reiterated that the actual distribution coefficient values could not be ascertained from the experimental data because the concentration in the matte phase is unknown.

Table 6.1.16: Summary table showing conditions, thermodynamic data and activity ratio calculations for barium, scandium, hafnium, cerium, thorium and tungsten.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature[K]</th>
<th>$pO_2$[atm]</th>
<th>$pS_2$[atm]</th>
<th>$K_a$</th>
<th>$K_b$</th>
<th>$\gamma_{MOx}/\gamma_M$</th>
<th>$\gamma_{MSx}/\gamma_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>1523</td>
<td>1x10^-9</td>
<td>3.1x10^-4</td>
<td>7.4x10^13</td>
<td>1.5x10^13</td>
<td>2.4x10^9</td>
<td>2.5x10^11</td>
</tr>
<tr>
<td>Sc</td>
<td>1523</td>
<td>1x10^-9</td>
<td>3.1x10^-4</td>
<td>1.3x10^25</td>
<td>1.6x10^16</td>
<td>2.3x10^18</td>
<td>3.7x10^13</td>
</tr>
<tr>
<td>Hf</td>
<td>1523</td>
<td>1x10^-9</td>
<td>3.1x10^-4</td>
<td>7.5x10^28</td>
<td>1.5x10^15</td>
<td>7.5x10^19</td>
<td>4.6x10^11</td>
</tr>
<tr>
<td>Ce</td>
<td>1523</td>
<td>1x10^-9</td>
<td>3.1x10^-4</td>
<td>8.9x10^23</td>
<td>3.1x10^15</td>
<td>8.8x10^16</td>
<td>7.2x10^12</td>
</tr>
<tr>
<td>Th</td>
<td>1523</td>
<td>1x10^-9</td>
<td>3.1x10^-4</td>
<td>8.6x10^10</td>
<td>9.4x10^10</td>
<td>1.2x10^12</td>
<td>1.7x10^9</td>
</tr>
<tr>
<td>W</td>
<td>1523</td>
<td>1x10^-9</td>
<td>3.1x10^-4</td>
<td>8.6x10^13</td>
<td>4.3x10^3</td>
<td>85.94</td>
<td>1.347</td>
</tr>
</tbody>
</table>

Table 6.1.17: Describing reactions, thermodynamic data and comparison between predicted distribution coefficients and data from literature.

<table>
<thead>
<tr>
<th>Element</th>
<th>Describing Reaction</th>
<th>$K$</th>
<th>$\gamma_a/\gamma_b$</th>
<th>$\nu_{M/s}$ Model</th>
<th>$\nu_{M/s}$ Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>BaS(s)+1/2O_2(g)=BaO(s)+1/2S_2(g)</td>
<td>5.15</td>
<td>1.0</td>
<td>88.7</td>
<td>&lt;0.18</td>
</tr>
<tr>
<td>Sc</td>
<td>ScS_1.5(s)+3/4O_2(g)=ScO_1.5(s)+3/4S_2(g)</td>
<td>8.2x10^8</td>
<td>1.0</td>
<td>1.3x10^-5</td>
<td>&lt;0.11</td>
</tr>
</tbody>
</table>
Summary of findings:

- The experiments using industrial samples provided an indication of the various microelements present in a matte smelting circuit and in a majority of cases the data have successfully given an indication of the distribution behavior of these elements.
- The model was shown to predict the distribution behavior well. Where distribution coefficient values could be ascertained from the experimental data, the model predicted very similar values.
- Where experimental data could only provide an indication of preferential distribution into one phase or the other, the model has successfully predicted the correct distribution behavior except in the case of barium.
- It is believed barium and other similar basic oxides do not model well because the activity coefficient ratio exerts more influence on the distribution coefficient than the equilibrium constant.

<table>
<thead>
<tr>
<th></th>
<th>Reaction</th>
<th>K_1</th>
<th>K_2</th>
<th>K_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf</td>
<td>HfS_2(s) + O_2(g) = HfO_2(s) + S_2(g)</td>
<td>5x10^{13}</td>
<td>1.0</td>
<td>5x10^{-7}</td>
</tr>
<tr>
<td>Ce</td>
<td>CeS_{1.5}(s) + 3/4O_2(g) = CeO_{1.5}(s) + 3/4S_2(g)</td>
<td>1.6x10^{8}</td>
<td>1.0</td>
<td>6.7x10^{-5}</td>
</tr>
<tr>
<td>Th</td>
<td>ThS(s) + 1/2O_2(g) = ThO(s) + 1/2S_2(g)</td>
<td>4.0x10^{5}</td>
<td>1.0</td>
<td>1.2x10^{-3}</td>
</tr>
<tr>
<td>W</td>
<td>WS_2(s) + O_2(g) = WO_2(s) + S_2(g)</td>
<td>2.0x10^{7}</td>
<td>1.0</td>
<td>0.01</td>
</tr>
</tbody>
</table>
6-2 SYNTHETIC EXPERIMENTS

6-2.1 COBALT

Cobalt was chosen to be examined experimentally for several reasons:

- Cobalt is strongly associated with copper in some sulfide concentrates, such as those from Gecamines in Zaire (Mwema et al., 1995) and is considered to be a valuable by-product.
- Comparison with existing literature data for cobalt distribution allows for validation of the experimental methods used in this study.
- Cobalt is readily available as cobalt (II) oxide and cobalt (II) sulfide, allowing experiments which approach equilibrium from both directions to be performed.
- Cobalt and its compounds do not present any occupational health and safety concerns.
- Cobalt concentration in the phases can be conveniently analyzed with sufficient accuracy using ICP-AES.

Two series of distribution experiments were conducted, the first with synthetic copper matte and iron silicate slag equilibrated at 1523 K with a small quantity of cobalt (II) sulfide (CoS) added to the matte and the second with cobalt (II) oxide (CoO) added to the slag. The resulting concentrations of CoS and CoO were within the Henry’s Law region (Teague et al., 2000; Sinha and Nagamori, 1982; Celmer and Toguri, 1986), i.e., the values of the respective activity coefficients are independent of concentration so the distribution coefficient is also independent of concentration.

Figure 6-2.1 shows the results of equilibrating iron silicate slag containing cobalt with copper matte for various durations under nitrogen gas at 1523 K.
Figure 6-2.1: Cobalt concentration as a function of time at 1523 K for master slag containing 0.6 wt% Co.

Figure 6-2.2 shows the results of equilibrating copper matte doped with cobalt (II) sulfide with iron silicate slag at 1523 K under nitrogen atmosphere.

