The Thermodynamic Behavior of Magnetite in Non-Ferrous Smelting

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Metallurgy and Materials Science
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ABSTRACT

The problems of magnetite build up have plagued the non-ferrous pyrometallurgical industry for many years. Traditionally, solutions to this problem were brought about add-hoc, as a means of survival, and not necessarily based on rigorous fundamental work. Until now, no comprehensive fundamental studies were available, in the area of nickel pyrometallurgy, which addressed the thermodynamic principles and how the pertinent factors such as temperature, oxygen and sulfur pressure and activities of iron and magnetite influenced the age old problems of magnetite saturation.

One of the main objectives of this study was to provide a sound investigation and subsequent analysis, obeying the guiding principles of thermodynamics (phase rule) in order to understand the mechanisms behind magnetite saturation during nickel smelting. By fulfilling this goal, methods which could be used to control the behavior of magnetite as well as obtaining metallurgical benefits would naturally follow. Of perhaps equal and even more significance, was the manner in which these experimental data and fundamental understanding could be applied on an industrial level.

In order to fulfill these objectives a series of equilibration studies were performed in the systems matte-gas and matte-slag (silica saturation)-gas. The thermodynamic variables of temperature, sulfur and oxygen pressure and matte grade were examined and their relationships to the magnetite activity were defined. In general, a lower sulfur pressure and higher temperature operation was proven to enhance the metallurgical benefits of nickel smelting by decreasing the magnetite activity.
Comparison of actual industrial data, with those of this experimental study indicated that even by incorporating these data into theoretical process models (heat and material balances) no matter how reliable they may be, the real situations may end up radically different to those predicted from the models. It should be recognized that these types of fundamental studies only provide a guideline which can be used to pursue larger scale testwork in an attempt to prove out real and attainable benefits. Without these types of studies to form the basis for development, a clear direction and significant progress would never be possible.
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I hope you find this document deserving of your efforts.
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1.0 Introduction

The main objective during the processing of nickel sulfide concentrates, by pyrometallurgical means, is elimination of the gangue and iron which can comprise up to 50% by mass of the concentrate. These phases are removed by oxidation at elevated temperatures, where the iron is oxidized and slugged (or combined) with the gangue to form a low density molten silicate. The nickel and/or copper and cobalt retain their sulfide form (for the most part) and coalesce into a more dense molten sulfide phase (matte) which separates from the slag (iron and gangue) by the density difference. Owing to the mineralogical complexities of various concentrates, it is seldom possible to perform the separation in one stage. In general, multiple stages are required to progressively upgrade the concentrate from a high iron content to a form comprising almost 100% nickel to various combinations of nickel+iron+sulfur, depending on the end use of the product. Irrespective of what the upgrading stage is (roasting, smelting, converting) control of the iron oxidation usually determines the success of the respective processing step. It is particularly important to avoid over-oxidation, as this generally results in high melting point iron oxides which build up and form solid accretions in the reactors at each processing stage. Iron oxidation in each processing stage is controlled mainly by temperature and oxygen partial pressure, each of which are not independent and are set by the process heat and mass balance requirements.

Typically, each step is characterized by the degree of oxidation and a certain amount, at a specified temperature, is required in each stage. If any more or any less occurs, the efficiency and metal recovery of that and each subsequent step will be effected. In traditional pyrometallurgical processing there are three stages defined as roasting, smelting and converting. Each smelter flowsheet is unique, depending on mineral characteristics of the ore and the final product desired, however each flowsheet will contain any or a combination of the three aforementioned processes.
Roasting (or Calcining)

Roasting can be characterized by a gas-solid reaction which selectively oxidizes iron-sulfides, contained in sulfide concentrates, into oxides or sulfates the resulting product is termed calcine. These processes typically occur at temperatures below 900 °C and can be autogenous. In the more modern smelters, this calcining stage typically occurs in fluid bed reactors.

A fluid bed reactor is a vertical cylindrical refractory lined steel shell which is sealed at the bottom with tuyeres or a grate to allow air flow into the vessel, Figure 1.0. Feeding is normally done through the top or sides and the feed material may be slurry, filter cake or partially dried agglomerated feed in the form of pellets or briquettes. Some reactors may also have provisions for adding water (sprays) to control the temperature of the process. The feed material drops toward the grate where it is suspended by the countercurrent flow of air. The bed is highly turbulent within which the primary gas-solid reactions take place to produce a selectively oxidized concentrate called calcine. The product may be removed either with the off-gases (through the top) or through the side or bottom. The degree of roasting is controlled by the air/feed ratio and the product typically has lost between 50-80% of the original sulfur in the concentrate feed.

If a particular processing flowsheet employs roasters to pre-treat the concentrate the next stage is typically characterized by smelting in an electric or reverberatory furnace. In the case of nickel smelting there are no reverberatory furnaces still in operation, the last known nickel smelting reverbs were shutdown in 1993 and were replaced by the modern flash smelting process at Copper Cliff by INCO Limited.
Smelting

In the case of electric smelting the roasted concentrate (calcine) is fed to the furnace through fettling pipes located along the roofline, Figure 1.1. In addition to calcined concentrate the furnace is fed with carbonaceous material (coal or coke) and siliceous flux. The carbon source is added for three reasons, for fuel, to achieve the desired metal recoveries in the furnace by chemically reducing any base metals which have been oxidized and to control the amount of iron retained into the product phase (matte). The siliceous flux is added to combine with the oxidized iron to form an iron silicate slag. This slag has a lower density than the matte, which contains the majority of the base metal sulfides. The slag and matte settle on the furnace hearth and are allowed to
separate. After sufficient separation has occurred the slag is removed from the furnace and discarded. The matte is removed and further upgraded in a separate stage called converting. Most of the energy required for this process is provided by electric power in the form of resistance heating in the slag phase. Electrical energy in the form of heat is generated by passing high voltage current between the furnace electrodes which are submerged in the slag phase. The slag provides a resistive path for the current which generates energy by Joule heating. Electric smelting processes typically operate between 1150 and 1400 °C, but can operate at higher temperature regimes, depending on particulars such as the slag and matte metallurgy.

Figure 1.1 Cutaway view of an electric furnace (Boldt and Queneau 1967).

Newer more efficient technologies used for smelting of nickel bearing concentrates are flash furnaces. In a flash smelting furnace the roasting step is combined with the traditional smelting step (melting). In the flash smelting process typically the concentrate is bone dried and mixed with siliceous flux and sometimes carbonaceous material. This mixed charge is blown into the furnace proper with tonnage oxygen (INCO), Figure 1.2, or oxygen enriched air (Outokumpu), Figure 1.3, via flash "burners". When this solids/oxygen mixture enters the heated furnace, reactions are very intense and smelting
is usually complete before the charge hits the molten bath. The molten mixture is allowed to settle on the furnace hearth and is removed periodically analogous to the electric furnace process. This process is characterized as highly energy efficient and environmentally friendly. Since it takes advantage of the concentrate fuel value (exothermic oxidation of sulfides), it is generally more energy efficient than the two step roasting-smelting processes. In most nickel smelting operations the flash reaction does not provide enough heat to sustain the process and additional heating is required from auxiliary burners. In the case of the INCO flash furnace, at Copper Cliff - Ontario, with the addition of coke in the flash burner, no additional fuel burners are required. Currently the Copper Cliff smelter of Inco Limited flash smelts a bulk (CuNi) concentrate. However, prior to 1993 a copper concentrate was being flash smelted and this operation was autogenous at a 45% Cu containing matte.

A unique and advantageous feature of flash furnaces is that all the off-gases can be collected in one concentrated stream and sulfur bearing gases may be more easily fixed in liquid SO₂ or sulfuric acid than for the electric furnace counterpart.

![Figure 1.2 Sectional view of an INCO flash furnace (Boldt and Queneau 1967).](image-url)
Problems with over oxidation are usually more serious for flash smelting furnaces than for electric furnace smelting. Since the flash furnaces operate typically at much higher sulfur and oxygen pressures and the residence times are much shorter, the over-oxidation of iron must be closely controlled. If this phenomenon is not controlled properly, major inefficiencies may result from magnetite accretions at various locations in the vessel and off-gas handling facilities. These build ups can lead to severe losses in metal recoveries and furnace on-line time.

Flash furnaces typically operate in the temperature regime of 1180 to 1400 °C, which is similar to electric furnace operation.
Converting

With the exception of the DON process (Kojo et al. 1997), all nickel converting operations employ Pierce Smith converters to finish upgrading the smelting furnace matte. In the converting process, the remaining iron and sulfur are selectively removed from the furnace matte. The Pierce Smith converter operates by feeding with molten furnace matte (through the mouth) and blowing air, or oxygen enriched air, (through side-blown tuyeres), with the addition of siliceous flux (through the mouth) to produce slag and converter matte containing varying amounts of iron and sulfur with the majority of the product being Ni, Figure 1.4. In the majority of cases, the oxidation process occurring in this vessel generates excess heat and scrap must be added as a coolant at various stages to maintain the correct heat balance. The Pierce Smith process is batch fed with typically one to two ladles of slag removed between blows. Typically more ladles of matte are added for the first blow (4 to 7) than for the additional blows in which 1-2 ladles are added. The amount of matte added and slag removed are dependent on the furnace matte grade and the final converting matte product requirements.

Figure 1.4 Cutaway view of a Pierce Smith converter (Boldt and Queneau 1967).
Since the converting stage is characterized by the highest oxygen pressures in the pyrometallurgical flowsheet extreme care must be taken to avoid the formation of solid magnetite. During converting it is extremely important to maintain correct silica control in the slag and correct vessel heat balance to avoid saturation with magnetite which results in solid build up in the vessel and tuyeres.

Pierce Smith converters typically operate in the temperature regime between 1150 and 1350 °C. They are generally lower temperature processes than smelting.

The most common, widespread and uncontrolled pyrometallurgical phenomenon which afflicts every copper and nickel producer, is the problem of magnetite formation. Magnetite typically manifests itself in the smelting and/or converting stages as a solid build up. This build up can form anywhere where conditions are favorable (T, P\text{O}_2), but in general are concentrated on the furnace hearth and gas offtakes, during smelting, and near the tuyeres and mouth, in converting.

The problem of magnetite control is a complex one that has been studied in great detail on laboratory and industrial scale. There are a number of issues that have made laboratory scale studies difficult to interpret, mainly having to do with correct experimentation technique and thermodynamic validity (application of the phase rule). These will be discussed in detail in the next chapter. In the case of industrial experience and testwork, however, there is extensive documentation of the problems caused by this build up in commercial smelting furnaces and converters (Peretti 1948, Ellwood and Henderson 1952, Mossman 1956, Lathe and Hodnett 1958, Barth 1960, Beals 1963, Brittingham 1965, Brittingham 1966, Michealson 1966, Verney 1969, Middlin 1970, Hart and Milne 1970, Milne et al. 1971, Minto and Davenport 1974, Kim et al. 1976, Goto 1976, Elliott et al. 1983, Moriyama et al. 1995, San Miguel et al. 1995) and the realities of the problems and remedies show many similarities among various operations.

As mentioned above, in general, all the experiences related by the various sources indicate similarities with respect to the issues. The main problem encountered with regards to smelting furnace operators was the massive build up of the magnetite layer in
the hearth areas of the furnace. This had a significant detrimental impact on furnace operation, metal recoveries and overall smelter economics. The main problems were associated with decreased vessel capacity, increased slag losses and increased furnace downtime for cleaning/removal of the magnetite layer. A number of control mechanisms were found to be useful and were very similar in nature, despite the application in very different geographical locations. The control strategies developed can be summarized below.

- Adding a reductant such as pig Fe, coke, ferrosilicon, etc.
- Adding dry concentrate and/or pyrrhotite.
- Better fluxing of slags from furnaces and converters (control of slag silica).
- Increasing matte and slag superheat.
- Strategic placement of tapping and skimming holes to improve bath movement.

These control mechanisms worked on the practical level and the reality was accepted. However, to date, there is no fundamental work which unites theory and practice, in a cohesive study, that indicates the thermodynamic reasons for magnetite behavior during smelting and converting and why certain control mechanisms are effective.

By rationalizing the effective magnetite control mechanisms used in the past by various furnace operators, it can be seen that on a thermodynamic basis there appear to be three main variables which need to be defined:

1. Oxygen potential.
2. Sulfur potential.
3. Temperature.

Controlling these three parameters should be the key to determining the behavior of magnetite, in terms of activity, thus defining the conditions necessary to avoid magnetite precipitation during particular smelting and converting operations.
Review of the literature shows that study of thermodynamics of nickel smelting is lacking. There have been extensive studies to investigate copper smelting and behavior of magnetite in copper mattes, but there remains much work to be done for the case in nickel.

It is the objective of this present study to investigate the smelting region by performing equilibrium studies between matte-gas and matte-slag-gas in order to understand the behavior of magnetite during smelting and converting of nickel sulfide concentrates. These two types of equilibrium studies are important to adequately define magnetite saturation conditions for the smelting and converting regimes. It may be argued that it is only necessary to study the matte-slag-gas system, since the equilibrium between matte and gas only does not simulate true smelting conditions. However, as will be shown in these studies, it is not always possible to achieve magnetite saturation in a system containing matte-slag and gas and therefore it is difficult to define saturation conditions. However, in the system containing matte and gas it is possible to adjust conditions such that magnetite saturation will occur, therefore an understanding of magnetite behavior as a function of temperature and oxygen and sulfur pressures can be investigated. These studies, when combined with the matte-slag-gas studies will constitute a cohesive thermodynamic representation which will describe why magnetite saturation occurs and what can be done to prevent magnetite formation during smelting and converting.

The experimental systems under study consist of Ni-Fe-S-O mattes in equilibrium with a gas phase containing CO-CO$_2$-SO$_2$. The gas mixture will fix the partial pressures of sulfur and oxygen. By fixing the temperature and the matte grade (Fe/Ni ratio) the experimental system will be completely, thermodynamically, defined according to the phase rule. Once saturation is achieved, the system will no longer be constrained by the Fe/Ni ratio, but merely by the sulfur and oxygen partial pressures at isothermal conditions.

In the case of the matte-slag-gas system, there will be five components Ni-Fe-S-O-SiO$_2$. The gas phase composition will again be controlled by a mixture containing CO-CO$_2$-SO$_2$. Testwork will be conducted at silica saturation and according to the phase rule,
under isothermal conditions and having fixed the partial pressures of oxygen and sulfur the experimental system will be completely thermodynamically defined. An additional component, cobalt, will be added for the case of matte-slag-gas equilibrium. Since cobalt is normally present in nickel sulfide ores and is a valuable metal, compared to nickel, it is important to learn cobalt behavior in these high temperature processes. Since cobalt can be regarded as a minor element in this study it will not be included as a component for the phase rule considerations.

More detail of the experimental theory and test conditions will be presented in Chapters 3 and 4.
References


2.0 Literature Review

The study of magnetite behavior during non-ferrous smelting or converting has in general been approached from very specific directions and many separate studies have been performed, with limited success. The different types of studies performed can be grouped into three major categories:

1. Study of phase equilibria.
2. Experimental study to determine various compositional relationships.
3. Thermodynamic studies resulting in activity data.

Phase equilibria studies can yield very useful information if performed properly. Often, however, phase equilibria work, in the systems of interest, has been conducted under inert atmospheres so that the condensed systems under study may be allowed to equilibrate with each other and not necessarily with the gas phase. However, in the case of smelting and converting systems the compositional relationships must be defined by a number of parameters including temperature and partial pressures of oxygen and sulfur. The systems of interest have significant solubilities of sulfur and oxygen from the gas phase. It is therefore important to have proper control of the gas phase activities in order to determine the response of the condensed phase compositions by varying the gas phase compositions. Since the condensed phase equilibrium state will depend on the gas atmosphere used, phase equilibria work conducted with inert gases (N₂ or Ar) do not provide sufficient understanding of magnetite behavior during smelting or converting.

A number of experimental studies have been performed to examine the equilibrium between matte and gas phases in an attempt to understand the behavior of magnetite in these simpler systems, without a slag phase. The majority of this work has been performed in copper mattes, with one study having been done with nickel mattes. The review of the literature will be presented below in sections 2.1 to 2.5.
During the 1970's there was an enormous interest in copper smelting systems and as a result a vast amount of fundamental testwork was carried out at various laboratories around the world. The stimulus for this research was to gain a better understanding of the smelting and converting processes to determine what parameters may be controlled in order to maximize metal recoveries. As a natural progression, many of these studies did investigate how magnetite affects the smelting parameters and especially metal losses to slags. A summary of pertinent testwork conducted with these, more realistic smelting systems, is also included in sections 2.6 and 2.7.

It is now more understood and accepted that magnetite behavior is influenced by the following variables:

- Temperature.
- Oxygen partial pressure.
- Sulfur partial pressure.

Each of these variables is related to the magnetite activity by its effect on the activity of iron and the free energy of formation of magnetite. In the past, although acknowledged by various authors, proper consideration of these factors, consequently the phase rule, were not always given and, as a result, the behavior of magnetite from these studies could not always be adequately explained. In going through the following review, it is important to keep in mind the main factors, mentioned above, which define and govern any particular smelting situation. In any experimental study it is the proper definition and manipulation of those variables that determines the value and practical usefulness of the testwork for industrial application.

The most basic system under study in this investigation is the quaternary Ni-Fe-S-O. It is therefore important to establish reliable experimental data on the oxygen free ternary systems so that a basis for thermodynamic study can be referenced. It will be extremely useful to have reliable information on the Ni-Fe-S system for study of real nickel mattes and also for the Cu-Fe-S system for study of real copper mattes. A number of thermodynamic studies in both the aforementioned ternaries have been performed in the past and are described below. In these cases the experimental work was complemented
by correct thermodynamic analyses and as a result the experimental data is presented in
the form of the resultant thermodynamic properties found from each study.

2.1 Activities in the Cu-Fe-S System

For the purpose of studying the thermodynamic properties of copper smelting mattes
reliable information of the ternary Cu-Fe-S system should be considered essential. In
order to define the properties of the Cu-Fe-S-O system the data of the base ternary system
is often used as the standard state in which information in the quaternary is referenced.

The most significant thermodynamic studies conducted in the Cu-Fe-S ternary were by
Krivsky and Schuhmann (1957), Bale and Toguri (1976) and Nagamori et al. (1989).
These authors employed various techniques to study the phase equilibria and determine
the activities of iron and copper in the ternary melts. Of particular importance was the
region which defined the most basic copper mattes, which is the region of homogeneous
molten Cu-Fe-S melts between 1200 to 1400 °C. In general, it was found that the
activities of iron and copper (subsequently those for Cu$_2$S and FeS) were strongly
dependent on the sulfur pressure.

Due to practical limitations of the Gibbs-Duhem (G.D.) integration technique used by
Krivsky and Schuhmann (1957) the component activities were only calculated at 1350
°C. Following their analyses, they found that the activities of Cu$_2$S and FeS could be
described fairly well, as a first approximation, by Temkin’s model.

Bale and Toguri (1976) conducted thermogravimetric testwork to determine the
thermodynamic properties of Cu-S, Fe-S and Cu-Fe-S melts at 1200 °C. In order to
determine the component activities in the region corresponding to homogeneous sulfide
liquids these authors employed the equilibrium established between these mattes and
alloy saturated liquid (copper rich side) and alloy saturated solid (iron rich side) to define
their standard state activities. By integrating the G.D. equation, at the alloy saturated-
matte boundary and continuing through into the homogeneous liquid matte field, the
variation of iron and copper activity was determined as a function of composition (Figure
2.1.1). With respect to Cu$_2$S and FeS, their findings were similar to those of Krivsky and Schuhmann (1957) and found that they could be fairly well represented by Temkin's model (Figure 2.1.2) which assumes random mixing of cations and anions on their respective sites.

Nagamori et al. (1989) re-established iron and copper activities, at 1200 °C, in the Cu-Fe-S ternary after updating the phase equilibria data. They claimed that previous researchers had missed part of the phase diagram which showed an additional solid alloy phase in equilibrium with the alloy saturated matte on the iron rich side. This new alloy had considerably higher S solubility than the previous estimates (which just assumed an Fe-Cu alloy with negligible S solubility).

The activities of iron and copper in the region of homogeneous matte liquid established by Nagamori et al. have been re-plotted and are shown in Figures 2.1.3 and 2.1.4.

![Figure 2.1.1 Iso-activity of iron curves in the homogeneous matte liquid field of the Cu-Fe-S system at 1200 °C after Bale and Toguri (1976).](image)
Figure 2.1.2 Activities of FeS and Cu$_2$S in the Cu-Fe-S System at 1200 °C (Bale and Toguri 1976) and 1350 °C (Krivsky and Schuhmann 1957).

Figure 2.1.3 Activity of Fe in the Cu-Fe-S system at 1200 °C after Nagamori et al. (1989).
Figure 2.1.4 Activity of Cu in the Cu-Fe-S system at 1200 °C after Nagamori et al. (1989).

2.2 Activities in the Ni-Fe-S System

Conard et al. (1986) investigated the thermodynamics of the Ni-Fe-S system at temperatures between 1200 to 1400 °C. They employed previous experimental work, from their laboratory, on Fe-Ni alloys and the equilibrium between the solid alloys and molten matts together with previous thermodynamic work by Meyer (1972) to determine iron and nickel activities in molten matts. At the time Meyer (1972) conducted his studies reliable data did not exist in the Fe-Ni binary, so all his thermodynamic calculations were referenced to standard states at specific Fe/Ni ratios in the homogeneous liquid matte field at a sulfur mole fraction of 0.50. He then derived the quantities Δlog γₙi and Δlog γ_fe which were the differences between the logarithms of the activity coefficients of nickel and iron in two solutions at the same temperature with the same Fe/Ni molar ratio. Conard et al. (1986) used the activity coefficient relationships of Meyer (1972) extrapolated to the liquidus representing equilibrium between homogeneous matts and Ni-Fe-S solid alloy, since they had determined the iron and
nickel activities from their own work. Knowing the variation of sulfur pressure over a wide range of matte compositions from alloy saturation into the region of homogeneous liquid mattes and the activity values at the alloy-matte boundary, a graphical integration technique was carried out to define iron and nickel activities over this broad range. Integration paths were along lines of constant Fe/Ni molar ratio at varying sulfur pressures using the liquidus as the standard state. Part of the results from Conard et al. (1986) at 1200 °C and 1300 °C have been re-plotted and are shown below in Figures 2.2.1 and 2.2.2. In the figures below the open circles represent values of iron activity and the solid lines correspond to iso-sulfur pressures.

![Graphical representation of Fe-Ni-S system at 1200 °C](image)

**Figure 2.2.1** Variation, with respect to mole fractions, of iron activity and iso-sulfur pressure lines in the Ni-Fe-S system at 1200 °C after Conard et al. (1986).
Figure 2.2.2 Variation, with respect to mole fractions, of Fe activity and iso-sulfur pressure lines in the Ni-Fe-S system at 1300 °C after Conard et al. (1986).

2.3 Experimental Testwork in Cu-Fe-S-O Quaternary

In terms of experimental studies into copper mattes, there were a number of experimental studies which investigated the characteristics of oxygen solubility. Some experimental work was performed without complete thermodynamic analyses (activity calculations) and are presented below. Some investigators used their experimental data and/or that of others to generate thermodynamic relationships to describe the behavior of magnetite in
the copper mattes containing oxygen. No thermodynamic studies were conducted in the Ni-Fe-S-O quaternary to date. A summary of the most pertinent experimental work will be covered in this section. Any thermodynamic studies or analyses from other studies are presented in section 2.4.

2.3.1 Phase equilibria in the Cu-Fe-S-O system.

Yazawa and Kameda (1955) were one of the first researchers to perform phase equilibria studies on more realistic Cu mattes, Figure 2.3.1.1. They were mainly interested in understanding the behavior of oxygen in these sulfide mixtures and to determine the most prominent form of iron oxides (ferrous or ferric). They believed, at the time, that in practice it would be very difficult to obtain iron oxides in the form of magnetite due to the fact that most industrial mattes contained significant proportions of FeS. From their perspective, thermodynamics would dictate that melts containing iron oxides could not exist in the ferric state due to the reducing effect of FeS on magnetite. In their experiments thermal arrest curves, quenching and metallography were used to study the microstructure of different Cu-Fe-S-O mixtures and a pseudo phase diagram was developed. Their testwork showed that a significant amount of oxygen could be dissolved into the sulfide melts and the oxygen content increased with the FeS content. Using a stannous chloride etch to distinguish between ferric and ferrous oxides, they confirmed that the majority of the iron oxides were in the form of wustite. This however is not so surprising when one considers they did all their experiments at either Fe or silica saturation.

Schmiedl and co workers (1971) developed a phase stability diagram of the Cu-Fe-S-O system at 1227 °C, based on a rationalization of previous testwork conducted in the corresponding the six ternaries which make up the Cu-Fe-S-O system, Figure 2.3.1.2. They were mainly interested in the region of coppermaking and thus their diagram reflects the region of converting corresponding to coppermaking and beyond towards blister formation. As a result the representation is at very low sulfur pressures, log \( PS_2 \leq -6.0 \), which is too low for interpretation of primary smelting processes.
Figure 2.3.1.1 Partial liquidus phase diagram for the Cu$_2$S-FeS-FeO system after Yazawa and Kameda (1955).

Figure 2.3.1.2 Representation of the Cu-Fe-S-O system at 1227 °C after Schmiedl et al. (1971).
2.3.2 Oxygen solubility studies using a fixed SO\textsubscript{2} partial pressure.

A number of equilibration studies were performed with regard to matte oxygen solubility in which the gas phase employed was either a combination of inert gas (Ar or N\textsubscript{2}) + SO\textsubscript{2} or pure SO\textsubscript{2} (Johannsen and Knahl 1963, Spira and Themelis 1969). In general the results of these studies concluded that the oxygen content in mattes was an inverse function of matte grade. However, according to phase rule constraints, for a system of matte-gas equilibrium (Cu-FeS-O or Ni-Fe-S-O) with a constant gas composition of SO\textsubscript{2}, it is only possible to control two degrees of freedom at a fixed temperature. Fixing the SO\textsubscript{2} pressure essentially fixes the partial pressures of sulfur and oxygen which means that no degrees of freedom remain. It is therefore not possible to independently control matte grade (which all the above authors in this section did) to derive any relationships of oxygen solubility. If true equilibrium were achieved in the testwork employing fixed SO\textsubscript{2} pressures all condensed phase compositions would have to converge to one set of values. However, due to mass constraints and the fact that most experiments were only conducted for a fixed time, data generated by this type of testwork generally only represents some metastable equilibrium state.

