

CHAPTER I INTRODUCTION

South Africa has more than 80% of the world's platinum reserves, and is the largest producer of platinum-group metals (PGMs) from ores containing copper, nickel and iron sulphide [JONES, 1999:42].

During treatment for metal recovery, sulphide ores are concentrated by flotation and smelted to a nickel or nickel-copper matte, which is further processed to nickel or nickel oxide by hydrometallurgical, pyrometallurgical, or vapometallurgical methods.

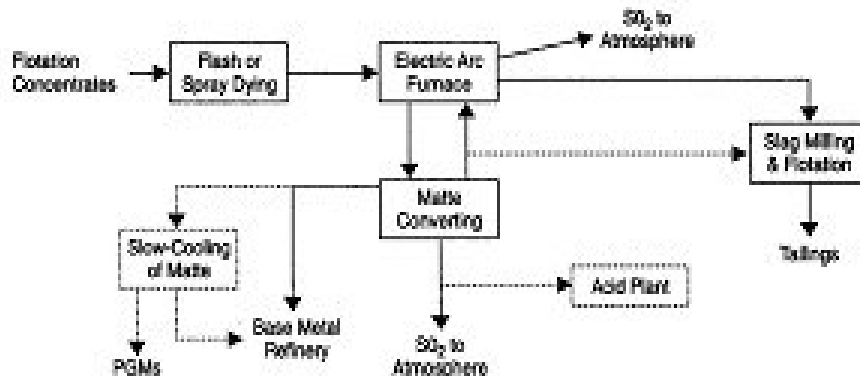


Figure 1-1. Simplified diagram showing the route to recover PGMs from sulphide flotation concentrates [CRAMER, 2001:7]

The main chemical reactions and aim each processing step are summarised below:

Smelting: A metallurgical thermal processing operation used to separate the gangue (oxide or silicate) minerals from the sulphide minerals associated with the noble metals in a furnace at high temperature, with little chemical reaction.

Converting: consists of eliminating most iron and much sulphur by injecting oxygen in the form of air, oxygen enriched air or pure oxygen. The endpoint is crucial to be determined to avoid oxidation of valuable metals from the matte causing loss of metals in slag.

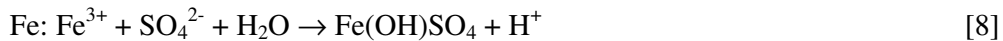
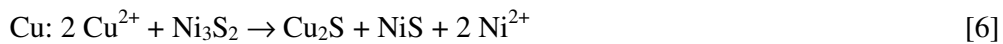
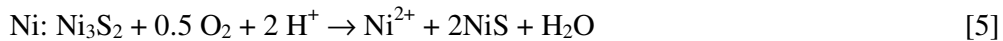
Main reactions





Refining: Hydrometallurgical refining is applied in the base metal refinery to dissolve and separate the iron, copper and nickel; the relevant reactions are given by equations (5) to (9). Its objective is to produce high-purity metal with a minimum consumption of energy.

Main reactions



In industry, the iron in the matte from the converting process must be controlled to a low level. An excess of Fe in the matte compared with the required level (average 0.5 to 3 wt% iron) affects hydrometallurgical refining.

In this study, the oxygen activity for decreasing iron content in a simulated converting matte has been investigated. Generally, the converting process decreases the amount of iron contained in the matte from approximately 37-wt% iron to approximately 1.4 wt% iron [JONES, 1999:41].

According to the Gibbs free energy calculated with FactSage at 1250°C, the driving force for reaction (2) is larger than reaction (4). During oxidation, reaction (2) will take place first until the equilibrium is reached and thereafter oxidation of copper by reaction (4) may start only if the minimum value of Fe in the matte is reached.

The Ellingham diagram shows that between these two reactions, the formation of NiO is possible and can therefore take place before reaction (4). The presence of NiO can be used as an indicator in the slag-matte system. If NiO concentration increases in the slag, reaction (2) is close to completion.

The introduction of probes as measurement elements could perhaps be used as an alternative to measure and accurately determine the endpoint of oxygen blowing.

Electrochemical oxygen probes are used extensively in the steel industry to measure the oxygen potential in liquid steel [GELDENHUIS, 2004:24]. The application of this type of sensor contributes to the optimisation of the deoxidation process of steel.

The commercial oxygen probes give signals of thermoelectric voltage (for the temperature measurement) and cell potential (for oxygen activity measurements).

When these signals attain stability, they are processed to provide a graph displaying the cell potential (emf).

The following are of particular interest in this study:

- the relationship between iron content in the matte and the electromotive force (emf);
- the effect of slag composition on the emf.

In the present study, the experimental method consisted of the use of different matte grades (FeS contents) in contact with a constant slag composition under a continuous gas flow at 1250°C (average temperature in industry). A fayalitic slag saturated in silica was obtained by mixing pure FeO and SiO₂, or pure FeO, Fe₂O₃ and SiO₂. Slag with a composition of 62mass% FeO_x-38 mass% SiO₂ was used in both cases.

A CO-CO₂-SO₂ gas mixture with controlled partial pressure of oxygen was used (pO₂ from 1.53 x 10⁻⁸ atm to 2.65 x 10⁻⁷ atm) at 1250°C; pure Ar was also used. The gas composition was varied to test whether the gas has any affect on the presumed local matte-slag equilibrium.

To determine the influence of iron in the Cu-Ni-Fe-S system, experiments were performed from 8.8 % Fe to 1.0 % Fe, in the matte. The Ni-Cu ratio was kept constant, and the matte was made up as a mixture of Ni₃S₂, Cu₂S and FeS.

CHAPTER II

LITTERATURE SURVEY.

One of the objectives of this work was to understand the thermodynamic principles of the Fe-Cu-Ni-S system at 1250°C and the links between this system and recovery of Platinum Group Metals (PGM).

The first section reviews the treatment of ore in order to obtain PGM as product. Section two reviews the phase and stability diagrams of the relevant binary, ternary and quaternary systems.

II.1.PGM in South Africa

Generally, the ore is treated by crushing, grinding and flotation to produce a concentrate, which is molten in a furnace to produce two immiscible melts: a denser sulphide melt (matte) and a less dense silicate melt (slag).

The slag and matte phases are tapped through separate furnace tap holes; the slag is discarded or processed further to recover valuable metals; the matte is treated further. The matte is converted by blowing air or air-oxygen mixtures into the system, oxidising most of the Fe to FeO, which reacts with added SiO₂ to form fayalite slag (Fe₂SiO₄). The converted matte contains Cu, Ni, S principally, Fe and Co as secondary elements, and small amounts of PGMs, gold and silver.

In South Africa, three broad ore types are exploited: the Merensky Reef, the Upper Group Chromitite Reef No.2 (UG2) and the Platreef [CRAMER, 2001:7].

According to Jones [1999:41], ore from the Merensky Reef contains up to 3% base-metal sulphide minerals, distributed as follows: pyrrhotite (45%), pentlandite (32%), chalcopyrite (16%) and pyrite (2-4%). The majority of the PGMs are associated with pentlandite, Pt-Pd sulphides such as braggite-coopertite, laurite or ferroplatinum.

The UG2 consists primarily of chromite (60-90%), interstitial orthopyroxene and plagioclase, together with secondary minerals such as talc, chlorite and phlogopite. The major base metal sulphide minerals are pentlandite, chalcopyrite, pyrrhotite and minor amounts of pyrite and millerite [JONES, 1999:41].

Table 2-1. Average grades of the individual precious metals in Merensky, UG2 and platreef ores [JONES: 1999:42].

| | Merensky ore | | UG2 ore | | Platreef ore | |
|---------------------|---------------------|------------|----------------|------------|---------------------|------------|
| | g/t | Mass%* | g/t | Mass%* | g/t | Mass%* |
| Pt | 3.25 | 59 | 2.46 | 41 | 1.26 | 42 |
| Pd | 1.38 | 25 | 2.04 | 34 | 1.38 | 46 |
| Rh | 0.17 | 3 | 0.54 | 9 | 0.09 | 3 |
| Ru | 0.44 | 8 | 0.72 | 12 | 0.12 | 4 |
| Ir | 0.06 | 1 | 0.11 | 1.9 | 0.02 | 0.8 |
| Os | 0.04 | 0.8 | 0.1 | 1.7 | 0.02 | 0.6 |
| Au | 0.18 | 3.2 | 0.02 | 0.4 | 0.1 | 3.4 |
| Total PGM+Au | 5.5 | 100 | 6.0 | 100 | 3.0 | 100 |

Mass%*: relative mass%

Each type of ore requires different approaches to metallurgical processing. UG2 ore has a much lower content of nickel and copper sulphides, and contains much more chromite than Merensky ore. The lower based-metal sulphide content of the UG2 indicates that a more sophisticated procedure is required for PGM recovery from UG2 ore. Nevertheless, UG2 ore is by far the richest source of rhodium, and the high demand for palladium makes processing of this ore very attractive [JONES, 1999:42].

II.1.1. General flow sheet

The general process consists of the classic operations which include milling, flotation, drying, smelting, converting, refining.

II.1.1.1. Concentrate preparation and drying

The ore is crushed and milled to reduce the size of the rock particles and to expose the minerals that contain the PGM. The particles are mixed with water and special reagents and air is

pumped through the liquid, creating bubbles to which the PGM-containing particles adhere. These float to the surface and are removed as a soapy froth. The PGM content of this flotation concentrate varies between 100 and 1000 grams per tonne [MATTHEY, 2005:52].

The concentrate is dried in a flash drier. The dry concentrate is transferred pneumatically from the drier into the furnace.

Table 2-2. Typical concentrate compositions [CRAMER, 2001:7]

| | Al ₂ O ₃ Mass% | CaO Mass% | Co Mass% | Cr ₂ O ₃ Mass% | Cu Mass% | FeO Mass% | MgO Mass% | Ni Mass% | S Mass% | SiO ₂ Mass% | PGM g/ton |
|---------|---|--------------|-------------|---|-------------|--------------|--------------|-------------|------------|---------------------------|--------------|
| Amplats | 3.2 | 4.7 | 0.08 | 0.80 | 2.1 | 20 | 15 | 3.6 | 9 | 34 | 143 |
| Impala | 4.1 | 2.9 | 0.06 | 1.1 | 1.3 | 18 | 18 | 2.1 | 5.6 | 42 | 138 |
| Lonmin | 1.8 | 2.8 | 0.08 | 0.4 | 2.0 | 23 | 18 | 3.0 | 9 | 41 | 130 |
| Northam | 2.6 | 3.0 | 0.05 | 0.87 | 1.3 | 17 | 18 | 2.5 | 5.4 | 47 | 132 |

II.1.1.2.Smelting

Smelting is used to separate the gangue (oxide or silicate) minerals from the sulphide minerals and the associated noble metals. Smelting uses an electric furnace at temperatures that can exceed 1500°C. Because of the low concentration of valuable minerals in the concentrate, the furnace is operated with a slag to matte production ratio of between 4 and 9.

The sulphide minerals form a denser molten matte with a relative density of about 4.8-5.3 g/cm³ containing the valuable metals. This separates from the unwanted minerals which form a lighter silicate and iron-rich slag with a relative density around 2.7-3.3 g/cm³; the slag is discarded [JONES, 1999:42].

Because of the low sulphur content of the UG2, it is not possible to matte smelt the UG2 on its own as an immiscible sulphide matte will not form. Therefore, UG2 concentrate is blended with Merensky concentrate prior to matte smelting. Matte temperature exceeds 1300°C for Merensky Reef concentrates and is in excess of 1500°C for UG2 concentrates [MERKLE, 2002:53].

The chromium, which is present as chromite in the furnace feed, can be a problem. Depending on the chromium content of the feed and the operating conditions of the furnace, it frequently happens that the slag becomes saturated with a chromium-rich spinel phase [NELL, 2004:63]. Usually a rough value of 3% by mass is used as the maximum allowable chromium content,

but studies have shown that the solubility of chromium in slag may be as low as 1% to 1.5% by mass chromium. The maximum chromium level that can be accommodated during smelting depends on: the smelting temperature, the proportion and type of fluxes used, and the exact concentrate blend being smelted [MERKLE, 2002:53].