Figure 6-2.2: Cobalt concentration as a function of time at 1523 K for master matte containing 0.6 wt% Co.
Both figures 6-2.1 and 6-2.2 show that equilibrium was achieved after approximately eight hours. The cobalt contents of the slags for both series of experiments are shown in Figure 6-2.3 for the approach to equilibrium from both directions. The convergence of both data sets confirms that true equilibrium has been achieved.

![Cobalt concentration in slag](image)

**Figure 6-2.3**: Concentration of cobalt in slag as a function of time at 1523 K under reducing conditions.

Examination of the raw data for the two sets of experiments in Table 6-2.1 shows a slight difference between the average cobalt distribution coefficients. The average distribution ratio only includes the data points which have been deemed to be at equilibrium, i.e., data points from 8 hours and above.

**Table 6-2.1**: Equilibrium cobalt contents of synthetic matte and silica saturated slag at 1523 K under reducing conditions.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Cobalt [wt%]</th>
<th>LCo\text{m/s}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Matte</td>
<td>Slag</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>0.61</td>
</tr>
<tr>
<td>4</td>
<td>0.38</td>
<td>0.21</td>
</tr>
<tr>
<td>6</td>
<td>0.45</td>
<td>0.21</td>
</tr>
<tr>
<td>8</td>
<td>0.47</td>
<td>0.18</td>
</tr>
<tr>
<td>16</td>
<td>0.46</td>
<td>0.14</td>
</tr>
<tr>
<td>32</td>
<td>0.46</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Chapter 6: Results & Discussion

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th></th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.60</td>
<td>-</td>
<td>0.34</td>
</tr>
<tr>
<td>4</td>
<td>0.60</td>
<td>0.13</td>
<td>4.62</td>
</tr>
<tr>
<td>6</td>
<td>0.63</td>
<td>0.11</td>
<td>5.73</td>
</tr>
<tr>
<td>8</td>
<td>0.60</td>
<td>0.13</td>
<td>4.62</td>
</tr>
<tr>
<td>16</td>
<td>0.61</td>
<td>0.12</td>
<td>5.08</td>
</tr>
<tr>
<td>32</td>
<td>0.51</td>
<td>0.13</td>
<td>3.92</td>
</tr>
</tbody>
</table>

**Average**

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th></th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.51</td>
<td></td>
<td>0.62</td>
</tr>
</tbody>
</table>

**Overall**

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th></th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.75</td>
<td></td>
<td>0.95</td>
</tr>
</tbody>
</table>

One series of experiments shows an average distribution ratio of 3.0, whereas the other series has a value of 4.5. The distribution ratio at equilibrium should be the same for both sets of experiments. This difference may be caused by errors involved in experimentation. These errors include fluctuations in furnace temperature as well as errors in chemical analysis. The relative error in analysis for impurity element concentrations below 1 wt% was 5% and so the relative error for the distribution ratio is 10%. Changes in temperature influence the distribution ratio through the equilibrium constant. The descriptive reaction for cobalt distribution between matte and slag was predicted using the activity ratio test to be:

\[
\text{CoS(l)} + \frac{1}{2} \text{O}_2(g) = \text{CoO(s)} + \frac{1}{2} \text{S}_2(g)
\]  

[6-2.1]

Table 6-2.2 shows the respective equilibrium constant values for the temperature range possible with the error in the temperature controller.

**Table 6-2.2**: Change in equilibrium constant of reaction [6-2.1] with fluctuations in temperature.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1520</td>
<td>8.482x10^2</td>
</tr>
<tr>
<td>1523</td>
<td>8.342x10^2</td>
</tr>
<tr>
<td>1526</td>
<td>8.204x10^2</td>
</tr>
</tbody>
</table>
There is approximately a 2% variation in the equilibrium constants within this temperature range. Taking into account the relative errors of chemical analysis and fluctuations in temperature, the maximum error that can be assumed for the distribution ratio is 12%. This is considered to be acceptable for microelement distribution studies where the concentration of the microelement is small. The difference in the value of the distribution ratio between the two sets of experiments falls outside the estimated maximum error for experimentation and thus there must be another source of error. It can be speculated that this additional error could come from the use of different standards for the different set of experiments because each set was sent for analysis separately. In retrospect, it would have been preferable to send samples from both sets of experiments for analysis simultaneously so that the conditions of analysis remain constant. The combined mean and standard deviation of the data points at equilibrium give a value of 3.75±0.95. This value is in good agreement with prior research performed by Mwema et al. (1995); which reported $L_{Co}^{m/s} \sim 3$ for matte grade of ~55 wt% Cu, and is slightly lower than that reported by Yazawa (1980); $L_{Co}^{m/s} \sim 5$ for matte grade of 55 wt% Cu. The agreement between literature results and the experimental results in this study demonstrates that the experimental methodology used in this study is reliable.

Cobalt distribution was also examined experimentally under oxidizing conditions corresponding to a constant sulfur dioxide partial pressure of 0.1atm. Similarly to the experiments conducted under reducing conditions, two sets of experiments were conducted to observe approach to equilibrium from both directions. Figure 6-2.4 shows the results of equilibrating synthetic matte doped with cobalt (II) sulfide with iron silicate slag at 1523 K. The system is observed to reach equilibrium after 8 hours.
Figure 6-2.4: Cobalt concentration as a function of time at 1523 K and $P_{SO_2} = 0.1$ atm when cobalt is doped into the matte.

Figure 6-2.5 shows the results of equilibrating synthetic matte and slag at 1523 K under oxidizing conditions with cobalt (II) oxide added to the slag phase. It is evident from Figure 6-2.5 that equilibrium is achieved after 4 hours.

Figure 6-2.5: Cobalt concentration as a function of time at 1523 K and $P_{SO_2} = 0.1$ atm when cobalt is doped into the slag.
The cobalt contents of the slags for both series of experiments are shown in Figure 6-2.6 for the approach to equilibrium from both directions. The convergence of both data sets confirms that equilibrium has been achieved.

![Cobalt Concentration in Slag](image)

**Figure 6-2.6**: Concentration of cobalt in slag as a function of time at 1523 K and $P_{SO_2} = 0.1$ atm.

All samples from both sets of experiments conducted under oxidizing conditions were sent for analysis together. Table 6-2.3 shows the raw data for both sets of experiments. When doping into the slag phase the average value of the cobalt distribution ratio is 1.55, whereas when doping into the matte phase the average value is 1.51. Unlike the experiments conducted under reducing conditions, both sets of data show very good agreement with each other, thus supporting earlier speculation that the errors incurred were caused by the use of different standards for chemical analysis. The calculated average distribution ratios only include data points at equilibrium.