Johannsen and Knahl (1963) sought to explain the sulfur deficiencies in industrial mattes by the dissolved oxygen content. Since their analyses of industrial mattes indicated very low levels of metallic Fe it was their belief that the non-stoichiometric nature of these mattes could be attributed to the dissolved oxygen contents. Another driving force for their studies, as they cited, was a deficiency of published data regarding the Cu-Fe-S-O system at temperatures above 1200 °C. In their studies, copper mattes of varying grades were equilibrated with 1 atm. SO\textsubscript{2} gas and solid magnetite which had been formed a priori in the test crucibles. Each charge was allowed to equilibrate for two hours, then sampled and a new charge of FeS and Cu\textsubscript{2}S added for a new melt equilibrium. By employing a combination of bromine-alcohol leaching and X-ray diffraction these authors speciated the contained oxygen into ferric and ferrous oxides. They found that the oxygen content increased dramatically inversely with matte grade and directly with temperature. Also, by their analyses, the oxygen was mainly in the form of magnetite at temperatures below 1250 °C and increased in FeO proportion (lower Fe\textsuperscript{3+}/Fe\textsuperscript{2+} oxides) at
temperatures above. Upon comparing the dissolved oxygen contents of their work with those of others (Rosenqvist and Hartvig 1958, Yazawa and Kameda 1955, 1962 and Lander 1954) they found there was good agreement. This however, should have led them to investigate further as not all of the previous work was conducted under magnetite saturation. Furthermore, according to the phase rule, their own studies should not have been valid since under constant partial pressure of SO2 and temperature in their experiments it would not be possible for mattes of different grades to exist. If all their tests had been allowed to come to true equilibrium, at a fixed temperature and sulfur and oxygen partial pressure (fixed pSO2), they should have attained the same matte grade in each case. They also attempted to correlate their results to industrial mattes to estimate the industrial matte smelting temperatures. However, in this regard, they failed to mention that since all the industrial mattes they investigated were relatively high grade (≤ 20 wt.% Fe) the oxygen solubility would not be expected to vary significantly in this range as a function of temperature, as cited by even their own studies.

2.3.3 Oxygen solubility in mattes using a controlled gas phase.

Luraschi and Elliott (1980) also used a controlled CO-CO2-SO2 gas atmosphere to control the sulfur and oxygen partial pressures and study the oxygen solubility in copper mattes at a fixed temperature of 1200 °C. These authors realized the importance that sulfur and oxygen pressures have on the sulfur and oxygen solubility in mattes and were able to demonstrate this theory from their test results, Figure 2.3.3.1. They developed a correlation equation for oxygen dissolution in the copper mattes which could be represented by

\[ Wt.\%O = 5.70 \left( P_{SO2}^{0.2005} P_{S2O3}^{-0.2004} \right) \]

This relation seemed to agree with the earlier work performed by Kameda and Yazawa (1969), but did not fit well with Lander's (1954) earlier testwork, Figure 2.3.3.2. This discrepancy was explained by the fact that the above equation may not be valid at the higher sulfur pressures such as those used by Lander (1954).
Figure 2.3.3.1 Solubility of oxygen in Cu-Fe-S-O melts at 1200 °C after Luraschi and Elliott (1980).

Figure 2.3.3.2 Representation of oxygen solubility correlation equation by Luraschi and Elliott (1980) and comparison with other studies.
Luraschi and Elliott (1980) also attempted to describe the nature of the melts using various thermodynamic parameters such as oxygen and sulfur activity coefficients, but were unsuccessful. The oxygen and sulfur contents of the mattes, from their study, were in excess of melts which could be described as mixtures of FeS-Cu₂S-FeO-Cu₂O which led them to conclude that the melts must contain Cu²⁺ and Fe³⁺ species. As a result, they indicated that the oxygen and sulfur behavior in these melts was too complex to be described by simple activity coefficients and recommended further fundamental studies to understand the structure of these melts.

Kaiser (1986) followed a similar approach to Luraschi and Elliott (1980) by conducting tests at fixed oxygen and sulfur pressures using CO-CO₂-SO₂ gas mixtures. The difference in this study is that Kaiser conducted experiments from low PO₂ up to values corresponding to saturation with solid magnetite. Luraschi and Elliott (1980) did not experiment under conditions which would result in magnetite saturation. There is good agreement between the testwork of Kaiser and Luraschi and Elliott at lower sulfur pressures than at the higher sulfur pressures. From Kaiser’s study of Cu-Fe-S-O melts correlation equations were developed which gave the oxygen and sulfur solubilities as a function of Fe weight fraction and partial pressures of sulfur and oxygen within the range of experimental conditions. At fixed sulfur pressures Kaiser defined magnetite saturation conditions (PO₂) as a function of iron weight fraction in the melt. However, by strict definition of the phase rule in this system at oxygen pressures greater than those required for saturation the oxygen solubility should be independent of initial weight fraction of Fe in the melt and thus all tests should have converged to a common curve. It appears that the researcher did not explicitly recognize this aspect of the phase rule. However, by re-plotting some of the experimental data, it can be seen that phase rule constraints were adhered to, Figure 2.3.3.3. The greater amount of scatter, defining the maximum oxygen solubility (magnetite saturation) and beyond, especially for lower matte grades, results from the fact that true equilibrium was not reached (all tests were carried out for fixed time intervals of 24 hrs.). For mattes containing higher iron contents it appears that more time was required to reach equilibrium at oxygen pressures higher than those corresponding to magnetite saturation.
2.4 Activities in the Cu-Fe-S-O System

Rosenqvist and Hartvig (1958) performed equilibrium studies between Cu-Fe-S-O melts and solid magnetite in an attempt to understand conditions which promote solid magnetite formation during smelting. They recognized the importance that magnetite behavior has on the efficiency and successful operation of smelting furnaces and therefore sought to provide fundamental studies whereby industrial operations could be improved by understanding the nature of the mattes.

Their testwork consisted of equilibrating melts containing Cu-Fe-S with solid magnetite, formed a priori, in alumina crucibles under conditions of controlled \( \text{S}_2\text{SO}_2 \) gas and temperature. The reason for choosing this particular gas mixture was to study the equilibrium:
3 FeS + 2 SO₂ = Fe₃O₄ + 2½ S₂

and thus correlate the oxygen solubility behavior with FeS activity. The results of their investigation are shown below in Figure 2.4.1. The activity behavior of FeS was surprising as it exhibited both a maximum and a minimum as a function of melt iron content. As a result of this behavior the Cu₂S activity also displayed the same effect only mirrored to the FeS activity. The strange behavior of FeS and Cu₂S activity could not be explained by analyzing the structure of melts using Flood or Temkin models. From examination of the experimental data and microscopic examination they explained this behavior by the possible influence of Fe³⁺/Fe²⁺ structure of the melts, especially in the case of the soluble oxide components. There appeared to be a change in the oxygen solubility behavior (Wt.% oxygen) with the solubility curve changing slope and becoming much steeper as the iron metal mole fraction increased beyond about 0.68, corresponding to the maxima in FeS activity. Furthermore, from metallographic examinations, it was observed that the crystallizing wustite phase did not appear until the melt compositions approached the same iron metal mole fraction corresponding to the maximum in the a₃FeS curve.

Figure 2.4.1 Activities of FeS and Cu₂S in mattes saturated with solid magnetite as a function of Fe metal mole fraction in the melt after Rosenqvist and Hartvig (1958).
After investigating the ternary Cu-Fe-S ternary melts, Nagamori and Yazawa (1988) performed experimental work with the quaternary Cu-Fe-S-O melts at 1200 °C and a fixed sulfur pressure of $10^{2.10}$ atm. Combining their experimental data with the results from Kaiser (1985), they developed an analytical expression of the G.D. equation for a quaternary system containing two volatile components. The solution of the G.D. equation involving four species could be simplified by performing the integrations along planes of constant Fe/Cu molar ratio and iso-potential surfaces of either sulfur or oxygen pressure. Their equations took the final form presented below:

$$\int_{N_2=0}^{N_2=N_2} \left( \frac{\partial \ln a_3}{\partial \ln N_2} \right) \, dN_2 = t_1 + t_2 + t_3$$

where:

$$t_1 = \int_{N_2=0}^{N_2=N_2} \left( \frac{-N_2}{(1 - N_1 - N_2)^2} \right) \left( \frac{\partial N_3}{\partial y} \right)_{N_2, P_1} \left( \frac{\partial \ln P_2}{\partial N_2} \right)_{N_2, P_1} \, dN_2$$

$$t_2 = \int_{N_2=0}^{N_2=N_2} \left( \frac{(1 - y)(1 - N_1)}{(1 - N_1 - N_2)^2} \right) \left( \frac{\partial \ln P_2}{\partial y} \right)_{N_2, P_1} \, dN_2$$

$$t_3 = \int_{N_2=0}^{N_2=N_2} \left( \frac{-N_2}{(1 - N_1 - N_2)} \right) \left( \frac{\partial \ln P_2}{\partial N_2} \right)_{N_2, P_1} \, dN_2$$

The LHS of the integral will simplify down to:

$$\int_{N_2=0}^{N_2=N_2} (d \ln a_3)_{x,P_1} = \ln \left[ \frac{a_3(x = \text{const}, P_1 = \text{const}, N_2 = N_2)}{a_3'(x = \text{const}, P_1 = \text{const}, 1 - 3 - 4)} \right]$$

where the activity of component 3 is referenced back to the 1-3-4 ternary system. The variables x and y are defined as:
In the case of the quaternary copper mattes the components are as follows: 1=S, 2=O, 3=Fe, 4=Cu. Activities of Fe, as a function of oxygen pressure and Fe/Cu molar ratio at a fixed sulfur pressure, calculated from Nagamori and Yazawa (1988) are shown below, replotted on an X-Y axis, Figure 2.4.2.

Figure 2.4.2 Activity of Fe in the Cu-Fe-S-O system at 1200 °C and log PS₂=-2.10 after Nagamori and Yazawa (1988).

Kaplan et al. (1995) used the equations developed by Nagamori and Yazawa (1988) only using a different standard state to define the activities of iron and copper in the quaternary Cu-Fe-S-O. Kaplan et al. (1995) used the experimental data of Kaiser (1985), as well as some of their own, but instead of choosing the ternary Cu-Fe-S system as the
standard state they chose magnetite saturation conditions (for iron activity) and stoichiometric Cu$_2$S (for copper activity). Nagamori and Yazawa (1988) could not use magnetite saturation conditions to define the iron activity since their experimental work did not employ oxygen pressures sufficiently high to achieve saturation. The results of Kaplan et al. (1995) are shown below for the case of copper matte with Fe/Cu molar ratio of $\frac{1}{4}$, Figure 2.4.3.

Somsiri and Gaskell (1995) conducted equilibration studies of copper mattes and platinum foil to determine component activities at 1300 °C. In these experiments magnetite saturation was also not achieved and the standard state was matte saturated Pt-Cu-Fe alloy at specified sulfur and oxygen pressures.

In their analysis of the component activities, Somsiri and Gaskell (1995) concluded that the activity of iron increases with increasing oxygen pressure and decreasing sulfur pressure, Figure 2.4.4. The trend with respect to oxygen pressure was contrary to the findings of both Nagamori and Yazawa (1988) and Kaplan et al. (1995). It appears that there may have been some errors in the way Somsiri and Gaskell (1995) calculated their Fe activities. It seems more likely that the iron activity decreases as the oxygen pressure increases at a fixed Fe/Cu molar fraction and a fixed sulfur pressure, which would be more consistent with behavior observed in the systems Fe-O (Darken and Gurry 1945, 1946) and Fe-O-SiO$_2$ (Michal and Schuhmann 1952, Muan 1955). However, since the change in iron activity, over the range of oxygen pressure investigated, did not change significantly, the activities of magnetite and wustite they calculated should not be significantly affected. One finding, of particular interest, from their study was the effect of sulfur pressure on the activity of iron and consequently magnetite. It is seen that the magnetite activity increases dramatically as the sulfur pressure decreases at constant Fe/Cu molar ratio and oxygen pressure (Figure 2.4.4).
Figure 2.4.3 Compound activities in the Cu-Fe-S-O system at 1200 °C after Kaplan et al. (1995).

Figure 2.4.4 Effect of sulfur pressure on the activity of magnetite at 1300 °C at a fixed Fe/Cu ratio and oxygen pressure, after Somsiri and Gaskell (1995).
2.5 Experimental Testwork in The Ni-Fe-S-O Quaternary

Hsieh and Chang (1986) and Yoshiki-Gravelsins (1988) performed investigations of the quaternary Ni-Fe-S-O system. The testwork of Hsieh and Chang (1986) was conducted at temperatures below 1000 °C and was carried out mainly as a study of the phase equilibria between solids. The testwork conducted by Yoshiki-Gravelsins (1988), however, was in the temperature regime corresponding to existence of homogeneous nickel smelting mattes.

Yoshiki-Gravelsins (1988) conducted equilibrium experiments using CO-CO₂-SO₂ gas mixtures with Ni-Fe-S-O melts of differing initial Fe/Ni ratios. This researcher was mainly interested in examining the behavior of oxygen in these sulfide melts and attempted to carry out experiments from the regime of magnetite unsaturated mattes to magnetite saturation and beyond. In her experimental work temperatures chosen were between 1200 and 1300 °C and partial pressures of sulfur between 10⁻³.⁰⁰ to 10⁻².⁰⁰ atm. In general the oxygen pressures employed varied between 10⁻¹¹.⁵⁰ and 10⁻⁸.⁵⁰ atm., the higher value depending on where magnetite saturation was achieved.

From the work of Yoshiki-Gravelsins (1988), it was found that the nickel mattes behaved in much the same way as do copper mattes. The trends of oxygen solubility are directly proportional to the Fe/Ni ratio (or conversely matte grade) and PO₂ (at PO₂'s lower than those for magnetite saturation) and indirectly proportional to temperature (at PO₂'s below saturation) and PS₂. Comparing the data from Kaiser (1985) to those of Yoshiki-Gravelsins (1988) it is observed that nickel mattes at the same Fe/(non-ferrous metal) molar ratio have a much lower oxygen solubility than do copper mattes.

In the study conducted by Yoshiki-Gravelsins (1988) a solid electrolyte was used to determine the attainment of equilibrium. From preliminary experiments it was determined that 24 hours would be sufficient to achieve equilibrium between melt and gas. However, upon examination of the experimental data, it appears that some experiments may not been given enough time to reach an equilibrium state, especially after saturation. For example, as was shown with the work of Kaiser (1985) above (Figure 2.3.3.2), according to phase rule constraints, once saturation is achieved, the
melts can no longer be controlled by fixing Fe/Ni ratio, rather this ratio will be determined from the temperature and sulfur and oxygen pressures. Figure 2.5.1 shows some of the experimental data from the study of Yoshiki-Gravelsins (1988) re-plotted. The data from this study does not seem to be as consistent as that from the copper mattes by Kaiser (1985). Strict attainment of equilibrium or some pseudo-equilibrium state, due to air inleakage, cracked crucible assembly, etc may have been the cause of the variation observed.

Figure 2.5.1 Oxygen solubility in Ni Mattes at 1200 °C and log PS2=−2.00 at different matte grades, after Yoshiki-Gravelsins (1988).

2.6 Experimental Testwork in The Cu-Fe-S-O-SiO2 System.

In the smelting system comprising matte, slag and gas phases, many experimental studies have been performed. Owing to the complexity of these systems, corrosiveness of the melts and experimental difficulties, there have not been a great deal of thermodynamic
studies to date. Due mainly to difficulties in fixing the appropriate degrees of freedom, the majority of the thermodynamic testwork has been conducted employing simplifying assumptions such as ideal behavior of matte components (typically Cu$_2$S and FeS). One such study is shown in section 2.8.

As mentioned previously, a vast majority of the smelting testwork has been conducted without proper phase rule constraints having been applied. This testwork was mostly conducted for the copper systems using either a fixed SO$_2$ pressure or inert gas atmospheres. Investigations of this type will be covered in the following sections 2.6.1 and 2.6.2.

2.6.1 Equilibration studies using a fixed SO$_2$ gas.

Generally, if the phase rule constraints are obeyed it is not possible to conduct equilibrium studies in the Cu-Fe-S-O-SiO$_2$ system using a gas composition containing a fixed SO$_2$ content and varying the condensed phase composition, if the gas phase is considered controlling. All of the researchers mentioned below used either a mixture of N$_2$/SO$_2$ or Ar/SO$_2$ to fix the gas phase composition. Therefore, none of these studies obeyed the phase rule and equilibrium was not established between the matte, slag and gas phases, merely some metastable equilibrium was achieved.

According to the phase rule, for a five component system (Cu-Fe-S-O-SiO$_2$) and four phases (matte-slag-gas-silica) the number of degrees of freedom are three. Therefore at a fixed temperature the remaining degrees of freedom which can be fixed are partial pressures of oxygen and sulfur. The condensed phase compositions will therefore vary with changes in either of the three degrees of freedom. By specifying different volume fractions of SO$_2$ gas in an inert gas stream will change the values of oxygen and sulfur pressures as the inert gas acts as a diluent if the total pressure is defined.

Tavera and Davenport (1979) were primarily interested in determining the equilibrium content of copper in fayalite slags. They conducted their experiments at silica saturation and determined the copper losses in slag as a function of matte grade at constant N$_2$/SO$_2$ gas mixtures and temperatures between 1150 and 1300 °C.
Johansen et al. (1970) carried out their studies in an attempt to better understand the phase equilibria and thermodynamics pertaining to continuous copper smelting. They cited a lack of data until then relating to continuous processing of copper versus the abundance of available data pertaining to conventional pyrometallurgical processing of copper ores. They attempted to study three different states of equilibrium between matte-metal-magnetite, metal-matte-slag-silica and matte-magnetite-slag-silica all under a constant and fixed flow of SO₂ gas. By examination of the phase rule each of their series of tests therefore only has one degree of freedom after fixing temperature. However, by fixing the SO₂ gas at one atmosphere the testwork essentially fixed both sulfur and oxygen pressures. It was therefore necessary for one of the phases to disappear for true equilibrium to be achieved. As a result their testwork showed wide compositional fluctuations, of the condensed phases, and did not agree well with previous studies (Sehnalek and Imris 1972).

Korakas (1964) carried out experimental work to investigate the phase relations between mattes and slags corresponding to smelting and converting. In the case of his smelting tests he attempted to equilibrate mattes and slags with two different N₂/SO₂ gas mixtures. As one of his independent variables he chose matte grade. For a five component system (Cu-Fe-S-O-SiO₂) and being silica saturated there remains three degrees of freedom. However, by fixing the volume fraction of SO₂ in the incoming gas mixture the sulfur and oxygen pressures are fixed. As mentioned above, if the gas phase is considered to control the equilibrium, matte grade cannot be an independent variable. For this reason he did not achieve equilibrium and the relationships developed do not obey phase rule constraints.

2.6.2 Equilibration studies without controlled gas phase.

Since the most basic typical smelting systems contain five components (Cu-Fe-S-O-SiO₂) at a fixed temperature with gas, matte and slag phases present there are at least three degrees of freedom to be fixed. If the system is studied under magnetite or silica saturation, two remaining degrees of freedom need to be fixed. In the latter cases,
testwork conducted in accordance with the phase rule typically will employ a gas phase which fixes the sulfur and oxygen pressure by mixing various gases in different proportions. In the cases where a purely inert or constant gas phase composition is used, equilibrium will never exist between all phases present and compositional variations of the condensed phases will no doubt be a result of some kind of metastable equilibrium set up between themselves. This type of testwork, although yielding some data, does not give a true indication of the condensed phase compositional dependence on the gas phase and thus should not be used to develop thermodynamic properties for the melts.

Yazawa (1956) conducted testwork using mattes and slags contained in iron crucibles to better understand the smelting system Cu-Fe-S-O-SiO$_2$ at 1200 °C. Having realized that smelting mattes may not necessarily be adequately described by the ternary system FeO-FeS-Cu$_2$S, from his previous work, due to presence of magnetite, this study was performed to determine the mutual solubility between mattes and slags in the five component system. However, since all his testwork was conducted in iron crucibles and under a N$_2$ atmosphere, the presence of Fe$^{3+}$ was not significant and he noted that FeO was deduced to be quite stable in the resulting condensed phases. From these experiments he found that the mutual solubility between matte and slag phases could be decreased by increasing the silica and Cu$_2$S content and decreasing the FeO content of the system.

Geveci and Rosenqvist (1973) also attempted to equilibrate molten copper-matte-slag and silica or magnetite under a flow of nitrogen. This again does not establish the importance of the gas phase, thus sulfur and oxygen pressures, on the condensed phase equilibrium and merely represents some metastable equilibrium between the condensed phases at some arbitrary value of gas phase composition. Their data showed a significant amount of scatter and even they indicated that the experimental data should be regarded as preliminary, with more work to follow.

Spira and Themelis (1969) investigated the nature of slag losses during copper smelting to explain the differences observed at various Noranda operations. In their experimental work, they attempted to equilibrate mattes and slags under an atmosphere generated by a gas-fired burner. They obtained certain relationships of slag losses vs. matte grade,
however the system under an uncontrolled gas phase is not at equilibrium. They should have been alerted to experimental error because the magnetite concentration in the slag was constant even though the matte grade varied. If the system had in fact been at equilibrium it would not be possible for the magnetite to remain constant since an increase in matte grade is only possible by increasing the oxygen pressure and thus magnetite content. Furthermore, they went on to derive a relationship of slag losses vs. the matte oxygen content and matte grade from the same experimental data that showed the constant slag magnetite levels as a function of matte grade. At the time they could not distinguish what the major factors which influenced the slag losses, oxygen content in mattes and the matte grades derived from examination of mattes and slags from their different operations. Since the thermodynamic conditions of their testwork are unknown, their slag loss relationships are not useful or applicable to actual situations.

Spira and Themelis (1971) conducted their experiments in order to clarify the effect that lime and alumina have on the solubility of oxygen in mattes which are in equilibrium with silica and iron saturated slag at 1200 °C. They employed a nitrogen atmosphere, they recognized and stated that equilibrium was not achieved, since the gas phase composition was not controlled. Results of their testwork showed that addition of lime and/or alumina did not have any appreciable affects on the oxygen solubility in mattes.

2.6.3 Equilibration studies using a controlled gas atmosphere.

It is well known and well accepted now that in order to carry out proper equilibration studies in the five component smelting systems, it is necessary to control both the partial pressures of sulfur and oxygen under isothermal conditions. This can be done in a variety of ways by employing different combinations of gas mixtures. But fixing the appropriate number of phases must also follow proper control of the gas atmosphere. In this section a number of studies will be reviewed in which proper gas phase control was maintained, but phase rule constraints were invalidated by attempting to simultaneously equilibrate too many phases.

Sehnalek and Imris (1972) were mainly interested in developing fundamental physico-chemical information for the Cu-Fe-S-O-SiO₂ system for purposes of developing
continuous coppermaking. Their main objectives were to determine optimum smelting and converting conditions to maximize recoverable metals under defined conditions of T, PO₂ and PS₂. They conducted two sets of testwork to simulate smelting and converting. Although they did follow the phase rule properly for the smelting case, the data from their testwork indicate that equilibrium was not achieved. For example, at a fixed sulfur and oxygen potential (used N₂-S₂-SO₂ gas mixtures) they report varying quantities of copper in slags and mattes. In the case of experimental work, for converting, they employed a gas mixture containing N₂ and SO₂. Furthermore, they claimed that they had achieved doubly saturated slag (magnetite and silica). However according to the phase rule, it would not be possible for their system to have been in equilibrium with four phases. Additionally, at a fixed SO₂ pressure it is impossible to vary the condensed phase compositions for a N₂-SO₂ gas mixture.

Tavera and Bedolla (1990) also conducted equilibration work with particular regards to determining the behavior of copper losses during converting processes. Their experimental set up consisted of five phases (metal-matte-slag-silica-gas) and five components (Cu-Fe-S-O-SiO₂), thus at a fixed temperature there was only one degree of freedom left. These authors claimed that the SO₂ pressure was essentially fixed by fixing the Ar-CO-CO₂-SO₂ gas mixture, but in effect that fixes two variables PS₂ and PO₂. Since the gas mixture essentially fixes two degrees of freedom one phase should have disappeared if the system had indeed achieved equilibrium. Since the silica saturation and gas phase was fixed this meant that either the metal, matte or slag phase would have had to disappear.

Toguri and Santander (1969) performed equilibrium studies on fayalite slags and gold-copper alloys. In this experimental work a gas phase containing CO and CO₂ were equilibrated with fayalite slag and gold-copper alloys at varying Cu/Au ratios and PO₂'s. Since the activities of copper in the alloy was known \textit{a priori}, by varying the oxygen pressures, the variation of copper activity, thus Cu₂O, could be found as a function of oxygen pressure. They found that the solubility of copper in fayalite slags varies linearly with the activity of copper in the metal phase, at constant oxygen pressure and varies linearly with PO₂\textsuperscript{16} at constant copper activity. In relating these studies to the real smelting systems containing sulfur they acknowledged that one should be cautious about
trying to correlate these relationships. Since it is unknown how the activities of copper and iron will vary in the case where sulfur is present in the slags and oxygen is present in the mattes, the slag loss relationships from this study should only be used as a general guide to understand how copper losses will be affected by matte grade (%Cu in matte) and the oxygen partial pressure.

Font et al. (1998) conducted equilibrium studies in the copper smelting system at MgO and silica saturation. The equilibrium gas phase was controlled using mixtures of $S_2/\text{SO}_2/\text{Ar}$. Therefore by fixing the temperature of the system, at 1300 °C, the phase rule was obeyed and the system was completely defined by fixing partial pressures of oxygen and sulfur at a fixed temperature. In the case of copper smelting, they found that slag losses were independent of the SO$_2$ pressure, Figure 2.6.3.1. Furthermore, their experimental work showed that slag losses were independent of matte grade in the range from 20 to 65% Cu. This behavior was quite different from what was observed in the case of nickel smelting, section 2.7.

![Figure 2.6.3.1 Solubility of copper in magnesia and silica saturated fayalite slag after Font et al. (1998).](image-url)
2.7 Experimental Testwork In The Ni-Fe-S-O-SiO₂ System.

Celmer (1987) conducted equilibration studies in the nickel smelting system under both fixed SO₂ pressures (1% and 10% SO₂ + Ar) and mixtures of CO-CO₂-SO₂ to simulate a 10% SO₂ atmosphere. The main goal of this study was to investigate the behavior of minor elements under simulated conditions of nickel smelting. According to prior arguments based on the phase rule for copper smelting testwork, it can be shown that tests conducted under fixed SO₂ pressures, and employing matte grade as an independent variable, will not necessarily reach equilibrium state. The matte and slag phases may attain some kind of metastable equilibrium, but will not necessarily be in equilibrium with the gas phase. Results from this study provide proof of the theory and was acknowledged by the researcher. In the study it was indicated that testwork carried out for 48 hours appeared to result in some state of equilibrium, whereas if the testwork was carried out for a longer time, the condensed phase compositions would continually change. As a result, all tests were carried out for 48 hours and did not achieve equilibrium.