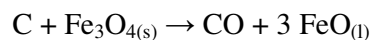
Table 2-3. Furnace matte compositions [JONES, 1999:42]

| | % Co | % Cr | % Cu | % Fe | % Ni | % S | PGM(g/t) |
|---------|------|------|------|------|------|-----|----------|
| Amplats | 0.5 | 0.5 | 9 | 41 | 17 | 27 | 640 |
| Impala | 0.4 | | 16 | 34 | 20 | 28 | 1050 |
| Lonmin | 0.5 | 0.23 | 9.7 | 37 | 17 | 28 | 1000 |
| Northam | 0.4 | | 7.9 | 41 | 16 | 27 | 724 |

Table 2-4. Furnace slag compositions [JONES, 1999:42]

| | Al ₂ O ₃ Mass% | CaO Mass% | Co Mass% | Cr ₂ O ₃ Mass% | Cu Mass% | FeO Mass% | MgO Mass% | Ni Mass% | S Mass% | SiO ₂ Mass% |
|---------|---|--------------|-------------|---|-------------|--------------|--------------|-------------|------------|---------------------------|
| Amplats | 3.3 | 6.4 | 0.05 | 0.80 | 0.11 | 31 | 15 | 0.19 | 0.5 | 46 |
| Impala | 6 | 8 | 0.03 | 1.2 | 0.11 | 21 | 18 | 0.11 | 0.25 | 47 |
| Lonmin | 2 | 9.8 | 0.05 | 1.2 | 0.09 | 28 | 19 | 0.15 | | 44 |
| Northam | 1.5 | 10 | 0.03 | 0.8 | 0.1 | 21 | 20 | 0.2 | | 44 |

During smelting, oxidising conditions can lead to a high ferric ion content in the slag, causing magnetite (Fe₃O₄) to form as a separate phase. Some operational problems can emerge like false bottom between slag and matte with reduced operational furnace volume, and increase base metal loss in the slag. Carbon additions can reduce magnetite in the slag to liquid FeO:



This reaction decreases slag viscosity and improves settling rates [DAVENPORT, 2002:9].

As said, during smelting the matte phase accumulates on the furnace floor, while the slag forms a layer on top of the matte. From a production point of view, it is important to know where the interface between matte and slag is, in order to optimise the tapping schedules for matte and slag. This slag/matte interface level changes continuously between tapping events and the rate is determined by different factors:

- the smelting rate,
- ‘matte fall’ of the concentrate feed
- the power input
- and the concentrate feed rate into the furnace.

[GELDENHUIS, 2004:24].

Some slag characteristics, which are important for the melting of PGM concentrates, are as follows:

- a low viscosity to allow clean slag-matte separation
- a low liquidus temperature to avoid excessive superheating of the matte
- the ability to dissolve all the chromium which is present in the concentrate to avoid the formation of refractory chromium-bearing spinel and to avoid the transfer of chromium to the matte
- a limited solubility of nickel, copper and cobalt as oxides
- chemical compatibility with the refractory lining in the furnace.

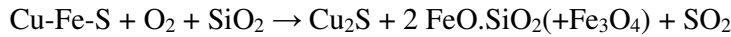
However, the slag composition is determined by the composition of the concentrate charged to the furnace, and there is a very little freedom to manipulate the slag composition [NELL, 2004:63].

II.1.1.3. Converting

Converting consists of eliminating some sulphur and most iron from the matte by injecting oxygen in form of air, air enriched with oxygen or pure oxygen. This increases the PGM grade. The main raw materials for converting are sulphide matte, silica flux, air and/or industrial oxygen.

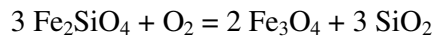
In the copper matte converting, the process is mostly done in the Peirce-Smith converter, which blows the blast into molten matte through submerged tuyeres. Several other processes are also used or are under development like Hoboken or siphon converter, Mitsubishi top-blown converter, Outokumpu flash converting and Noranda continuous converting [DAVENPORT, 2002:9].

Converting of platinum-bearing Fe-Cu-Ni-S follows the same principle as for Cu-Fe-S mattes. Air (or oxygen) is blown into the matte, which originates from the matte-smelting furnace (often termed ‘green matte’); this leads to removal of iron and sulphur from the matte by oxidation according to the main reactions:



The oxidation reaction is sufficiently exothermic to maintain a temperature around 1250°C in the converter and no external energy is required. The temperature is controlled by adding cold feed or revert materials (such as spillages) to the converter if it becomes too hot [JONES, 1999:42].

The melting point of FeO and Fe₃O₄ are 1385°C and 1597°C respectively, and silica flux is added during this stage by means of a flux gun to combine with the FeO and part of the Fe₃O₄ as liquid fayalitic slag; the sulphur leaving the system as SO₂ is captured to form sulphuric acid. The slag-forming stage is finished when the FeS in the matte has been almost completely oxidised i.e. to a point when the matte contains less than 5% Fe. Liquid fayalite (2FeO.SiO₂) slag, saturated with magnetite, is poured off at various times during slag forming but cannot be discarded due to its high base metal content. The oxygen partial pressure in converter slag is stated to be close to that of the quartz-fayalite-magnetite (QFM) redox buffer, which defines an oxygen partial pressure of 10^{-8.4} bar at 1200°C [NELL, 2004:63].



At 1200°C, NiFe₂O₄ coexists with a nickel-rich monoxide phase at oxygen partial pressures that are more oxidizing than 10^{-10.5} bar. The oxidizing nature of the converting conditions means that high losses of cobalt, nickel and copper as oxides might be encountered unless blowing conditions are carefully controlled and monitored [NELL, 2004:63].

The converter matte (known as the 'white matte') consists of copper and nickel sulphide and copper–nickel alloy and smaller amounts of iron sulphide, cobalt and PGE [MERKLE, 2002:53]. Impurities such as chromium, selenium, tellurium, arsenic, lead, tin, antimony and bismuth may concentrate in the white matte. Generally, the white matte is cast into ingots or granulated prior to treatment in the base metal refinery except at Anglo Platinum where it is cast into large ingots and slow-cooled [MERKLE, 2002:53].

To improve the SO₂ emission and air pollution which are associated with Peirce-Smith converters, many projects have been directed to develop new and competitive technology for Cu matte smelting, with lower capital and operational costs compared with conventional technology, while achieving virtually total capture of the sulphur as SO₂ for acid production.

Examples include:

- The Kennecott-Outokumpu flash converting process uses advanced technology of continuously converting copper matte and permits the capture of virtually 100% of the SO₂ generated for acid production [Internet, 2005].

- The innovative DON (Direct Outokumpu Nickel) process eliminates the need for Peirce-Smith converting and the ladle transfer of molten matte [Internet, 2005].
- The Anglo Platinum Converting Process (ACP) aims to improve the control of sulphur dioxide emissions while increasing the available converter capacity. The converter, developed in conjunction with Ausmelt and others, utilises a Siros melt process adapted to the requirements of nickel-copper matte smelting. The Ausmelt converter is a totally contained vessel, which makes it possible to contain all the gas generated in the converting process. The off-gas from the Ausmelt converter is then fed to a new acid plant, consisting of two sections, specifically selected for its ability to treat both the high strength Ausmelt converter gas and the low-strength gas from the existing electric furnaces [Internet, 2005].

❖ Difference between the Peirce-Smith Converter and Ausmelt Converter.

- Ausmelt converter can be much smaller than the Peirce-Smith converter due to the rapidity of furnace reactions and a short residence time required to process most materials.
- The electric furnace matte is hot charged to the Peirce-Smith converter while the Ausmelt converter is fed with granulated electric furnace matte.
- Improve sulphur fixation levels of converter gas from the present 55% to more than 95%.

The end-point iron content is important in this study because:

- an iron excess in the matte compared with the specification has an impact on hydrometallurgical refining of the matte.
- an iron deficit in the metal compared with the specification has an impact on refining as iron is needed to increase the exothermicity of the refining.
- alloy formation during solidification of matte in ingots (slow cooling) depends on the iron content.

Table 2-5. Converter matte analyses [JONES, 1999:42]

| | % Co | % Cu | % Fe | % Ni | % S | PGM(g/t) |
|----------------|------|------|------|------|-----|----------|
| Amplats | 0.5 | 26 | 2.9 | 47 | 21 | 2100 |
| Impala | 0.4 | 31 | 0.5 | 47 | 21 | 3430 |
| Lonmin | 0.6 | 29 | 1.4 | 48 | 20 | 6000 |
| Northam | 0.5 | 27 | 1.0 | 51 | 19 | 2570 |

Table 2-6. Converter slag analyses [JONES, 1999:42]

| | %Al ₂ O ₃ | %CaO | %Co | %Cr ₂ O ₃ | %Cu |
|----------------|---------------------------------|------|------|---------------------------------|-------------------|
| Amplats | 0.7 | 0.4 | 0.45 | 0.4 | 1.17 |
| | %FeO | %MgO | %Ni | %S | %SiO ₂ |
| Amplats | 63 | 1.1 | 2.25 | 2.4 | 27 |
| | %Al ₂ O ₃ | %CaO | %Co | %Cr ₂ O ₃ | %Cu |
| Impala | 1.8 | 0.3 | 0.43 | 1.4 | 1.06 |
| | %FeO | %MgO | %Ni | %S | %SiO ₂ |
| Impala | 64 | 0.71 | 1.9 | 1.0 | 27 |
| | %Al ₂ O ₃ | %CaO | %Co | %Cr ₂ O ₃ | %Cu |
| Lonmin | 0.7 | 0.5 | 0.39 | 1.4 | 0.94 |
| | %FeO | %MgO | %Ni | %S | %SiO ₂ |
| Lonmin | 65 | 0.78 | 1.43 | 1.7 | 28 |
| | %Al ₂ O ₃ | %CaO | %Co | %Cr ₂ O ₃ | %Cu |
| Northam | 1.3 | 0.7 | 0.4 | 0.36 | 1.37 |
| | %FeO | %MgO | %Ni | %S | %SiO ₂ |
| Northam | 64 | 0.82 | 2.18 | | 27 |

II.1.1.4. Off-gas handling

Some of the sulphur leaves the system in the gas phase as sulphur dioxide (SO_2). Of the sulphur entering the smelter, 60% leaves in the converter gases, 20% in the smelter gases, 15% in the converter matte, and 5% in the furnace slag [JONES, 1999:42].

SO_2 from converting is almost always made into sulphuric acid, and occasionally liquid SO_2 or gypsum.

II.1.1.5. Refining

The objective of the refinery is to produce high-purity metals with a minimum consumption of energy.

According to Jones [1999:42], the converter matte is usually milled prior to treatment in the base-metal refinery, where the copper and nickel are extracted by sulphuric-acid leaching. The leach residue makes up the high-grade PGM concentrate that is supplied to the precious metals refinery for the final separation of the pure precious metals.

There are mainly two processes used in the base-metals refinery: The Outokumpu and Sherritt-Gordon processes. Both processes have the same rationale and operate in several steps of increasingly aggressive conditions:

- the initial stage operates under mild conditions to leach some Ni and Co, and uses fresh matte to remove Cu from nickel sulphate solution
- the middle stage operates under harsher conditions and aims at dissolving all the remaining nickel and cobalt, as well as some copper from the matte
- the final stage aims at dissolving all the remaining copper and some iron from the matte.

A simplified process flowsheet for both processes is illustrated below.

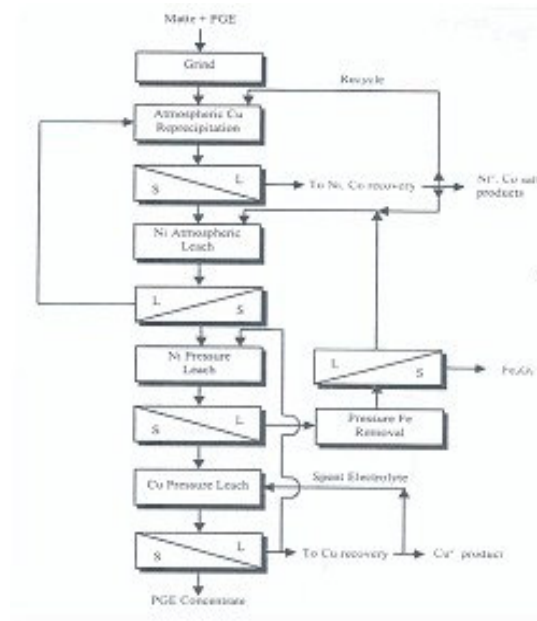


Figure 2.1. The Outokumpu process (Hartley platinum refinery)[COLE, 2002:6]

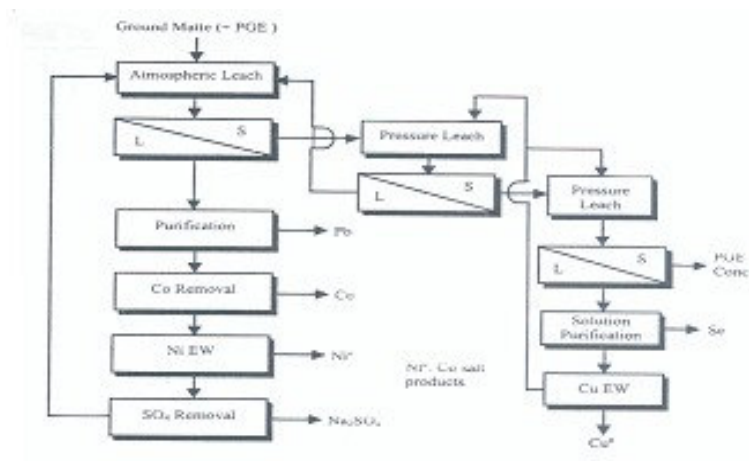


Figure 2.2. The Sherritt-Gordon process (Rustenburg base metals refinery) [COLE, 2002:6]

The precious-metal refining process consists of transforming the high-grade PGM concentrate (30% to 60% PGM) into high-purity (>99%) individual elements such as platinum, palladium, iridium, osmium, ruthenium, rhodium as well as recovering the gold and silver usually accompanying the PGM, see figure 2.3. [COLE, 2002:6].