**Table 6-2.3**: Equilibrium cobalt contents of synthetic matte and silica saturated slag at 1523 K under oxidizing conditions.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Cobalt [wt%]</th>
<th>$L_{Co^{m/s}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Matte</td>
<td>Slag</td>
</tr>
<tr>
<td>0</td>
<td>0.62</td>
<td>0.24</td>
</tr>
<tr>
<td>4</td>
<td>0.38</td>
<td>1.58</td>
</tr>
</tbody>
</table>
Cobalt distribution was modeled at 1523 K under both reducing and oxidizing conditions as used in the experimental work. Under reducing condition, the oxygen and sulfur partial pressures were set as $1 \times 10^{-9}$ atm and $3.1 \times 10^{-4}$ atm respectively. Under oxidizing conditions the oxygen and sulfur partial pressures were set as $1 \times 10^{-8}$ atm and $4.3 \times 10^{-3}$ atm respectively corresponding to a matte grade of 55 wt% Cu and a constant $p_{SO_2}$ of 0.1 atm.

The activity ratio test is used to establish the nature of the species in which cobalt exists in the matte and slag. Under reducing conditions, in the slag phase:

$$\frac{a_{Co|\text{S}}}{a_{Co|\text{S}}^{\infty}} = K_a \cdot p_{O_2}^{1/2} = 0.7137$$  \[6-2.2\]

The value of the activity ratio in equation [6-2.2] suggests cobalt dissolves as the oxide in slag. In the matte phase:

$$\frac{a_{Co|\text{M}}}{a_{Co|\text{M}}^{\infty}} = K_b \cdot p_{S_2}^{1/2} = 0.4763$$  \[6-2.3\]
The value of the activity ratio in equation [6-2.3] suggests that the sulfide species is likely the more predominant species. Similar calculations were performed for cobalt distribution under oxidizing conditions, the results of which are shown in Table 6-2.4.

Table 6-2.4: Summary of conditions, thermodynamic data and activity ratio calculations for modeling cobalt distribution.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature[K]</th>
<th>$p_{O_2}$[atm]</th>
<th>$p_{S_2}$[atm]</th>
<th>$K_a$</th>
<th>$K_b$</th>
<th>$a_{MOx}/a_M$</th>
<th>$a_{MSx}/a_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1523</td>
<td>$1 \times 10^{-9}$</td>
<td>$3.1 \times 10^{-4}$</td>
<td>$2.26 \times 10^4$</td>
<td>$2.71 \times 10^1$</td>
<td>0.7137</td>
<td>0.4763</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$4.3 \times 10^{-5}$</td>
<td>$2.26 \times 10^4$</td>
<td>$2.71 \times 10^1$</td>
<td>2.2570</td>
<td>1.7800</td>
<td></td>
</tr>
</tbody>
</table>

From the activity ratio tests, the descriptive reaction for the distribution of cobalt between matte and slag can thus be expressed as:

$$\text{CoS}(l) + \frac{1}{2} \text{O}_2(g) = \text{CoO}(s) + \frac{1}{2} \text{S}_2(g)$$  \[6-2.4\]

From equation [6-2.4], the equilibrium expression can be expressed and the distribution coefficient term derived as discussed in Section 4-1. The describing reaction in equation [6-2.4] corresponds to Case 4 in Table 4-1.2 (Section 4-1). The distribution coefficient expression for this case is defined as:

$$L_{\text{Co} m/s} = \frac{0.82 \left( \gamma_{\text{CoO}} \right) p_{S_2}^{1/2}}{K \left( \gamma_{\text{CoS}} \right) p_{O_2}^{1/2}}$$  \[6-2.5\]

The activity coefficient of cobalt (II) oxide in slag with reference to the solid reference state is 2.0 (Section 4-3) and the activity coefficient of cobalt (II) sulfide with reference to the liquid reference state is 0.4 (Section 4-2). Under oxidizing conditions, the model gives a cobalt distribution ratio of 3.23 which compares well with the value of 1.54 obtained experimentally. Under reducing conditions, the thermodynamic model gives a cobalt distribution coefficient ($L_{\text{Co} m/s}$) value of 2.74, favoring the matte. This value is in good agreement with the experimentally determined distribution ratio of 3.75.

Table 6-2.5: Describing reaction, thermodynamic data and comparison between predicted distribution coefficients and experimental data.

<table>
<thead>
<tr>
<th>Element</th>
<th>Describing Reaction</th>
<th>$K$</th>
<th>$(\gamma_a)/\gamma_b$</th>
<th>$L_{\text{Co} m/s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_{\text{CoS}(l)} + \frac{1}{2} \text{O}_2(g) = \text{CoO}(s) + \frac{1}{2} \text{S}_2(g)$</td>
<td>8.34$\times 10^2$</td>
<td>5.0</td>
<td>2.74</td>
</tr>
<tr>
<td></td>
<td>$\gamma_{\text{CoS}(l)} + \frac{1}{2} \text{O}_2(g) = \text{CoO}(s) + \frac{1}{2} \text{S}_2(g)$</td>
<td>8.34$\times 10^2$</td>
<td>5.0</td>
<td>3.23</td>
</tr>
</tbody>
</table>

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Summary of findings:

- Under reducing conditions, the distribution ratio of cobalt, \( L^{m/s} \), was found to be 3.75±0.95.
- Under oxidizing conditions the distribution ratio of cobalt, \( L^{m/s} \), was found to be 1.54±0.055.
- The distribution data found experimentally are in good agreement with literature data thus providing confidence in the experimental methodology used in this study.
- Under both conditions, the thermodynamic model predicted values which are in good agreement with those found experimentally.

6-2 SYNTHETIC EXPERIMENTS

6-2.2 TUNGSTEN

Tungsten is one of the microelements of interest nominated by Boliden Minerals AB. It was chosen to be examined experimentally for several reasons:

- Small amounts of tungsten have been reported in concentrates purchased by Boliden so there is an interest to know how it behaves, in accord with the Precautionary Principle of Environmental Management\(^1\).
- From earlier tests using the thermodynamic model, the distribution ratio of tungsten was predicted to be neither so large nor so small that the concentration of tungsten in one of the phases would be too small to be chemically analyzed with sufficient accuracy.
- Tungsten is readily available in both the oxide and sulfide compound forms, allowing equilibrium to be observed from both directions.
- Tungsten and its compounds do not present any occupational health and safety issues.
- Tungsten represents a microelement for which no activity coefficient data are available and is therefore useful for testing the methodology developed for predicting the distribution behavior for less studied/encountered elements.