Font et al. (1998) conducted equilibrium studies in the nickel smelting system at MgO and silica saturation. The equilibrium gas phase was controlled using mixtures of S₂/SO₂/Ar. Therefore by fixing the temperature of the system, at 1300 °C, the phase rule was obeyed and the system was completely defined by fixing partial pressures of oxygen and sulfur at a fixed temperature. Their experimental work concentrated on the solubility behavior of Ni in slag which they related to the SO₂ pressure and matte grade. The results of this study showed that the nickel losses in slags were most dependent on the matte grade and SO₂ pressure and in the range of matte grade from 15% to 45% Ni, losses to the slag were virtually constant, Figure 2.7.1. Nickel losses to the slag increase dramatically at matte grades above 60% Ni.
2.8 Activities in the Cu-Fe-S-O-SiO₂ System

Yazawa (1974) constructed a copper smelting diagram (at 1200 °C and 1300 °C) which indicated the equilibrium phases under different combinations of PS₂ and PO₂, Figures 2.8.1 and 2.8.2. In constructing this diagram, he used data collected from his studies and other experimental work available at the time. He concluded from his analysis that the oxygen and sulfur partial pressures change very little in the matte smelting region (0% Cu to 70% Cu). However, from 70% Cu to 80% Cu and towards blister production, there is a tremendous increase in the oxygen pressure and a corresponding decrease in the sulfur pressure. In the matte smelting region (up to 80% Cu) the slags were assumed to be silica saturated and thus the activity of FeO in the system was assumed to be fixed at a value of 0.35. Based on this assumption, he calculated the variations in activities of magnetite, FeS, Cu₂S, Cu₂O and copper which would be expected. The partial pressure of SO₂ was
assumed to be constant at 10%, essentially fixing the variation of sulfur and oxygen pressures. In order to calculate the component activities (iron and copper) the activities of FeS and Cu2S were assumed to behave ideally in the matte. The results of the thermodynamic analyses are shown in Figure 2.8.3. Consistent with his smelting diagrams he shows that the variation of magnetite activity is very small until matte grade is increased past about 70% Cu. At matte grades from 70% to 80%, the activities of copper, Cu2O and Fe3O4 are shown to drastically increase.

![Diagram](image)

Figure 2.8.1 Copper smelting diagram at 1200 °C after Yazawa (1974).
Figure 2.8.2 Copper smelting diagram at 1300 °C after Yazawa (1974).

Figure 2.8.3 Activities in the copper smelting system after Yazawa (1974).
2.9 Rationalization of Proposed Study

In order to study the oxygen solubility in nickel mattes and consequent magnetite behavior, it is important to conduct experimental work in the simpler systems of matte-gas equilibrium. If a slag phase is present, experimental conditions may not permit the attainment of magnetite saturation under practical smelting situations. After review of the literature, it appears that there is a need for the fundamental data of the Ni-Fe-S-O quaternary, if not only to confirm the results of a previous researcher (Yoshiki-Gravelsins 1988), but to extend the knowledge not attained in the previous work. It is also necessary to perform the studies in a way that valid thermodynamic relationships, such as component activities, may be obtained from the experimental data. It is therefore the intention of the present study to investigate the oxygen solubility behavior in nickel mattes at temperatures between 1200 to 1300 °C and sulfur pressures between log PS2=-2.00 to -4.50, in order that a complete understanding of magnetite behavior can be realized. These studies will be used to complement the real smelting and converting experimental systems (containing a slag phase) in order to develop a cohesive picture of the high temperature processes of interest.

Since it is apparent that actual thermodynamic relationships in the realistic smelting system (matte-slag-gas) is lacking, it is necessary to conduct further studies in an attempt to define and understand them. The study conducted by Yazawa (1974) seems to be reasonable and one can not pass judgement as to the trends observed from his activity calculations since no other practical data is available. Obviously the assumptions made by Yazawa (1974) about the ideal behavior of FeS and Cu2S in the matte phase are not strictly accurate over the whole smelting range depicted in his diagrams (Figures 2.8.1 and 2.8.2) since the stoichiometry may change significantly depending on the PS2 and PO2 combinations being considered. However, in the copper smelting system this assumption may not be inaccurate since the variation in matte composition as a function of sulfur pressure does not appear to be significant. By examination of the base Cu-Fe-S system, Figure 2.9.1, it is readily apparent that compositional deviations from the pseudo-binary join, representing FeS-Cu2S, do not appear to be very significant until the sulfur pressures drop below about 10^-4.0 atm.
Figure 2.9.1 Iso-sulfur pressure lines at 1200 °C in the Cu-Fe-S system after Bale and Toguri (1976).

This may indeed have been the reason why Bale and Toguri (1976) and Krivsky and Schuhmann (1957) did observe the mattes in the ternary system to behave close to idealality.

In the case of nickel smelting however, the compositional changes in the matte phase may be much more affected by the sulfur pressures than in the case of copper. In support of this theory, one has to only look at the observed trends in the Ni-Fe-S ternary (Figures 2.2.1 and 2.2.2). It is easily seen that the variation in matte composition, away from the pseudo-binary FeS-Ni$_3$S$_2$, as a function of sulfur pressure, is more dramatic in the case of nickel than for copper. Looking further at the corresponding iron activities and their variation with sulfur pressure, it is reasonable to suspect nickel smelting systems will be affected by changes in sulfur pressure. Furthermore, in terms of reliable experimental work, there appears to be only one applicable study to date (Font et al. 1998). It is the objective of the present study to obtain reliable equilibrium data for the nickel smelting system of matte-slag-gas at silica saturation, to determine the thermodynamic properties of the components. Having an understanding of these relationships, thus, the
oxidation/sulfidization processes which occur during nickel smelting and converting will enable proper process modeling with valid thermodynamic data.
References


Yazawa A., "Fundamental Studies on Copper Smelting (V): Mutual Dissolution Between Matte and Slag Produced in System Cu₂S-FeS-FeO-SiO₂", Tech. Reports, Tohoku University, Sendai, Japan, No. 21, 1956, pp. 31-50.


3.0 Experimental Theory

3.1 The Ni-Fe-S-O System

According to the phase rule, in a four component system consisting of two phases (matte-gas) there will remain four degrees of freedom. The variables to be fixed in these experiments are temperature, sulfur and oxygen pressures and the Fe/Ni molar ratio. By conducting experiments at a fixed Fe/Ni ratio and sulfur pressure, under isothermal conditions, the oxygen pressure can be gradually increased from low values to the point where saturation occurs and magnetite precipitation occurs. Once magnetite saturation is achieved there will be an additional solid phase present in the system which means one degree of freedom is lost. In this case the system will no longer be constrained by the Fe/Ni ratio because the precipitation of solid magnetite has depleted the melt of iron. As the oxygen pressure is increased beyond the onset of saturation, the system is completely defined by the temperature and sulfur and oxygen pressures. As a result, irrespective of the initial Fe/Ni ratios of the Ni-Fe-S-O melts once each melt has saturated, the oxygen solubility must be defined by a common curve controlled by temperature, sulfur and oxygen pressures (Figure 3.1.1).

![Oxygen Solubility in Matte at Constant Sulfur Pressure and Temperature](image)

Figure 3.1.1 Schematic of oxygen solubility characteristics in a quaternary system defined by proper phase rule limitations.
The major problem in most thermodynamic testwork is having a convenient, available standard state in which to reference the information being gathered. In the case of the matte-gas equilibria for the quaternary Ni-Fe-S-O, melt the logical standard state may be chosen is the oxygen free system under a given set of conditions (T, sulfur pressure, Fe/Ni molar ratio). The activities in the Ni-Fe-S system were defined previously by Conard et al. (1986) at three fixed Fe/Ni ratios (0.25, 1.0 and 4.0). Therefore if this system is to be used as the standard state for the quaternary melt, the same Fe/Ni ratios must be employed.

The classical binary and ternary Gibbs-Duhem integration method was given by Gokcen (1960) to enable treatment of a quaternary system. The important factors for this method are manipulating the independent variables to achieve a reasonable integral, or alternatively graphical representation. For a quaternary system with components Fe, Ni, S and O the graphical integration can be carried out as shown below.

\[
y = \frac{N_2 + N_4}{N_2 + N_3 + N_4}
\]

\[
a = \frac{N_3}{N_4}
\]

\[
N_2 = (1 - N_1)(1 - y)
\]

\[
N_3 = \frac{y(1 + N_1)}{(1 + a)}
\]

Elimination of \(N_2\), \(N_3\) and \(N_4\) yields an integrable equation of the form:

\[
\frac{\partial \mu_2}{\partial \mu_1} \bigg|_{\gamma_a} = \frac{y}{(1 - N_1)^2} \frac{\partial N_1}{\partial y} \bigg|_{\mu_a} - \left( \frac{N_1}{(1 - N_1)} \right)
\]

or, alternatively
\[ \left( \frac{\partial \mu_2}{\partial N_1} \right)_{y,a} = \frac{y}{(1-N_1)^2} \left( \frac{\partial \mu_1}{\partial y} \right)_{N_2} - \left( \frac{N_1}{(1-N_1)} \right) \left( \frac{\partial \mu_1}{\partial N_1} \right)_{y,a} \]

Integration of the above equation is carried out at constant \( y \) and \( a \), along varying compositions of \( N_1 \). Graphically the equation is represented by:

\[ \mu_2(y,a,N_1) - \mu_2(y,a,N_1=b) = \int_b^N \left( \frac{\partial \mu_1}{\partial N_1} \right)_{\mu_1,N_2,N_4} \, d\mu_1(y,a) \]

Further expanding the RHS of the above equation yields:

\[ \left( \frac{\partial n_1}{\partial n_2} \right)_{\mu_1,n_3,n_4} = \frac{N_3 \left( \frac{\partial N_1}{\partial N_3} \right) - N_1}{N_3 \left( \frac{\partial N_2}{\partial N_3} \right) - N_2} = \frac{2 - A}{1 - A} = \left( \frac{N_1}{N_2} \right)_{\mu_1,n_3,n_4} \]

To solve the thermodynamic properties of component 3, the following equation is manipulated:

\[ \left( \frac{\partial \mu_3}{\partial \mu_1} \right) = \left( \begin{array}{c} \frac{N_1}{N_2} \\ \frac{N_2}{N_3} \\ \frac{N_3}{N_4} \end{array} \right)_{\mu_1,n_3,n_4} \]

and the integral can be represented by

\[ \mu_3 \left( y, \frac{n_3}{n_4}, N_1 \right) - \mu_3 \left( y, \frac{n_3}{n_4}, N_1 = b \right) = -\int_b^N \left( \frac{\partial n_1}{\partial n_3} \right)_{\mu_1,n_3,n_4} \, d\mu_1 \left| \text{const.} \, y, \frac{n_3}{n_4} \right| \]

where \( n \) refers to moles and \( N \) refers to mole fractions.

In the case of the Ni-Fe-S-O system the components are numbered as follows O=1, S=2, Fe=3 and Ni=4. It can be shown that in order to carry out the graphical integration
(Figure 3.1.2), the integration path must be defined along planes of constant Ni/Fe and Ni/S ratios. The integration path will be along the line representing iso-oxygen pressures from the oxygen free system to oxygen saturation (magnetite precipitation). Since this method can only be applied in a homogeneous phase field, the onset of magnetite precipitation will define the endpoint of the integral.

Figure 3.1.2 Quaternary graphical integration after Gokcen (1960).
An alternative integration method was proposed by Nagamori and Yazawa (1988). It provides an equation which can be integrated by parts assuming proper representation of the experimental data has been carried out \textit{a priori}. The final form of the equation is shown below.

\[
\int_{N_2=0}^{N=N_2} \left( \frac{\partial \ln a^3}{\partial \ln N_2} \right)_{y,P_i} \, dN_2 = t_1 + t_2 + t_3
\]

where:

\[
t_1 = \int_{N_2=0}^{N=N_2} \left( \frac{-(1-y)N_2}{(1-N_1-N_2)^2} \right) \left( \frac{\partial N_1}{\partial y} \right)_{P_2,P_i} \left( \frac{\partial \ln P_2}{\partial N_2} \right)_{y,P_i} \, dN_2
\]

\[
t_2 = \int_{N_2=0}^{N=N_2} \left( \frac{(1-y)(1-N_1)}{(1-N_1-N_2)^2} \right) \left( \frac{\partial \ln P_2}{\partial y} \right)_{N_1,P_i} \, dN_2
\]

\[
t_3 = \int_{N_2=0}^{N=N_2} \left( \frac{-N_2}{(1-N_1-N_2)} \right) \left( \frac{\partial \ln P_2}{\partial N_2} \right)_{y,P_i} \, dN_2
\]

The LHS of the integral will simplify to:

\[
\int_{N_2=0}^{N=N_2} (d \ln a^3)_{x,P_i} = \ln \left[ \frac{a_3(x = \text{const.}, P_i = \text{const.}, N_2 = N_2))}{a_3(x = \text{const}, P_i = \text{const.}, l - 3 - 4))} \right]
\]

where the activity of component 3 is referenced to the 1-3-4 ternary system.

In order to carry out the integration the partial derivatives \(t_1 \text{-} t_3\), must be correctly. The following variables must be correctly expressed:

\[P_2 = f(y,N_2)\]
Similarly, the measured values of $N_1$ may be best expressed as a function of $y$ and $P_2$ under constant $P_1$ by:

$$[N_1 = f(y, P_2)]_{P_1}$$

Also the following relationships will be found useful:

$$\left( \frac{\partial \ln P_2}{\partial N_2} \right)_y = \frac{1}{P_2} \left( \frac{\partial P_2}{\partial N_2} \right)_y$$

and,

$$\left( \frac{\partial \ln P_2}{\partial y} \right)_{N_1} = \frac{1}{P_2} \left( \frac{\partial P_2}{\partial y} \right)_{N_1}$$

As always,

$$x = \frac{N_3}{N_4}$$

$$y = \frac{N_3}{N_3 + N_4}$$

In the case of the quaternary nickel mattes the components are as follows: 1=S, 2=O, 3=Fe, 4=Ni.

In choosing the reference state for the integration methods covered above, it was not mentioned previously that in the case of iron, the oxygen saturation point may be used as an alternative to the oxygen free system. At conditions where oxygen saturation occurs, the magnetite activity will be assumed to be unity, since solid magnetite is precipitating at that point. With the oxygen pressure and molar fractions of Ni/Fe and Ni/S defined, the iron activity can be calculated from the free energy of formation of magnetite at given temperatures. Kaplan et al. (1995) used this approach with the experimental work generated by Kaiser (1985). By employing the equations developed by Nagamori and
Yazawa (1988), he calculated the iron and copper activities in the Cu-Fe-S-O mattes as a function of $PS_2$ and $PO_2$ at 1200 °C.

3.2 The Ni-Fe-S-O-SiO$_2$ (sat.) System

Finding a suitable reference state for the case of nickel or copper smelting is not straightforward. Due to the difficulties in fixing the experimental degrees of freedom, reliable thermodynamic data in base smelting systems is difficult to obtain. In order to resolve the problem of reference state activities an attempt will be made to estimate the thermodynamic properties of the base smelting system (Fe-S-O-SiO$_2$) based on phase equilibria work and experimental studies of the related systems (Fe-S-O and Fe-O-SiO$_2$).

The quaternary Fe-S-O-SiO$_2$ can be considered the most basic smelting system since at 0% matte grade, of copper or nickel, all quinary smelting can be described by it. Phase equilibria studies were conducted in this system by Yazawa and Kameda (1953), Maclean (1969) and Li and Rankin (1994), but no thermodynamic treatment of the data was performed in either case. No activity data can be derived from either of these studies.

If one considers the two ternary systems which make up the quaternary, it can be seen that there exists a set of reliable activity data. Stofko et al. (1974) and Nagamori and Kameda (1965) conducted studies of the Fe-S-O system at varying oxygen and sulfur pressures at a fixed temperature of 1200 °C. Bog and Rosenqvist (1959) also conducted investigations into the Fe-S-O system at 1120 and 1400 °C, but at sulfur pressures outside the range of interest for the present study. The testwork performed by Stofko et al. (1974) was conducted at fairly high sulfur pressures (log $PS_2$=-1.68 to -1.17) and are therefore considered too high to be applicable to this study. The limited (and high) range of sulfur pressures employed by Stofko et al. was as a result of the gas phase chosen for equilibration, they controlled the gas atmosphere using a $N_2/\text{SO}_2/\text{S}_2$ mixture. Nagamori and Kameda (1965) employed CO-CO$_2$-SO$_2$ gases to equilibrate the oxysulfide melts, thus had much better control over the sulfur and oxygen pressures. The range of sulfur pressures employed in their study was between $10^{-2.60}$ and $10^{-1.05}$ atm. and the oxygen pressures were in the range $10^{-12.00}$ to $10^{-9.39}$ atm. After conducting tests in the Fe-S
system to obtain the reference state iron activities, they performed a Gibbs-Duhem integration in the ternary from the oxygen free system into the ternary phase field along lines of constant sulfur pressures. Results for the iron activities are shown in Figure 3.2.1 below.

![Figure 3.2.1 Activities of Fe in the ternary Fe-S-O after Nagamori and Kameda (1965).](image)

In order to estimate the iron activity at a given set of sulfur and oxygen pressures these experimental numbers are shown below in Table 3.2.1.

<table>
<thead>
<tr>
<th>Series</th>
<th>log PO\textsubscript{2}</th>
<th>log PS\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-12.00</td>
<td>--</td>
</tr>
<tr>
<td>B</td>
<td>-11.05</td>
<td>--</td>
</tr>
<tr>
<td>C</td>
<td>-10.31</td>
<td>--</td>
</tr>
<tr>
<td>D</td>
<td>-9.77</td>
<td>--</td>
</tr>
<tr>
<td>E</td>
<td>-9.39</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>--</td>
<td>-2.60</td>
</tr>
<tr>
<td>3</td>
<td>--</td>
<td>-2.09</td>
</tr>
<tr>
<td>4</td>
<td>--</td>
<td>-1.50</td>
</tr>
<tr>
<td>5</td>
<td>--</td>
<td>-1.05</td>
</tr>
</tbody>
</table>
In order to obtain reliable estimates for iron activity outside the range investigated by Nagamori and Kameda (1965), a compilation was made of the available literature data for the Fe-S binary system at different temperatures and sulfur pressures and are shown below in Figure 3.2.2. From examination of the iron activity data presented by Nagamori and Kameda (1965) it does not appear that there is a significant change from the oxygen free system to oxygen pressures up to \(10^{-9.39}\) atm. at constant sulfur pressures. It is reasonable to use iron activity data in the Fe-S binary as a first approximation in the Fe-S-O system for sulfur pressures outside the range studied by Nagamori and Kameda (1965).

![Activity of Fe in the Fe-S System](image)

**Figure 3.2.2** Variation of Fe activity as a function of sulfur pressure and temperature in the binary Fe-S system.

A comparison of the iron activity data in the Fe-O-SiO\(_2\) system is also needed in order to estimate the expected iron activity in the Fe-S-O-SiO\(_2\) under a given set of oxygen and sulfur pressures corresponding to a 0% matte grade smelting situation. A number of reliable studies were conducted in the iron-silicate systems from which iron activities may be calculated (Michal and Schuhmann 1952, Muan 1955 and Muan and Osborne
The region of silica saturation is of most importance in these studies and the variation of iron activity as a function of oxygen pressure, along lines of constant silica saturation, are shown in Figure 3.2.3.

Figure 3.2.3 Activity of Fe as a function of oxygen pressure in the system FeO-Fe_2O_3-SiO_2 at silica saturation.

Data from the analyses conducted by Korakas (1963) are also shown in Figure 3.2.3. The calculations performed by Korakas were based on average values from all previous information available to him and are seen to be in good agreement with the present analysis of the experimental data from Muan and Osborne (1960) and Michal and Schuhmann (1952).

Once the reference state activities are obtained, it will be necessary to obtain component activities in the Ni-Fe-S-O-SiO_2 system by integration using the Gibbs-Duhem equation. Application of the Gibbs-Duhem equation to the case of nickel smelting is shown below.
Slag:  \[ X_{(M)} d \log a_M + X_{(Fe)} d \log a_{Fe} + X_{(S)} d \log P_{S^2} + X_{(O)} \frac{1}{P_{O^2}} + X_{(SO_2)} d \log a_{SO_3} = 0 \]

Matte:  \[ X_{(M)} d \log a_M + X_{(Fe)} d \log a_{Fe} + X_{(S)} d \log P_{S^2} + X_{(O)} \frac{1}{P_{O^2}} + X_{(SO_2)} d \log a_{SO_3} = 0 \]

Where the subscripts ( ) represent the slag phase mole fractions and the [ ] represent the matte phase mole fractions. When both phases are in equilibrium the activities of each component, in each phase, will be equal. Furthermore, by conducting the test work at constant sulfur pressure and silica saturation both the third and fifth terms of each equation will be eliminated. As a result the two equations may be used to calculate for the activities of Fe and/or Ni as a function of oxygen pressure. An example of one of the mathematical constraints is shown below. In theory, there are a number of different manipulations which may be performed on the above equations to yield integrable equations.

\[ d \log a_{Fe} = \left[ \frac{X_{(M)} X_{[O]} X_{(O)} - X_{(O)}^2 X_{[M]}}{X_{(Fe)} X_{[M]} X_{(M)}} \right] d \log P_{O^2} \]

or

\[ d \log a_{Fe} = \left[ \frac{X_{(M)} X_{[O]} - X_{(O)} X_{[M]}}{X_{(Fe)} X_{[M]} - X_{(M)} X_{[Fe]}} \right] d \log P_{O^2} \]

A similar equation may be obtained in order to solve for the activity of Ni as a function of oxygen pressure or iron activity. In this case it is preferable to obtain an equation for activity of Ni as a function of Fe activity since the standard state activity of Fe was estimated from the ternary Fe-S-O and Fe-O-SiO_2 systems. One form of this equation can be as follows:

\[ d \log a_{Ni} = \left[ \frac{X_{(Fe)} X_{[O]} - X_{(O)} X_{[Fe]}}{X_{(O)} X_{[Ni]} - X_{(Ni)} X_{[O]}} \right] d \log a_{Fe} \]
References


Maclean W.H., “Liquidus Phase Relations in the FeS-FeO-Fe\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} System, and their Application in Geology”, Econ. Geol., Vol. 64, 1969, pp. 863-884.


4.0 Experimental

4.1 Experimental approach

For the experimental studies under investigation, it was decided to operate with a flow through system. As applied to the matte-gas or matte-slag-gas studies this means that equilibration, of condensed phases, was achieved by means of a flowing stream of reactive gas at a fixed composition. Flowing systems permit the imposition of precise thermodynamic conditions (fixed activities) of the compounds in the gas phase. By fixing these conditions in the gas phase, which is continuously replenished, forces the condensed phase(s) to respond by dynamic mass exchange between phases. The attainment of equilibrium can then be monitored by following the compositional changes of the condensed phases(s) with time. Application of the phase rule is outlined below for the two systems investigated in this study.

*Four Component System (Ni-Fe-S-O).*

No. of phases: 2 (matte + gas) and 3 (matte-spinel-gas)
Degrees of freedom: 4 (T, PS₂, PO₂, Fe/Ni) and 3 (T, PS₂, PO₂)
Gas mixture: CO-CO₂-SO₂
Mass of initial charge: 250 g

*Five Component System (Ni-Fe-S-O-SiO₂) silica saturated.*

No. of phases: 4 (matte-slag-gas-silica)
Degrees of freedom: 3 (T, PS₂, PO₂)
Gas mixture: CO-CO₂-SO₂
Mass of initial charges: 400 g matte + 500 g slag
Application of the phase rule in these studies is done with the assumption that the pressure is constant across all phase boundaries and that gravitational, magnetic, electrical and surface forces all have an insignificant effect on the equilibrium state.

Examination of testwork conducted by various researchers (Chapter 2.0) indicated that one of the main concerns common to all equilibration studies was the uncertainty in the attainment of equilibrium. For example, studies conducted by Johansen et al. (1970), Rosenqvist and Hartvig (1958), Bog and Rosenqvist (1959), Kaiser (1985), Celmer (1987) and Yoshiki-Gravelins (1988) clearly indicate concerns relating to the attainment of equilibrium. Therefore, owing to experimental limitations from previous workers, it was decided to equilibrate not for a set time, but to carry out compositional monitoring with each test. The approach taken in both matte-gas and matte-slag-gas studies was to fix the sulfur pressure in the gas phase and temperature, then progressively change the oxygen pressure. In the case of the matte-gas tests, the initial Fe/Ni ratio was also fixed. By following this experimental technique, the compositional changes of the condensed phases could easily be monitored as a function of oxygen pressure by obtaining suction pin samples at various time intervals. Once the condensed phase(s) compositional changes had ceased, equilibrium was assumed to be achieved and a new oxygen pressure was imposed on the system by changing the inlet gas composition.

4.2 Reagent Preparation

In all testwork, synthetic materials were used. Mattes were prepared using Ni powder, Fe powder and Cu powder (Fisher >99.999 mass basis) combined with sulfur flour. Samples were prepared in 1 kg batches. The solid powder mixtures were put into graphite crucibles and ignited in an induction furnace using a heated graphite rod as the reaction initiator. Owing to the exothermic nature of the formation reactions, fusion of the powdered charge occurred usually in less than 1 minute. The normal procedure is to mix the reagents assuming a 90-95% sulfur retention, adding a slight excess of the sulfur flour. In this manner the material is always slightly sulfur sufficient. After cooling, the
fused metal sulfides are crushed and submitted for chemical assay. The crushed material is re-melted at 1000 °C in graphite crucibles and the metal contents adjusted using metal powders. A pin sample is taken of the melt via 6 mm vycor lance fitted with a suction device and again analyzed chemically. The melts may be adjusted further until stoichiometric FeS, Cu₂S and Ni₃S₂ compositions are obtained and usually less than three attempts are necessary to achieve this.

For matte-slag-gas equilibration testwork a common master slag was used as starting material for every test. The master slag consisted of a mixture of “FeO” and silica which was briquetted and placed on top of the initial (pre-made) matte crystals formed as described above. Since the initial slags were free of non-ferrous metals and sulfur, the approach to equilibrium could easily be monitored by following the compositional progression of any of these elements. The “FeO” was prepared by mixing metallic iron powder and hematite in an iron crucible, fusing under a nitrogen atmosphere at 1250 °C for two to three hours, cooled to 1100 °C for one hour, then water quenched. The solidified mass is crushed, ground and chemically assayed. If the analysis was acceptable the charge was ground to fine powder (-65 mesh) for briquetting. Fine silica sand was used in the synthetic fayalite slag mixture.

4.3 Furnace – Crucible Assembly

Matte-gas

The furnace–crucible assembly is shown in Figure 4.3.1. Fused alumina crucibles (99.8% Al₂O₃, 2.0” Ø I.D. x 2¾” Ø O.D. x 4.0” high) were employed which were covered using an alumina castable lid. Three tubes were inserted in through the castable lid to enable bubbling, blowing and sampling of the melt. The bubbling and blowing tubes were made of alumina whereas the sampling tube consisted of quartz. It was found that due to the thermal cycling experienced by the sample tube it was necessary to use quartz since it possesses more favorable thermal shock resistance characteristics over alumina. The
crucible assembly was backed up in a larger diameter (7.5" Φ I.D. x 9.0" Φ O.D. x 8.0" high) fireclay crucible covered with a fireclay lid and sealed with MgO based cement, Figure 4.3.2. Inside the fireclay crucible the alumina crucibles were held in place using a combination of MgO based ramming mix and back up powder.