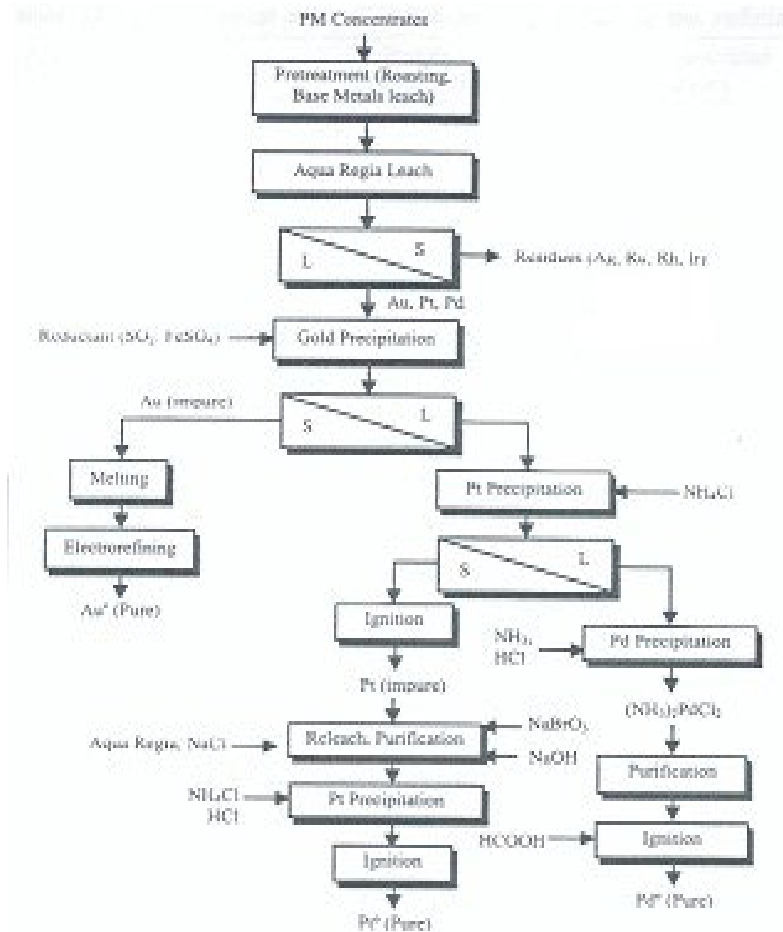


Figure 2.3. Refining process for Au, Pt, Pd (Inco Acton refinery)[COLE, 2002:6]

The refined PGMs have a purity of over 99.95 per cent, and can be produced in a number of forms: ingot, grain or a fine powder known as “sponge” [MERKLE, 2002:53].

The time between mining of the ore and production of pure metal typically ranges from around 6 weeks for palladium to up 20 weeks for rhodium [MATTHEY, 2005:52].

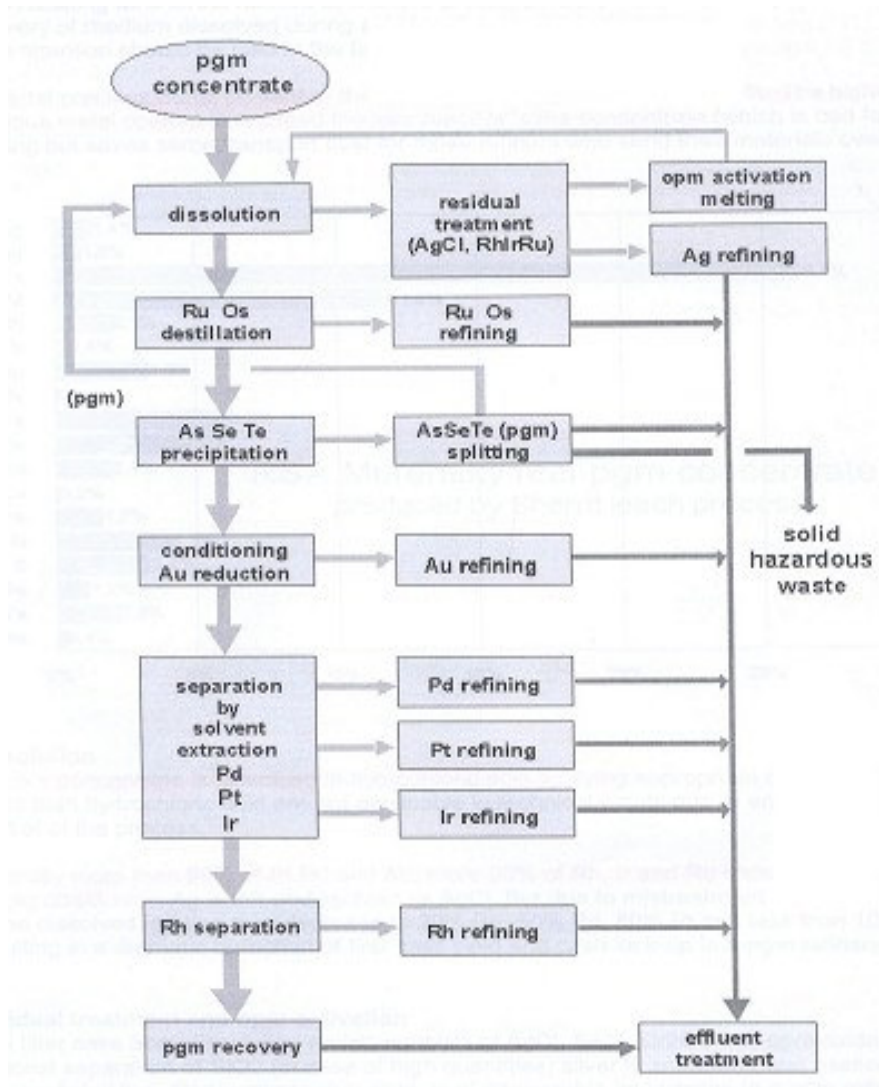


Figure 2-4. Refining of PGM converter matte [Internet, 2005]

General flow sheet

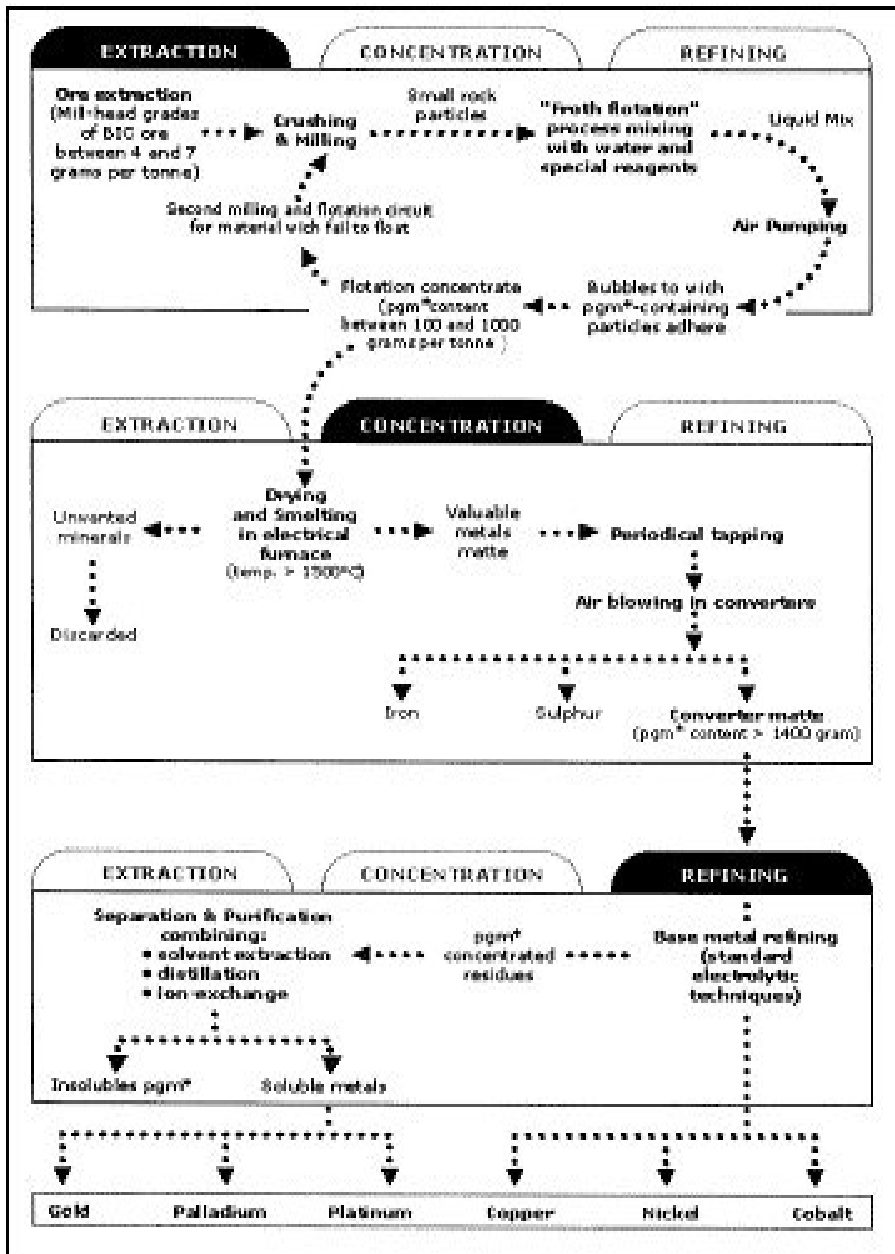


Figure 2-5. General flow sheet of PGMs [Internet, 2005]

II.2. Binary, ternary and quaternary systems

The understanding of the Cu-Ni-Fe-S system is discussed below to estimate converter matte and slag composition as functions of temperature and oxygen potential. Stability diagrams of the relevant binary and ternary systems are reviewed, and are presented to describe ores and natural mineral assemblages.

II.2.1. The binary system

II.2.1.1. The binary system FeO-Fe₂O₃

The FeO-Fe₂O₃ system is shown in figure 2.6. At 1250°C, the FeO-Fe₂O₃ system contains five phase fields appearing with the increase of FeO oxidation:

γ -Iron+wüstite , wüstite , wüstite+magnetite , magnetite and magnetite+hematite .

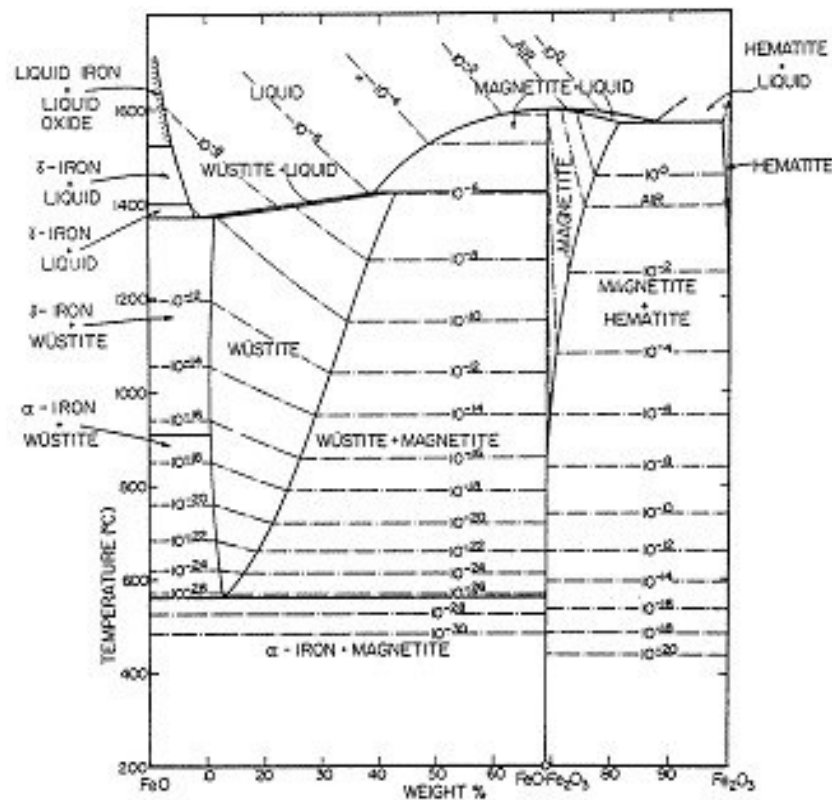


Figure 2-6. Diagram of the Fe-O system [ELLIOT, 1976:12]*

*: FeO is a simplified formula of wüstite. Its formula is more accurately written Fe_xO where the average value of x is 0.95 if the oxide is in contact with Fe metal.