\(^1\) “Foresight principle” requiring precautionary measures to be taken when an activity raises threat of harm to human health or environment even if some cause and effect relationships have yet to be fully established scientifically.
The copper matte-iron silicate slag-tungsten system is not one that has been examined previously, so the solubility of the tungsten compounds in the molten phases is unknown. As discussed in Section 2-5.2, when dealing with such a system, the distribution ratio must be determined as a function of the amount of element added to ensure that the measured distribution ratio has not been affected by saturation of tungsten species in either molten phase. Tungsten was doped into the matte phase as the compound tungsten (IV) sulfide in various concentrations as shown in Table 6-2.6. Table 6-2.6 also highlights a consistent difference of approximately 28% between the target and actual composition. This could be due to volatilization of a tungsten species during preparation of the master matte. The master matte is prepared in air, thus making it likely for tungsten (IV) sulfide to become oxidized following reaction [6-2.6].

\[
WS_2(s) + \frac{3}{2}O_2(g) = WO_3(g) + S_2(g) \quad \Delta G^\circ_{1473 \text{ K}} = -96.554 \text{ kJ} \quad [6-2.6]
\]

**Table 6-2.6**: Comparison between target and actual composition in synthetic master mattes.

<table>
<thead>
<tr>
<th>Target W [ppm]</th>
<th>Actual W [ppm]</th>
<th>Actual W/Target W</th>
</tr>
</thead>
<tbody>
<tr>
<td>2200</td>
<td>1600</td>
<td>0.727</td>
</tr>
<tr>
<td>4400</td>
<td>3090</td>
<td>0.702</td>
</tr>
<tr>
<td>8800</td>
<td>6490</td>
<td>0.738</td>
</tr>
</tbody>
</table>

Each master matte shown in Table 6-2.6 was then equilibrated with tungsten-free iron silicate slag for various durations under nitrogen gas at 1523 K and the results are shown on Figures 6-2.7 to 6-2.9. It is apparent that equilibrium is achieved after approximately four hours.
Chapter 6: Results & Discussion

**Figure 6-2.7:** Tungsten concentration as a function of time at 1523 K for master matte containing 1600 ppm W.

**Figure 6-2.8:** Tungsten concentration as a function of time at 1523 K for master matte containing 3090 ppm W.
As mentioned earlier, the solubility of tungsten (IV) sulfide in copper matte is not known and neither is the solubility of tungsten (VI) oxide in iron silicate slag. When neither phase is saturated, then the distribution ratio will be independent of the concentration of tungsten in either phase, provided that these concentrations are relatively small such that the activity coefficients of the species are constant i.e. obeying Henry’s Law. When tungsten (IV) sulfide is added to copper matte, then saturation of either phase would cause the distribution ratio to be larger than the true value and to increase linearly with the amount of tungsten (IV) added to the system. Figure 6-2.10 shows tungsten distribution ratio as a function of tungsten concentration in the system. The data seems to indicate that the distribution coefficient is decreasing slightly with increasing tungsten concentration. Under the conditions used, the possible outcome should either be a constant distribution ratio or a sharp increase in the distribution ratio with increasing tungsten concentration and therefore the apparent downwards slope cannot be supported by any theoretical consideration except for a systematic change in activity coefficient of one of the species which is unlikely considering the small changes in tungsten concentration.

The apparent decreasing trend in the results shown in Figure 6-2.10 is more likely to be caused by the errors involved in experimentation. These errors include fluctuations in operating temperature as well as errors in chemical analysis. The error analysis from Section 5-4.4 stated that the relative error in microelement concentration for concentrations below 1 wt% for each phase was 5% and so the relative error for the distribution ratio is 10%. Fluctuations in temperature influence the distribution coefficient.
through the equilibrium constant. The describing reaction for tungsten distribution between matte and slag was predicted using the activity ratio test to be:

\[
\text{WS}_2(s) + \text{O}_2(g) = \text{WO}_2(s) + \text{S}_2(g)
\]  

The respective equilibrium constant values for the temperature range possible with the error in the thermal controller is shown in Table 6-2.7:

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1520</td>
<td>2.043x10^7</td>
</tr>
<tr>
<td>1523</td>
<td>1.978x10^7</td>
</tr>
<tr>
<td>1526</td>
<td>1.916x10^7</td>
</tr>
</tbody>
</table>

There is a 3% to 3.5% variation in the equilibrium constants within this range. Taking into account the relative errors in chemical analysis and fluctuations in temperature, the maximum error that can be assumed for the distribution ratio is 13.5%. This value is high but is acceptable for microelement distribution studies where microelement concentration is small. The inclusion of maximum relative error to the data points in Figure 6-2.10 (in the form of error bars), leads to the conclusion that the distribution ratio can be considered constant within experimental error and that saturation of either phase with tungsten species does not occur at the concentrations used.

![Figure 6-2.10](image)

**Figure 6-2.10**: Tungsten distribution ratio as a function of tungsten concentration.
Statistical analysis was also performed on the raw data. Table 6-2.8 gives the results of the distribution experiments using the three different master mattes. Since it is evident from Figures 6-2.7 to 6-2.9 that equilibrium is achieved after four hours, the average distribution ratio includes data at all three experimental durations for each initial tungsten concentration. It is clear from Table 6-2.8 that the average distribution ratio at each initial concentration of tungsten in matte does not differ significantly. It can be concluded that the values of distribution ratio in Table 6-2.8 are not affected by saturation of either the matte or slag with tungsten.

**Table 6-2.8**: Tungsten distribution as a function of initial tungsten concentration in copper matte at 1523 K.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Tungsten [ppm]</th>
<th>Lu(^{IV})/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Matte</td>
<td>Slag</td>
</tr>
<tr>
<td>0</td>
<td>1600</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>120</td>
<td>1680</td>
</tr>
<tr>
<td>8</td>
<td>68</td>
<td>1630</td>
</tr>
<tr>
<td>16</td>
<td>100</td>
<td>1660</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
</tr>
<tr>
<td>St. Dev.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3090</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>130</td>
<td>3130</td>
</tr>
<tr>
<td>8</td>
<td>180</td>
<td>2870</td>
</tr>
<tr>
<td>16</td>
<td>180</td>
<td>3090</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
</tr>
<tr>
<td>St. Dev.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>6490</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>245</td>
<td>6440</td>
</tr>
<tr>
<td>8</td>
<td>281</td>
<td>6520</td>
</tr>
<tr>
<td>16</td>
<td>360</td>
<td>6350</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
</tr>
<tr>
<td>St. Dev.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
</tr>
<tr>
<td>St. Dev.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Having established that tungsten saturation does not occur in either the matte or slag phase at the levels of doping used, experiments with tungsten (VI) oxide doped into the slag phase equilibrated with tungsten-free matte were performed to confirm that true equilibrium was achieved. In order to observe equilibrium from both directions, the same amount of tungsten must be used in both sets of experiments so that the concentration of tungsten in each phase will converge. Alternatively, a plot of distribution ratio as a function of time can be used to show approach to equilibrium from both directions irrespective of the amount of tungsten doped, provided the activity coefficients remain constant. An attempt was thus made to have the tungsten concentration in the master slag to be 3090 ppm. Loss of tungsten to volatilization was observed when doping tungsten (IV) sulfide into the matte, and so similar losses were accounted for when doping tungsten (VI) oxide into the slag. Table 6-2.9 shows a comparison between the targeted and actual amount of tungsten in the slag. It is to be noted that unlike the preparation of master matte, there is very little difference between the actual and targeted concentration of tungsten when doping into the slag.