Temperature of the furnace hot zone was controlled using a type R thermocouple calibrated against gold (melting point 1064.4 °C) in conjunction with a Eurotherm° 818 furnace controller.

Figure 4.3.1 Experimental apparatus for matte-gas equilibration studies.
Figure 4.3.2 View of crucible assembly used for study of the matte-gas systems.

Matte-slag-gas

For the testwork involving matte-slag and gas, the crucible-furnace set up was much simpler, Figure 4.3.3. The bubbling tube consisted of quartz (3.0 mm Ø I.D. x 8.0 mm Ø O.D.) which was found to also be useful as an indicator as to how quickly saturation conditions were reached. In this case only one alumina tube was used to introduce both the bubbling and sampling tube. When a sample was required, the bubbling tube was taken out of the melt and a smaller diameter quartz tube (2.0 mm Ø I.D. x 6.0 mm Ø O.D.) inserted to obtain a matte and slag sample. Since it was important in this study to obtain silica saturation conditions, the back up lining and lid of the crucible assembly was made with as much quartz containing material as was possible, Figure 4.3.4.
Figure 4.3.3  Experimental apparatus for matte-slag-gas equilibration studies.

Figure 4.3.4  View of crucible assembly used for study of the matte-gas systems.
4.4 Gas Train

For both the matte-gas and the matte-gas-slag-silica equilibration studies, the condensed phases were equilibrated using a gas mixture of CO-CO$_2$-SO$_2$. The gas preparation system is shown in Figures 4.3.1 and 4.3.3. Compressed gases were supplied by Praxair Canada and their specifications are listed below in Table 4.4.1. All gas flows were controlled using Brooks$^\circ$ 5850 mass flow controllers and Analog Devices$^\circ$ data acquisition and control software on a centralized PC. Individual flows were further metered into the crucibles using Brooks$^\circ$ RB-215 rotameters employing R215 SS floats.

Table 4.4.1 Specification for compressed gases supplied by Praxair.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Grade</th>
<th>Purity (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>3.0</td>
<td>99.90</td>
</tr>
<tr>
<td>CO</td>
<td>2.5</td>
<td>99.50</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>3.8</td>
<td>99.98</td>
</tr>
</tbody>
</table>

In order to ensure thermal segregation did not occur, a gas flow of 1000 ml/min was used in all experiments. Furthermore, an in line mixer (turbulator) was employed in the outlet line from the gas mixer and ahead of the crucible assembly. The linear flowrate of the reaction gases was calculated to be 52.6 cm/s which is more than sufficient to avoid segregation (0.6 cm/s) according to Darken and Gurry (1945).

Cold gas mixtures required to generate the desired oxygen and sulfur pressures, at a given temperature, were calculated by F*A*C*T. The F*A*C*T system has been found to be one of the most consistent and reliable thermodynamic databases for equilibration testwork involving systems where the gas phase plays an integral role. The calculation algorithm employed by F*A*C*T is based on the constrained chemical potential method (Bale et al. 1981 and Melancon and Bale 1982). One example of how useful, F*A*C*T
can be in determining equilibrium gas compositions is demonstrated by examining the equilibrium dissociation of SO₂ gas, Figure 4.4.1. In order to determine the equilibrium partial pressures of oxygen and sulfur from the dissociation of sulfur dioxide, it is necessary to consider species which will affect the overall equilibrium. By considering just sulfur, oxygen and sulfur dioxide may be misleading as Figure 4.4.1 shows. Using the calculation algorithm from F*A*C*T enables quick, easy and reliable equilibrium calculations to be performed to determine equilibrium gas compositions from various mixtures at different temperatures. It has been found to provide much more reliable data than other alternatives such as HSC (1994). As an example, comparison of F*A*C*T data with that of HSC is shown in Figure 4.4.2 (the comparison was made at 1250 °C). The difference in oxygen and sulfur pressure between the two programs, for a fixed cold gas composition, is more than two orders of magnitude (lower in the case of HSC). It appears that the solver in F*A*C*T may be more reliable than that used by HSC, since the reference data utilized by both programs is the same. Furthermore, previous investigations conducted in this laboratory examining the equilibrium relationships in the Fe-S, Fe-O-SiO₂ and Ca-S-O systems have confirmed the reliability of F*A*C*T.
Figure 4.4.1 Equilibrium dissociation of sulfur dioxide according to F^A^C^T.
The range of oxygen and sulfur partial pressures employed in these studies were between $10^{-2.0}$ to $10^{-4.5}$ atm. for sulfur and $10^{-12.0}$ to $10^{-7.0}$ atm. for oxygen. According to calculations performed by F*A*C*T there should be no difficulty attaining these equilibrium partial pressures with the gas mixtures of CO-CO$_2$-SO$_2$. Previous investigations by various researchers (Celmer 1987, Yoshiki-Gravelsins 1988) using the F*A*C*T system confirm the possible operating range of sulfur and oxygen pressures with CO-CO$_2$-SO$_2$ cold gas mixtures, Figures 4.4.3 and 4.4.4. A more recent Russian publication (Makhov et al. 1991) have presented suggestions of gas mixtures which may be used in the laboratory to attain various combinations of sulfur and oxygen pressures, Figure 4.4.5. In this study, as mentioned previously, all conditions were met using the desired gas mixture.
Figure 4.4.3 Attainable operating range of sulfur and oxygen pressures at 1300 °C using various gas mixtures after Celmer (1987).

Figure 4.4.4 Range of attainable oxygen and sulfur pressures at 1200 °C utilizing an Ar-CO-CO$_2$-SO$_2$ cold gas mixture after Yoshiki-Gravelsins (1988).
Figure 4.4.5 Range of attainable sulfur and oxygen pressures at 1300 °C using various combinations of cold gas mixtures after Makhov et al. (1991).

Aside from the thermodynamics associated with the equilibrium gas species, there is also the practical side of being able to attain low partial pressures of certain species due to constraints in laboratory measurement and control equipment. For example, in the case of experiments where low sulfur and oxygen pressures were required, such as log PS₂= -4.50 and log PO₂= -10.0 at 1300 °C, thermodynamically, they could be attained easily with the aforementioned gas mixture. But for a total gas flowrate of 1000 ml/min., the required SO₂ flow would have to be as low as 20 ml/min. Utilizing typical flowmeters of 150 to 250 ml/min. capacity would introduce too much error in the metering of gases at these flowrates. In order to alleviate this problem, a combination of flowmeters rated for between 10 and 25 ml/min. were employed to meter SO₂ gas at the low end.
In order to ensure proper inlet gas mixtures, routine gas samples are taken by suction syringe and analyzed using gas chromatography. Normally 3 to 4 samples are analyzed separately and mass flow controllers adjusted accordingly. This also aided in confirming the accuracy of the flow control and measurement equipment.

4.5 Equilibration Time

In this study the approach was taken to continuously sample the condensed phase to determine whether or not equilibrium had been achieved. It is the feeling of the author that this is a much more reliable way to ensure that equilibrium has been achieved than to pre-determine an equilibrium time based on conditions which were adequate under a different set of conditions than the ones under study.

For the matte-gas studies, oxygen in the matte phase was monitored as a function of time. Once the charge was molten and a specific oxygen and sulfur pressure established, by the gas phase, samples of the melt were taken (about 1-3 grams) every twenty four hours. Once the oxygen concentration in the melt had stabilized, the final sample was analyzed for the remaining elements (Ni, Fe and S). The experimental conditions were then changed and allowed to equilibrate again. Magnetite saturation conditions were defined as the point where further increases in the oxygen pressure (at fixed temperature and sulfur pressure) resulted in decreasing oxygen concentration in the melt, resulting in a maximum in oxygen solubility. At this point the Fe/Ni ratio also changed since magnetite saturation also corresponded to a depletion of dissolved iron in the melt.

In the case of the matte-slag-gas equilibration testwork, the attainment of equilibrium was determined by monitoring the following:

- Oxygen concentration in matte.
- Sulfur, cobalt or nickel concentration in slag.
Since the slag was initially free of sulfur and non-ferrous metals (Cu, Ni or Co), it is natural that these elements be chosen for equilibrium monitoring. The same rational applies for determination of oxygen in the matte phase. In general, it was found that matte oxygen and slag sulfur were more rate limiting than nickel or cobalt in slags which seemed to achieve their equilibrium state very quickly. A similar approach to the matte-gas tests were taken in these studies, in that the temperature and sulfur pressure were fixed and the oxygen pressure varied progressively at each equilibrium value.

4.6 Analytical Techniques

The types of analytical techniques and their descriptions used in the course of this study can be found in Appendix A. There were a number of established and common instrumental techniques used for determination of the base metals assays (Atomic Absorption, Induction Coupled Plasma Analysis, LECO Oxygen and Sulfur combustion analyses, etc.). There were also a number of analytical techniques, procedures and sample preparation methods that are non-traditional and unique to the laboratory in which the work was carried out (Bromine alcohol leaching, Ferric iron analyses, LECO Oxygen analysis of high sulfur materials, etc.).

In general, the preliminary stages of sample preparation were identical for every assay technique. Samples of matte or slag obtained from the equilibration experiments were always first ground to -100 mesh (149 μm) before any assaying was performed. The only instances where this was not the case was when mattes were to be analyzed by SEM and for oxygen content. It has been found by previous investigations at this laboratory that matte oxygen determinations can be artificially biased from oxidation which may occur during sample preparation (grinding in a Bleuhler mill). For this reason all mattes which are to be analyzed for oxygen are done so as pin samples (approx. 2mm x 3mm x 2mm).
References


5.0 Experimental Results

This chapter describes the experimental results obtained from equilibration studies involving the systems nickel matte-gas and nickel matte-nickel slag-gas. The application of the experimental theory (Chapter 3.0) and set up of the experimental system (Chapter 4.0) were carried out in such a way as to ensure proper thermodynamic constraints were followed, thus resulting in reliable test data. The results from testwork conducted with the matte-gas system will be presented first, followed by the results from the matte-slag-gas system.

5.1 Matte-Gas Equilibration

As mentioned in section 4.1, the experimental approach taken in the matte-gas studies was to define magnetite saturation by progressively increasing oxygen pressure of the system held at constant sulfur pressure, temperature and Fe/Ni ratio. The onset of magnetite saturation is indicated by a maximum in matte oxygen concentration. The system behavior then changes and a subsequent decrease in oxygen concentration and Fe/Ni ratio is observed as the oxygen pressure is increased further beyond the onset of saturation conditions.

5.1.1 Attainment of equilibrium

For the purposes of this testwork it was decided to continually monitor compositional changes with time for each test point, rather than equilibrating all tests for a predetermined time period. In the current testwork, the oxygen content in matte was used to determine equilibrium conditions. In general, it was found that equilibrium was achieved in about fifty hours, but experimental conditions were not changed until at least two consecutive samples indicated steady compositions (on the curve plateau). Examples of typical equilibrium monitoring curves are shown in Figure 5.1.1.1 and 5.1.1.2.
The importance of monitoring compositional changes with time, as opposed to equilibrating for a set time, may not be readily obvious by examination of Figures 5.1.1.1 and 5.1.1.2. These plots may suggest that even in cases where conditions are significantly different (compare sulfur and oxygen pressures), it appears that the same time was required to reach equilibrium. This may indeed be the case when conditions (oxygen pressure) are far away from saturation but in the vicinity of saturation this may not be true. In fact, from this testwork it has been shown that in some cases, the equilibrium composition was only achieved after about six days (144 hours) at fixed conditions (Figure 5.1.1.3).

![Graph showing oxygen in matte vs time for 36% Nickel Matte Equilibration at 1250 °C](image)

Figure 5.1.1.1 Equilibrium monitoring of test from the matte-gas studies.
Figure 5.1.1.2 Equilibrium monitoring of test from the matte-gas studies.

Figure 5.1.1.3 Equilibrium monitoring of a 14% nickel grade test after saturation has been achieved. Saturation occurred at log PO₂ = -8.80.
5.1.1 Oxygen solubility test results

In this study, three series of sulfur pressure were investigated \( \log P S_2 = -2.00, -2.50 \) and \(-4.50\). At these three sulfur pressures, the temperature was varied between 1200 °C and 1300 °C. In this type of testwork it is important to ensure that phase rule limitations have been obeyed. One of the most controversial points of these types of tests is the reliability of the condensed phase composition. It is important that the melt be controlled by the gas phase present and not be affected by external factors such as air inleakage from cracked or flawed crucible assemblies. One way to ensure this has not happened is to monitor the melt composition to determine whether or not the phase rule is being adhered to. Figure 5.1.2.1 shows results of the melt composition from an equilibration test. The important characteristic to observe is the constant Fe/Ni ratio with increasing oxygen content, until magnetite saturation is achieved. Once magnetite saturation occurs Fe/Ni ratio is no longer a degree of freedom and thus must change with oxygen pressure. The trends observed in Figure 5.1.2.1 are what would be expected from proper equilibration testwork in this system. The validity of all testwork was checked using the same procedures as shown in Figure 5.1.2.1. Experimental test results which define magnetite saturation conditions as a function of temperature, sulfur pressure, oxygen pressure and matte grade, for nickel mattes are presented in Figures 5.1.2.2 to 5.1.2.4 for one series of sulfur pressure \( \log P S_2 = -2.50 \). The remaining experimental data is presented in Appendix B.
Figure 5.1.2.1 Variation in nickel matte composition as a function of oxygen pressure at 1200 °C and a sulfur pressure of $10^{-2.50}$ atm.

Figure 5.1.2.2 Oxygen solubility characteristics of nickel mattes at 1200 °C and a sulfur pressure of $10^{-2.50}$ atm.
Figure 5.1.2.3 Oxygen solubility characteristics of nickel mattes at 1250 °C and a sulfur pressure of $10^{-2.50}$ atm.

Figure 5.1.2.4 Oxygen solubility characteristics of nickel mattes at 1300 °C and a sulfur pressure of $10^{-2.50}$ atm.
Examination of Figures 5.1.2.2 to 5.1.2.4 show that as the temperature increases the oxygen pressure needed for saturation increases. This means that as the temperature of the system rises, the mattes can be exposed to a higher oxygen pressure before magnetite precipitation occurs. Also, consistent with other studies (Kaiser 1985 and Yoshiki-Gravelsins 1988), it appears that the oxygen solubility at saturation increases with temperature. These observations are demonstrated in Figures 5.1.2.5 and 5.1.2.6.

One puzzling observation, consistent from all the experimental work performed, is related to the oxygen solubility as a function of temperature at oxygen pressures below saturation. Examination of Figures 5.1.2.5 to 5.1.2.7 indicates that the mattes dissolve less oxygen as the temperature increases, at oxygen pressures below saturation, again consistent with Yoshiki-Gravelsins (1988). The reason for this will be discussed later in Chapter 6.0 in relation to the magnetite activity.

The effect of sulfur pressure on oxygen solubility, under isothermal conditions, is shown in Figure 5.1.2.8. These results indicate that the nickel mattes can dissolve more oxygen, at oxygen pressures below saturation, as the sulfur pressure decreases. Figures 5.1.2.8 and 5.1.2.9 also indicate that at lower sulfur pressures mattes will saturate at lower oxygen pressures. Furthermore, the effects of sulfur pressure on the oxygen saturation pressure are much more dramatic than those of temperature (Figure 5.1.2.6).

The effect of copper on the oxygen solubility behavior was also examined as part of the matte-gas experimental program. Bulk mattes (defined as Ni/Cu = 1.0 w/w) were equilibrated with the same gas mixtures as used for the nickel mattes. Results of one experimental series (at sulfur pressure $10^{-50}$ atm. and 1250 °C) are shown in Figure 5.1.2.10.
Figure 5.1.2.5 Oxygen solubility, for a 14% nickel matte, as a function of temperature at a fixed sulfur pressure of $10^{-2.50}$ atm.

Figure 5.1.2.6 Oxygen solubility, for a 35% nickel matte, as a function of temperature at a fixed sulfur pressure of $10^{-2.50}$ atm.
Figure 5.1.2.7 Oxygen solubility, for a 58% nickel matte, as a function of temperature at a fixed sulfur pressure of $10^{-1.50}$ atm.

Figure 5.1.2.8 Oxygen solubility, for a 35% nickel matte, as a function of sulfur pressure at 1250 °C.
Figure 5.1.2.9  Oxygen solubility, for a 35% nickel matte, as a function of sulfur pressure at 1300 °C.

Figure 5.1.2.10  Oxygen solubility, for bulk mattes (Cu/Ni = 1.0, by mass), at a sulfur pressure of $10^{-2.50}$ atm. and 1250 °C.
5.1.3 Identification of saturating phase

In order to confirm that the saturating phase was magnetite, examination by scanning electron microscope was performed. The details of the instrument and its operation were described in section 4.6.6. Samples of the crucible materials, after completion of a test, were obtained by sectioning using a diamond saw. These were mounted in epoxy, polished and analyzed by the microscope. Typical magnetite crystals were observed, Figure 5.1.3.1, and are consistent with those by previous researchers (Kaiser 1985, Yoshiki-Gravelsins 1988). Typical EDXA scans of the magnetite phase indicated about 0.5% w/w dissolved nickel in the oxide. This was confirmation that the precipitating phase could be taken as pure magnetite and not a nickel ferrite spinel.

![Figure 5.1.3.1 Typical SEM micrograph of precipitated magnetite crystals from matte-gas equilibration testwork. Magnification is 20X.](image)

5.2 Matte-Slag-Gas Equilibration

As mentioned in section 4.1, the experimental approach taken in the matte-gas studies was to study the smelting system by progressively increasing oxygen pressure of the
system held at constant sulfur pressure and temperature as per phase rule constraints. The compositional relationships, then will be defined with respect to the changing oxygen pressure under isothermal and iso-sulfur pressure constraints. Two series of sulfur pressure were used in these tests $10^{-2.50}$ and $10^{-4.50}$ atm. at a fixed temperature of 1250 °C. Silica saturation was maintained in all testwork by employing a silica crucible to contain the mattes and slags.

5.2.1 Attainment of equilibrium

For the purposes of this testwork it was decided to continually monitor compositional changes with time for each test point, rather than equilibrating all tests for a predetermined time period. In the current testwork, the oxygen content in matte, nickel, cobalt and sulfur contents in slag were used to determine equilibrium conditions. In general, it was found that these parameters were reliable indicators to determine the attainment of equilibrium Figures 5.2.1.1 to 5.2.1.4.

![Attainment of Equilibrium](image)

**Figure 5.2.1.1** Equilibrium monitoring of the nickel matte phase at a sulfur pressure of $10^{-2.50}$ atm. and 1250 °C.
Figure 5.2.1.2  Equilibrium monitoring of the nickel slag phase at a sulfur pressure of $10^{-2.50}$ atm. and 1250 °C.

Figure 5.2.1.3  Equilibrium monitoring of the nickel matte phase at a sulfur pressure of $10^{-4.50}$ atm. and 1250 °C.
5.2.2 Compositional relationships

The effects of oxygen pressure, at fixed temperature and sulfur pressure can be seen in Figures 5.2.2.1 to 5.2.2.4 for the $10^{-2.50}$ atm. sulfur pressure and Figures 5.2.2.5 to 5.2.2.8 for the $10^{-4.50}$ atm. sulfur pressure. In general, it is observed that the matte grade and nickel, cobalt and magnetite contents in the slag increase with the oxygen pressure. Iron and oxygen contents in the matte and sulfur in slags decrease with increasing oxygen pressure. Sulfur content in the matte appears to go through a maximum as a function of oxygen pressure. This behavior for sulfur is similar to that observed in previous studies of copper smelting (Kameda and Yazawa 1969). They attributed this behavior to a lowering of FeS concentration (high matte grades) and high oxygen concentrations (low matte grade). In general, these trends are consistent with those observed in this work on nickel mattes.
Figure 5.2.1.1 Variation of nickel matte composition as a function of oxygen pressure at fixed sulfur pressure (10^{-2.50} atm.) and temperature (1250 °C).

Figure 5.2.2.2 Variation of nickel matte composition as a function of matte grade at fixed sulfur pressure (10^{-2.50} atm.) and temperature (1250 °C).
Figure 5.2.2.3 Variation of nickel slag composition as a function of oxygen pressure at fixed sulfur pressure ($10^{-2.50}$ atm.) and temperature (1250°C).

Figure 5.2.2.4 Variation of nickel slag composition as a function of matte grade at fixed sulfur pressure ($10^{-2.50}$ atm.) and temperature (1250°C).
Figure 5.2.2.5 Variation of nickel matte composition as a function of oxygen pressure at fixed sulfur pressure (10^{-4.50} atm.) and temperature (1250 °C).

Figure 5.2.2.6 Variation of nickel matte composition as a function of matte grade at fixed sulfur pressure (10^{-4.50} atm.) and temperature (1250 °C).
Figure 5.2.2.7 Variation of nickel slag composition as a function of oxygen pressure at fixed sulfur pressure ($10^{-4.50}\text{ atm.}$) and temperature (1250 °C).

Figure 5.2.2.8 Variation of nickel slag composition as a function of matte grade at fixed sulfur pressure ($10^{-4.50}\text{ atm.}$) and temperature (1250 °C).
Compositionally, mattes from the testwork conducted at the lower sulfur pressure (10^{-4.50} atm.) contain less oxygen (Figure 5.2.2.9) and sulfur (Figure 5.2.2.10) and higher iron contents (Figure 5.2.2.11) than the mattes equilibrated at a sulfur pressure of 10^{-2.50} atm. This is not overly surprising given the fact that simple calculation shows the mattes from the testwork conducted at the lower sulfur pressure to be more sulfur deficient. In this case, sulfur deficient is defined as the amount of sulfur below the stoichiometric amount to satisfy nickel and cobalt as sulfides (Ni₃S₂ and Co₉S₄) and the iron, not present as an oxide (oxygen in matte is assumed to be present all as Fe₂O₃), as FeS. If a matte is sulfur deficient, usually there will be metallics present which are typically iron or ferronickel.

![Equilibration Tests - Ni System](image)

Equilibration Tests - Ni System
Varying Sulfur Pressure and 1250 °C

Figure 5.2.2.9 Comparison of matte oxygen contents for the two sulfur pressure series.

It is difficult to compare the oxygen solubility data, as function of oxygen and sulfur pressure, obtained in the matte-gas study with those obtained in the matte-slag-gas study. This is due to the fact that the Fe/Ni ratio, or matte grade, cannot be used as an independent variable in the matte-slag-gas system. The mattes obtained from the latter study can only exist at one distinct oxygen pressure (cannot exist at different oxygen pressures) if temperature and sulfur pressure are fixed.
Figure 5.2.2.10 Comparison of matte sulfur contents for the two sulfur pressure series.

Figure 5.2.2.11 Comparison of matte iron contents for the two sulfur pressure series.
The reliability of bench scale studies is particularly important in the area of slag loss. Since the relationship of slag metal losses as a function of matte grade can be studied under controlled conditions it is possible to define soluble slag losses without influence of matte entrainment. This information is invaluable and can be used to define the optimum limits from any smelting operation. Since the lowest slag losses, at a given matte grade, will correspond to the case where no entrainment is present.

In the matte-slag-gas equilibration studies, a special technique was used to analyze the slag samples to ensure that the metal loss numbers were reliable. Employing the suction pin-quenching sampling technique analyzed by electron microprobe analysis (EMPA) and atomic absorption (AA) a true metal dissolved content could be obtained and also used to ensure that the suction sample had been free of matte entrainment. An example of this type of analysis is presented below in Table 5.2.2.1 and Figure 5.2.2.12. As a slag sample is obtained by the 6 mm vycor tube an initial frozen (quenched) layer is formed immediately adjacent to the sampling tube (Figure 5.2.2.12). This region is typically free of any matte entrainment, thus only contains metals in the dissolved form. Performing a microprobe analysis on this frozen edge will enable determination of the dissolved metals content and this will represent the true equilibrium value coexisting with the particular matte and slag under defined conditions of sulfur and oxygen pressures. Taking another section of the sample and analyzing by atomic absorption will enable quantitative determination of the total metal content of the slag sample. If matte had been sucked into the slag during sampling the metal assay would be greater than the microprobe assay. On the condition that no matte entrainment occurred the microprobe assay of the pin edge and the atomic absorption assay of the bulk slag sample should be identical. All slag samples obtained in these studies were confirmed by EMPA (section 4.6.8). In general, it was found that the suction pin sampling technique was very successful in avoiding matte entrainment. An example of a typical analysis for a slag sample is shown below in Table 5.2.2.1.
Table 5.2.2.1  Typical slag assay comparison (Wt.%) by EMPA and AA.

<table>
<thead>
<tr>
<th>Method</th>
<th>Log PO₂</th>
<th>Log PS₂</th>
<th>Ni</th>
<th>Fe</th>
<th>S</th>
<th>Co</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>10.50</td>
<td>4.50</td>
<td>0.16</td>
<td>49.50</td>
<td>2.33</td>
<td>0.10</td>
<td>15.41</td>
</tr>
<tr>
<td>EMPA</td>
<td>10.50</td>
<td>4.50</td>
<td>0.16</td>
<td>49.97</td>
<td>2.82</td>
<td>0.09</td>
<td>14.75</td>
</tr>
<tr>
<td>AA</td>
<td>8.50</td>
<td>2.50</td>
<td>0.89</td>
<td>48.00</td>
<td>0.23</td>
<td>0.72</td>
<td>16.58</td>
</tr>
<tr>
<td>EMPA</td>
<td>8.50</td>
<td>2.50</td>
<td>0.73</td>
<td>47.96</td>
<td>0.24</td>
<td>0.78</td>
<td>16.53</td>
</tr>
</tbody>
</table>

Figure 5.2.2.12  Micrograph of suction pin sample lateral section. EMPA is performed on either the left or right frozen edge which is free of matte entrainment. Magnification is 30X.

The nickel losses to slag appear to follow the same dependency on oxygen pressure as does matte grade. For example, in the case of testwork conducted at a sulfur pressure of $10^{-2.50}$ atm. there appears to be three distinct slopes on the curve representing nickel content in matte as a function of oxygen pressure. The three slopes appear to be in the following regions:
- **Region I** - from 0% matte grade to 45% matte grade (-9.75 \leq \log \text{PO}_2 \leq -9.00).
- **Region II** - from 45% matte grade to 60% matte grade (-9.00 \leq \log \text{PO}_2 \leq -8.50).
- **Region III** - from 60% matte grade to 68% matte grade (-8.50 \leq \log \text{PO}_2 \leq -7.25).

In each of these distinct regions it can be seen that the behavior of nickel and magnetite in slags changes. For example, in region I, the slag loss is very gradual, whereas the losses in region II become more significant with matte grade and in region III change very rapidly with small changes in matte grade (Figure 5.2.2.8). The significance of this behavior is suspected to be related to the oxygen pressure as shown in Figure 5.2.2.1. Similar behavior is observed in the test results at the lower sulfur pressure (log PS\textsubscript{2} = -4.50), except the location of region III is displaced to a higher matte grade. The three defined regions are shown with respect to nickel and magnetite contents in slag in Figures 5.2.2.13 and 5.2.2.14.