II.2.1.2. The binary system FeO-SiO₂

All laboratory tests in this thesis were done with slag composed of 62 mass% FeO-38 mass%SiO₂. To assure a condition of silica saturation, SiO₂ was added in excess of saturation level. On the figure below, the range in which fayalite is liquid at 1250°C is approximately between 62 and 82 mass% FeO.

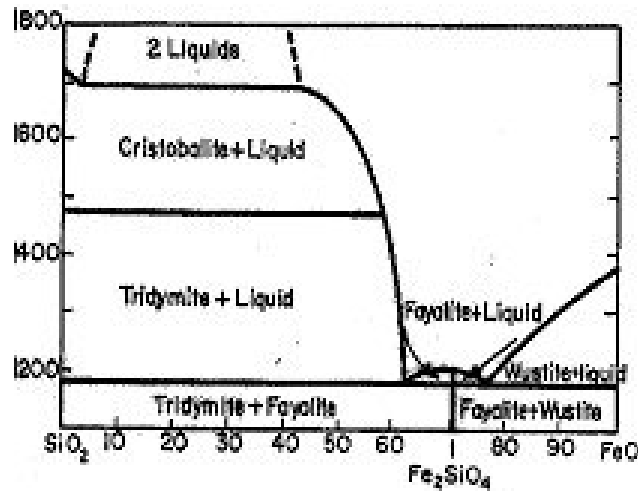
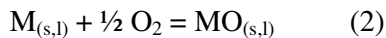
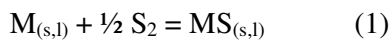


Figure 2-7. FeO-SiO₂ binary diagram [LEVIN, 1964:46]*

*: The phase diagram is based on equilibrium with metallic iron.

- Yazawa diagram

The stability of a metal relative to its oxide or sulphide depends on two reactions:



By knowing the $\log K_1$ and $\log K_2$ at a given temperature, by assuming $a_M = a_{MS} = a_{MO}$, figure 2-8 was constructed [Yazawa, 1974:93].

The sulphides of iron, copper and nickel tend to change into oxide during the converting process. For example, iron sulphide can change to iron oxide at 1300°C for p_{O_2} values higher than the line between the FeS and FeO fields, starting at values of $\log(p_{S_2}/atm) = -4.8$ and $\log(p_{O_2}/atm) = -10.8$

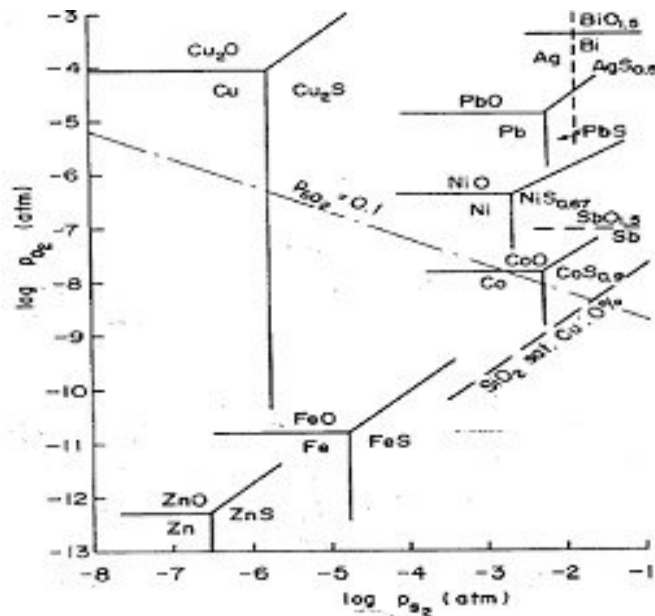


Figure 2-8. Sulphur-oxygen potential diagram for various metal-sulphur-oxygen systems at 1300°C [Yazawa, 1974]

II.2.2. Ternary systems

II.2.2.1. The ternary system FeO-FeS-SiO₂

This ternary system is the simplest to show the effect of silica on matte/slag separation.

The miscibility gap between the silicate and sulphide liquids is a prerequisite for matte-slag separation. The figure below shows that liquid FeO and FeS alone are miscible. In silica-free melts with FeS concentrations above approximately 31mass%, a single oxysulphide liquid is formed. However, the presence of SiO₂ introduces a miscibility gap causing the separation into two immiscible liquid phases. The gap becomes larger as more silica is added. The tie lines, a, b, c, d on the curve ACB showed below represent the equilibrium compositions of the two liquids, the sulphide-rich melt (matte) and the oxide-rich melt (slag)[DAVENPORT, 2002:9].

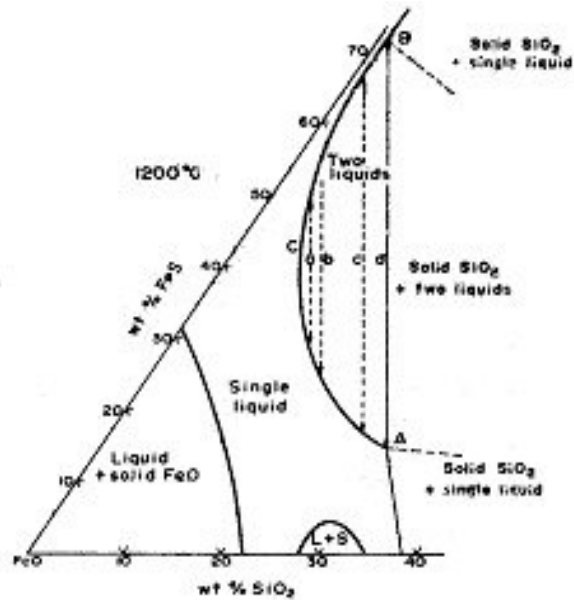


Figure 2-9. Phase diagram (1200°C) for the FeO-FeS-SiO₂ system showing the liquid-liquid immiscibility region created by the presence of silica [DAVENPORT, 2002:9]. *

*: The phase diagram is based on equilibrium with metallic iron.

An increased SiO₂ content induces liquid immiscibility between the sulphide and oxide-silicate phases, an effect that is maximal at SiO₂ saturation. This silica saturation condition forms a convenient boundary position used for the experimental investigation of this study.

II.2.2.2. The ternary system FeO-Fe₂O₃-SiO₂

As figure 2-10 shows, the SiO₂ content at saturation is affected little by the Fe₂O₃ content of the slag.

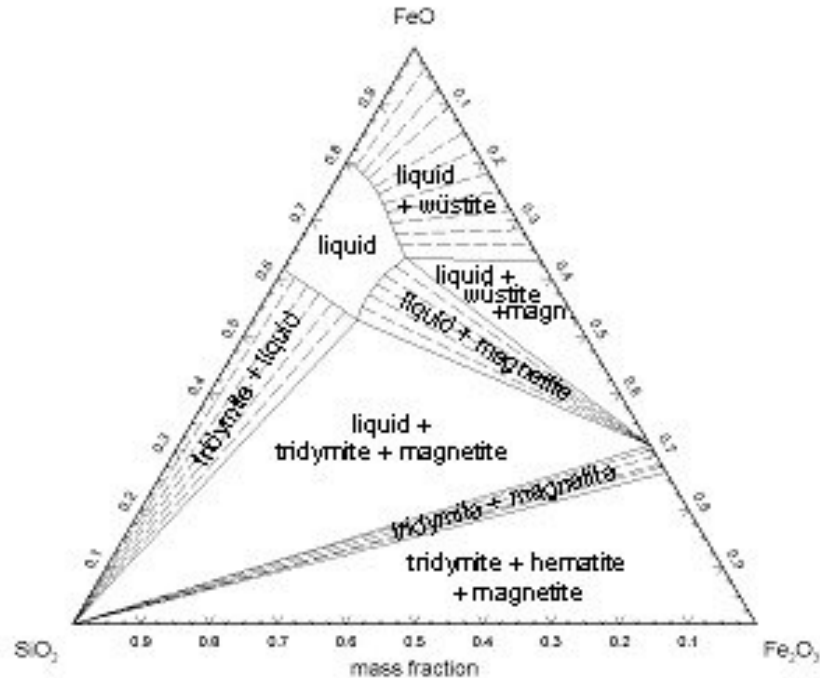


Figure 2-10. FeO-Fe₂O₃-SiO₂ diagram at 1250°C (FactSage).

II.2.3. The quaternary Fe-S-O-SiO₂ system

The stability diagram for the Fe-S-O-SiO₂ system for 1573K is shown below in terms of oxygen and sulphur potentials and the ratio $\frac{\%SiO_2}{(\%Fe + \%SiO_2)}$.

The volume, which represents the region of stability for iron silicate slags, is bounded at its surfaces by Fe₃O₄ (top), Fe (bottom), and SiO₂ (far face). At the left of the diagram, at low p_{S₂}, there is an alternative representation of the well-known FeO-Fe₂O₃-SiO₂ ternary. Muan and Osborn gave oxygen potentials and liquidus boundaries, and Nagamori estimated activities of FeO and Fe₃O₄ at 1473 and 1573K. The surface of liquid oxysulfide stability is defined by points NOPQRN [CELMER, 1987:3].

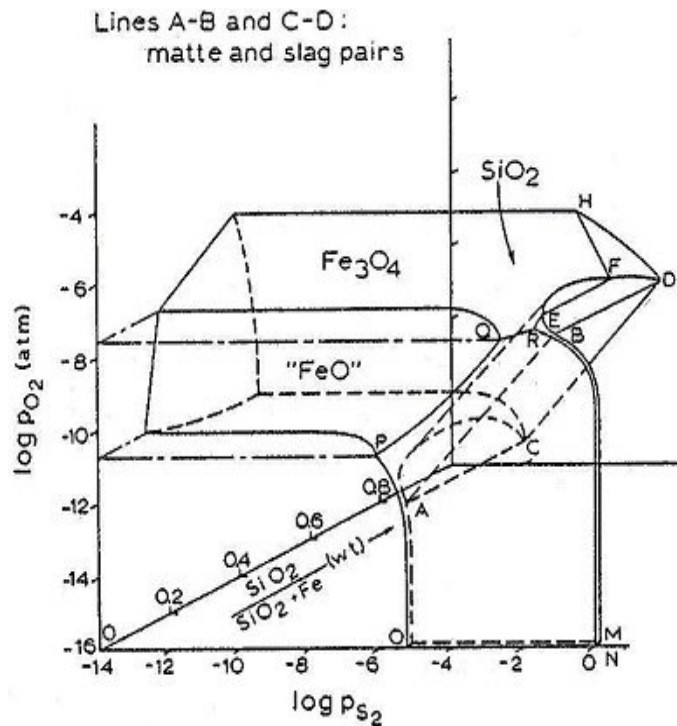


Figure 2-11. Stability diagram for the Fe-S-O-SiO₂ system at 1573K[CELMER, 1987:3].

II.3. Components and phase systems obtained with the Gibbs phase rule.

The selection of different variables is important in this study to determine the variance of the system. A variable is a component, which may be independently altered in value without disturbing the equilibrium of the system.

The variables that must be measured or controlled to define the equilibrium in the system are imposed by the degrees of freedom obtained with the Gibbs phase rule:

$$F = C + 2 - P$$

where F is the variance of the system or number of degrees of freedom,

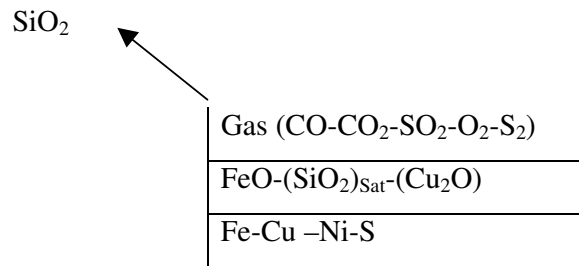
C is the number of components and P is the number of phases. The number of degrees of freedom, F , is defined as the maximum number of variables, which may be independently altered in value without disturbing the equilibrium in the system.

If the system contains N species among which there are R independent reaction equilibria, then

$$F = (N-R) + 2 - P. \text{ [GASKELL, 1981:21]}$$

The phase rule gives

$$F = (12 - 6) - 3 + 2 = 5 \text{ (see appendix C)}$$



According to Celmer[1987:3], matte is not a rigorous thermodynamic variable because the activities of individual components (a_{Fe} , a_{Ni} , p_{O_2} , p_{S_2}) are not necessarily constant at any value of matte grade. In practice, matte grade does closely define the matte composition in a smelting system, such that the activities of the constituent sulphides (FeS , $\text{CuS}_{0.5}$) are fixed [CELMER, 1987:3].

Some studies have been done on the phase equilibrium between the $\text{Ni}_3\text{S}_2\text{-FeS}$ or $\text{Ni}_3\text{S}_2\text{-Cu}_2\text{S-FeS}$ matte and the iron-silicate-based slag with the composition of 64 mass% $\text{FeO}_x\text{-36 mass\% SiO}_2$ [FONT, 1999:16].

By applying the same principle in the Font experiments, the degree of freedom is found to be three: $N = 10$ (all species used in the experiment)

$$R = 6 \text{ (obtained with the rank of the echelon matrix)}$$

$$P = 3 \text{ (solid, liquid and gas phase)}$$

Thus, all the thermodynamic parameters can be defined by three variables chosen as: temperature, matte grade, the slag composition and the SO_2 partial pressure.