Table 6-2.9: Comparison between target and actual tungsten composition in synthetic master slag.

<table>
<thead>
<tr>
<th>Target W [ppm]</th>
<th>Actual W [ppm]</th>
<th>Actual W/Target W</th>
</tr>
</thead>
<tbody>
<tr>
<td>3200</td>
<td>3080</td>
<td>0.963</td>
</tr>
</tbody>
</table>

Figure 6-2.11 shows the results of the distribution experiments. Similarly to the earlier experiments, tungsten displayed preferential distribution into the slag phase with the system achieving equilibrium after four hours.
Figure 6-2.11: Tungsten concentration as a function of time at 1523 K for master slag containing 3080 ppm W.

The tungsten contents of the mattes for experiments commencing with 3090 ppm tungsten added to the matte in one series and with 3080 ppm tungsten added to the slag in the other series are shown in Figure 6-2.12 for the approach to equilibrium from both directions. The convergence of both data sets confirms that true chemical equilibrium has been achieved.

Figure 6-2.12: Concentration of tungsten in matte as a function of time at 1523 K.
Careful examination of the raw data for the two sets of experiments in Table 6-2.10 reveals a consistent difference between the tungsten distribution ratios. One set shows an average distribution ratio of 0.021, whereas the other set has a value of 0.054. The distribution ratio at equilibrium should be the same for both sets of experiments. The difference is too large to be attributed to experimental error alone and is likely to be caused by a systematic error in chemical analysis (eg. different standards used for different sets of experiments) although there is no way to clarify this without further experimentation. The recommendation is that in the future, samples from both sets of experiments be sent for analysis simultaneously so that analysis conditions remain constant.

### Table 6-2.10: Tungsten distribution data observing approach to equilibrium from both directions.

<table>
<thead>
<tr>
<th>Time [Hours]</th>
<th>Tungsten [ppm]</th>
<th>( L_W^{M/s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Matte</td>
<td>Slag</td>
</tr>
<tr>
<td>4</td>
<td>47</td>
<td>2960</td>
</tr>
<tr>
<td>8</td>
<td>72</td>
<td>2960</td>
</tr>
<tr>
<td>16</td>
<td>71</td>
<td>2990</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td><strong>0.021</strong></td>
</tr>
<tr>
<td><strong>St. Dev.</strong></td>
<td></td>
<td><strong>0.005</strong></td>
</tr>
</tbody>
</table>

|              | Matte          | Slag            |                |
| 4            | 130            | 3130            | 0.042          |
| 8            | 180            | 2870            | 0.063          |
| 16           | 180            | 3090            | 0.058          |
| **Average**  |                | **0.054**       |                |
| **St. Dev.** |                | **0.011**       |                |

The objective of the tungsten distribution experiments was to generate data to validate the thermodynamic model of microelement distribution, so while there is a slight discrepancy in the distribution ratio values, the difference is not so large that this objective cannot be achieved. Taking an average of all the data collected, the distribution ratio of tungsten at 1523 K under reducing conditions was found to be 0.045±0.005.
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Tungsten distribution was modeled at 1523 K with an oxygen partial pressure of $1 \times 10^{-9}$ atm and a sulfur partial pressure of $3.1 \times 10^{-4}$ atm corresponding to reducing conditions as used in the experimental work.

Having defined the conditions, the activity ratio test is used to establish the nature of the species in which tungsten exists in slag and matte. In the slag phase:

$$\frac{a_{\text{WO}_2(s)}}{a_{\text{W}(s)}} = K_a \ p_{\text{O}_2} = 86$$ \hspace{1cm} [6-2.8]

The value of the activity ratio in equation [6-2.8] suggests tungsten dissolves as the oxide in slag. In the matte phase:

$$\frac{a_{\text{WS}_2(s)}}{a_{\text{W}(s)}} = K_b \ p_{\text{S}_2} = 1.35$$ \hspace{1cm} [6-2.9]

The value of the activity ratio test in equation [6-2.9] shows that the sulfide species is only slightly more likely to be the predominant species, however the activity coefficient for metals in matte is usually much larger than for sulfides in matte and thus in terms of mole fractions the sulfide species can be assumed to predominate. Tungsten distribution was also modeled under more oxidizing conditions, the results of which are shown in Table 6-2.11 and 6-2.12.

**Table 6-2.11**: Summary of conditions, thermodynamic data and activity ratio calculations for modeling tungsten distribution.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature[K]</th>
<th>$p_{\text{O}_2}$[atm]</th>
<th>$p_{\text{S}_2}$[atm]</th>
<th>$K_a$</th>
<th>$K_b$</th>
<th>$a_{\text{MO}<em>x}/a</em>{\text{M}}$</th>
<th>$a_{\text{MS}<em>x}/a</em>{\text{M}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>1523</td>
<td>$1 \times 10^{-9}$</td>
<td>$3.1 \times 10^{-4}$</td>
<td>8.59$x10^{10}$</td>
<td>4.34$x10^{3}$</td>
<td>85.94</td>
<td>1.347</td>
</tr>
<tr>
<td></td>
<td>1523</td>
<td>$1 \times 10^{-8}$</td>
<td>$5.5 \times 10^{-3}$</td>
<td>8.59$x10^{10}$</td>
<td>4.34$x10^{3}$</td>
<td>859.4</td>
<td>23.89</td>
</tr>
</tbody>
</table>

From the activity ratio tests, the describing reaction for the distribution of tungsten between matte and slag can thus be expressed as:

$$\text{WS}_2(s) + \text{O}_2(g) = \text{WO}_2(s) + \text{S}_2(g)$$ \hspace{1cm} [6-2.10]

From equation [6-2.10], the equilibrium expression can be expressed and the distribution coefficient term derived as discussed in Section 4-1. The describing reaction in equation [6-2.10] corresponds to Case 4 in Table 4-1.2 (Section 4-1). The distribution coefficient expression for this case is defined as:

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The activity coefficients of tungsten (IV) oxide in slag and tungsten (IV) sulfide in matte are not known and are therefore assumed to be unity. The thermodynamic model gives a tungsten distribution coefficient \(L_W^{m/s}\) value of 0.01, heavily favoring the slag. This value is in good agreement with the experimentally determined distribution ratio of 0.045. In order for the predicted value to match the experimental data, the activity coefficient ratio \(\gamma_{WO_2}/\gamma_{WS_2}\) would have to have a value of approximately 5, which is possible. An approximation of the activity coefficient ratio could be made by examining the activity coefficients of elements surrounding tungsten in the Periodic Table. Among the closer elements, cobalt has an “oxide/sulfide” activity coefficient ratio of 5 and nickel has an activity coefficient ratio of approximately 2.