![Equilibration Tests - Ni System](image-url)

**Figure 5.2.2.13** Variation of nickel in slag as a function of matte grade.
Figure 5.2.2.14 Variation of magnetite in slag as a function of matte grade.

The seemingly coincidental behavior of nickel in slag to that of magnetite in slag needs to be further defined. Their dependence on oxygen pressure is apparent from the relationship observed in Figures 5.2.2.3 and 5.2.2.7. Supporting this apparent strong relationship of nickel losses in slag to oxygen pressure is the seemingly unrelated behavior of dissolved sulfur content in slags. This may suggest that nickel losses in silica saturated fayalite slags is most affected by oxygen pressure as is the slag magnetite contents. These relationships will be covered in more detail in Chapter 6.0 with reference to the magnetite activities in these systems.
References


6.0 Discussion

With respect to different trends observed in the experimental data for either the matte-gas or matte-slag-gas equilibration systems, previous studies were found to be lacking in thermodynamic interpretation (see Chapter 2.0). Examining the experimental data and formulating hypotheses to explain the compositional relationships can be done in a fairly straightforward and obvious manner. However, it is important to understand the fundamentals and be able to extract proper thermodynamic information and apply them in order to interpret and utilize this data in a truly meaningful and correct way. That does not mean the value of the experimentally observed data alone are any less important than the thermodynamic treatment, since reliable thermodynamic treatment is only possible with reliable experimental data. Simply put, it means that the fundamental understanding that comes with proper thermodynamic treatment is most important and is the only way any practical and significant benefit can be derived from experimental testwork.

6.1 Matte-gas equilibria.

The first phase of the present investigation focussed on the behavior of oxygen in nickel mattes, in particular, magnetite behavior. The variables which were investigated in this study were oxygen and sulfur pressure, temperature and nickel concentration in the matte phase (Fe/Ni, matte grade, WFe, etc.). From the results presented in Chapter 5.0 it is seen that the general trends observed for oxygen solubility, with respect to these independent variables, were consistent with previous work performed by various investigators. However, the present study had the advantage of a more comprehensive thermodynamic treatment of the experimental data. From this treatment it was possible to explain the behavior of oxygen solubility in nickel mattes in terms of precisely defined thermodynamic relationships that exist between temperature, oxygen and sulfur pressures and the activities of iron and magnetite.
6.1.1 Oxygen solubility as a function of nickel content in matte.

Any of Figures 5.12.2 to 5.12.4 can be used to describe the effect of nickel concentration on the solubility of oxygen in matte. This behavior has been well documented in previous studies conducted in the copper matte system (section 2.3.3). In particular, the studies conducted by Kaiser (1985) show clearly the dependence of oxygen solubility on the copper content of the matte phase. It appears that the behavior of oxygen is very strongly dependent on the iron content in mattes whether they are nickel or copper based. Irrespective of the non-ferrous system, the oxygen solubility increases with iron concentration in the matte.

From the experimental data generated in this study, it was possible to carry out thermodynamic analyses (section 3.1) to calculate the iron and magnetite activities under the different conditions. Comparison of these activities, at different matte grades, appears to provide an explanation for the trends observed. Figures 6.1.1.1 and 6.1.1.2 indicates that as the mattes become richer in iron content, or conversely poorer in nickel, both iron and magnetite activities are higher at a given oxygen pressure. Intuitively, this would appear to be an acceptable result since the activity of iron and its concentration in the melt should be directly related (Figure 6.1.1.1). By virtue of the thermodynamic relationship between iron and magnetite, it also follows that the magnetite activity is higher for the lower grade matte at a given oxygen pressure (Figure 6.1.1.2). These trends then indicate that as the magnetite activity increases, the oxygen solubility also increases. Previous testwork, such as those by Kaiser (1985) and Yoshiki-Gravelsins (1988), did not carry the investigation through to the point where iron or magnetite activities were found. As a result, the oxygen solubility behavior in mattes of different grades was attributed to some dependency, not explicitly defined, being related to the iron contents in the matte phase.
Figure 6.1.1.1  Comparison of iron activity as a function of oxygen pressure for nickel mattes at 1250 °C and a sulfur pressure of $10^{-2.50}$ atm.

Figure 6.1.1.2  Comparison of magnetite activity as a function of oxygen pressure for nickel mattes at 1250 °C and a sulfur pressure of $10^{-2.50}$ atm.
6.1.2 Oxygen solubility as a function of sulfur pressure.

In Figures 5.1.2.8 and 5.1.2.9 the relationships of oxygen solubility in nickel mattes as a function of sulfur pressure were presented. As the figures indicate, the solubility of oxygen in mattes, at a given nickel concentration, increase as the sulfur pressure decreases at oxygen pressures below those required for saturation. Also, the oxygen pressure required to reach saturation decreases with sulfur pressure under isothermal conditions. Similar behavior was observed in studies conducted with copper mattes (Kaiser 1985, Somsiri and Gaskell 1995), Figures 6.1.2.1 and 6.1.2.2 respectively and in nickel mattes (Yoshiki-Gravelsins 1988), Figure 6.1.2.3.

![Graph of Oxygen Solubility in Mattes](image)

Figure 6.1.2.1 Comparison of oxygen solubility behavior of nickel and copper mattes as a function of sulfur pressure at 1200 °C and non-ferrous metal content in matte (35% MG).
Figure 6.1.2.3  Comparison of oxygen solubility behavior of nickel and copper melts as a function of sulfur pressure at 1200 °C after Yoshiki-Cravatins (1988).

Figure 6.1.2.4  Oxygen solubility in melts at 1300 °C.
Examination of the matte composition from data presented in Figure 5.1.2.8 shows that the sulfur content of the matte phase decreases with sulfur pressure. Or in other words, as the sulfur pressure decreases, the sulfur deficiency of the mattes increases. The sulfur deficiency, defined in section 5.2.2, is calculated from a mass balance of the matte phase speciated into compounds such as chalcocite (Cu₂S for copper matte), heazlewoodite (Ni₃S₂ for nickel matte), troilite (FeS) and magnetite (Fe₃O₄). The degree of sulfur deficiency of a matte can also be reflected by the amount of iron existing in the metallic state, the more sulfur deficient a matte, the higher is the metallic iron content. The amount of iron present as metallics is determined by subtracting the total iron content (from chemical assay) from that combined as magnetite and troilite. This is done assuming all the oxygen in matte is present as magnetite and the iron remaining as troilite is that required stoichiometrically to satisfy the sulfur balance after speciation of all the nickel as heazlewoodite. It would be expected that the degree of metallization of the matte (metallic iron) should be closely related to the sulfur pressure and thus the iron activity. The degree of metallization for mattes presented in Figure 5.1.2.8 are shown in Figure 6.1.2.4.

![Metallic Iron in Nickel Mattes](image)

**Figure 6.1.2.4** Comparison of nickel matte iron metallization as a function of sulfur pressure for matte containing 35 wt.% nickel at 1250 °C.
The matte sulfur deficiency, as indicated by iron metallization, shows the expected trends. As the sulfur pressure decreases, the amount of metallic iron present in a matte of fixed Fe/Ni ratio increases. The significance of this behavior on the iron activity should be obvious, as mentioned above, and is evident from Figure 6.1.2.5. As the matte becomes depleted in sulfur (higher amount of iron metallized), reflected by the sulfur pressure, the iron activity increases. By virtue of the thermodynamic relationship that exists between iron, magnetite and oxygen pressure (under isothermal conditions), this means that at a given oxygen pressure, the magnetite activity will increase as the sulfur pressure decreases. Comparing the trend in magnetite activity (Figure 6.1.2.6) with that of the oxygen solubility (Figure 5.1.2.8) provides an explanation for the observed increase in oxygen solubility in nickel mattes as a function of sulfur pressure. The oxygen solubility appears to be directly related to the magnetite activity.

It is important to note that the same behavior was observed with regards to the experimental data from Kaiser (1985) presented in Figure 6.1.2.1 and Yoshiki-Gravelsins (1988) in Figure 6.1.2.3. In both of the previous studies the oxygen solubility of the mattes at a fixed grade, temperature and oxygen pressure, increased with an increase in matte iron metallization, or a decrease in sulfur pressure, consistent with this study. However, at the time, neither Kaiser (1985) nor Yoshiki-Gravelsins (1988) could explain the significance of the sulfur pressure and matte sulfur deficiency in terms of thermodynamic factors, due to a lack of iron and magnetite activity data.
Figure 6.1.2.5 Comparison of iron activity as a function of sulfur pressure at a constant temperature (1250 °C) and nickel concentration in the matte phase (35 Wt.%).

Figure 6.1.2.6 Comparison of magnetite activity as a function of sulfur pressure at a constant temperature (1250 °C) and nickel concentration in the matte phase (35 Wt.%).
6.1.3 Oxygen solubility as a function of temperature.

The experimental data showing the dependence of oxygen solubility in nickel mattes as a function of temperature were shown in Figures 5.1.2.5 to 5.1.2.7. The data presented for all three matte grades are consistent and indicate that at oxygen pressures below those required for magnetite saturation the oxygen solubility increases as the temperature is decreased. This trend is consistent with data reported by Yoshiki-Gravelsins (1988), shown in Figure 6.1.3.1.

![Graph showing oxygen solubility in nickel matte as a function of temperature](image)

**Figure 6.1.3.1** Oxygen solubility in nickel matte (fixed Fe/Ni ratio) at oxygen pressures below those required for magnetite saturation as a function of temperature (after Yoshiki-Gravelsins 1988).

In order to explain the observed trends from this study (with respect to temperature), the data shown in Figure 5.1.2.6 for a matte containing 35 wt.% nickel will be analyzed below. In section 6.1.2 the significance of sulfur deficiency on the iron activity and consequently the magnetite activity and its relationship to oxygen solubility was explained. It was found that the iron activity increased as the sulfur deficiency increased or, conversely, as the amount of metallized iron in the matte increased. Analyzing the
mattes from Figure 5.1.2.6 to determine the relationship of metallic iron as a function of temperature are shown in Figure 6.1.3.2.

![Metallic Iron in Nickel Mattes](image)

**Figure 6.1.3.2** Comparison of metallized iron in nickel mattes at different temperature at a fixed Fe/Ni ratio (1.0 by mole) and a sulfur pressure of $10^{-2.50}$ atm.

Ignoring the data at 1250 °C, due to scatter, Figure 6.1.3.2 indicates that as the temperature increases, the nickel mattes becomes more sulfur deficient or more metallized in iron content. The resultant effect on the activity of iron is shown in Figure 6.1.3.3 and is consistent with the findings reported in section 6.1.2. It can easily be seen that the iron activity in the nickel mattes of a fixed grade and sulfur pressure increases with temperature. The trend observed with respect to temperature and magnetite activity, however, is the reverse of that for iron activity, Figure 6.1.3.4. The reasons for the reverse behavior can be explained by the thermodynamic relationship that exists between the activities of iron, magnetite and oxygen pressure as a function of temperature. The dependence of magnetite activity on iron activity, temperature and oxygen pressure is defined as shown below.

$$3Fe(s) + 2O_2(g) = Fe_3O_4(s)$$
This relationship is defined at different temperatures by the reaction constant, \( K(T) \).

\[
K(T) = \left[ \frac{a_{FeO}a}{a^{3} \cdot P^{2}O_{2}} \right]
\]

The values of \( K(T) \) at temperatures between 1200 to 1300 °C are shown in Table 6.3.1.1.

Table 6.3.1.1 Variation of reaction constant, \( K(T) \), as a function of temperature.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( K(T) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>( 8.30397 \times 10^{22} )</td>
</tr>
<tr>
<td>1250</td>
<td>( 4.45127 \times 10^{21} )</td>
</tr>
<tr>
<td>1300</td>
<td>( 2.87389 \times 10^{20} )</td>
</tr>
</tbody>
</table>

This thermodynamic information indicates that even though the iron activity increases with temperature, at a given oxygen pressure, (Figure 6.1.3.3) the resultant magnetite activity will be greater, at a lower temperature (Figure 6.1.3.4). The behavior of magnetite activity as a function of temperature again is consistent with the observed oxygen solubility shown in Figure 5.1.2.6 and indicates that for nickel mattes the oxygen solubility increases with increasing magnetite activity.
Figure 6.1.3.3 Iron activity as a function of temperature at a fixed sulfur pressure and nickel content in the matte phase.

Figure 6.1.3.4 Magnetite activity as a function of temperature for nickel mattes at fixed sulfur pressure and nickel content.
6.1.4 Effect of copper on oxygen solubility.

The experimental data from Kaiser (1985), Figure 6.1.2.1, was used to calculate the corresponding iron and magnetite activities in the copper mattes. The trends appear to be consistent with those observed in the nickel mattes, from this study, with regard to oxygen solubility and magnetite activity as a function of sulfur pressure (Figures 6.1.4.1 and 6.1.4.2). Since Kaiser did not conduct experiments at temperatures other than 1200 °C, the effect of temperature on the activities of iron, magnetite and oxygen solubility could not be confirmed.

Somsiri and Gaskell (1995) conducted testwork with copper mattes at different sulfur pressures at 1300 °C. From their experimental data they calculated iron activities as a function of oxygen pressure at fixed sulfur pressure, temperature and copper concentration in the matte phase, Figure 6.1.4.3. Their data shows the same dependency of iron on the sulfur pressure, as found from this study (Figure 6.1.2.5), and the analyses done here with Kaiser's data (Figure 6.1.4.1). It appears however, that there may be an error in their calculations. The trend in iron activity, as a function of oxygen pressure, from these authors are contrary to the findings of this study and of other iron-oxygen-sulfur related systems as mentioned in section 2.4. It does not seem possible for the activity of iron to be increasing as the oxygen pressure increases at a fixed temperature, sulfur pressure and matte grade. However, since the range of oxygen pressure investigated was quite limited, the effect of their errors on the magnetite activity (Figure 6.1.4.4) should be minimal. Furthermore, those small errors are not significant enough to change the trend observed for dependency of iron and magnetite activity on the sulfur pressure.
Figure 6.1.4.1 Iron activity as a function of sulfur pressure in copper mattes (35% MG) from Kaiser's (1985) experimental data.

Figure 6.1.4.2 Magnetite activity as a function of sulfur pressure in copper mattes (35% MG) from Kaiser's (1985) experimental data.
Figure 6.1.4.3 Iron activity in copper matte (35% MG) as a function of sulfur pressure at 1300 °C, after Somsiri and Gaskell (1995).

Figure 6.1.4.4 Magnetite activity in copper matte (35% MG) as a function of sulfur pressure at 1300 °C, after Somsiri and Gaskell (1995).
Examination of oxygen solubility data for copper mattes, Kaiser (1985), indicates that they can dissolve more oxygen than nickel mattes under similar conditions (Figure 6.1.2.1). Furthermore, it appears that the oxygen pressure required for magnetite saturation is also higher for the copper mattes. The effect of copper on the oxygen solubility and oxygen pressure required for saturation was investigated in this study by equilibrating mattes containing nickel and copper at similar conditions of non-ferrous metals content, oxygen and sulfur pressure and temperature. The findings were consistent with observations made in the two separate systems Figure 6.1.4.5. The addition of copper to the nickel mattes (Cu/Ni ratio = 1.0 by mass) at the same matte grades (% by mass of non-ferrous metals concentration) increased the oxygen solubility and saturation oxygen pressure as compared to the corresponding nickel mattes (Figure 6.1.4.5).

Figure 6.1.4.5 The effect of copper on the oxygen solubility and magnetite saturation of nickel mattes at the same matte grades, temperature and sulfur pressure.

The iron and magnetite activities have not been calculated for the bulk mattes (Cu/Ni = 1.0) in Figure 6.1.4.5, but the expected behavior can be surmised from comparison of
these activities in nickel and copper mattes. Figures 6.1.4.6 and 6.1.4.7 show iron and magnetite activities calculated from Kaiser's (1985) testwork, for copper mattes, and nickel mattes from this study. The findings appear to be consistent with the trends observed in the experimental data (Figure 6.1.2.1). At equivalent non-ferrous metal concentration (mass % nickel or copper in matte), oxygen pressure, sulfur pressure and temperature, the iron and magnetite activity are not too different until oxygen pressures close to saturation are achieved. Close to saturation, the increase in magnetite activity for nickel matte is much steeper than for the copper matte. As a result, magnetite saturation for the nickel matte is achieved at lower oxygen pressure than in the case of the copper matte (Figure 6.1.4.7).

![Graph comparing iron activity in nickel and copper mattes at 1200 °C, 35% matte grade and a sulfur pressure of 10^{-2.50} atm.](image)

Figure 6.1.4.6 Comparison of iron activity in nickel and copper mattes at 1200 °C, 35% matte grade and a sulfur pressure of $10^{-2.50}$ atm.
Figure 6.1.4.7 Comparison of magnetite activity in nickel and copper mattes at 1200 °C, 35% matte grade and a sulfur pressure of $10^{-2.50}$ atm.

It is interesting to note the large differences in oxygen solubility behavior between copper and nickel mattes under the same thermodynamic conditions of temperature, sulfur and oxygen pressures and non-ferrous metal concentration (Figure 6.1.2.1). Yet, examination of Figures 6.1.4.6 and 6.1.4.7 show that there is very little difference in iron and magnetite activity in these two mattes.

The reason for the improved solubility of copper mattes over their nickel counterparts cannot be rigorously explained at this time. It is however evident that the activity coefficient of oxygen is much higher for nickel mattes than for copper mattes (Figure 6.1.4.8), but this should be expected from relationship of oxygen solubility and oxygen pressure (Figure 6.1.2.1). All that can be said is that the oxygen solubility behavior of copper mattes is similar to that of nickel mattes with respect to the thermodynamic variables of sulfur pressure, oxygen pressure, temperature and concentration of nickel or copper.
Figure 6.1.4.8 Comparison of oxygen activity coefficient in nickel and copper mattes at 35% matte grade.

6.1.5. Oxygen solubility and magnetite activity.

Following with the behavior consistent in both nickel and copper mattes, it would be expected that the copper or nickel free oxysulfide would saturate at the lowest oxygen pressure with the highest solubility of oxygen. Extrapolation of Nagamori and Kameda’s data (1965) show that this does, in fact, occur (Figures 6.1.5.1 and 6.1.5.2).
Figure 6.1.5.1 Comparison of oxygen solubility in different mattes at 1200 °C and similar sulfur pressure.

Figure 6.1.5.2 Activity of magnetite in mattes at 1200 °C and similar sulfur pressures. The activities shown for the Fe-S-O are from Nagamori and Kameda (1965) those for copper and nickel mattes were calculated in this study.
Since the most basic mattes consist of iron, sulfur and oxygen (0% matte grade), it is useful to compare the behavior of oxygen solubility and magnetite activity in this system with either of the copper or nickel mattes. Comparing the oxygen solubility of the copper and nickel mattes with the iron-sulfur-oxygen system under similar conditions, shows that non-ferrous metal additions to an initially iron oxysulfide melt decreases the oxygen solubility capabilities (Figure 6.1.5.1). Furthermore, nickel appears to have a greater effect on depressing the oxygen solubility, in iron oxysulfide melts, than does addition of copper.

The consistency of the oxygen solubility and magnetite activity relationship can be summarized by comparing Figures 6.1.5.1 with 6.1.5.2. Comparing the Fe-S-O curve with copper matte (for copper system) and the Fe-S-O curve with nickel matte (for nickel system), below saturation, shows that the oxygen solubility is directly related to the magnetite activity for a given system. Aside from Figures 6.1.5.1 and 6.1.5.2, comparison of Figure 6.1.2.1 with Figures 6.1.2.6 and 6.1.4.2 (for copper mattes) or Figure 5.1.2.6 with Figure 6.1.3.4 (for nickel mattes) shows the same behavior for a given system.

It is important to note at this point the differences between oxygen content and magnetite activity. As mentioned above, the experimental data along with the thermodynamic analyses performed with the nickel matte studies showed that the oxygen solubility and magnetite activity appeared to be directly related. At oxygen pressures below saturation, conditions (sulfur pressure, temperature) which resulted in higher oxygen solubilities also corresponded to higher magnetite activities. But this correlation did not hold true when comparing two different systems (nickel vs. copper). For example, under the same conditions, copper mattes possess higher oxygen solubility (Figure 6.1.2.1) and lower magnetite activities (Figure 6.1.4.7 or Figure 6.1.5.2) than nickel mattes. In this case it does not appear that oxygen solubility and magnetite activity can be used as correlating factors.

The measurement of activity merely provides an indication as to how close a given matte is to being saturated with the pure solid phase under consideration, in this case magnetite. It does not necessarily follow that the activity indicates what the concentration of that
species will be in the matte phase. For example, Figure 5.1.2.6 showed the relationship of oxygen solubility as a function of temperature at a fixed nickel matte concentration and sulfur pressure. That plot indicates that as the temperature increases the oxygen pressure and corresponding oxygen solubility required for magnetite saturation increases. At oxygen pressures below saturation, the oxygen solubility and magnetite activity correlation is evident (higher dissolved oxygen relates to higher magnetite activity). However, at magnetite saturation, the activity is always unity even though the amount of oxygen dissolved in the matte phase at each temperature is different (Table 6.1.5.1).

Table 6.1.5.1 Summary of magnetite saturation conditions as a function of temperature for 35% nickel mattes at a sulfur pressure of $10^{-2.50}$ atm.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Oxygen concentration, Wt.%</th>
<th>Magnetite Activity</th>
<th>Log PO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>1.53</td>
<td>1.0</td>
<td>-9.00</td>
</tr>
<tr>
<td>1250</td>
<td>2.13</td>
<td>1.0</td>
<td>-8.70</td>
</tr>
<tr>
<td>1300</td>
<td>2.50</td>
<td>1.0</td>
<td>-8.30</td>
</tr>
</tbody>
</table>

It is important to recognize the correlation between oxygen solubility and magnetite activity within a given system, however, at the same time be able to recognize the distinct differences in their behavior. In particular, it is important to not generalize the correlation observed between the oxygen solubility and magnetite activity, in a given system, when comparing two distinct systems, e.g. copper and nickel mattes.

6.1.6 Practical application of matte-gas equilibria testwork.

As mentioned in the introduction, the major common plague that has infected copper and nickel producers over history and into present times has been with regards to magnetite build up in smelting vessels. Many attempts have been made (industrial and laboratory scale) to understand the magnetite build up phenomenon and thus find ways of eliminating it. However, to date, there is/are no comprehensive document(s) which relate experimental and thermodynamic data in a such a way as to provide definitive measures
which can be taken to tackle the problem of magnetite accretions, until now. The experimental and thermodynamic studies carried out in this investigation provides a set of guidelines which may be followed in order to eliminate magnetite build up in pyrometallurgical vessels. The remedies provided from this study may seem obvious when considering the physico-chemico properties of the high temperature melts (mattes) and solids (magnetite), but nevertheless are considered to be reliable due to the close agreement between the experimental observations and the corresponding thermodynamic analyses.

Controlling or eliminating magnetite build up in copper or nickel mattes translates directly into keeping the magnetite activity in the matte phase below unity. Since it is only under conditions that make the magnetite activity equal to unity which results in solid magnetite precipitating from the molten matte phase. Based on the relationships developed here, the most significant factors which can be used to control magnetite precipitation in molten mattes can be summarized in Figure 6.1.6.1.

![Activity of Magnetite in Fe-Ni-S-O System](image)

**Figure 6.1.6.1 Activity of magnetite as a function of temperature, nickel concentration temperature and oxygen pressure.**
The main variables and the relative significance of how each affects the magnetite activity in nickel mattes are easily seen in Figure 6.1.6.1. This diagram indicates that the magnetite activity, at a given matte grade is most affected by the sulfur pressure of the smelting operation. The effect of changing the matte grade, in the range shown, is not as great as the effect of temperature or sulfur pressure at a fixed matte grade. For example, increasing the matte grade from 14% to 35% nickel decreases the magnetite activity by a factor of around 1.5 (from unity to 0.70) and increases the oxygen required for saturation from $10^{-4.80}$ to $10^{-8.70}$ atm. However, by increasing the sulfur pressure during smelting of nickel mattes, at a fixed matte grade of 35% and a temperature of 1250 °C, from $10^{-2.50}$ to $10^{-2.00}$ atm. lowers the magnetite activity by almost 7 times (from 1.0 to 0.15) at an oxygen pressure of $10^{-8.70}$ atm., but it also increases the saturation pressure to around $10^{-8.18}$ atm. For the same grade matte at a sulfur pressure of $10^{-2.50}$ atm., increasing the temperature from 1250 to 1300 °C only decreases the magnetite activity by 4.5 times (from unity to 0.22) at the same oxygen pressure of $10^{-8.70}$ atm and increases the saturation pressure to $10^{-8.30}$ atm.

These studies now provide a sound thermodynamic argument which can be used to develop basic furnace control operating parameters in order to eliminate/control solid magnetite formation. It is necessary, however, to look at these factors in conjunction with the matte-slag-gas studies in order to properly apply the control strategies to real smelting situations. It will be shown, in the following sections, that when a slag phase is present the behavior of magnetite in relation to the thermodynamic variables of oxygen and sulfur pressures, under isothermal conditions, are not necessarily the same as the slag free system. This arises from the fact that in the matte-slag-gas system, matte grade is no longer an independent variable and thus the compositional relationships must constrain to the limitations imposed by only temperature and oxygen and sulfur pressures.
6.2 Matte-slag-gas equilibria.

In the matte-slag-gas equilibria studies, the independent variables used for investigation were temperature, oxygen and sulfur pressure. With the additional phases present (silica saturation and slag) the matte grade was no longer a controlling variable (as was the case in the matte-gas tests). It is easy to understand why this would be the case. As the oxygen pressure of the system increases, iron transfers from the matte phase into the slag phase (as is the case in real smelting). In conjunction with this phenomenon, the matte grade changes, becoming richer in nickel concentration. It therefore becomes very difficult to compare the data trends between the testwork in the matte-slag-gas system with those from the first phase of the study in the matte-gas system.

6.2.1 Oxygen solubility in mattes.

Comparison of Figures 5.2.2.1 and 5.2.2.5 indicates that at a given oxygen pressure, nickel mattes can dissolve more oxygen as the sulfur pressure increases. This is contradictory to the trends observed in the slag free system (Figure 5.1.2.8). The reason for this behavior can be explained by examination of Figure 6.2.1.1. At a given oxygen pressure, the matte grade corresponding to the lower sulfur pressure, in the matte-slag-gas system, is substantially higher. However, even at the same matte grade, according to Figure 6.2.1.1, the oxygen solubility will decrease with the sulfur pressure, again in contradiction to the results obtained in the matte-gas studies. The reason for this behavior once more relates to the impact of oxygen pressure. At equivalent matte grades, the oxygen pressure required at the lower sulfur pressure is significantly lower than that which is required at the higher sulfur pressure, which again is evident from Figure 6.2.1.1.
In the slag free system, it was found that within a given system, the oxygen solubility in mattes was closely related to the iron and magnetite activity. It was also observed that the iron activity increased by decreasing the sulfur pressure or increasing the temperature for a matte at constant grade. Furthermore, the relative amount of iron existing in the matte phase, as metallic iron, provided an indication of the differences in iron activity between two given mattes possessing identical nickel concentrations. Following from the thermodynamic relationship between iron and magnetite, at a given oxygen pressure the activity of magnetite would increase as the iron activity increased. It was then shown, consistently, that as the magnetite activity increased so would the solubility of oxygen.