CHAPTER III

EXPERIMENTAL APPARATUS AND PRELIMINARY TESTWORK

III.1. Furnace assembly

Experiments were performed in a sealed vertical furnace tube. The furnace shell is of dimensions of 600 mm length, 600 mm width and 550 mm height. Silicon carbide (SiC) heating elements were used to provide external heat to the work tube. The hotrods (heating elements) of SiC can operate in the furnace up to 1550°C.

The heating elements were concentrically arranged in the centre of the furnace and connected in series providing a zone of high temperature about 100 mm in length. Kaowool stuffing was used at the top of the furnace and around the thermocouple protection to prevent heat losses.

A mullite tube with a closed end was used as work tube with an inner diameter of 64 mm, an outer diameter of 73 mm and 520 mm length.

The system was closed gas tight by water-cooled brass end caps joined to the tube by compression 'O'-ring.

❖ Temperature profile

The objective of preliminary tests was to check and find the operating conditions required for accurate tests. These runs were used to check the gas flows, the gas tightness, and whether the temperature in the furnace remains constant over periods of time.

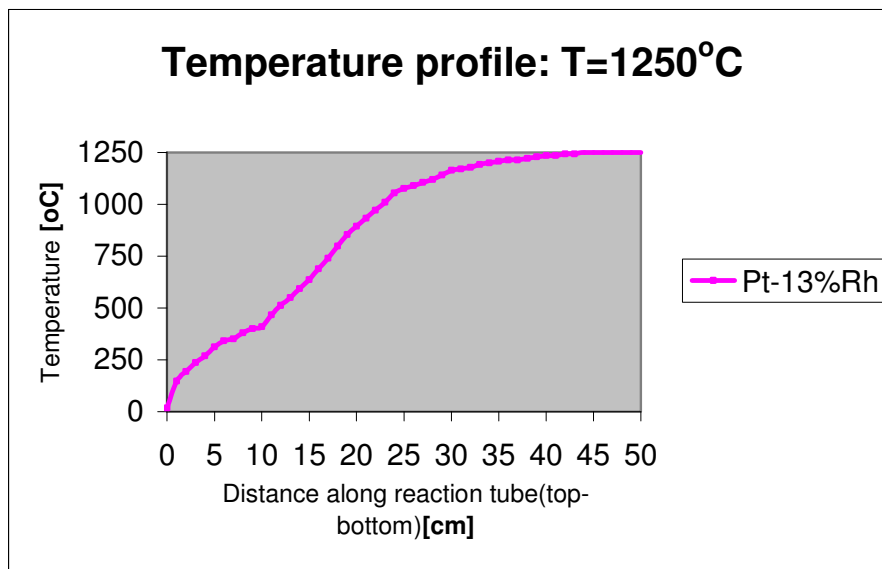


Figure 3-1 Temperature profile in the furnace

The temperature profile of the furnace showed a plateau region measuring 1523 K over a length of 6 cm. This was satisfactory for a depth of 10-20 mm of molten charge contained in the sample crucibles.

III.2. Apparatus

Experimental apparatus used in this study consisted of

- Zirconia electrolyte (4mm I.D., 6mm O.D., and 50mm in length) containing a mixture of Cr and Cr₂O₃ for the first experiments and Fe and FeO for the last experiments (as oxygen reference).
- An iron rod (2mm O.D and 75 mm in height) used as an electrical lead to the reference electrode, cemented onto the zirconia tube with alumina cement.
The probe protection tube was a silica tube to minimise reaction of iron rod with the furnace content.
- Platinum wire (0.5mm diameter) to complete the electrical circuit of the cell, shielded with a mullite tube, immersed in the matte.
- A thermocouple (Pt-13%Rh) used to measure the temperature.

The thermocouple protection tube was a mullite tube, 6 mm O.D., 2 mm I.D for each holes; the tip of the thermocouple was positioned approximately 1 cm from the crucible.

- The CO/CO₂/SO₂ inlet gas mixture was supplied through a 6 mm O.D., 4 mm I.D., silica tube . The gas left the furnace via a copper exit tube in the end cap. The tip of the gas inlet tube was approximately 2 cm from the top of the crucible.

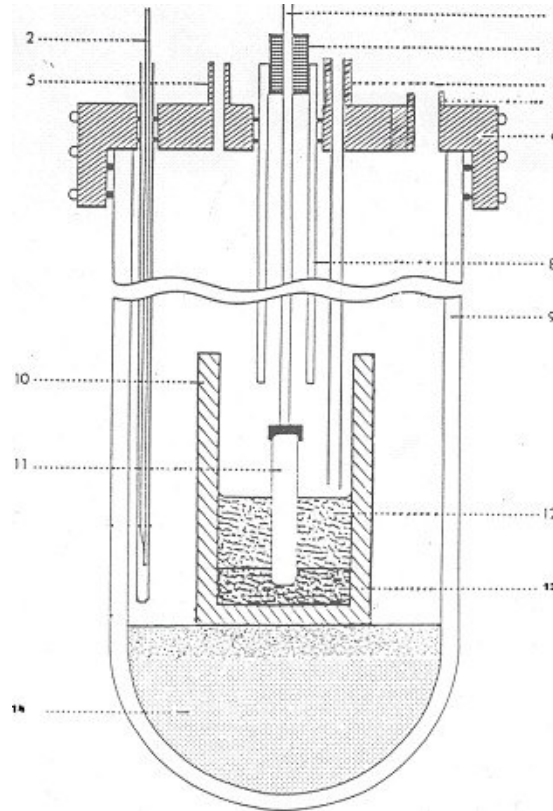


Figure 3-2. Reaction tube and crucible assembly used in the thesis.

- | | |
|-------------------------------|---------------------------|
| 1. Iron rod | 8. Alumina guide tube |
| 2. Pt13Rh thermocouple | 9. Mullite reaction tube |
| 3. Rubber stopper | 10. Silica crucible |
| 4. Platinum wire guide tube | 11. Zirconia oxygen probe |
| 5. Gas inlet | 12. Liquid slag |
| 6. Water-cooled brass fitting | 13. Liquid matte |
| 7. Gas outlet | 14. Alumina beads |

Samples were removed from the furnace and carefully separated from the silica crucible. The samples were ground in a mortar to obtain small pieces and then mounted for further analysis with SEM and the electron probe microanalyser. The matte composition was determined by an average value of the solidified matte.

Samples were analysed by scanning electron microscope (SEM) and also with an electron probe microanalyser (WDS). SEM measurements were performed with the following parameters: acceleration voltage of 25 kV, working distance of 20 mm, Norvar window and silica-lithium detector.

Samples were also analysed with an electron probe microanalyser (CAMECA SX-100), with four WDS spectrometers and a Röntek Xflash SDD detector. The beam conditions were 20 kV and 20 μ A with measurement times (real time) of 120 s.

III.3.Zirconia solid electrolyte

According to Iwase [IWASE, 1992:34], the solid electrolyte is a diagnostic sensor that permits rapid determination of various elements dissolved in hot metal and liquid steel. Pure zirconia has a monoclinic crystal structure at room temperature and transforms to tetragonal and cubic forms at increasing temperatures. The volume expansion caused by the cubic to tetragonal to monoclinic transformations induces very large stresses, and causes pure zirconia to crack upon cooling from high temperatures. Several different oxides can be added to zirconia to stabilize the tetragonal and/or cubic phases such as magnesium oxide (MgO), yttrium oxide, (Y_2O_3), calcium oxide (CaO), and cerium oxide (CeO) [Internet,2005].

➤ Properties of ZrO_2 [JANKE, 1977:38]

| | |
|--|---------------------|
| ZrO₂ | |
| Structure | Monoclinic |
| Transformation mono.↔ tetra., °C | 800 to 1200 |
| Transformation tetra.↔ cub., °C | ≈ 2300 |
| Melting point, °C | 2680 |
| Density at 20°C, g.cm ⁻³ | 6.1 |
| Free energy of formation ΔG° , kJ.mol ⁻¹ | -1082.74 + 0.17806T |
| Log pO ₂ (1600°C), atm | -20.88 |

Stabilized zirconia is predominantly an oxygen anion conductor because of the presence of a large amount of oxygen anion vacancies. Stabilized zirconia is used because the unstabilized zirconia has electronic conduction causing polarization of the electrolyte and incorrect readings [NAUDE, 2003:62]. Therefore, the addition of magnesia in the zirconia probe composition is important to ensure proper readings due to ionic conduction.

The accurate measurement of oxygen activity can be ensured only if the e.m.f. response has a stable e.m.f. plateau, a short response time, and good reproducibility. [VAN WIJNGAARDEN, 1987:86]

Solid zirconia electrolytes are used in high-temperature thermodynamic studies of slag-metal systems such as the production of iron, ferrochromium, and steel. The construction of the solid electrolyte oxygen cell is different depending on the practical conditions and the component to be measured: iron, matte, slag or steel. The use of zirconia electrolytes at high temperature and low oxygen potentials introduces a mixed ionic and n -type electronic conduction.

According to Schmalzried's analysis [GELDENHUIS, 2004:24], the cell EMF for a mixed ionic and electronic conduction of the oxide electrolyte at low oxygen partial pressures follows the equation:

$$E = \frac{RT}{F} \ln \left[\frac{(P''_{O_2})^{\frac{1}{4}} + (P_e)^{\frac{1}{4}}}{(P'_{O_2})^{\frac{1}{4}} + (P_e)^{\frac{1}{4}}} \right]$$

Where P'_{O_2} and P''_{O_2} are the respective partial pressures of oxygen at the two electrolyte-electrode interfaces, P_e is the oxygen partial pressure at which the n -type and ionic conductivities are equal, R is the gas constant, F the Faraday constant, and T the absolute temperature.

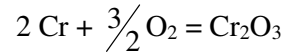
According to Van Wijngaarden[1988:84], the electrical properties of solid electrolytes are influenced by the type and concentration of the stabilizing oxide, the phase composition, the impurities in the electrolyte, and the microstructure of the electrolyte and can therefore be influenced by the chemical and physical properties of the original raw materials, as well as by the heat treatment to which the electrolyte is exposed during fabrication.

Two different reference electrodes have been used in this thesis to see their behaviour in the melt at a given temperature.

a. Electrochemical oxygen probe with Cr/Cr₂O₃ reference.

A mixture of Cr-Cr₂O₃ was used as reference electrolyte.

The principal reaction is



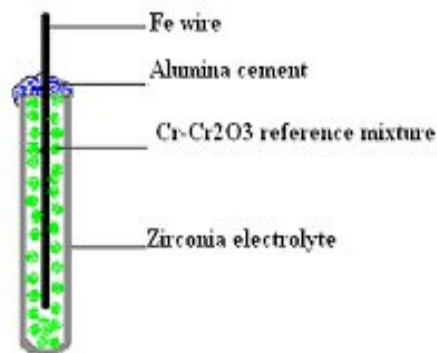
Chromium and chromium oxides used were laboratory chemicals (see Appendix –E).

The equilibrium constant $K = \frac{a_{\text{Cr}_2\text{O}_3}}{a_{\text{Cr}}^2 \cdot p_{\text{O}_2}^{1.5}}$, therefore $p_{\text{O}_2} = \left(\frac{a_{\text{Cr}_2\text{O}_3}}{K} \right)^{\frac{2}{3}} \cdot \frac{1}{a_{\text{Cr}}^3}$

Oxygen partial pressure depends on temperature, activities of chromium and chromium oxide.

If Cr₂O₃ and Cr are pure, $p_{\text{O}_2} = 6.48 \times 10^{-18}$ atm (FactSage, 1250°C)

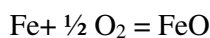
The Cr-Cr₂O₃ mixture was placed in a zirconia electrolyte tube stabilized with MgO (see appendix-I) of 50 mm length, 5 mm I.D and 6 mm O.D. An iron wire served as the electrical lead to the reference electrode used for electrical contact and was cemented into the zirconia tube with alumina cement. No alloying between Fe and Cr was observed after use of the probe at 1250°C.



The electrolyte was heated at 300°C in a resistance furnace for about a day to dry and harden the alumina cement.

b. Electrochemical oxygen probe with Fe/FeO reference.

The reaction for this reference electrode is



Fe was a laboratory chemical (see Appendix-E) while FeO was prepared from FeC₂O₄·2H₂O by using a muffle furnace at 1000°C according to the reaction:

Ar

$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}_{[S]} \rightarrow \text{FeO}_{[S]} + \text{CO}_{[g]} + \text{CO}_2_{[g]} + 2\text{H}_2\text{O}_{[g]}$. Details are presented in Appendix-F.