Table 6-2.12: Describing reaction, thermodynamic data and comparison between predicted distribution coefficients and experimental data.

<table>
<thead>
<tr>
<th>Element</th>
<th>Describing Reaction</th>
<th>(K)</th>
<th>(\gamma_a/\gamma_b)</th>
<th>(L_W^{m/s}) Model</th>
<th>(L_W^{m/s}) Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>(WS_2(s)+O_2(g)=WO_2(s)+S_2(g))</td>
<td>1.98x10^7</td>
<td>1.0</td>
<td>0.01</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>(WS_2(s)+O_2(g)=WO_2(s)+S_2(g))</td>
<td>1.98x10^7</td>
<td>1.0</td>
<td>0.02</td>
<td>-</td>
</tr>
</tbody>
</table>

Summary of findings:

- The distribution ratio of tungsten was found to be 0.045±0.005, heavily favoring the slag phase.
- The thermodynamic model predicted the distribution coefficient of tungsten to have a value of 0.01 when the activity coefficients were assumed to be 1. This value is in very good agreement with that found experimentally.
- When the oxide/sulfide activity coefficient ratio was given values similar to that applicable to elements near tungsten in the Periodic Table, the agreement between experimental and modeled distribution coefficients was further improved.
CHAPTER 7: CONCLUSIONS

The precautionary principle of sustainable development is subscribed to by many smelters in that the behavior of all elements entering the smelter needs to be quantified and understood. Element distribution studies provide part of the necessary framework for improving the sustainability of base metal production by opening future opportunities for profitable recovery or by anticipating future legislative restrictions that impact on profitability. The distribution data produced through experiments such as in this study are the tools for operators and researchers to improve smelting operations. The experiments, however, are resource intensive and can be inconvenient for several reasons. The thermodynamic model developed in this study was shown to reliably predict the distribution behavior of elements between matte and slag at accuracies sufficient for many purposes.

The main finding from the present study with regards to validating the model was that, in comparison with literature data, the majority of predicted distribution coefficient values were of the correct order of magnitude. The distribution ratio for cobalt \((L_{Co}^{m/s})\) between matte and silica-saturated iron silicate slag was found experimentally to be 3.75±0.95 under reducing conditions and 1.54±0.055 under oxidizing conditions. The predicted values of 2.74 and 3.23 respectively, are in satisfactory agreement with the experimental data. The distribution coefficient for tungsten \((L_{W}^{m/s})\) between matte and silica-saturated iron silicate slag was found experimentally to be 0.045±0.005 which is in good agreement with the predicted value of 0.01.

Experiments using industrial samples containing a number of microelements originating from the raw materials and which displayed a large range of distribution behavior strengthened the conclusion that the model had general applicability. Where distribution coefficient values could be calculated, the model predicted very similar values. In cases where the experimental data could only show preferential distribution into one phase or the other because the concentration of the element in one of the phases was below the detectable limit, the model also successfully predicted the observed distribution behavior.

The predictive ability of the model is mostly limited by the difficulty of estimating the activity coefficients of species in both slag and matte. Where such data exists, the model generally predicts distribution behavior very well. Where such data is unavailable, as is often the case, the model prediction is much less reliable. Nevertheless, for many purposes the model will prove to be a very useful tool.
CHAPTER 8: REFERENCES


Lehner, T. “European Smelting and Environmental Considerations.” The Brimacombe Memorial Symposium, Vancouver, Canada, 159-171.


Outokumpu Research Oy. HSC Chemistry 5.11.


CHAPTER 9: APPENDIX

9-1 RESPONSE TO EXAMINER’S COMMENTS

9-1.1 EXAMINER #1: PROFESSOR BART BLANPAIN

1. Page 3, second paragraph, line 7 corrected to read “can be analyzed” instead of “can been analyzed”.

2. Page 4, first paragraph, line 5 corrected to read “greater precision than available” instead of “greater precision that available”.

3. Line after equation 2-1.2 on page 8 corrected to read “Gibbs” instead of “Gibb’s”.

4. Compounds in reactions such as equation 2-2.3 edited to include the standard reference state of the compounds. This has been corrected throughout the thesis.

5. Examiner’s suggestion has been noted. Section 2-3 has been left in as it is still a useful section to have available.

6. Page 11, second paragraph, line 4 corrected to read “The shaded region of the diagram” instead of “The left hand of the diagram”. Aforementioned region now shaded in Figure 2-2.1.

7. Line after equation 2-2.10 on page 13 corrected to read “activity of magnetite is proportional to the third power of the activity of FeO” instead of “proportional to the activity”.

8. Examiner’s comment noted.

9. Examiner’s comment noted, but decided that no change is necessary.

10. Line after Figure 2-5.2 on page 33 corrected to read “Yazawa et al. (1983) give” instead of “Yazawa et al. (1983) gives”.

11. List of common symbols and their definitions added on page xvii.
12. Page 36, equation 2-5.8: No, because required thermodynamic data is unavailable.

13. Page 54: Accept that it is dual saturation at the indicated point; however disagree that the value of MgO would be significantly different to 4%.

14. Equation 2-5.29 on page 55 corrected to read “ΔG°” instead of “ΔG”

15. Page 64, second paragraph, line 6 corrected to read “than that” instead of “that that”.

16. Examiner’s comment has been noted, however no changes were made. Chapter 4-1 already covers the details requested by the examiner albeit in a different order. The current structure details the necessary information and assumptions at each step of the model as opposed to at the beginning of the section as per examiner’s suggestion.

17. Statement added before Table 4-1.4 explaining the derivation of the factor 0.82 in the distribution coefficient expressions.

18. Line after Figure 4-2.3 on page 144 corrected to read “clear difference” instead of “clear different”.

19. Line after Figure 4-2.4 on page 145 corrected to read “activities in the metal” instead of “activities in the matte”.