As mentioned above, in the matte-gas system with a slag phase present, the trend of oxygen solubility with regards sulfur pressure appears to be in contradiction to the findings observed in the case where no slag exists (matte-gas). In an attempt to explain these differences, data were presented in Figure 6.2.1.1 which indicates that the contradictions appear to be related to the intimate relationship between matte grade and oxygen pressure in the smelting system. In order to more accurately describe the reasons...
for the behavior observed with respect to the oxygen solubility, the focus must again turn to discussion of the behavior of the iron and magnetite activities.

In Figure 6.2.1.2, the matte iron metallization as a function of matte grade and sulfur pressure, under isothermal conditions, are shown. As expected, it shows that mattes at conditions of lower sulfur pressure are more metallized. Also, following with trends observed previously (section 6.1.2), the more metallized mattes exhibit higher iron activity at a given matte grade (Figure 6.2.1.3). However, due to the nature of the relationship between matte grade, sulfur pressure and oxygen pressure, under isothermal conditions, the magnetite activity is actually lower for the lower sulfur pressure at a given matte grade (Figure 6.2.1.4).

![Equilibration Tests - Ni System](image)

*Figure 6.2.1.2 Comparison of metallized iron in nickel matte at different sulfur pressures.*
Equilibration Tests - Ni System
Varying Sulfur Pressure and 1250 °C

Figure 6.2.1.3 Iron activity as a function of matte grade and sulfur pressure.

Activity vs. Matte Grade in Nickel System
At 1250 °C and Varying Sulfur Pressure

Figure 6.2.1.4 Magnetite activity as a function of matte grade and sulfur pressure.
After consideration for the behavior of magnetite activity, it appears that its relationship with regard to the oxygen solubility, in the matte-slag-gas system, agrees closely with those from the matte-gas studies. Comparison of equivalent matte grades at the two sulfur pressures shows that the increase in oxygen solubility for the mattes at higher sulfur pressures corresponds to higher magnetite activities (Figure 6.2.1.5). However, contrary to the findings reported in section 6.1.6, it appears that under real smelting conditions (matte-slag-gas equilibria) operating at lower sulfur pressures offers greater advantages with regard to eliminating magnetite build up.

![Diagram](Image)

Figure 6.2.1.5 Comparison of oxygen solubility and magnetite activity in nickel smelting mattes.

### 6.2.2 Practical application of matte-slag-gas equilibria studies.

It is interesting to compare the thermodynamic relationships which follow from the matte-slag-gas equilibria studies to those which were found from the slag free investigation in the first phase of the project. In order to alleviate magnetite precipitation in the nickel mattes it was demonstrated that one of the most significant factors was to
control the sulfur pressure. In Figure 6.1.6.1 the effect of sulfur pressure, at a fixed
temperature and matte grade, on magnetite saturation was shown. The implications were
that in order to eliminate magnetite precipitation, it is more advantageous to operate at
higher sulfur pressures. At a given matte grade and oxygen pressure, operating at higher
sulfur pressures could significantly lower the magnetite activity. However, under real
smelting conditions, the matte grade and oxygen pressure are intimately related and it is
not possible to independently control the two. Each matte grade corresponds to a specific
oxygen solubility providing the temperature and sulfur pressure are defined. Furthermore, it has been shown that in the real system it is more beneficial to operate at
lower sulfur pressures if magnetite saturation is to be avoided, which contradicts the
findings of the slag free studies (Figure 6.1.6.1).

Therefore, in order to decide which conditions would be most favorable for avoiding
magnetite build up under practical smelting situations a new control chart, similar to
Figure 6.1.6.1, can again be constructed. In this case, however, there are a number of
additional factors which must be taken into account. These include, metal losses to the
slag (or consequently partition coefficient), matte grade and magnetite activity. To
optimize a particular smelting operation, it is necessary to determine what conditions can
be controlled to balance the economics of metal recoveries versus other process
requirements such as additional refining stages. For a given smelting operation, the
following areas must be considered in order to optimize the metallurgical benefits:

- Magnetite build up.
- Distribution of valuable metal to the product phase (Partition coefficient, \(P_{Ni}\)).
- Recovery of valuable metal to product phase.
- Number of operating vessels.
- Workplace and surrounding environment.

Each one of these areas will be covered below in order to demonstrate how the
experimental data may be used to define optimal operating conditions for a typical
smelter.
Avoiding magnetite build up.

The magnetite activity and matte grade show a very close relationship, both being highly dependent on the prevailing oxygen pressure. The advantages, with regards to magnetite build up, of operating at lower sulfur pressures can be seen from Figure 6.2.2.1. At a given matte grade, the magnetite activity is lower for the lower sulfur pressure operation.

![Activity and Matte Grade vs. Oxygen Pressure - Nickel System](image)

**Figure 6.2.2.1** Relationship between matte grade and magnetite activity as a function of oxygen and sulfur pressure.

Nickel recovery and partition coefficient.

In section 5.2.2 the behavior of metal losses to slags was discussed and the relationship as a function of matte grade and slag magnetite was shown to delineate three regions of differing slag loss behavior. In Figure 6.2.1.5 the activity of magnetite as a function of matte grade shows the same type of behavior which would indicate that the metal loss to slag, slag magnetite concentration and magnetite activity are closely related. Furthermore, as mentioned in section 5.2.2, this behavior is a direct result of the relationship between matte grade and oxygen pressure (Figures 5.2.2.1 and 5.2.2.5). The interrelationship of these variables and the significance to determination of the optimum smelting conditions will be explained below.
In general, higher matte grades impact detrimentally on metal recovery by increasing losses to slags (Figure 5.2.2.13). Furthermore, the metal losses to slag, at a given matte grade, are lower for the lower sulfur pressure operation. This again leads to the implications that operating at lower sulfur pressures is conducive to more favorable metallurgy.

The matte grade target of a given smelting operation is usually based on the downstream refining requirements as well as consideration to a certain level of metal recovery determined to be economic. The recovery of nickel is directly related to the metal losses in the smelting slags. It is the objective of any smelting operation to maximize recovery, given specific process requirements. For example, to balance downstream refining costs with acceptable recoveries, the matte grade and slag loss relationship becomes one which is essential to have knowledge of.

Issues relating to the type of operation preferred to avoid magnetite build up have already been determined to be lower sulfur pressure operation. According to the apparent relationships which also appear to exist between sulfur pressure, oxygen pressure, matte grade and metal losses, it is clear that the lower sulfur pressure operation offers significant metallurgical benefits. In Figure 5.2.2.13, the metal losses to slag, for a given matte grade, are lower in the case of the lower sulfur pressure. This would indicate that at the lower sulfur pressure, the separation of nickel into the matte phase is more effective. In order to define the effectiveness of the metal separation between the matte and slag phases, a new parameter now may be defined called the partition coefficient. The partition coefficient is defined as the mass % ratio of a certain element between the matte and slag phases. The maximum partition coefficient will define conditions where the most effective separation of that element will take place, maximizing its concentration in the matte phase. The partition coefficients have been determined from the experimental data and are presented in Figure 6.2.2.2. Also included in this plot is the magnetite activity. As expected, the partition coefficient of nickel appears to be closely related to the magnetite activity.
Figure 6.2.2.2 Nickel partition coefficient and magnetite activity as a function of matte grade and sulfur pressure.

Although the nickel partition will define the conditions which give the optimal metal separation, they do not indicate which conditions will maximize the recovery of valuable metal. As mentioned in Chapter 1.0, the main objective of every pyrometallurgical step is to refine a feed by removing unwanted material, which is, mostly in the form of iron and gangue. In order to do this, the metal recovery at each stage will necessarily have to be lower than 100%, otherwise, the feed material also represents the product. Obtaining partition data, from experimental work, is invaluable, since it represents the behavior of the metal system when subjected to the high temperature pyrometallurgical process. This partition data then can be used in process heat and material balances to determine the relationship between processing (upgrading) the feed material and the metal recoveries which are possible under different conditions. Such a procedure was carried out, using a theoretical nickel flash furnace smelting concentrate and flux to produce a molten matte and slag stream at a temperature of 1250 °C. Employing the partition data generated from the matte-slag-gas experimental work, in conjunction with the integrated flash furnace heat and mass balance model, make it possible to explore the effects of different sulfur pressure operation (Figure 6.2.2.3).
Figure 6.2.2.3  Results from theoretical process modeling of a nickel flash furnace operation using experimental data from this study.

The results of the modeling show that the lower sulfur pressure operation can have very significant benefits with regard to metal recoveries. For example, looking at Figure 6.2.2.3, it has been shown that by operating at the lower sulfur pressure, at an equivalent matte grade, (say 45 wt.% nickel) the furnace recovery can be increased by around 1%, which is a very significant gain. The recovery benefits of the lower sulfur pressure operation, at a given matte grade, should have been evident simply by examination of Figure 5.2.2.13. However, in order to determine more realistic benefits it is essential to carry out the process modeling. This is due to the intimate relationship between the heat and material balances which interact in such a way that do not always make the end result intuitively obvious. For example, Figure 6.2.2.3 also indicates that it is possible to operate the flash furnace at equivalent recovery by producing a higher matte grade in the lower sulfur pressure operation. This can have significant beneficial impact on the downstream refining requirements and workplace environment.
The usefulness of the experimental data generated from the matte-slag-gas equilibria studies were demonstrated above pertaining to the benefits of lower sulfur pressure operation on the avoidance of magnetite build up and increased nickel recovery. The value of how this experimental study can be used to tailor specific smelting operations to meet other criteria, such as lowering operating costs or meeting other requirements such as environmental constraints (sulfur dioxide emissions) will be demonstrated by examining a theoretical case study shown below in section 6.2.3. This case study concerns a nickel smelting operation employing one flash furnace for primary smelting and Pierce-Smith converters for matte upgrading. The product from the smelter consists of converter matte with virtually no iron present (thus basically a mixture of nickel and sulfur).

### 6.2.3 Example Case I - Options for operation of a nickel flash smelter.

**Objective.**
The main objective of this modeling study was to scope out various options which could be employed to significantly decrease sulfur dioxide emissions from a nickel smelter.

**Background.**
As mentioned above, the smelter product consists of converter matte, which contains virtually no iron. The sulfur dioxide produced in the furnace is fully captured and fixed in an acid plant. The converter off-gases are not captured in the current flowsheet which means that the sulfur dioxide emissions are all attributed to the converting operation (Figure 6.2.3.1). The particulars of the furnace and converting operation are shown below.

**Flask furnace**

<table>
<thead>
<tr>
<th>Operating temperature:</th>
<th>1250 °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matte grade:</td>
<td>45% nickel by mass.</td>
</tr>
<tr>
<td>Matte production:</td>
<td>25 metric tonnes per hour (mtph).</td>
</tr>
<tr>
<td>Slag nickel content:</td>
<td>0.38% by mass.</td>
</tr>
<tr>
<td>Slag production:</td>
<td>55.9 mtph.</td>
</tr>
</tbody>
</table>
O$_2$/Conc.: ~25%
Flux: 10.2 mtp, 80% silica by mass.
SO$_2$ gas: 39.7 mtp.

Converter

Operating temperature: 1250 °C.
Matte grade: 73% nickel by mass.
Matte production: 15.2 metric tonnes per hour (mtp).
Slag production: 9.8 mtp.
SO$_2$ production: 5.53 mtp.
Air: 11.9 mtp.
Flux: 2.6 mtp, 94% silica by mass.

Figure 6.2.3.1 Current smelter flowsheet for production of converter matte.
Proposed solution.

The option which will be presented here consists of a higher matte grade, lower sulfur pressure, furnace operation, which would lower the sulfur dioxide emissions from the converters by fixing more in the furnaces.

The first criteria which must be met, is in regards to production rate. Consideration of a viable alternative flowsheet must not impact negatively on the amount of product nickel converter matte being produced. The conditions, which would be used to control the flash furnace in such a way as to produce equivalent nickel units in the matte phase, are easily found from Figure 6.2.2.3. It seen that for the existing operation, at 45% matte grade, the nickel recovery in the furnace is around 98%. For an equivalent nickel recovery at the lower sulfur pressure means increasing the furnace matte grade to around 59%. The equivalent recovery results from the fact that even though additional slag is being produced, at the higher matte grade, the nickel partition is high enough to offset the mass changes so that the equivalent mass units of nickel are being produced (Figure 6.2.3.2).

![Nickel Flash Smelting Operation](image)

Figure 6.2.3.2 Effect of sulfur pressure and matte grade on matte and slag production in the flash furnace.
The data presented in Figure 6.2.2.3 can be used in conjunction with the equation,

\[
Recovery(\%) = \left( \frac{P_{NI}}{P_{NI} + \frac{Slag}{Matte}} \right) \times 100\%
\]

to determine what effects the partition coefficient and slag/matte mass ratio have on the recovery in a single unit such as the flash furnace. The changes to the flash furnace product streams are summarized below:

### Flash furnace

**Operating temperature:** 1250 °C.

**Matte grade:** 59% nickel by mass.

**Matte production:** 19 metric tonnes per hour (mtph).

**Slag nickel content:** 0.36% by mass.

**Slag production:** 61.3 mtph.

**O₂/Conc.:** ~30%

**Flux:** 12.4 mtph, 80% silica by mass.

**SO₂ gas:** 45.7 mtph.

Comparing these parameters with the ones from the current operation show that, in the flash furnace, the proposed operation requires more tonnage oxygen and flux and produces more slag and sulfur dioxide gas.

The implication of these changes to the converting operation can be summarized below:

### Converter

**Operating temperature:** 1250 °C.

**Matte grade:** 73% nickel by mass.

**Matte production:** 15.2 metric tonnes per hour (mtph).

**Slag production:** 6.2 mtph.

**SO₂ production:** 0.43 mtph.

**Air:** 4.3 mtph.

**Flux:** 1.6 mtph, 94% silica by mass.
Comparing the new converter operation with the current one indicates that indeed a significant reduction in sulfur dioxide emissions is possible (over 90% reduction from current) with the proposed changes to the flash smelting operation (i.e. higher matte grade – lower sulfur pressure). The reason for the dramatic differences in sulfur dioxide emissions from the converting operation can be explained by examination of Table 6.2.3.1.

Table 6.2.3.1 Summary of smelter operational details pertaining to different flash furnace sulfur pressure operation.

| Flash Furnace Sulfur Pressure | Flash Furnace Matte | Converter | SO$_2$ | mtpH |
|------------------------------|---------------------|-----------|--------|
|                              | Mass mtpH | Ni$_3$S$_2$ Wt.% | FeS Wt.% | Metallic Fe Wt.% | SO$_2$ mtpH |
| Current (log PS$_2$=-2.50)   | 25        | 62.3         | 30.3    | 0.3             | 5.526       |
| Proposed (log PS$_2$=-4.50)  | 19        | 81.9         | 3.1     | 14.3            | 0.433       |

The furnace mattes produced at the lower sulfur pressure are more metallized and contain less troilite. Since the iron phase (as metallic and sulfide) is the one eliminated during converting it is easily seen, from Table 6.2.3.1, that operating the flash furnace at a lower sulfur pressure can dramatically reduce the converter sulfur dioxide emission.

However, sulfur dioxide emissions are not the only advantages which are evident from the proposed operation. In terms of the furnace operation, Figure 6.2.2.1 also indicates that the higher matte grade-lower sulfur pressure operation corresponds to lower magnetite activity, thus increasing the possibilities of avoiding solid magnetite formation. As for the additional benefits potentially available for converting, the flash furnace matte production also decreases with the higher matte grade operation. This has the possible implications that shorter converting times and lower reagent (flux and air) requirements will result. The implications on reagent costs are already evident, since the modeling results indicate that the converter flux requirements decrease by about 1.6 times and the
air requirements decrease by about 2.8 times. If the air delivery system on the converter stays the same (thus constant blowing rates) the lower air requirements combined with lower furnace matte production rate will obviously lead to shorter converting times. In addition to these advantages, one other and possibly very significant, advantage of the lower sulfur pressure furnace operation relates to lower operating costs for the converters. This aspect deals with the number of converting vessels required to handle the tonnage of furnace matte produced. For example, if one converter could handle 5 mtpfh of furnace matte the proposed flowsheet producing 19 mtpfh of furnace matte requires four converters, whereas in the current flowsheet, 5 converters would be required. The savings in operating costs by running 4 vs. 5 converters is obvious.

The complete cost benefit analysis is beyond the scope of this example. In summary, the objective of this case study was to display how experimental work, similar to that generated in this investigation, can be used to either design more efficient smelting operations or to re-design existing ones depending on the specific objectives. In this specific case, changing the flash furnace operation, operating at lower sulfur pressure, indicated that the same production of nickel in converter matte could be attained while also acquiring the following potential benefits:

- Much lower sulfur dioxide emissions (0.433 vs. 5.526 mtpfh).
- Lower refining (converting) requirements (less furnace matte production, lower air and flux requirements).
- Lower operating costs (possibility of eliminating one operating converter).

These benefits would, of course, have to be weighed against the potential disadvantages cited such as higher furnace flux and tonnage oxygen requirements and increased sulfur dioxide gas volume going to the acid plant from the flash furnace.

6.2.4 Optimizing smelting conditions.

In section 6.2.2., it was stated that one of the objectives of the matte-slag-gas equilibria studies would be to use the experimental data in order to construct a control chart, similar
to Figure 6.1.6.1, to define parameters which could be controlled for optimum smelting conditions. It was further stated that in order to do so, certain factors had to be simultaneously considered such as magnetite precipitation, metal recovery and partition, downstream refining requirements, etc. The analyses presented in sections 6.2.1 to 6.2.3 indicate that construction of this control chart, for application to all nickel smelting operations, is impossible. It is possible though, to compile the relationships developed in sections 6.2.1 to 6.2.3 and generate control charts for specific operations in order to optimize the smelting operation depending on what the overall objectives are (e.g. increasing metal recoveries, eliminating magnetite build up, or decreasing sulfur dioxide emissions).

Finally, it can be stated that the construction of these control charts can be performed in a very reliable manner, since their development was based on consistent and correct application of thermodynamic principles applied to experimental work conducted in both matte-gas and matte-gas-slag equilibria studies.
References


7.0 Conclusions

In Chapter 1.0 the historical problem of magnetite build up in the area of non-ferrous pyrometallurgy was outlined. The experiences of many smelting operations were summarized and it was found that many similarities existed between the problems observed and the control measures taken to deal with the magnetite problem. Typically though, the remedies that were instituted were based merely on the operators' instinct and past experiences (adding scrap iron, increasing temperature, adding coke, etc.). An understanding of the fundamentals was lacking and therefore, a sound basis in which to develop efficient and optimized smelting processes was not available.

The main focus of this study was to develop an understanding of the thermodynamic principles that promote magnetite precipitation during smelting, by conducting properly controlled experiments in a matte-gas equilibria study. At the same time, it was recognized that in order to develop a thorough understanding of real smelting, it would be necessary to conduct experimental studies in the matte-slag-gas system. Keeping in mind proper phase rule limitations, to ensure reliable experimental data, it was anticipated that the fundamental behavior of the systems would be controlled by three main variables (temperature and pressures of oxygen and sulfur). It would follow then that the behavior of magnetite could be controlled by adjusting any of the aforementioned variables. Incorporating these experimental variables into real situations would then provide the furnace operator with the proper guidelines in which to design more efficient and optimum smelting processes.

7.1 Matte-gas equilibria.

The combination of experimental data and thermodynamic analyses was successful at relating the behavior of iron and magnetite to the oxygen solubility in mattes and how they are affected by temperature and pressures of oxygen and sulfur. In general, it can be said that the most important factor is how these variables affect the activity of iron, in
these non-ferrous systems, since the activity of magnetite will logically follow by virtue of its thermodynamic relationship with iron and oxygen.

In these studies it was found that the temperature and sulfur pressure had the most significant effects on the iron activity in nickel mattes. The iron activity increased directly with temperature and inversely with sulfur pressure. The relationship of sulfur pressure was confirmed by performing the same thermodynamic analyses applied to data generated in the copper system from Kaiser (1986). The resulting effects on magnetite activity were straightforward, in the case of sulfur pressure, but not so with regard to temperature. For example, at a given oxygen pressure and temperature, the increase in iron activity (due to lowering of the sulfur pressure) resulted in an increase in magnetite activity which also corresponded to an increase in matte oxygen solubility. However, at a given oxygen and sulfur pressure, an increase in iron activity (due to increasing temperature) resulted in a lower magnetite activity and a corresponding decrease in the matte oxygen solubility. The lower magnetite activity as a function of temperature was discussed in section 6.1.3 and essentially relates to the lower stability of magnetite at higher temperatures due to the associated changes in Gibbs free energy (more positive at higher temperature).

In order to avoid magnetite build up, based on the matte-gas equilibria studies, a control chart was constructed, Figure 6.1.6.1, which indicated that sulfur pressure and temperature are the most significant factors. The most effective control parameters, for lowering the magnetite activity, were found to be increasing sulfur pressure and temperature.

7.1 Matte-slag-gas equilibria.

Applying the same thermodynamic analyses to the experimental data from the matte-slag-gas equilibria study again made it possible for determination of iron and magnetite activities. In this particular study, the thermodynamic variables of sulfur and oxygen pressure were examined, however, only one temperature was employed (1250 °C). The
data trends observed and relationships to the iron and magnetite activities, developed from this study, were quite interesting and the significance of sulfur and oxygen pressures are quite striking and evident.

The interdependence of oxygen and sulfur pressures was very clearly demonstrated from this study. It was found that as the sulfur pressure decreased, the oxygen pressure required to produce a matte of equivalent grade is substantially lower. The resulting effect on the relationship between oxygen solubility in mattes and magnetite activity was still shown to be consistent from that observed in the matte-gas equilibria studies. That is to say, as the oxygen solubility decreased so did the magnetite activity. Besides the oxygen solubility in mattes, behavior of the magnetite activity, at a fixed temperature and sulfur pressure, as a function of oxygen pressure showed very definite similarities to the matte grade, dissolved nickel and magnetite contents in the slag. As would be expected then, the relationship between magnetite activity and the nickel partition was very clear, higher partitions were associated with the lower magnetite activities.

Similar to the matte-gas testwork, the effects of sulfur pressure on the smelting characteristics were quite significant. As would be expected, it was again demonstrated that the effect of sulfur pressure was related, inversely, to the iron activity. However, due to the interrelationship of the oxygen and sulfur pressures, mentioned above, it was found that the lower sulfur pressure operation offers substantial metallurgical benefits over the higher sulfur pressure option. Furthermore, it can be said that these benefits are a direct result of the magnetite behavior (activity) due to the close relationship observed with the aforementioned variables (matte grade, oxygen solubility, nickel and magnetite in slag). The potential metallurgical benefits, possible by operating at lower sulfur pressure, were outlined in sections 6.2.2 and 6.2.3. In these two sections, the experimental data from this study were incorporated into a theoretical heat and material balance model which was used to predict how an existing smelter flowsheet could be optimized by changing the smelting conditions in the flash furnace. The benefits are clearly evident and show that operation of the flash furnace at the lower sulfur pressure relates to significant recovery gains at a fixed matte grade.
7.2 Summary

The overall objective, as stated previously, was to conduct this fundamental study in such a way as to ultimately result in viable options which may be employed to optimize the pyrometallurgical processing of nickel. It should be considered that the importance of each of the studies (matte-gas and matte-slag-gas) are equivalent, even though the most favorable operating conditions from the two did not necessarily agree.

It has been found, from the limited experience of the author, that conditions prevailing in real smelting vessels do not always correspond to equilibrium. It is very rare, suffice it to say, *extremely* rare, to find equilibrium conditions in a smelting vessel between the matte, slag and gas phases (highly turbulent vessels like the Pierce-Smith converters being the exception). Aside from the fact that these phases do not spend a significant amount of time in intimate contact, there is almost always a temperature difference among them. In the case of flash furnaces, the highest temperature typically occurs in the gas phase, decreasing in the slag and even more in the matte. For electric smelting furnaces, the gas phase is typically the coldest with the hottest phase being the slag.

Taking these considerations into account, the ideal fundamental study would be to investigate an unlimited combination of sulfur pressures, oxygen pressures and temperatures. But this is not practically possible. Keeping in mind the main objective, which is to understand how to eliminate magnetite build up, it was fitting that the matte-gas system was studied in more detail, than the matte-slag-gas system. This is perhaps even more significant when considering the practical application, since, typically, magnetite precipitation occurs in the hearth areas of the vessels where temperatures, especially, are lower than in the main reaction zone. Furthermore, as mentioned in Chapter 1.0, under equilibrium conditions it would not even be possible to achieve magnetite saturation for the matte-slag-gas testwork, due to the interrelationship between matte grade and pressures of oxygen and sulfur under isothermal conditions and silica saturation.
The end result of this investigation was supposed to provide a basis for developing a variety of options which could be employed in order to optimize any particular nickel smelting operation. According to the matte-gas testwork, the conditions, which would ensure avoiding magnetite precipitation, were stated to be higher sulfur pressure and temperature. The higher sulfur pressure operation ensured a lower magnetite activity by decreasing the iron activity under given conditions of matte grade and temperature. The advantages of higher temperature are attributed to the lower magnetite stability (free energy), even though the iron activity increased, under given conditions of sulfur pressure and matte grade. The results from the matte-slag-gas testwork indicated that a lower sulfur pressure would not only be more advantageous in terms of avoiding magnetite saturation, but also provided significant metallurgical benefits (e.g. partition coefficient of nickel). Even though the iron activity increased at the lower sulfur pressure, the resulting magnetite activity, at a given matte grade, was lower due to the oxygen-sulfur pressure effects. The effect of temperature was not investigated for the case of matte-slag-gas equilibria. However, given the results from the matte-gas study, the potential advantages of operating at higher temperatures should not be ignored. It is possible that a lower sulfur pressure operation at even higher temperatures (than 1250 °C) would be even more beneficial with regard to magnetite saturation and metallurgical gains.

7.3 Practical applications and final remarks.

It is now evident from the bench scale experimental work that the conditions necessary to optimize the metallurgical benefits of a smelting operation translate into minimizing the magnetite activity. Not only does this provide obvious advantages with regard to magnetite saturation, but it also has been shown to result in significant improvements in other metallurgical parameters such as partition coefficients and metal recoveries.