The equilibrium constant $K_T = \frac{a_{\text{FeO}}}{a_{\text{Fe}} \cdot x(p_{\text{O}_2})^{0.5}} \Rightarrow p_{\text{O}_2} = \left[\frac{a_{\text{FeO}}}{K_T \cdot a_{\text{Fe}}} \right]^2$

$a_{\text{Fe}} = a_{\text{FeO}} = 1$ (solid reference)

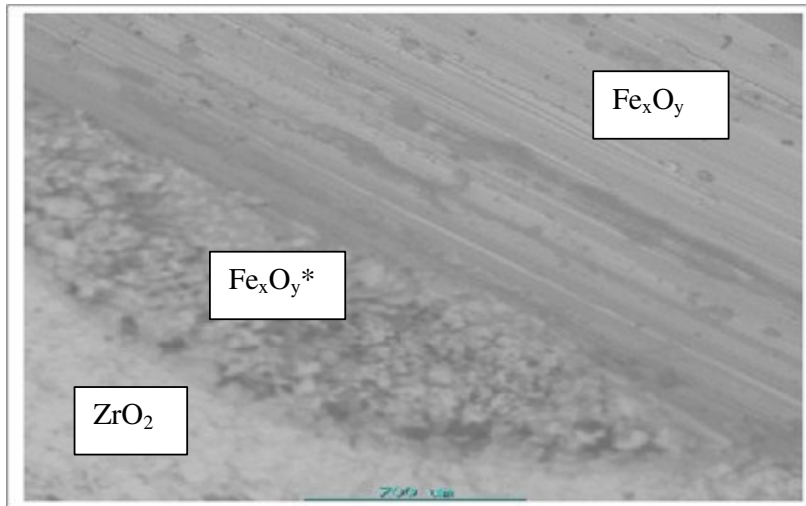
$K_T = 591720$ (1523K)

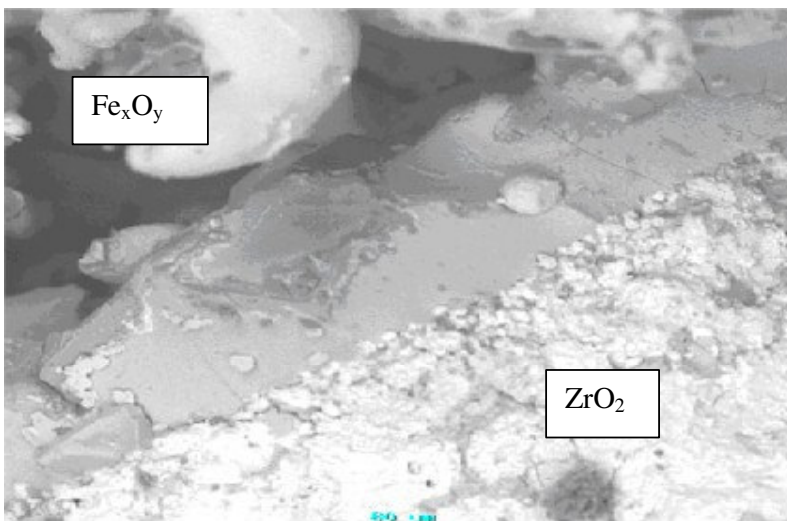
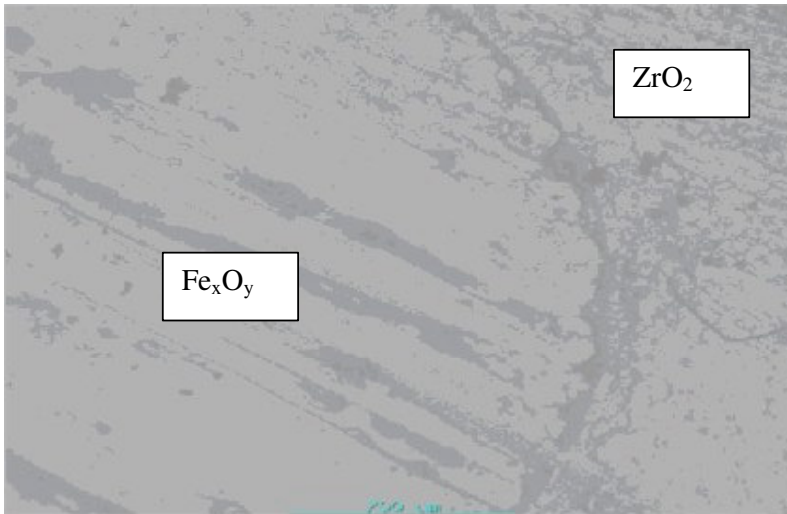
$P_{\text{O}_2} = 2.86 \times 10^{-12} \text{ atm}$

❖ Fe/FeO reference with added silver.

The iron –iron oxide reference electrode was improved in terms of conductivity by adding silver in the reference electrode. Silver was used in the electrode to enhance the electronic conductivity of the electrodes [XIA, 2002:91] and served as stabiliser for the EMF measurements and reading.

The cross section of the zirconia probe after the test did not show any reaction between zirconia, iron oxide and silver. SEM pictures of the cross section are presented below





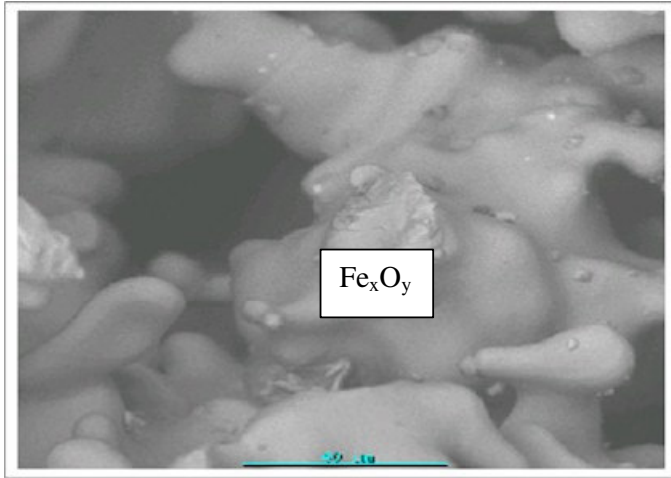
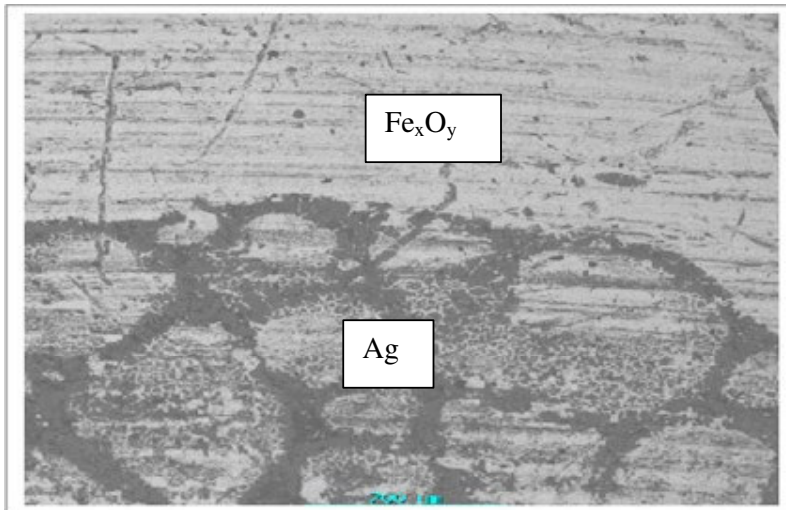


Figure 3-3. SEM micrograph of zirconia cross-section showing the boundary between zirconia probe and iron oxide solid reference electrolyte.

The cross section of zirconia probe shows a net separation between zirconia and iron oxide. No reactions take place between the two compounds. Fe_xO_y differ from Fe_xO_y^* in terms of microstructure probably because of a temperature gradient.



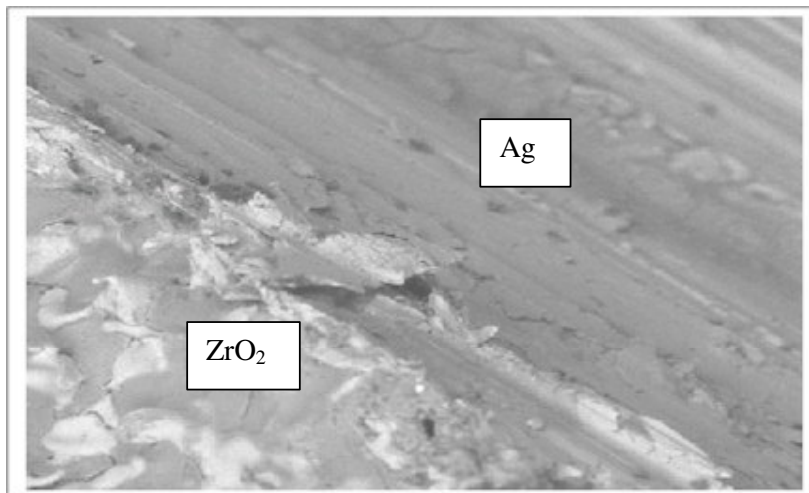


Figure 3-4. SEM micrograph of zirconia cross-section showing the boundary between zirconia probe and silver used as stabiliser.

C. Preliminary tests

The purpose of these tests was firstly to compare the two different reference electrodes at 1250°C and secondly to see the impact of different gas composition on the results.

Table 3-1 shown below presents the EMF results for Cr/Cr₂O₃ and Fe/FeO solid electrolytes obtained at 1250°C using Cu and Cu₂O as melts (fig. 3-5). The expected oxygen activity using the Ellingham diagram was about 6×10^{-4} atm; the value obtained with FactSage was 1×10^{-4} atm.

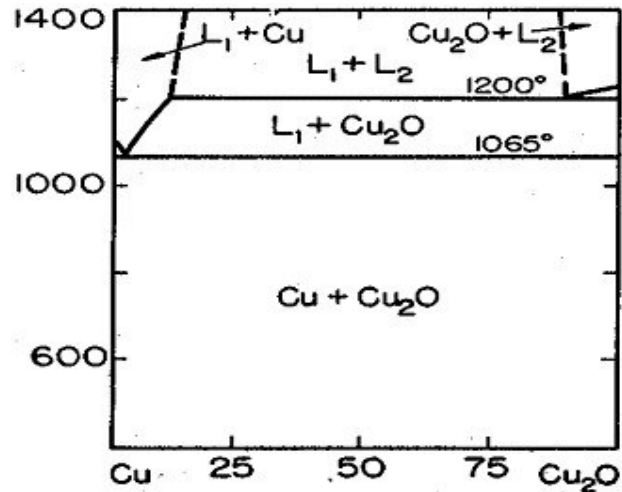
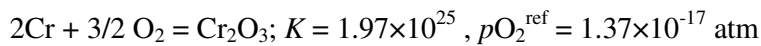


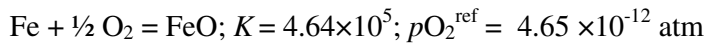
Figure 3-5. Phase diagram of Cu-Cu₂O

Details of calculation (for 1523 K):

Cr/Cr₂O₃ reference



Fe/FeO reference



| Cr/Cr ₂ O ₃ reference | | Fe/FeO reference | |
|---|----------------------------|------------------|----------------------------|
| E [mV] | log (pO ₂ /atm) | E [mV] | log (pO ₂ /atm) |
| -124 | -15.22 | -621 | -3.11 |
| -116 | -15.33 | -603 | -3.35 |
| -111 | -15.39 | -589 | -3.53 |
| -108 | -15.43 | -567 | -3.82 |

Table 3-1. EMF results when testing oxygen probes with Cr/Cr₂O₃ and Fe/FeO references in a Cu melt in contact with Cu₂O, at 1523 K. Different values are for repeat tests.

The oxygen partial pressure for both reference electrodes are completely different, values obtained with Fe/FeO reference electrodes are close to the expected results.

A second test was performed with the experimental matte and slag in a CO-CO₂-SO₂ gas mixture. The results obtained with the Cr/Cr₂O₃ solid electrolyte are presented in this chapter while the results obtained with Fe/FeO solid electrolyte are presented in the next chapter.

❖ Tests run using Cr/Cr₂O₃ reference electrode.

EMF results obtained using Cr/Cr₂O₃ as reference in different tests, the iron content varying from 8.8 % to 4 % in the matte, with CO/CO₂/SO₂ gas mixture are given below.

| Test 1 | 8.4wt%Fe | Test 2 | 4.2wt%Fe | Test 3 | 2.2wt%Fe | Test 4 | 1.3wt%Fe |
|----------|---------------------------|----------|---------------------------|----------|---------------------------|----------|---------------------------|
| EMF (mV) | log pO ₂ (atm) | EMF (mV) | log pO ₂ (atm) | EMF (mV) | log pO ₂ (atm) | EMF (mV) | log pO ₂ (atm) |
| -297 | -12.87 | -286 | -13.02 | -129 | -15.10 | -124 | -15.16 |
| -268 | -13.26 | -231 | -13.75 | -128 | -15.11 | -116 | -15.27 |
| -201 | -14.14 | -176 | -14.47 | -119 | -15.23 | -111 | -15.33 |
| -186 | -14.34 | -129 | -15.10 | -112 | -15.32 | -108 | -15.37 |

Table 3-2. Results of pO₂ measurements in different experimental runs with different Fe contents in the matte in contact with silica-saturated slag, using a Cr/Cr₂O₃ reference. Different values at each matte composition are from repeat tests. The values are erroneous because of the unreliability of this reference under the experimental conditions used here.