20. Caption for Figure 4-2.4 on page 145 corrected to read “quaternary” instead of “quarternary”.

21. Page 181, Table 5-4.1 added providing detection limits for elements analyzed by Neutron Activation Analysis.

9-1.2 EXAMINER #2: PROFESSOR ERIC GRIMSEY

Detailed Assessment

Literature Review:
1. The section on copper production technology is not crucial to the main content of the thesis (see Section 9-1.1, comment 5) but has been retained as a useful section to have available. Thus the section does not warrant extra attention at this point.

2. Page 55, first paragraph, second line edited to read “This section examines matte smelting distribution data available from literature over the full range of copper smelting conditions”. The only prior mention of reducing conditions being the focus of this thesis was made in reference to the experimental portion of the study (page 32, last paragraph).

3. Section has been added from page 39 onwards to address the examiner’s comment.

4. See section 9-1.1, comment 4.

5. See section 9-1.1, comment 7.

6. First paragraph on page 13, where reference is made to the activity of magnetite the relative standard state “pure solid magnetite” has been included.

7. Page 14, first paragraph, line 4 has been corrected to include the relative standard states of copper and copper sulfide; the activities of both being relative to the respective pure liquids.

8. Page 15, second paragraph. This section discusses the construction of the diagram beginning with the use of the Gibb’s phase rule to determine the variables needed to properly define the system. The inclusion of silica saturation of the slag as a defined variable was in fact stated in the following paragraph on page 16.

9. Page 15, second paragraph, line 2 has been corrected to read “…sulfur potential as the variables…” instead of “…sulfur potential as the dependent and independent variables…”

10. Page 16, first paragraph, first line has been corrected to read: “Slag has been assumed to be present in all regions of the potential diagram with the
exception of the region marked Fe in the lower left hand corner (where it breaks down into Fe and SiO$_2$) and at any $pO_2$ above line s-t (where it gradually breaks down into Fe$_3$O$_4$ and SiO$_2$)."

11. Page 16, last paragraph, line 2 has been corrected to include the reference standard state of FeO i.e. “relative to pure liquid FeO”. In addition, Figure 2-2.4 has been added to show $a_{FeO(l)}$ at 1623 K varies from 0.3 at magnetite saturation to 0.4 at iron saturation. Sentence has been added to state that Yazawa chose a value of $a_{FeO(l)}$ of 0.3 when constructing the chemical potential diagram.

12. Page 17, third paragraph, line 3 has been corrected to include the reference standard state of magnetite i.e. “relative to the pure solid magnetite”.

13. Page 36, equation 2-5.6 has been added. Line following equation 2-5.6 has been corrected to read “…equations 2-5.5 and 2-5.6 into equation 2-5.2” instead of “…equation 2-5.5 into equation 2-5.2”.

14. Page 38, last paragraph has been corrected to include the temperature at which the activities are defined, i.e. 1573 K.

15. Page 39, second paragraph has been corrected to address examiner’s comment.

16. Page 43, Section 2-5.2 has been re-examined.

a] Paragraph has been added on page 50 discussing the limitations of the test.

b] Re-examination of Section 2-5.2 shows that the test is still thermodynamically valid. It is correct that the activity of a species in both phases will be the same at equilibrium. However there are two species involved here, MO in the slag and MS in the matte such that at equilibrium $a_{MO}$ would be the same in both phases and $a_{MS}$ the same in both phases, but $a_{MO}$ does not necessarily have to be equal to $a_{MS}$. This has been clarified throughout the section using equation [2-5.20].

17. See comment 16 above.

18. See section 9-1.1, comment 4.
19. See section 9-1.1, comment 4.

20. Page 91, last sentence has been corrected to read “...prevailing oxygen potential and temperature, a decrease...” instead of “...prevailing oxygen potential, a decrease...”

21. Page 108, last paragraph. Statement amended to include observed trend of increasing \( L_{Sn}^{m/s} \) with decreasing oxygen partial pressure. The distribution coefficient reported by Louey et al. (1999) under reducing conditions is shown to conform to this trend via comparison with data by Koike and Yazawa (1994) and is therefore concluded to be of reasonable magnitude.

Thermodynamic Model

1. a] The point to make is that while the activity coefficient ratio influences the value of the distribution coefficient, it is often sufficient to assume ideality to get a good picture of the distribution behavior of elements.

b] The values of the activity coefficients of species in matte and slags were examined in Sections 4-2 and 4-3. The conclusion made from the two sections was that there is not enough data to get a feel for any periodic trends relating to the activity coefficients of species in the molten phases.

c] The activity ratio test was set up to determine the form of dissolution of the element in the molten phases when activity coefficient data is not available. Examiner’s comment regarding the extension of the activity ratio test to other metals is valid; however the lack of distribution data for other elements such as antimony where the predominance of the dissolved species changes with varying conditions prevents further validation of the criteria.

With regards to the prediction of distribution coefficients using the model, there are two important points to emphasize. Firstly, the values predicted using the model when activity coefficient values are available are reasonably close to experimental data. This means the activity ratio test is reasonably predicting the correct dissolved species in the molten phases. Secondly, where the activity coefficient ratio is assumed to be 1, some predicted values compare well with experimental data. This would seem to indicate that the other
parameters, e.g. the equilibrium constant are likely to outweigh the effect of the activity coefficient ratio on the distribution coefficient.

2. Examiner makes a valid point. It is noted that the liquid standard state should be preferred with exceptions made when the required thermodynamic data is not available.

3. Page 136, second paragraph describes how a value of 0.01 may be a suitable value for the lower limit of the activity ratio test. On page 137, the activity ratio test was used to determine the species of antimony in the slag and produced a value smaller than 0.01. Based on the criteria outlined for the activity ratio test, a value smaller than 0.01 would indicate the metallic species being predominant, which is confirmed by experimental data in Figure 4-1.3. It should be reiterated that the purpose of the activity ratio test is to predict the form of dissolution of an element in molten matte and slag at a fixed condition when activity coefficient data is not available.

4. The issue of defining the conditions (including temperature) for the model was discussed earlier in Chapter 4-1, and is not fixed at 1573 K. The statement regarding selection of standard states was made on page 150, however it is noted that the liquid standard state should be a preference.

5. Refer to comment “1c” above.

6. Examiner makes a very valid comment; however in this particular case, it was far more convenient to use the solid reference state for comparison of nickel oxide activity coefficients because of the availability of the necessary thermodynamic data.

7. The limiting activity ratios for the MO/M and MS/M predictions are calculated at the temperature selected for testing the model (shown in the 2nd column of Table 4-4.2) and not limited to 1573 K.

8. Page 164, Table 4-4.2. The temperatures for each row in Table 4-4.2 correspond to the same row in Table 4-4.1. The K-values in Table 4-4.2 are for the describing reactions given in Table 4-4.2. Therefore \( K_a \) in Table 4-4.1 and the K-value in Table 4-4.2 will only be the same if the describing reaction corresponds to Case 2 from Table 4-1.4. Similarly, \( K \) and \( K_b \) will only be the same for Case 3 in Table 4-1.4.
9. Possible explanations for the five elements which did not model well are given on the second dot point on page 172.