The advantages of operating at higher temperature have not been completely scoped out yet, (the benefits in the isolated matte-gas system are clear) however, indications are that this may also have a significant impact on improving the metallurgy of nickel smelting. In order to interpret why these conditions offer such significant advantages, and be able
to apply them industrially, it is essential to understand the intimate nature of the thermodynamics (oxygen pressure, sulfur pressure, temperature and activities of iron and magnetite) and how they relate to practical measures such as matte, slag and gas compositions. Some of the practical measures, which have been shown to be representative of the thermodynamic trends, are metal partitions and matte compositions. In particular cobalt partitions and metallic iron contents of the matte have been shown (in this study and previous ones) to be good indicators of the thermodynamic state of a nickel smelting system. The reliability of the cobalt partition is high since it is very insensitive to matte entrainment (the overwhelming majority of cobalt in slag is dissolved) and it has been shown to be excellent as an indicator of the relative oxidation state of the system (INCO Reports). Metallic iron contents in the matte phase reflect the relative sulfur pressures, since lower sulfur pressure operations correspond to mattes higher in metallic iron content. Although it is not always possible to obtain accurate information from industrial operations (matte and slag compositions, temperatures, etc.) an examination and comparison of some industrial data with the experimental work of this study can be used to demonstrate the relevance of the above comments. Table 7.3.1 and Figure 7.3.1 show the range of different cobalt partitions obtained at various nickel smelters. Again, the obvious advantages of lower sulfur pressure operation is evident (from the experimental curves), but what is also clear is how industrial data supports these findings. Comparing Table 7.3.1 with Figure 7.3.1, shows that the cobalt partition has a definite correlation to the sulfur pressure for a given matte (as reflected by the metallic iron contents). This can be demonstrated by examination of Figure 7.3.2 where the cobalt partitions are shown as a function of metallic iron in the mattes. The representation of the data in Figure 7.3.2 is not strictly correct, since they do not adequately show the effect of matte grade, but the trend is evident. In addition to the obvious advantages evident at lower sulfur pressures, the data in Table 7.3.1 also indicates that the assumption of further metallurgical benefits possible with higher temperatures (inferred from the matte-gas studies) may have merit industrially.
Table 7.3.1 Comparison of matte compositions, cobalt partitions and matte temperatures from various nickel smelting operations.

<table>
<thead>
<tr>
<th>Operation</th>
<th>MG Wt.% (CuNiCo)</th>
<th>Fe Wt.%</th>
<th>S Wt.%</th>
<th>Metallic Fe, Wt.%</th>
<th>Co Partition</th>
<th>Matte Temp.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT INCO-EF</td>
<td>32.70</td>
<td>57.00</td>
<td>10.00</td>
<td>56.23</td>
<td>29.0</td>
<td>1377</td>
</tr>
<tr>
<td>INCO-RRS-EF</td>
<td>52.75</td>
<td>30.58</td>
<td>15.22</td>
<td>26.84</td>
<td>17.6</td>
<td>1250</td>
</tr>
<tr>
<td>FALCO Slag Cleaner</td>
<td>36.55</td>
<td>37.00</td>
<td>23.46</td>
<td>7.24</td>
<td>9.61</td>
<td>1207†</td>
</tr>
<tr>
<td>WMC-NEW-FSF† (WMC-N)</td>
<td>50.35</td>
<td>21.80</td>
<td>25.96</td>
<td>2.45</td>
<td>6.00</td>
<td>N.A.</td>
</tr>
<tr>
<td>BCL-NiCu-FSF</td>
<td>32.00</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>6.00</td>
<td>1280</td>
</tr>
<tr>
<td>INCO-CuNi-(#2 FF)</td>
<td>30.14</td>
<td>40.10</td>
<td>27.60</td>
<td>2.10</td>
<td>5.82</td>
<td>1220</td>
</tr>
<tr>
<td>WMC-OLD-FSF* (WMC-O)</td>
<td>49.95</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>4.38</td>
<td>N.A.</td>
</tr>
<tr>
<td>INCO-NiCu-(#9 FF)</td>
<td>40.94</td>
<td>28.50</td>
<td>27.10</td>
<td>0.00</td>
<td>4.27</td>
<td>1185</td>
</tr>
<tr>
<td>This study (log PS_f=4.50)</td>
<td>42.83</td>
<td>29.50</td>
<td>25.10</td>
<td>10.13</td>
<td>8.30</td>
<td>1250</td>
</tr>
<tr>
<td>This study (log PS_f=2.50)</td>
<td>46.40</td>
<td>24.50</td>
<td>27.75</td>
<td>4.75</td>
<td>4.89</td>
<td>1250</td>
</tr>
</tbody>
</table>

† Operation of FSF with appendage, commissioned in 1978
‡ Operation of FSF with two separate slag cleaning furnaces (prior to 1978).

EF – Electric Furnace.
FF – Flash Furnace.
FSF – Flash Smelting Furnace.
RRS – Roast Reduction Smelting. (Diaz et al. 1993)
FALCO – Falconbridge Limited, Sudbury Ontario. (Kaiura et al. 1989)
WMC – Western Mining Corporation (Kalgoorlie Nickel Smelter). (Sridhar 1998)
BCL – Bougainville Copper Limited, Botswana. (Elliot et al. 1983)
INCO – International Nickel Company. (Internal Reports)
MD – Manitoba Division (INCO), Thompson Manitoba.
OD – Ontario Division (INCO), Sudbury Ontario.
Figure 7.3.1 Comparison of cobalt partitions from different nickel smelting operations.

Figure 7.3.2 Effect of metallic iron on the cobalt partition.
A very relevant and significant finding, from examination of Figures 7.3.1 and 7.3.2, is that the cobalt partition appears to be highly dependent on the type of smelting vessel employed. For example, the two smelting operations, which correspond to the highest cobalt partitions, employ electric smelting furnaces. In general, at a given matte grade, the metallurgy of electric furnaces appears to be much superior to those of the flash smelting furnaces. A couple of exceptions to this observation correspond to the flash smelting operation of BCL (Elliot et al. 1983) and WMC (INCO internal report). These two operations employ unique methods in order to attain higher cobalt partitions (thus better metallurgy) than the traditional flash smelting methods employed by companies like INCO. Western Mining Corporation utilizes an Outokumpu flash smelting vessel which has been modified to comprise a slag cleaning appendage. Flash smelted matte and slag flow from the main settler into this appendage, which is heated by electrodes and held at a low sulfur and oxygen pressure by addition of reductants. As a result, slags which exit the furnace are much lower in metal contents than that which has entered from the settler. The highly metallized appendage matte (low sulfur and oxygen potential) backmix with the settler matte to obtain a matte product which is only slightly metallized. Instead of employing an appendage, the method adopted by BCL has been to maintain a reducing atmosphere at the slag-gas interface in the furnace (Outokumpu design) by employing lump coal in the 10-45 mm size range. The lump coal addition is made at the top of the reaction shaft and is successful at maintaining a covering of the slag layer so that all hot molten material originating from the flash smelting burner is forced to contact it before entering the slag and matte layers. It has been stated (Elliot et al. 1983) that this practice generates benefits of magnetite reduction and increased cobalt partitions by forcing all the smelted material to contact the reductant layer. Adoption of this practice has significantly increased metal recoveries and eliminated solid magnetite build up on the furnace hearth.

Normal flash smelting operations, without additional precautions to control oxygen and sulfur pressures, do not display as favorable metallurgy. This should not be unexpected since it would be very difficult to obtain exact and perfect combustion and control in a flash burner flame. Furthermore, without additional provisions to back reduce (chemically) any over oxidized particles emanating from the flame (such as a coke cover
on the slag surface) it would be extremely difficult, if not close to impossible, to obtain high metal partitions and avoid magnetite saturation. The additional flexibility and benefits, in the flash smelting operations, which arises from practices such as local oxygen and sulfur pressure control (reductant additions) are evident by comparing the operations shown in Figure 7.3.1, in particular:

- BCL or WMC, operation \( P_{\text{Co}} = 6.0 \) vs. any INCO operation \( P_{\text{Co}} \sim 4.5 \).
- WMC's new process, \( P_{\text{Co}} = 6.0 \) (WMC-N) vs. their old operation (conventional flash smelting), \( P_{\text{Co}} = 4.4 \) (WMC-O).

Further proof of the metallurgical advantages possible with localized control is the fact that BCL reports very little or no magnetite build up on the hearth of their flash furnace, whereas current INCO flash furnaces are operated with a significant amount of build up (which was the main thrust for conducting this study).

The importance of localized control is now more evident and can explain why the electric furnace processes display better metallurgy than their flash smelting counterparts. In an electric furnace operation, feed is typically in the form of calcine. The calcine represents pre-conditioned feed, which has been selectively oxidized, so that the sulfur control in the furnace is already set. All that is required from the furnace, then is to melt the feed and establish an oxygen pressure based on the amount of reductant added with the calcine. This means that the electric furnace only has to perform oxygen pressure control as opposed to a flash furnace which has to combine the functions of roasting and smelting thus both sulfur and oxygen pressure control. Furthermore, control of these parameters in the flame is next to impossible. Therefore, in the case of flash smelting it seems that it would be necessary to independently control the sulfur and oxygen pressure, from the flame, by either adding another reactor to the main vessel, or forming another reaction zone to adjust matte and slag compositions.

The characteristics of actual industrial operations raise an interesting and vitally important fact with regards to the applicability of fundamental bench scale studies. In
sections 6.2.2 and 6.2.3 examples were provided of how the experimental data could be combined with theoretical process models to develop new or modify existing flowsheets. The benefits obtainable in a paper study, however, do not provide the complete solution. For example, operation of a flash furnace at two sulfur pressures is possible in the theoretical model by simply controlling the feed and oxygen requirements, to obtain the desired matte and slag chemistries. However, upon examination and comparison of various industrial smelting operations, it can be shown that the theoretical metallurgy may not be achievable unless the reactor is operated in such a way that it is treated in separate reaction zones. This means that the actual process in the flash smelting flame may have to be operated under different conditions as the actual slag and matte zones in order to obtain the desired metallurgy predicted by the experimental data. For example, to generate a matte of specific grade, at a low sulfur potential, it may be necessary to flash the feed to a higher matte grade (eliminating the required amount of sulfur), then reacting the slag and matte with some reductant (to metallize the iron which was oxidized with the sulfur) to obtain the desired matte and slag compositions as predicted from the experimental work. One way to perform this can be inferred, from the experiences provided by BCL (Elliot at al. 1983), by ensuring all flash flame products contact a reductant before entering the matte and slag phases. The appropriate amount of flashing (oxygen, air, concentrate, alternative feed, etc.) and back-reducing (coke, coal, metallic iron, etc.) can only be determined by conducting larger scale tests (mini, pilot or full), they cannot be determined from bench scale equilibria studies. The bench scale studies only provide a guideline and initial justification to pursue larger scale studies to prove out the attainable benefits. This however, is the first step and the most crucial in the development of new and/or modification of old processes. Without these types of studies, which form the basis for development, a clear direction and significant progress is not possible.
References


Internal INCO Reports.


APPENDIX A - Analytical Techniques Used For Chemical and Instrumental Analyses
**Atomic Absorption (AA)**

The atomic absorption analysis technique was used mainly for assaying of Cu, Ni, Co and Fe. The theory of an AA unit is based upon the energy radiated or absorbed by elements at specific wavelengths. When an element is chosen to be analyzed, the wavelength selected is the one which will provide maximum energy and maximum absorbance. The radiation source used in AA spectrophotometers is the hollow cathode or electrodeless discharge lamp. These lamps contain the same element(s) as those sought in the material to be analyzed. The element to be analyzed is introduced into the light beam by spraying a solution of the element into a flame through which the beam passes. The flame vaporizes the water and the compounds containing the elements are decomposed into atoms. Those atoms in a low state of excitation, i.e. unionized, absorb radiation from the lamp, the amount depending on the number of atoms present which depends in turn on the concentration of the element.

The instrument utilized in this study was a Perkin Elmer model 5000. This instrument is a double beam type which means that the photomultiplier received in rapid succession a signal first directly from the lamp followed by one which has passed through the flame. The two signals are compared and the difference is related to the element concentration. Variations in lamp output, detector sensitivity, etc. are automatically compensated in this arrangement.

In preparing a solution of a sample for AA analysis, the main concern is to dissolve the sample, or that portion of the sample, to include all of the element of concern and without any loss of this element during the process as by volatilization. For mattes, a combination of concentrated hydrochloric acid and nitric acid is used for the initial attack, followed by some hydrofluoric acid and finally sulfuric or perchloric acid. In the case of slags, the use of hydrochloric acid initially, followed by nitric and sulfuric acids, is the best method of solution. The preparation of a solution sample for nickel analysis will be described below.

For slags, the one gram sample is placed in a 400 ml beaker along with 5 ml of water, 30 ml of hydrochloric acid, and 1 ml of hydrofluoric acid. The mixture is left to digest on a hotplate, then 10 ml of nitric acid is added and left to digest again. The beaker is rinsed down beaker with water and 10 ml of perchloric acid is added then evaporated to dryness. The salts are dissolved in
hydrochloric acid so that the final concentration will be 5% after dilution to volume, i.e., if the final volume is to be 100 ml, add 5 ml of acid. Addition of 30 ml of water is made and heated to dissolve all soluble salts. Filtering of the solution is performed through a Whatman #40 paper and pulped into a volumetric flask and washed five times with hot water. The solution is allowed to cool to room temperature and then the volume is made up. The new solution should be well mixed. If further dilutions are necessary, the aliquots are diluted with 5% hydrochloric acid.

For mattes, the one gram sample is placed into a 400 ml beaker with 20 ml of water and 20 ml of nitric acid then allowed to digest on a hotplate. After the mixture is cooled, 0.5 ml of hydrofluoric acid and 10 ml of hydrochloric acid are added and allowed digest again. Addition of 10 ml of 1:1 of sulfuric acid is made and allowed to evaporate to dryness. Addition of 30 ml of water is made and heated to dissolve all soluble salts. Filtering of the solution is performed through a Whatman #40 paper and pulped into a volumetric flask and washed five times with hot water. The solution is allowed to cool to room temperature and then the volume is made up. The new solution should be well mixed. If further dilutions are necessary, the aliquots are diluted with 5% hydrochloric acid.

Calibrating samples are made for each element to be analyzed. In the case of nickel, the standard calibration solution is made by using a burette or pipette, to transfer to each of seven 1000 ml one-mark volumetric flasks, 0; 5.0; 10.0; 25.0; 50.0 and 100 ml of a nickel standard solution. The nickel standard solution (1.0 g/L) is prepared by adding 1.000 g of nickel metal (minimum 99.99% (w/w)) into a 400 ml beaker with 20 ml of water and 20 ml of nitric acid (\(\rho_{20} = 1.41 \text{ g/ml}\)), covered with a watchglass and heated to complete dissolution. Once the solids have been dissolved the solution is evaporated to incipient dryness and cooled. Addition of 50 ml of water and 50 ml of hydrochloric acid (\(\rho_{20} = 1.18 \text{ g/ml}\)) is made and heated until a homogeneous solution is obtained. The solution is then transferred to a 1000 ml one mark volumetric flask, diluted to the mark with water, cooled to room temperature, diluted again to the mark, then transferred and stored in a glass or polypropylene bottle. Standard solutions of different concentrations can then be prepared from the 1.0 g/l standard by dilution with hydrochloric acid and water. Addition of 50 ml hydrochloric acid (\(\rho_{20} = 1.18 \text{ g/ml}\)) is made to each flask, diluted with water to the mark and mixed. These calibrating solutions correspond to 0; 1; 2; 5; 10; 15 and 20 mg/l of nickel.
**Bromine Alcohol (Br./Alc.) Leaching**

Bromine alcohol leaching is carried out in order to determine the distribution of metal species that may be present as metallics and sulfides apart from those present as oxides. In general, when a solid sample is subjected to the bromine alcohol leaching solution, the metal species present as oxides will remain in the leach residue and the metal species present as metallics and sulfides will remain with the leach solution. The specific procedure is outlined below.

- In a 300 ml beaker add about 1-2 grams of sample with 150 ml of dry 5% bromine alcohol solution.
- Stir with mechanical stirring apparatus for twenty minutes, ensuring there is a good dispersion of solids. Baffle plates inserted into the beaker is recommended to ensure good liquid/solids contact.
- Constantly maintain a CO₂ cover to ensure contact with ambient atmosphere is minimized.
- After the completion of stirring remove the stirring rod from the solution while washing with methanol. Leave the solution settle for a few minutes.
- Combine a 7 cm #42 Whatman filter paper with a 98 mm watch glass and dry for 30 minutes at 105 °C. Cool and weigh.
- Filter the bromine leach solution through the tared #42 paper, set in a Buchner funnel, using water vacuum, wash well with methanol and transfer the paper and precipitate to the 98 mm watchglass retaining the residue for a weight percent determination and the solution for evaporation and subsequent analysis.
- Dry the residue containing paper at 105 °C for 30 minutes. Cool and weigh and calculate the residue weight percent in the normal fashion.
- The filtered solution is transferred to the original beaker, 10 ml hydrochloric acid is added and the solution evaporated to dryness on a low temperature hot plate. The dried salts are cooled, treated with nitric acid to destroy the bromides, made aqua regia and boiled.
- Cool and add two drops hydrofluoric acid, 10 ml perchloric acid and evaporate to dryness.
- Re-dissolve the salts for atomic absorption analysis.
• If sulfur is to be determined on the solution add some sodium chloride to ensure the sulfates are not lost during the evaporation step.

**Ferric Iron Determination**

Ferric iron determinations are typically performed on the remaining residue from the bromine alcohol leaching. It is necessary to carry out Br./Alc. leaching prior to the ferric iron assay to remove any sulfides or metallics which are reducing towards ferric iron.

The analytical technique involves reduction of the ferric iron to ferrous iron with a known excess of standard stannous chloride and back-titration with standard iodine solution. To do a ferric iron determination, a separate sample is leached and remains wet when transferred to the reaction flask, which is continually being flushed with CO₂ gas to prevent sample oxidation with the atmosphere. In order to obtain a residue weight percent, another separate sample is dried and weighed after the Br./Alc. leaching. Approximately 2-3 minutes of flushing are required during the standardization of the stannous chloride solution. A 25 ml pipet of stannous chloride solution is introduced into the flask followed by 50 ml 12N hydrochloric acid and 1-2 ml 48% hydrofluoric acid while maintaining the carbon dioxide gas cover. The flask is positioned on top of a hotplate to boil for about 5 minutes or until all solids are dissolved, adding more hydrofluoric acid if necessary. If the solution has any yellow color, it is likely that all the ferric iron has not been reduced and a further 25 ml aliquot of stannous chloride solution should be added. If chromate is present in sample, it usually remains un-dissolved and can be ignored. After dissolution is complete, the flask is removed from the hot plate, 100 ml of boric acid solution is added to react with the excess hydrofluoric acid and the flask is placed in a cooling bath until cold, keeping the carbon dioxide flush running during all operations. When the solution is cold a 1 ml starch indicator is added and the excess stannous chloride is titrated with standard iodine solution to the first blue tinge agitating either by swirling or a magnetic stirrer, taking care to exclude air.
The ferric iron content is then determined by the following calculations:

\[ \%Fe^{3+} = \frac{(A - B) \times 0.05585 \times 100}{D} \]

where

A = Volume of iodine solution used in the standardization of 25 ml of the stannous chloride solution.
B = Volume of iodine solution used in the sample titration (ml).
D = Sample wt. (g)

**Oxygen Analyses**

A quick reliable method for oxygen determination in high sulfur bearing materials (mattes) has been under development in this laboratory for some time. It is well known and accepted that the most reliable method for oxygen determination in mattes is the hydrogen reduction method (Yazawa and Kameda 1959, Kaiser 1985), however this method is very labor intensive and does not allow for rapid turnover rates.

In 1995 an in-house method was developed by this laboratory to enable reliable oxygen determinations on high sulfur materials (mattes) by use of traditional LECO infrared oxygen analyzers. Typically the application of these analyzers in oxygen determinations of high sulfur materials have failed due to volatilization and stability of carbo-sulfide and carbo-oxy-sulfide compounds in the analysis stream of the detecting equipment. The past and present day oxygen analyzers manufactured by LECO have been mainly marketed in the iron and steel industry where test samples typically contained very low amounts of sulfur <0.5%.

The basis for the analysis was fusion of a sample contained in a graphite crucible, under a nitrogen carrier gas, at temperatures up to 3000 °C and chemical reaction of the oxygen contained in the sample with the graphite crucible to form CO gas. The CO gas emitted from the sample is then carried past infrared analyzers, which convert the signal into quantitative assay after proper calibration using established standards. As mentioned above, since traditional application of these analyzers was for samples essentially free of sulfur, virtually the only gases
emitted from the combustion was CO. However, in the case of materials containing both oxygen and sulfur, combustion in a graphite crucible may result in the production of various gases containing any combination of sulfur, oxygen and carbon (e.g. CS, COS, CS₂, etc.). As a result the infrared detectors, not designed to detect these gases, would become "confused" often yielding erroneous results.

In order to take advantage of the rapid analysis benefits of the combustion analysis technique, modified procedures were developed, at this laboratory, between the period 1994-1995, which could provide a means for reliable oxygen determinations in mattes using the LECO instruments. A procedure was developed, and verified using the classical hydrogen reduction technique, that enables the oxygen analyses to be performed using a LECO RO-X16 analyzer. The report written to describe the method and development work is described below.

1.0 INTRODUCTION

Studies on matte-slag-gas equilibrium are essential components to pyrometallurgical process design. An understanding of the solubility of oxygen in copper, nickel and bulk mattes under varying temperature conditions having predetermined partial pressures for sulfur and oxygen is necessary in these studies. Accurate oxygen analysis is necessary to determine the attainment of equilibrium and to determine a point in time when a change to one of the parameters can be made and then continue equilibration under the new conditions.

It has become apparent that the analysis of oxygen in mattes is not a simple analysis. Historically the most reliable technique for determining oxygen content is the hydrogen extraction method whereby a matte sample is completely reduced at about 900°C and the gas phase is passed through a phosphorus pentoxide \(\text{P}_2\text{O}_5\) absorption tube to selectively capture the \(\text{H}_2\text{O}\) and not the \(\text{H}_2\text{S}\).

Based on the method described in "Standard Methods Of Chemical Analysis ", 6\text{th} Edition Vol. One, N. Howell Furman, Ph.D., Editor, March 1962, the method determines the occluded oxygen and the oxygen combined with metals such as copper, nickel, cobalt and iron, but does not determine oxygen combined with manganese, aluminum and silica as these oxides are not reduced by hydrogen. The method itself is very labour intense, requiring 4-24 hours to carry out a single analysis. The method was applied by Kameda and Yazawa\(^{10}\) for the determination of oxygen in
copper mattes and D.L. Kaiser in copper-iron mattes. In these papers grinding of samples in preparation for analysis, with the possibility of oxidation, or melting of the sample during reduction, thereby preventing complete removal of sulfur and oxygen, was not considered.

2.0 THE EVOLUTION OF INSTRUMENTAL TECHNOLOGY

Gases are introduced to a metal by physical and chemical absorption. The type of metal atom available and its compatibility with the type and concentration of gas available under the temperature and pressures to which the material is exposed, determines the type of metallic compound formed. The metallic compounds formed become more stable as temperature increases and the physical bond becomes a chemical bond. With inert gas fusion, the physical and chemical bonding between the gas and the metals are reversed to dissociate the gases. Bonds can only be broken by heating the specimen above the highest temperature at which the gas/metal bonding occurs. The use of a graphite crucible to carry the sample and acting as a resistor is heated to 3000°C. Oxygen being highly reactive bonds to the carbon to form carbon monoxide. This isolates the oxygen from further reactions. As the sample fuses to a molten state, the other gas/metal compounds absorb and dissociate as hydrogen and nitrogen.

The application of inert gas fusion has been known and applied since about 1940 when the method was first applied by L. Singer for the determination of oxygen in steel. The sample was fused in a tin bath and the carbon monoxide formed was carried in a stream of nitrogen over heated copper oxide and the resulting carbon dioxide collected on askerite and weighed. Improvements in technology soon had the evolved carbon dioxide being absorbed into caustic and the solution conductivity measured and related to oxygen concentration. As the chemical, mechanical and electronic technologies evolved Leco corporation developed for the steel industry, an automated instrument capable of carrying out an inert gas fusion of a sample quantitatively in about one minute.

3.0 PRESENT DAY INSTRUMENT OPERATION

In the Leco RO-X16 series of instruments, mechanisms exist for having very accurately controlled constant pressures and gas flows. The carrier gas, nitrogen or argon, passes the sample
gases directly through an infrared cell which detects carbon monoxide. The infrared source is a nichrome wire which is resistance heated to about 850°C. The infrared source radiates visible energy as well as all the wavelengths in the IR spectrum. Carbon monoxide absorbs infrared energy at a specific wavelength. Thus at the detector less energy is received. All other infrared energy is eliminated from reaching the detector by a precise wavelength filter.

In the Leco TC-X36 series of instruments having similar gas flow and pressure control capabilities, simultaneous analysis of oxygen and nitrogen occurs. With argon as the carrier gas the sample gases are swept through a heated rare earth copper oxide catalyst to first convert all the carbon monoxide to carbon dioxide before passing through the infrared cell which detects carbon dioxide. The carbon dioxide is then removed by askerite and the remaining gases pass through a thermal conductivity cell which detects nitrogen.

4.0 INTERFERENCES IN OXYGEN ANALYSIS USING PRESENT TECHNOLOGY

The analysis of sulphur bearing matte samples for oxygen on the TC-X36 instrument has been found to be affected by the sulphur present in the sample. The sulphur distils out of the crucible, most likely as COS or CS₂ and this poisons the rare earth copper oxide catalyst. The catalyst's subsequent inability to convert carbon monoxide to carbon dioxide results in poor analysis for both oxygen and nitrogen. This is because the infrared detector is set to measure carbon dioxide in the gas stream and if carbon monoxide is not removed by the askerite it will interfere in the thermal conductivity measurement of nitrogen.

The analysis of matte samples for oxygen on the RO-X16 series of instruments is also susceptible to a sulphur interference because the volatile sulphur compounds, COS and CS₂, will be carried by the gas stream through the infrared detector and is measured as an interference. The only way to prevent this interference is to reduce or eliminate the possibility for sulphur to be volatilized from the sample crucible. This can be done by significantly lowering the sulphur vapour pressure with the addition of copper as a starting bath in the graphite crucible.

It is known that a saturated nickel/sulphur bath exhibits a very low vapour pressure at 800°C but as the temperature rises above 1300-1400°C the vapour pressure rises to 10⁻¹ mm and
sulphur is volatilized. During an analysis when this phenomena occurs the typical instrument behaviour significantly changes. The analytical time cycle for analysis on the Leco analyzer is normally completed after 20 seconds. In the presence of volatilized sulfur this time can extend from 40-200 seconds and during this time the detector is sensing what it suspects is carbon monoxide but is actually the volatile sulphur species. If the low vapour pressure could be maintained in the graphite crucible during the analysis the volatility of the sulphur would be reduced dramatically eliminating or reducing this interference. This can be accomplished by loading the crucible with a 10 fold excess of copper (~1 gm). The advantage for using copper (TABLE 1) is that the vapour pressure of a saturated copper/sulphur bath at 1400°C is $10^{-3}$ mm pressure, sufficiently low to prevent volatilization of sulphur during the analysis.