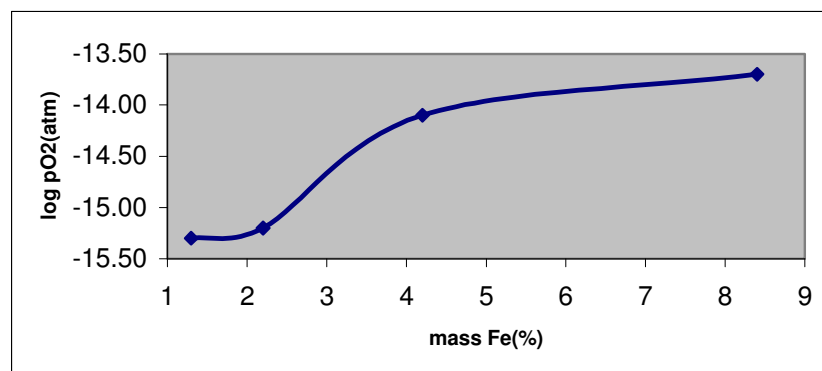


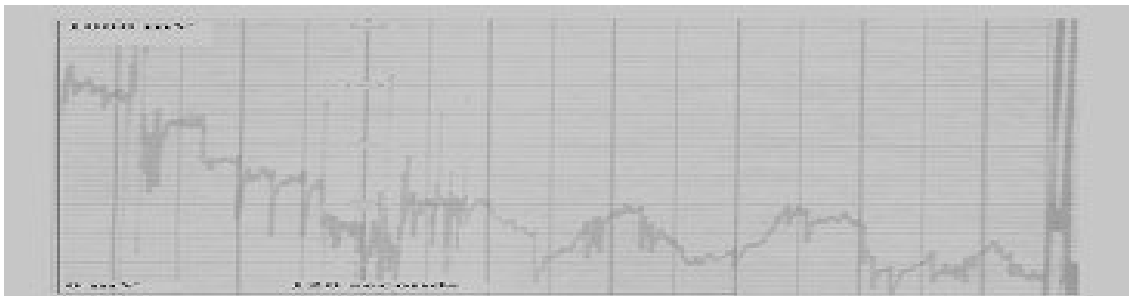
Figure 3-6. Apparent (erroneous) relationship between matte Fe content and measured oxygen activity, for a Cr/Cr₂O₃ reference.

Results presented on table 3.2 shows a trend of increasing pO₂ with a decrease of iron content in matte. The expectation was a decrease of pO₂ with a decrease of (%Fe)_{matte}. Measurements on different rows show results as a function of (%Fe) decrease in the matte.

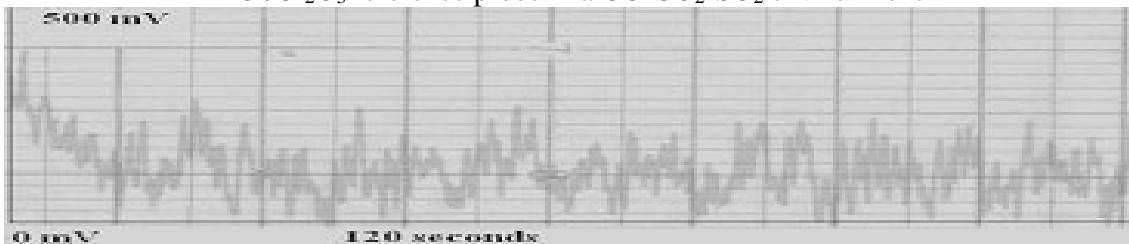
The oxygen partial pressure obtained was very low compare with the expected value, which was about 10⁻⁹ atm (see next chapter for predicted values). Analysis of the zirconia probe after the test revealed that:

- There was possible poor contact between the chrome-chrome oxide (oxygen reference) and the iron wire.
- The surface of the iron wire in the zirconia tube discoloured, more so close to the point of entry into the probe.
- The oxygen partial pressure in the reference electrode is unstable due to gas leakage through the alumina cement on top of the zirconia tube.

It is essential for all the experiments to obtain a stable e.m.f. plateau in order to classify the reading as successful in terms of the exact oxygen potential of the melt. A typical signal trace from Cr/Cr₂O₃ and Fe/FeO probes is given in figure 3-7. The Cr-Cr₂O₃ reference electrode used in the first part of this project was not successful. Several factors could strongly affect oxygen potential measurements when electrochemical oxygen probes were applied in slag-matte melts, such as polarization effects on the electrodes. In the case of polarization effects, the e.m.f. signal declines as a function of time.



Cr/Cr₂O₃ reference probe in a CO-CO₂-SO₂ environment



Fe/FeO reference probe in a CO-CO₂-SO₂ environment

Figure 3-7. Potential vs. time produced by the Cr/Cr₂O₃ and Fe/FeO reference probes.

For these reasons, it was imperative to find an alternative to the chrome-chrome oxide reference electrode utilized in the first phase of experiments.

As the wire used is iron, a mixture of iron-iron oxide was used as reference electrode. The advantage of the use of iron-iron oxide is:

- Oxygen concentration should be constant in all the zirconia tube, avoiding the different colour in the zirconia tube.
- Any excess of iron does not affect the measurement of oxygen activity according to the relation $\text{Fe}_{\text{powder, wire}} + \frac{1}{2} \text{O}_2 = \text{FeO}_{\text{powder}}$

Figure 3-8 shows SEM micrographs of different samples of Cr/Cr₂O₃ before (room temperature) and after the test (1250°C).

For the Cr/Cr₂O₃ grains are not uniform in size and shape before and after, although there is a slight growth of grain after the test observed with an image magnification of 8000. Some researchers [MARTIN, 2003:51] have shown that a much more open pore structure is observed after sintering at 1250°C, which can have an implication for a reduction of the electrode surface area.

Although the colour is different: Bright green before the test and dark green after the test.

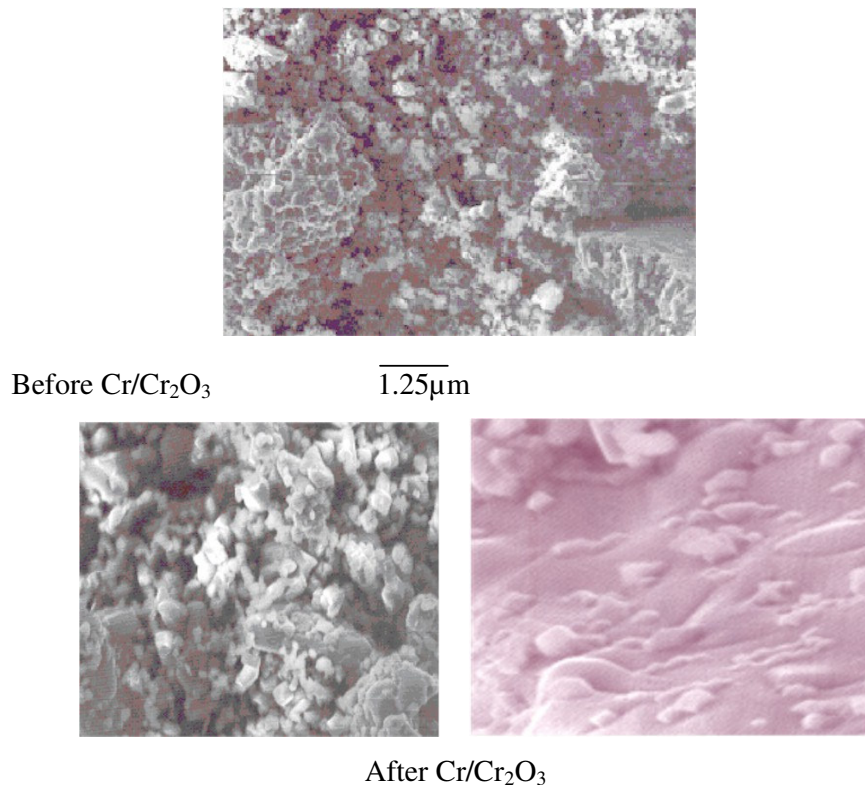


Figure 3-8. SEM micrograph of Cr/Cr₂O₃ solid reference before and after use.

For Fe/FeO, the situation is completely different. Figure 3-9 shows SEM micrographs of Fe/FeO before (room temperature) and after the test (1250°C). At room temperature, the microstructure reveals a non-uniform distribution of grains with small and large grains, and formation of small rods. However a uniform size distribution is observed after the test with a

low porosity. The change in grain size of the FeO is because of sintering at 1250°C as the temperature is not far below the melting point of wustite.

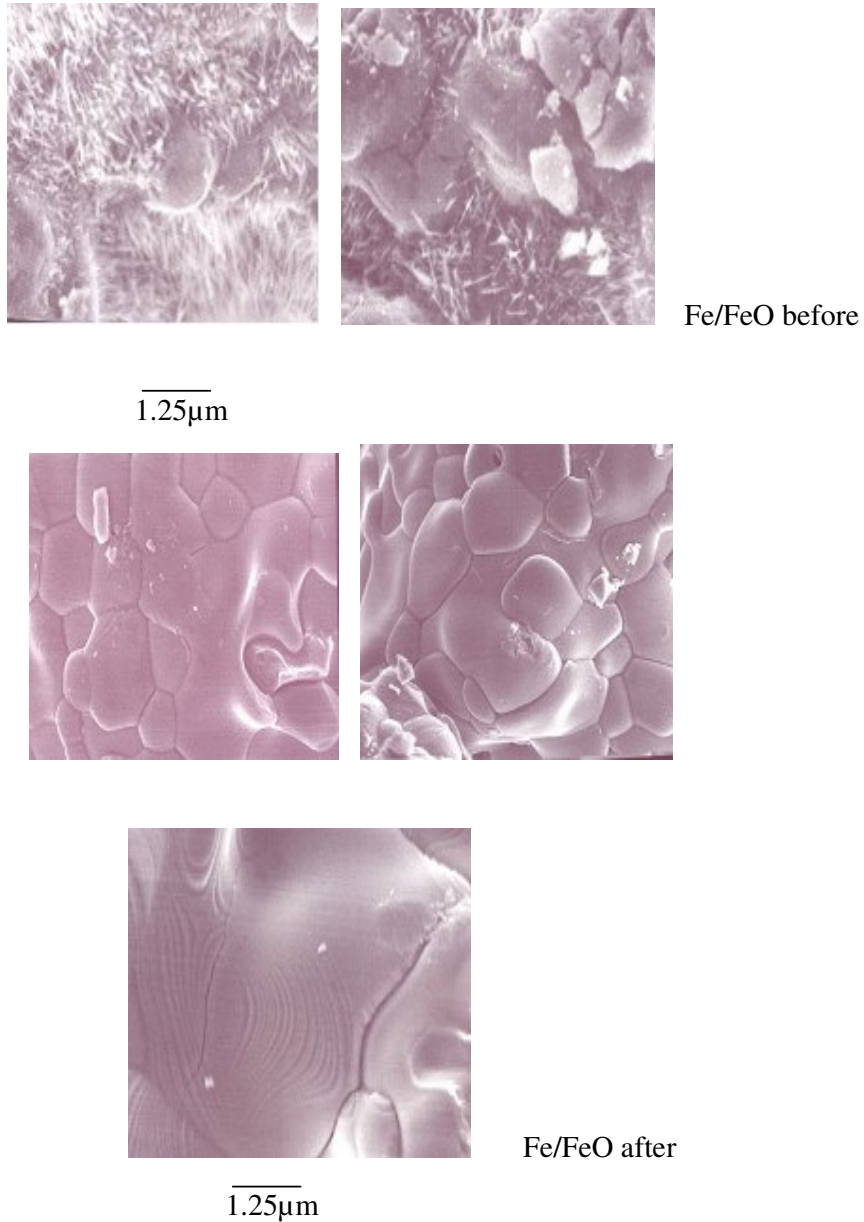


Figure 3-9. SEM micrograph of Fe/FeO solid reference before and after use.

On the basis of these differences between chromium and iron references, the iron reference was preferred to chromium reference as it gave more accurate and stable reading measurements compared to the chromium reference.

❖ Effect of gas mixture in the furnace on the results

Different gas compositions have been used to see their effect on the melt results. Same matte were used for all tests performed at 1250°C: 6.4 wt%Fe, 22.8 wt%Cu, 48.9 wt%Ni and 21.8 wt%S; 6.0 wt%Fe, 22.5 wt%Cu, 50.7 wt%Ni and 21.5 wt%S; 3.7 wt%Fe, 21.5 wt%Cu, 52.8 wt%Ni and 21.9 wt%S. The average slag composition was 54.8 wt%Fe, 16.3 wt%Si and 28.9 wt%O. The iron reference was slowly introduced from the top of the furnace until it reached the liquid melt in a silica crucible. The gas composition used was: 0.44 atm SO₂, 0.45 atm CO₂ and 0.02 atm CO. The expected pO₂ and EMF if equilibrium with the gas was achieved were 3.6x10⁻⁸atm and -294 mV respectively; with a total pressure of 0.91 atm. The gas mixture of CO/CO₂/SO₂ was flown through the gas inlet tube for the whole tests. After a determined time (five minutes for each test), the iron reference was slowly removed from the crucible. EMF values obtained were compared to those obtained in the same conditions but with Ar gas as furnace atmosphere.