10. See comment 7 above.

11. Refer to comment 1c above.

Experimental Section plus Results and Discussion

1. Examiner’s comment noted. Values in Table 5-1.1 have been reduced to two decimal places. Similar correction has been made for Table 5-1.2.

2. Page 183, second paragraph, line 5 corrected to read “basic oxides in acidic slags” instead of “basic oxides in slags”.

3. Refer to comment 1c in “Thermodynamic Model” section.

Text Corrections

1. a] Refer to 9-1.1 comment 11.
b] All references checked and amended.
c] Temperature corrected to be consistently referred to in units K.

2. The use of the word “data” as plural and the word “datum” as singular has been corrected throughout the thesis. It is noted however, that many sources consider “data” acceptable as either singular or plural.1

3. All occurrences of “Pierce-Smith” in the thesis corrected to read “Peirce-Smith”.

4. Page 18, fourth paragraph, line 3, the value of $p_{SO_2}$ in air has been corrected to “0.1 atm” instead of “0.2 atm”.


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6. Refer to “Text Corrections” comment 1.

7. Page 39, last paragraph: The decrease in the distribution coefficient due to decreasing silica content in slag is in fact immediately obvious from equation 2-5.17a. The influence of \( a_{\mathrm{FeO}} \) is taken into account in equation 2-5.16a and substituted into equation 2-5.13 to arrive at equation 2-5.17a, which when compared to 2-5.17 shows the distribution coefficient at lower silica contents in slag to be smaller by a factor of 2/3, if all other factors remain the same.

8. Page 57, first line after sub-chapter heading “d. Procedure” corrected to read “procedures” instead of “procedure”.

9. Page 62, Figure 2-5.18 edited to include point C’.

10. Page 62, last sentence has been corrected to read “From” instead of “from”.

11. Page 63, equations 2-5.32 to 2-5.34 “lower case \( k \)” replaced with “upper case \( K \)”.

12. Page 64, second line corrected to read “Q=0 are” instead of “Q=0 is” and the temperature for the chemical potential diagram (Figure 2-5.18) has been included in the caption.

13. Page 67, second paragraph, last line corrected to read “Table 2-5.6 shows” instead of “Table 2-5.6 shows”.

14. Page 70, first paragraph, line 7 corrected to read “effect” instead of “affect”.

15. Page 70, last line, no change has been made. While equation [2-5.12] could be changed to include \( p_{\mathrm{SO}_2} \) as a variable by use of equation [2-2.20], the subsequent analysis does not use the \( p_{\mathrm{SO}_2} \) term. The sulfur dioxide partial pressures are instead translated to oxygen and sulfur partial pressures respectively by reading the values off the chemical potential diagram (Figure 2-5.18) for a specific matte grade. Taking this into consideration, the \( p_{\mathrm{O}_2} \) and \( p_{\mathrm{S}_2} \) terms used in equation [2-5.12] are appropriate.

16. Page 72, first paragraph, line 4 corrected to read “…slope of 0.5. The slope…” instead of “…slope of 0.5, the slope…”
17. Page 62, Figure 2-5.18 edited to include line of 50% matte grade.

18. Page 74, second dot point in summary of findings corrected to read “approximately” instead of “roughly”.

19. Page 76, first paragraph, reference “Nishikawa and Yazawa, 1980” was wrongly referenced. Correct reference “Kashima et al., 1980” has been added to text and reference list.

20. Page 82, third paragraph, line 2 corrected to read “…in both phases, they…” instead of “…in both phases; they…”

21. Page 93, second last dot point in summary of findings: No change, it already reads “increases”.

22. Page 96, caption for Figure 2-5.41 corrected to include temperature for the diagram.

23. Page 97, first paragraph, line 6: PbO and PbS are terms used by Kaiura et al. (1980) to represent oxidic and sulfidic dissolution of lead in slag respectively as opposed to representing the species of dissolution of lead i.e. lead (II) oxide (PbO) and lead (II) sulfide (PbS).

24. Refer to point 23 above.


26. Page 113, top paragraph, line 7 corrected to read “oxygen pressures” instead of “oxygen potentials”.

27. Pages 121-126, figure captions have been edited to include temperature.

28. Page 35, first paragraph, second line. Statement has been added making reference to the development of the distribution ratio expression (from the series of equations on pages 35 and 36) as the “Yazawa thermodynamic model” for the purpose of this thesis.

29. Page 133, first paragraph, line 4. Sentence added regarding the availability of the sulfur-oxygen chemical potential diagram at 1473 K.
30. Page 134, second paragraph, last line. Statement has been made to clarify the issue. In addition, equations [4-1.3] and [4-1.6] have been edited to include the use of ( ) and { } in reference to components in the slag and matte phase, respectively.

31. Page 141, first paragraph, line 2 has been amended to make reference to Table 4-2.1 as a summary of available data from literature for the activity coefficients of species in matte at infinite dilution. The caption for Table 4-2.1 has also been corrected to include "at infinite dilution".


33. Page 142, first line after "Arsenic" subheading: No change. The reference Itagaki et al. (1983) here refers to the paper by Itagaki, K., Hino, M., and Yazawa, A. (1983), which does indeed have 3 authors.

34. Refer to section 9-1, comment 18.

35. Page 152, reference "Azuma et al. (1970)" has been added to reference list.

36. Page 159, last sentence has been corrected to read "Fe/SiO_2" instead of "Fe/SiO2".

37. Page 161, third paragraph, line 4 has been corrected to read "oxygen pressure" instead of "oxygen potential".

38. Page 162, first dot point in summary of findings has been corrected to read "to discern any" instead of "to get a feel for any".

39. Page 163. The source of the K values in Table 4-4.1, i.e. HSC Chemistry v5.11, has been included in the text in paragraph 3, line 3 to clarify the issue. The discussion of Table 4-4.1 makes reference to Section 4-1, where a similar table (Table 4-1.1) was discussed in more detail. The only difference between Table 4-1.1 and Table 4-4.1 is that the latter summarizes data for many elements whereas the former only does so for cobalt.
40. Page 175, paragraph 4, line 5 and 7. Reference Louey (1999) refers to the Masters thesis of the said author. This reference has been added to the reference list.

41. Page 183, third line after “Elements at Equilibrium” subheading has been corrected to read “some discrepancy” instead of “a bit of discrepancy”.

42. Page 199, Section 6-2.2, first dot point: Footnote added to define the Precautionary Principle of Environmental Management.