TABLE 1
AFFECT OF COPPER BATH ON SULPHUR INTERFERENCE

<table>
<thead>
<tr>
<th>Sample</th>
<th>Burn Time (sec) No Copper Added</th>
<th>Oxygen (%)</th>
<th>Burn Time (sec) Copper Added</th>
<th>Oxygen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HK 2212</td>
<td>135, 151</td>
<td>2.24, 2.38</td>
<td>20, 20</td>
<td>1.44, 1.47</td>
</tr>
</tbody>
</table>

5.0 CALIBRATION OF OXYGEN ANALYZERS

Analytical instruments designed for oxygen analysis were originally developed for the purpose of satisfying the needs of the steel industry. Used as a control tool for analyzing oxygen in the 100-2000 ppm range, sample weights of up to 2 grams could easily be handled on instruments calibrated using primary standards prepared using the method by Singer. During the 50's and 60's the technique of "Hot Extraction" was used to analyze and develop calibration materials of even lower oxygen concentration. The typical oxygen concentration level in these reference materials was in the order of 10-2000 ppm oxygen. None of these calibrating materials contained significant quantities of sulphur (<0.1%).

It is generally agreed that in the nickel matte smelting process higher matte grades and higher ferric/ferrous iron ratios in slag led to greater nickel losses in slag (10.4). It is also accepted that as the oxygen content of a matte increases there will be increased metal losses to the slag. High sulphur mattes generated from the non ferrous metals industry contain significant
concentrations of oxygen and part of the control of the oxygen levels is the ability for rapid analysis of the matte for oxygen thereby attaining better quality control. Generally the concentration level of oxygen in mattes can be in the range of 0.2-5.0%. The only known material for calibration at this concentration level is copper oxide which when analyzed for copper (79.9%) assumes a difference of 20% for oxygen content.

Today's instrumentation with its infrared detectors are designed to determine the combined oxygen in the carrier gas stream. If the concentration of combined oxygen in the gas stream increases above the sensing level of the detector, errors will occur in the analysis. This can be partially compensated by reducing the sample weight sufficiently such that the total evolved gases from the sample does not exceed the maximum sensing level of the detector. When dealing with matte samples at the 0.2-5.0% oxygen concentration range the sample size must be reduced to below 0.4 grams and the calibrating standard weight reduced to 0.1 gram. When reducing the weight of the sample and standard the possibility of errors due to inhomogeneity may be introduced into the analysis. Although the homogeneity problem can easily be overcome the problem of standard and sample matrix differences with respect to sulphur content is the major potential for error in the calibration of the oxygen analyzer.

Tests were carried out on a sample of Ni$_3$S$_2$ (X3126), in chunk form which was stored under nitrogen and believed to contained <0.1% oxygen. This sample was analyzed directly without any additional metal present in the crucible and using copper oxide to calibrate the instrument with the resulting value of 1.27% oxygen. The sample was then assayed with a starting bath of 1 gram nickel and finally a starting bath of 1/2 gram copper (TABLE 2). Check analysis was then performed on 3 samples and the results (TABLE 3) demonstrate the improvement when using a copper bath. Results from these tests are given below.

<table>
<thead>
<tr>
<th>TABLE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXYGEN ANALYSIS ON HIGH SULFUR MATERIAL (%)</td>
</tr>
<tr>
<td>SAMPLE NO.</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>X3126</td>
</tr>
<tr>
<td>&quot;</td>
</tr>
</tbody>
</table>
Additional testing was carried out with copper. It was found that when varying the amount of copper in the bath from between 0.75 - 1.5 grams random oxygen results were obtained on a high sulphur matte sample with a standard deviation of 3.6%. This is well within the accepted range of instrumental capability. It was concluded that a one gram copper bath would be used for all future testing.

With the impetus for the development of oxygen analysis analytical instrumentation coming from the steel industry, instruments were designed to allow for solid samples in the form of pins or squares not exceeding 6 mm in diameter to be introduced into the instrument via the sample inlet. Test samples generated from equilibrium studies could easily be made in the form of pin samples. Powder samples presented a different problem. The test sample used in this program was a bulk sample prepared as a powder. Attempts at pelletizing powders may cause oxidation of the sample. The only alternative was to transfer the sample in an oxygen free container whose size was small enough to fit the sample inlet. This was accomplished by weighing all powder samples into tin capsules which were developed to contain powdered or fine grained materials. There was a positive affect from using tin capsules to transfer the powdered sample into the furnace. In combination with powder samples there was improved retention of the sulphur even without the copper bath. Test results on copper sulfide MR #8106 and nickel sulfide MR #9106 indicated that the copper bath was still necessary (TABLE 4).

**TABLE 3**

<table>
<thead>
<tr>
<th>SAMPLE NO.</th>
<th>ORIGINAL OXYGEN</th>
<th>REASSAY OXYGEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>X3618A</td>
<td>4.42</td>
<td>3.56</td>
</tr>
<tr>
<td>X3619A</td>
<td>1.91</td>
<td>1.17</td>
</tr>
<tr>
<td>X3620A</td>
<td>3.78</td>
<td>3.00</td>
</tr>
</tbody>
</table>
TABLE 4
CALIBRATION WITH COPPER OXIDE

<table>
<thead>
<tr>
<th>Sample and Size</th>
<th>No Copper Added Burn Time (Sec)</th>
<th>Oxygen (%)</th>
<th>Copper Added Burn Time (Sec)</th>
<th>Oxygen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR. #8 (75mg)</td>
<td>25</td>
<td>1.10</td>
<td>20</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>1.16</td>
<td>23</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>1.18</td>
<td>20</td>
<td>1.05</td>
</tr>
<tr>
<td>MR. #9 (75mg)</td>
<td>26</td>
<td>1.24</td>
<td>20</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>1.29</td>
<td>20</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.23</td>
<td>20</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Even when the problem of containing the sulfur in the sample during analysis was solved there still remained the need to calibrate the instrument with sulfur containing high oxygen bearing standards.

To eliminate the possible affect the difference in matrix between the calibrating standard and the sample might have on the analytical result a high sulphur matrix oxygen standard was sought. None could be found available from the major standard sources. A request was made that a method be developed which could provide accurate oxygen analysis in sulphur bearing copper/nickel/iron mattes with a standard deviation of <3%. If such a method could be developed then the resulting materials analyzed using this method could be used as matched matrix calibrating materials for the oxygen analyzer. This would ensure that rapid oxygen analysis would be available with improved accuracy because of matrix matching. An investigation was initiated to develop such a method.

The method described in Standard Methods\(^{10,3}\) and later modified by Kameda and Yawaza\(^1\) and more recently by Kaiser\(^{10,2}\) was further modified for these tests. The outcome of these modifications was the improvement in quality of hydrogen used during the reduction. Temperature ramping was incorporated to fully reduce and remove the sulfur from the sample of matte just below the matte's melting point of 700°C before raising the temperature to 950°C to ensure complete reduction of the oxides. The bulk smelting process used by INCO provided a matte material of ideal composition for testing.
6.0 **GRAVIMETRIC OXYGEN ANALYTICAL SYSTEM DESCRIPTION**

Using short lengths of rubber and tygon tubing as connectors, pyrex tubing was used to connect all the critical components. The hydrogen reduction was performed by passing commercially available hydrogen gas (Union Carbide), set to a flow of 40 mL/minute, through a 1" ID quartz tube containing copper turnings heated in a tube furnace to 950°C to eliminate impurities such as carbon monoxide and carbon dioxide and then through two absorption tubes containing magnesium perchlorate (Anhydrite) followed by two absorption tubes containing phosphorus pentoxide (Sicapent) to remove the water by-products from the gas stream. A second furnace with ramping ability contained a 1" ID quartz tube into which the matte sample positioned in a silica boat was placed. Oxygen and sulfur in the sample reacts with the hydrogen gas to form H₂O and H₂S. The water vapour is absorbed by two containers of phosphorus pentoxide while the hydrogen sulphide passes through the absorbers and is absorbed in a caustic scrubber. The first absorber was employed to collect the sample while the second absorber was used as a backup (FIGURE 1).
A1 Magnesium Perchlorate Container
A2 Magnesium Perchlorate Container
A3 Phosphorus Pentoxide Container
A4 Phosphorus Pentoxide Container
S1 Weighing Tube
  - Phosphorus Pentoxide
S2 Back-up Weighing Tube
  - Phosphorus Pentoxide
F1 Gas Reduction Furnace
F2 Combustion Furnace
R₀ Potometer (40mL/min)
B₁ Container for Hydrogen-sulfide Absorbant
T Reaction Tube

Figure 1 Gravimetric Apparatus for Oxygen Determination in Mattes
A part of the test program involved studies on the anhydride and phosphorus pentoxide absorbers. The first anhydride scrubber required changing weekly while as a precaution the second scrubber was changed monthly. It was not necessary to change the phosphorus pentoxide scrubbers in the gas cleaning circuit more often than every three months. The primary sample absorber requires changing weekly. The secondary absorber should be changed monthly.

The anhydride scrubbers are prepared by placing some glass wool in the bottom of the container, filling with +20 mesh anhydride, topping with glass wool and close the filled container with a stopper-valve after wiping the ground glass joint and regrease with a very thin layer of Corning #4 stopcock grease. The phosphorus pentoxide is extremely hygroscopic and should be handled in a fumehood equipped preferably with a nitrogen purged glove box. Into the container alternately place layers of glass wool and phosphorus pentoxide, shaking between additions to disperse the phosphorus pentoxide and prevent channelling. Once the container is full top it with glass wool and close the filled container with a stopper-valve after wiping the ground glass joint and regrease with a very thin layer of Corning #4 stopcock grease.

The furnace containing the copper turnings will require maintenance periodically. Prolonged heating of the copper turnings will cause them to compress and replenishment of the copper in the 1" quartz tube is essential to ensure complete contact of the hydrogen gas to the hot copper metal to ensure reduction of all contaminants.

7.0 PROCEDURE

The system is assembled as outlined in FIGURE 1 with an empty sample boat and purged with nitrogen to remove air and stabilize the absorbers. A trickle flow of hydrogen is introduced into the system and gradually increased to 40 mL/min and the nitrogen flow is shut off after a ten minute hydrogen purge. After flushing the system for one hour with hydrogen the heated copper furnace is turned on and allowed to reach temperature. Thirty minutes after this furnace reaches temperature remove the absorbing tubes and weigh, ensuring no hydrogen is displaced by air in the tubes. This is accomplished by reducing the gas flow rate to 5 mL/minute then quickly closing the entry valve to S1 and the valve on S2 and disconnecting the tubes to prevent a pressure buildup in the system. Close the exit S1 and separate the absorbers. Make a quick single rotation of the
valves on both S1 and S2 to eliminate any hydrogen pressure in the absorbers. Weigh and record the sample tube weights. Reconnect the absorber tubes to the apparatus, open the valves on S1 and S2, reset the hydrogen flow to 40 mL/minute and turn on sample furnace and allow the program to run to completion. The oxygen content of the blank is determined by the weight gains of the absorbers. When carrying out sample analysis allow sufficient purge time after loading the sample tube with the sample before connecting the absorbers.

A 24 hour program (TABLE 5) was developed for the furnace which allowed nickel and bulk matte samples to be fully sintered before melting occurred. Sintering before fusion ensured that access to the hydrogen gas was available to all the sample sulfides and oxides. Completion of reduction of the test sample was verified by residue sulfur analysis (<1%) using a LECO CS-244 sulphur induction furnace calibrated using BCS 371 (0.013% sulphur). A temperature profile (Figure 2) was computer generated for the 24 hour sampling procedure.

**TABLE 5**

**RAMP PROGRAM FOR HIGH SULPHUR MATTE SAMPLES**

<table>
<thead>
<tr>
<th>STEP</th>
<th>START TEMPERATURE °C</th>
<th>RAMP RATE °C/Hr</th>
<th>HOLD TEMPERATURE °C</th>
<th>HOLD TIME HOURS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>240</td>
<td>450</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>450</td>
<td>120</td>
<td>600</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>25</td>
<td>700</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>700</td>
<td>120</td>
<td>950</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>950</td>
<td>600</td>
<td>25</td>
<td>END</td>
</tr>
</tbody>
</table>
8.0 RESULTS AND DISCUSSION

A sample of Bulk matte<sup>106</sup>, -100 mesh, assaying 18.4 Cu, 18.4 Ni, 32.7 Fe, 27.1 S and 0.26 SiO<sub>2</sub> and identified as MR #10 was used as the test sample for this program. Analysis of this material for total oxygen using a one gram copper bath and calibration of the RO-116 by copper oxide as described above reported a value ranging from 3.4 - 3.9% oxygen. Significant noise levels were observed in the calibrating standards results. This is due to either the small sample (50-75 mg) size taken for calibration or the lack of matched sulphur concentration between the calibrating standard and the sample.

The major handicap in the development of a standard material is the presence of silica in the sample. Analysis of MR #10 indicated the presence of 0.26% silica or 0.14% oxygen in silica. This indicated that a correction to the gravimetric value determined in the hydrogen reduction would be required in setting the final value for total oxygen in MR #10.

The affect of atmospheric temperature and pressure on the weight of the sample tube was measured by keeping an empty tube next to the balance overnight and weighing it at the same time the sample tube was weighed. Results from a large number of tests indicated that small variations in blank, both positive and negative (±0.5mg), resulted. Results from a series of 15 sample blanks taken during the test program gave values for the primary absorber of 1.0 mg and 0.9 mg for the backup absorber. For blanks run for two days consecutively the day 2 blank was in the range of
±0.2mg. This seems to indicate that a 24 conditioning period is necessary for the system before analysis could be started.

The sample absorber tubes used in these tests were U shaped tubes as indicated in FIGURE 1. The fully loaded absorbing tube weighed in excess of 60 grams. A four decimal place mettler balance, AE 163, was used for all weighings. Possible day to day variations in the absorbing tube weights could be in the order of ±2.5 mgs (0.0002/60.0000gm) indicating the low blanks determined during the tests approached zero. For these reasons the results for MR#10 are not blank corrected.

The sample of MR #10 was assayed repeatedly using the hydrogen reduction method. Completeness of reduction was verified by the sulfur level of the sample after the test was completed. Low recoveries were obtained when one gram samples were used and high residue sulfur levels (3-7%) were determined in the reduced product. A reduced sample weight (0.5 g) was used with the sample evenly distributed along the sample boat bottom. The results indicated reduction of the sulphur (residue analysis of <1%) over the 24 hour test cycle and consistent oxygen recoveries. Sample absorber weight gains of 15-25 mgs were typical during testing. Results for tests on MR #10 are tabulated in TABLE 6.

<table>
<thead>
<tr>
<th>TEST NO.</th>
<th>OXYGEN (%)</th>
<th>BLANK (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.09</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>0.0000</td>
</tr>
<tr>
<td>4</td>
<td>2.94</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>0.0004</td>
</tr>
<tr>
<td>6</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3.11</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3.09</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE 7</th>
</tr>
</thead>
</table>
OXYGEN CONTENT OF MR #8 AND MR #9 BY HYDROGEN REDUCTION

<table>
<thead>
<tr>
<th>TEST NO.</th>
<th>MR #8 % OXYGEN</th>
<th>MR #9 % OXYGEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.95</td>
<td>1.03</td>
</tr>
<tr>
<td>2</td>
<td>0.96</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>1.03</td>
<td>1.11</td>
</tr>
<tr>
<td>4</td>
<td>0.93</td>
<td>0.96</td>
</tr>
<tr>
<td>5</td>
<td>0.98</td>
<td>1.05</td>
</tr>
<tr>
<td>6</td>
<td>0.98</td>
<td>1.06</td>
</tr>
</tbody>
</table>

TABLE 8
CALIBRATION OF LECO WITH MR#10

<table>
<thead>
<tr>
<th>Sample and Size</th>
<th>No Copper Added Burn Time (Sec)</th>
<th>Copper oxide Calibration</th>
<th>Oxygen (%)</th>
<th>Copper Added Burn Time (sec)</th>
<th>MR #10 Calibration</th>
<th>Oxygen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR #8 (75mg)</td>
<td>20</td>
<td></td>
<td>1.03</td>
<td>20</td>
<td>0.96</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td></td>
<td>1.06</td>
<td>20</td>
<td>1.01, 1.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td></td>
<td>1.01</td>
<td>20</td>
<td>1.03, 1.01</td>
<td></td>
</tr>
<tr>
<td>MR #9 (75mg)</td>
<td>21</td>
<td></td>
<td>1.27</td>
<td>20</td>
<td>1.07, 1.11</td>
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<td></td>
<td>20</td>
<td></td>
<td>1.17</td>
<td>20</td>
<td>1.04, 1.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21</td>
<td></td>
<td>1.16</td>
<td>20</td>
<td>1.04, 1.11</td>
<td></td>
</tr>
<tr>
<td>MR #9 (200mg)</td>
<td>35</td>
<td></td>
<td>1.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>23</td>
<td></td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To see the affect of a matched matrix calibration standard vs a non sulfur containing standard on results generated from the Leco RO-116 tests were carried out using the proposed MR #10, rated at 3.20±0.06% (3.06± 0.06% gravimetric oxygen + 0.14% silica oxygen) and copper oxide (20.0%) as the calibrating samples. All test samples were weighed into tin capsules and a 1 gram starting bath of copper was used. These tests (TABLE 8) indicate bias higher results from the copper oxide calibration. The results in both tests indicate shorter burn times and significant improvement in precision with copper present. Results generated from the LECO RO 116 (TABLE

...
8) compared well with gravimetric results (TABLE 7). Both MR #8 and #9 require a correction to the gravimetric results of 0.04% for oxygen contained in 0.07% silica content. A summary of replicate gravimetric analysis corrected for oxygen related to silica content is given in TABLE 9.

TABLE 9
TOTAL OXYGEN BY GRAVIMETRIC ANALYSIS (%)

<table>
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<tr>
<th>Source of Oxygen</th>
<th>MR #8</th>
<th>MR #9</th>
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<tr>
<td>Gravimetric</td>
<td>0.97 ± 0.034</td>
<td>1.04 ± 0.049</td>
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<tr>
<td>Silica Oxygen</td>
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<td>0.04</td>
</tr>
<tr>
<td>Total Oxygen</td>
<td>1.01 ± 0.034</td>
<td>1.08 ± 0.049</td>
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Leco values for total oxygen using MR#10 for calibration gave 1.01±0.039 for MR#8 and 1.07±0.031 for MR#9. (Results calculated from TABLE 8)

9.0 REAL SAMPLE ANALYSIS

Real samples from equilibrium studies are taken as pin samples. These pin samples are then analysed by the Leco RO-116 as the pin to prevent oxidation from occurring. Occasional analysis of the test samples by hydrogen reduction has been requested. Since the samples are initially taken as pin samples it would be difficult to reduce the samples in this form. It was found that by shattering the samples in a shatter box no oxidation occurred and the sample could be completely hydrogen reduced. TABLE 10 is presented as a summary of the analytical data generated over the test period. Included are results for analysis of hydrogen reduction residue sulfur levels. From these results it is seen that the retention ability of copper (MR#8) to hold sulfur under strongly reducing conditions is apparent. The high residue sulfur content and reproducible oxygen analysis demonstrates the positive affect the copper bath has in the LECO analysis. As time permits reduction conditions will be modified to determine if complete sulfur removal is possible during the hydrogen reduction gravimetric oxygen analysis of MR#8.
TABLE 10
REAL SAMPLE ANALYSIS COMPARISON

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<tr>
<th>SAMPLE NO.</th>
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<th>HYDROGEN REDUCTION OXYGEN (%)</th>
<th>REDUCTION RESIDUE SULFUR (%)</th>
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10.0 REFERENCES


Sulfur Determination

Two methods are used for sulfur determination depending on the concentration in the specific sample. For high sulfur bearing materials (>1.5% w/w) a combustion/titration technique is used, whereas for low sulfur materials (0.01 to 1.5% w/w) an infrared technique is employed.

For mattes, the combustion/titration technique first combusts a 0.1 g sample in a sealed induction furnace (Zirconia crucible) with a stream of oxygen which converts the sulfur to sulfur dioxide. The sulfur dioxide gas is swept into a solution of hydrogen peroxide where it is converted to sulfuric acid. The acid is then titrated to pH 5.0 using an automatic titration unit, with a standard alkali solution. Calibration of the titrant is by combustion of a standard sulfur sample. For the high range, a high (5-25% w/w S) sample for the standardization of approximately 0.0625N sodium hydroxide (1.0 ml = 1.0 mg S).

For slags, the infrared sulfur analysis is performed in this laboratory using a LECO CS-244. In a sealed induction furnace, the sample to be analyzed is combusted (in a zirconia crucible) in a stream of oxygen and the gases swept past an infrared source. The infrared (IR) source radiates visible energy as well as all wavelengths in the infrared spectrum. Sulfur dioxide absorbs infrared energy at a precise wavelength within the IR spectrum. The sulfur dioxide absorbs energy from the radiated source and results in a lower energy being received by the IR detector. All other IR energy is eliminated from reaching the detector by means of a precise wavelength filter. Therefore, the absorption of infrared energy can only be attributed to sulfur dioxide. These changes in energy at the detector are thus converted to sulfur dioxide concentration. Instrument calibration is performed employing standard samples produced by LECO and the Bureau of Analyzed Standards (BAS).

Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) was used to carry out phase identification and relative standardless quantitative assays on various phases observed in solidified pin samples of the condensed phases. In particular it was used to carry out phase identification in an attempt to
distinguish between primary and secondary magnetite formed in solidified pin samples of the mottes in the oxygen solubility experiments. The instrument used for all the analyses was a JEOL 6400 equipped with an energy dispersive x-ray detector (EDXA).

**Electron Microprobe Analysis (EMPA)**

In order to reliably determine soluble metal contents in the fayalite based slags, an electron microprobe was employed. Even though extreme care was taken to ensure no matte entrainment occurred during suction sampling of the slag phase (matte-slag-gas tests), the chemical analyses were routinely verified using EMPA. During sampling of the molten slag it is possible to obtain a quench layer in the slag pin immediately adjacent to the sampling tube wall which is about 1mm thick. In this region, the elements in solution may be analyzed by microprobe to determine true concentrations of various species in solution. This is extremely important especially for the study of slag losses and determination of metal partition coefficients (wt.% element in matte/wt.% element in slag). The instrument used for all microprobe work was an Acton Cameca MS-64 electron microprobe (1966). This instrument operated at a focused beam diameter of 5-10 µm and an accelerating voltage of 25 kV at 300X magnification.
APPENDIX B – Experimental data for the matte gas equilibria studies.
Matte-Gas Equilibration Tests at 1200 °C and log PS\textsubscript{2}= -2.50.

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**Matte-Gas Equilibration Tests at 1200 °C and log PS₂=−4.50.**

58% Matte Grade

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**Matte-Gas Equilibration Tests at 1250 °C and log PS\textsubscript{2}=4.50.**

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### Matte-Gas Equilibration Tests at 1300 °C and log PS$_2$=-2.00.

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APPENDIX C – Integration example to find iron activity in the Fe-Ni-S-O system at 1300 °C and a sulfur pressure of 10^{-2.60} atm.
Oxygen Pressure vs. Oxygen Mole %
Projection onto Fe-O-(Ni+S) Plane at 1300 °C

Figure C1 Oxygen pressure as a function of oxygen (mole %) in the Fe-O-(Ni+S) ternary representation of the Fe-Ni-S-O quaternary.
Figure C2 Example of integration plane at fixed Fe/Ni and Ni/S molar ratios. Round markers indicate the experimental data while the lines represent isobaric planes of oxygen pressure.
Tangent Intercept vs. Oxygen Pressure
Projection onto Fe-O-(Ni+S) Plane, 1300 °C, log PS₂=-2.50

Figure C3 Example of integration graph showing the tangent intercepts at each oxygen pressure isobar.
### 14% MG, 1300 °C, log PS₂=2.50

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<th>Cum Area</th>
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Figure C4  Activity of iron associated species in the Fe-Ni-S-O system (14% matte grade) at 1300 °C and log PS$_2$=-2.50.
Activity of Fe-Associated Species in Fe-Ni-S-O System
At 1300 °C, Log PS$_2$=-2.50, Fe/Ni = 1.0

Figure C5 Activity of iron associated species in the Fe-Ni-S-O system (35% matte grade) at 1300 °C and log PS$_2$=-2.50.
APPENDIX D – Experimental data for matte-slag-gas equilibria studies at 1250 °C and two sulfur pressures (10^{-2.50} and 10^{-4.50} atm.).
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<td>0.63</td>
<td>26.90</td>
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<td>0.73</td>
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<td>8.55</td>
<td>0.65</td>
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<td>99.75</td>
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<td>15.59</td>
<td>0.36</td>
<td>33.00</td>
<td>99.59</td>
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APPENDIX E – Integration method example for matte-slag-gas equilibria studies at 1250 °C and a sulfur pressure of $10^{-2.60}$ atm.
Integration data for calculation of iron activity in the matte-slag-gas system at 1250 °C and log PS₂= -2.50.

<table>
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<th>log PO₂</th>
<th>area</th>
<th>Const Area</th>
<th>Cum Area</th>
<th>log a₇₅₂</th>
<th>a₇₅₂</th>
<th>a₇₅₀₃₀₄</th>
<th>a₇₅₀</th>
<th>a₇₅₅</th>
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<tbody>
<tr>
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<td>-0.098</td>
<td>-0.105</td>
<td>-1.260</td>
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<td>-0.340</td>
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<td>0.0550</td>
<td>0.0739</td>
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<td>0.6609</td>
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<tr>
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<td>-0.590</td>
<td>-1.745</td>
<td>0.0320</td>
<td>0.1458</td>
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<td>-0.850</td>
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<td>0.2593</td>
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<td>-2.414</td>
<td>0.0039</td>
<td>0.8082</td>
<td>0.3410</td>
<td>0.0464</td>
</tr>
</tbody>
</table>

A new variable was introduced called the y-factor. This is the variable represented on the y-axis in the integration plot and represents the integrable term, determined from the Gibbs-Duhem equation applied to this system. It was defined in Chapter 3.0 and is shown again below:

\[
d \log a_{Fe} = \left[ \frac{X_{(N)}X_{(O)}X_{(O)} - X_{(O)}X_{(N)}^2}{X_{(N)}X_{(O)}X_{(O)} - X_{(O)}X_{(N)}X_{[Fe]}} \right] d \log P_{O_2}^{1/2}
\]

the y-factor as represented from the above equation represents the term in the square brackets. The ( ) represent slag components whereas the [ ] represent matte components. The \(X_i\)'s represent mole fractions.
Figure E1  Integration plot for the calculation of iron activity in the matte-slag-gas system at 1250 °C and log PS$_2$=-2.50.
Figure E2 Activities of iron associated species in the nickel smelting system at 1250 °C and $\log PS_2 = -2.50$. 

Activity vs. Matte Grade in Nickel System

$log PS_2 = -2.50$, Temp. = 1250°C