Results obtained with Cr-Cr₂O₃ reference electrode showed pO₂ values far too low and unstable compare to Fe-FeO reference electrode in the same conditions.

| (%Fe) _{matte} | Measured EMF (mV) | |
|------------------------|-------------------------------------|-------|
| | CO-CO ₂ -SO ₂ | Ar |
| 6.4 | - 194 | - 196 |
| 6.0 | - 229 | - 230 |
| 3.7 | - 232 | - 234 |

Table 3.3. EMF measurements corrected for the thermal EMF between the Pt and the Fe with the Fe/FeO reference, for different gas atmospheres and for matte compositions, in contact with silica-saturated fayalite slag.

Results of oxygen measurements obtained with CO-CO₂-SO₂ gas mixture and Ar gas using Fe-FeO reference electrode present similar tendency of EMF stability for both cases. The oxygen activity was similar independently on the gas mixture. As the oxygen partial pressure did not affect the values of the results, Ar was chosen as inlet gas for all the subsequent tests.

III.4. Thermal EMF of Pt-Fe

The thermal EMF of a Pt/Fe thermocouple was measured at 1250°C. This was necessary to determine the correct value of the final emf by subtracting the thermal emf from cell voltage measured during oxygen probe measurements.

The Pt/Fe thermocouple was made of reference grade platinum of 99.999% purity and iron of 99+% purity wires (0.5-mm diameter for platinum and 1.8mm diameter for iron) and 55-cm length. The wires were cleaned with alcohol, and inserted in twin bore alumina tube of 2 mm inside diameter. Pt was the negative pole while the Fe was the positive pole during the potential measurements. All of the EMF measurements were made with a calibrated digital voltmeter.

The average EMF of the thermocouple at 1250°C was +17.7 mV.

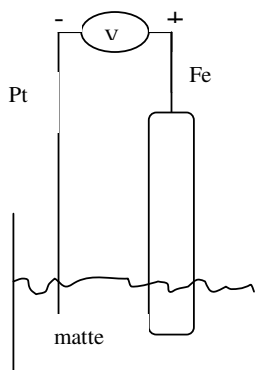


Figure 3-10. Schematic representation of Fe-Pt

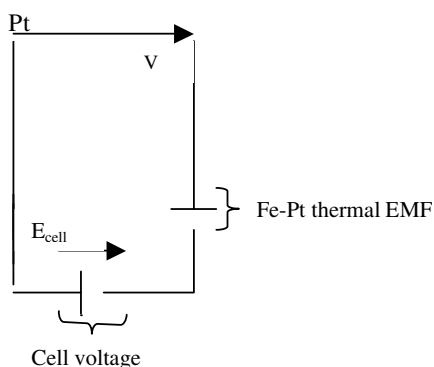


Figure 3-11. Fe-Pt circuit

$$E_{\text{cell}} = E_{\text{meas}} - \text{Thermal EMF}_{\text{Fe-Pt}}$$

$$= E_{\text{meas}} - 0.017 \text{ V}$$

The following graph on figure 3-12 was calculated for values between 0°C and 1000°C and was extrapolated beyond that temperature to estimate the EMF value at 1250°C. The following formula was used in that purpose:

$$S_{AB}(T) = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta U}{\Delta T} \right) = S_B(T) - S_A(T) \text{ [HELLWEGE, 1985:27]}$$

where S is the absolute thermopower of a material, T is absolute temperature, ΔU is the voltage and A, B are the materials forming the thermocouple.

Extrapolation to 1250°C was necessary since the source that was used contained Seebeck coefficients for iron up to 1000°C only.

The graph was extrapolated from two different assumptions:

- the absolute thermopower was kept constant
- the trend of the slope was kept constant

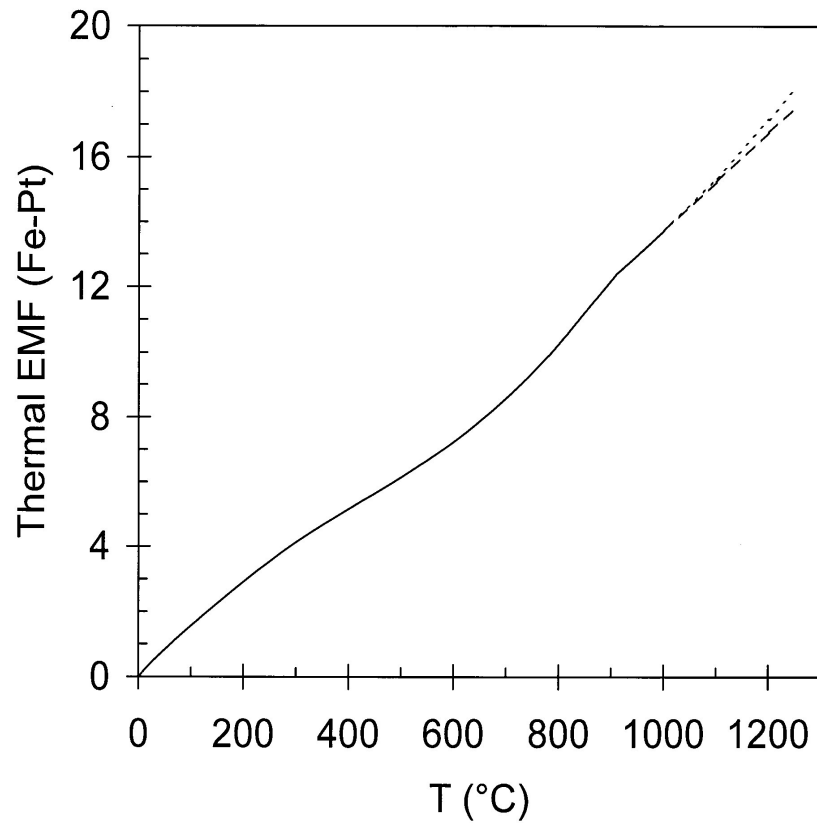


Figure 3-12. Thermal EMF vs temperature for Fe-Pt system

The predicted thermal EMF can be seen to agree with the measured value.

III.5. Experimental apparatus and procedure

III.5.1. Gas system

The choice of CO-CO₂-SO₂ gas mixture was made to provide oxygen and sulphur partial pressure in the furnace environment which may affect the equilibrium with the matte-slag system under conditions of constant temperature.

The gas system supplied high purity CO, CO₂ and SO₂ inlet gas at constant flowrates controlled by means of a digital readout and control system E-7000 supplied by BRONKHORST HIGH-TECH B.V. The oxygen potential in the gas at equilibrium with iron sulphide at 1250°C was calculated (details in Appendix-A) and was in the range of 1.53×10^{-8} to 2.78×10^{-7} atm. The CO/CO₂ ratio for all tests was of the order of 5.85×10^{-2} to 4.34×10^{-2} .

III.5.2. Experimental procedure.

The matte and slag were prepared in the laboratory from chemically pure or high quality commercial materials. Ni₃S₂, Cu₂S and FeS for the matte components were premelted in a silica crucible. The slag with the composition of 62 mass% FeO-38 mass% SiO₂ was premelted by fusing FeO powder and SiO₂ powder under argon atmosphere in an iron crucible. SiO₂ was added in excess of saturation (62mass% FeO-38mass%SiO₂) to assure a condition of silica saturation.

Slag was premelted in a furnace at 1400°C in an argon atmosphere to form fayalite. The cooled slag melt was milled and charged to the furnace as powder form. 5g of slag were used for each test. The matte was also preheated in the same furnace and milled before use in experiments.

Slag and matte powders were mixed intimately. 5g of matte and 5g of slag were put in a SiO₂ crucible with an inner diameter of 33 mm and a height of 37mm.

The charged silica crucible was carefully introduced into the furnace, which was then preflushed with Ar for 30 min to expel all the air. The gas mixture of CO/CO₂/SO₂ (or Ar) flowed through the gas inlet tube. The furnace was heated to 1250°C at 100°C per hour.

After a determined time (1h, 2h, 3h and 4h), samples were sucked into a silica tube by using a syringe at the end of the tube, which is introduced through the sampling hole. Some samples

withdrawn before the end of the complete experiment were quenched in water. The sampling procedure was not easy to apply because of the small melt quantity.

At the end of the experiment the gas mixture was replaced with Ar, and the crucible cooled with the furnace. Each measurement was performed twice.

○ Behaviour of iron

A test of experimental accuracy was performed to study the behaviour of iron content in matte as shown on figure 3.13 and 3.14.

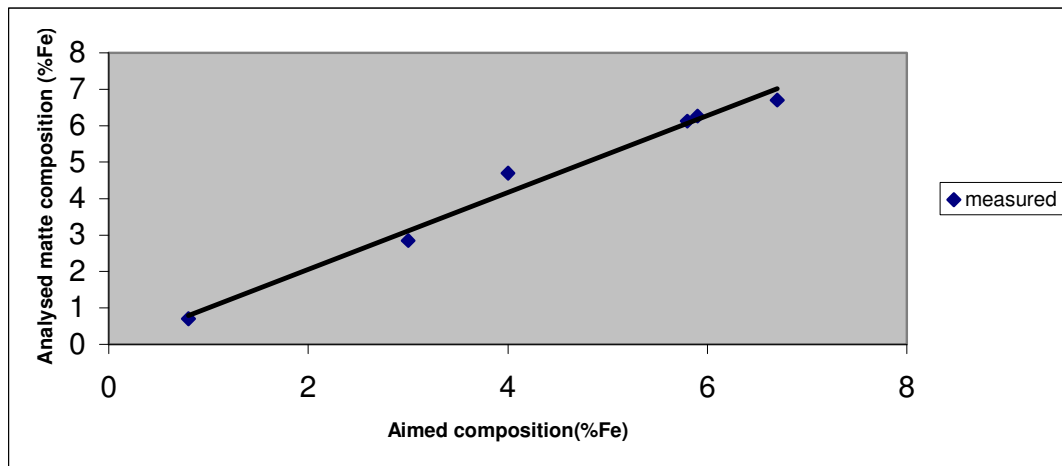


Figure 3-13. Tendency of iron for aimed composition matte vs. analysed matte (FeO slag)

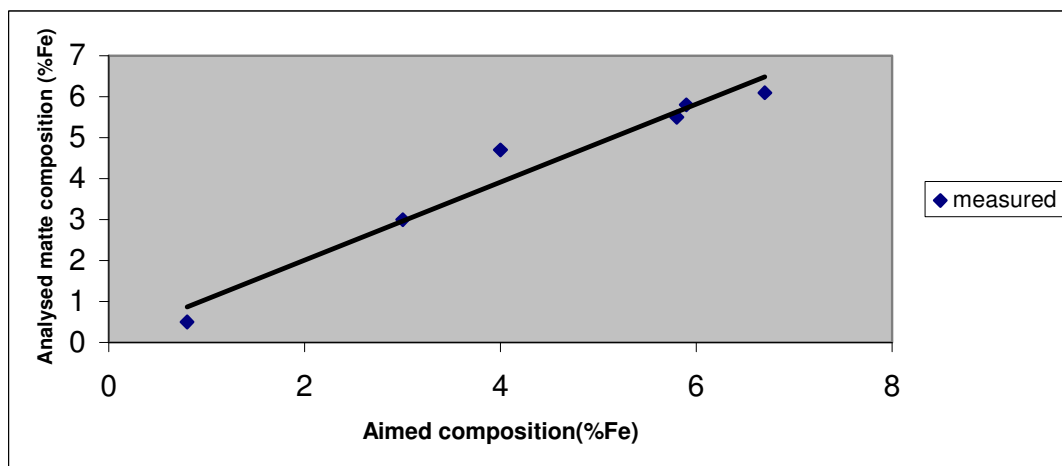


Figure 3-14. Tendency of iron for aimed composition matte vs. analysed matte (FeO/Fe₂O₃ slag)

Figure 3-13 and figure 3-14 show the aimed composition and analysed iron of the matte. Good agreement is shown between the expected values and the measured values.

III.6. Error analysis

The error involved in the different measurements after sampling the melt, cooling the crucible were significant and could change values of the matte-slag composition. These errors were due to

- the delicate manipulation of the probe according to the short height of the melt.
- the disturbance of gas composition in the furnace due to the opening on the top of the furnace for each experiment and sampling.

Confidence intervals (95%) on the potential measurements of all tests were calculated by using the t distribution.

For microprobe measurements, the total amount of the four components in the matte (iron, nickel, copper, and sulphur) varied from 99.6% to 100.4% for analyses done with Fe-FeO reference electrode.