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#### **Synopsis**

Four sulphide minerals – pyrite (FeS $_2$ ), pyrrhotite (Fe $_{1-x}S$ ), pentlandite ([Ni,Fe]<sub>9</sub>S<sub>8</sub>), and chalcopyrite (CuFeS<sub>2</sub>) - contain the base metals and most of the iron in concentrates of platinum group metals (PGMs). In the pyrometallurgical processing of PGM concentrates these sulphides form a matte during smelting, and iron and sulphur are removed from the matte during the converting process. This paper discusses the roasting of Merensky concentrate in air before smelting, with the purpose of reducing the matte load to the converter.

Roasting tests were conducted in a bench-scale rotary kiln at temperatures from 350°C to 700°C. The concentrate tested contained 17.4% sulphur and consisted of 23% pyrrhotite, 16% pentlandite, 11%chalcopyrite, and 2% pyrite. The particles were fine ( $d_{50} = 22 \mu m$ ), and all the sulphide particles were liberated. Roasting in air at 550°C and 650°C for 20 minutes removed respectively 60% and 70% of the sulphur. The iron in the sulphides was oxidized to Fe<sub>3</sub>O<sub>4</sub> (magnetite) at temperatures below  $500^{\circ}\text{C}$  and to Fe<sub>2</sub>O<sub>3</sub> (haematite) at temperatures above  $550^{\circ}\text{C}$ . At  $700^{\circ}\text{C}$  the bed sintered and copper oxides formed. At temperatures below 450  $^{\circ}\text{C}$ oxidation was incomplete: pyrrhotite remained and only 30% of the sulphur was removed. Smelting tests were conducted to assess matte fall and the deportment of copper and nickel to matte. It was evident that roasting resulted in lower matte falls (a drop of approximately 60%) compared with matte falls from unroasted concentrate. The iron and sulphur levels in the matte were reduced to below 3.5% and 22% respec-

This paper also briefly describes the mechanisms by which pyrrhotite, chalcopyrite, and pentlandite are oxidized during roasting. For chalcopyrite, the mechanism proceeds through an intermediate solid solution phase, which extends from  $\text{Cu}_{1.02}\text{Fe}_{1.04}\text{S}_2$  to  $\text{Cu}_{2.04}\text{Fe}_{0.72}\text{S}_2$  to a copper-rich solid solution of bornite ( $Cu_4Fe_{1.4}S_4$ – $Cu_2S$ ). The oxidation of pentlandite proceeds through a monosulphide solid solution (Ni<sub>0.39</sub>Fe<sub>0.53</sub>S–Ni<sub>0.74</sub>Fe<sub>0.15</sub>S) to a solid solution of heazlewoodite ([Ni,Fe]<sub>3±x</sub>S<sub>2</sub>). These mechanisms are explored in relation to chemical thermodynamics and microstructures.

roasting, PGM, concentrate, pyrrhotite, pentlandite, chalcopyrite, smelting, matte, base metal.

# Introduction

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Producers of nickel and copper have been partially roasting concentrates to reduce levels of sulphur and volatile impurities such as arsenic, antimony, and lead for many years (US Environmental Protection Agency, 1995). At Sudbury (Glencore) and Thompson (Vale Inco), concentrate is roasted in fluidized beds (two at each plant) before smelting. The grate diameters of the roasters at Sudbury are 5.6

m, and the freeboard 8 m, while the grate diameters at Thompson are 5.5 m, and the freeboard 6.4 m. The expanded freeboard begins 6.5 m above the grate (Warner et al., 2007). The roasters at Thompson process approximately 50 dry t/h of concentrate. The bed temperatures of the roasters at Thompson and Sudbury are respectively  $600^{\circ}\text{C}$  and 760°C. Both roasters operate under oxidizing atmospheres of air or oxygen-enriched air. Approximately 40% of the sulphur is removed from the concentrate at Thompson, and 70% at Sudbury (Pandher and Utigard, 2010).

Roasting can in principle be applied to PGM concentrates, which besides gangue minerals (mostly minerals in the pyroxene group) comprise pyrite (FeS<sub>2</sub>), pyrrhotite (Fe<sub>1-x</sub>S), chalcopyrite (CuFeS<sub>2</sub>), and pentlandite ([Ni,Fe] $_9S_8$ ). The base metal sulphides are the very same minerals roasted in the copper and nickel industries. In the ConRoast process developed at Mintek, PGM concentrates are dead-roasted to remove all of the sulphur (Jones, 1999). Subsequent smelting under reducing conditions produces a Cu-Ni-bearing alloy, which collects the PGMs. Many of the aims of roasting could be met by partially oxidizing the base metal sulphides. Partial roasting would desulphurize the concentrate, oxidize some or most of the iron, and the roasted concentrate would still produce a matte.

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This study focused on partial roasting of a Merensky concentrate. It examined how the conditions of roasting affect the degree of desulphurization, which phases form, how these phases affect matte fall, and the deportment of base metals to the matte. Mechanisms for the oxidation of pyrrhotite, pentlandite, and chalcopyrite were also determined.

#### **Experimental**

#### Sample

The concentrate sample — a product of flotation — originated from the Merensky Reef in Limpopo Province, South Africa. The bulk modal analysis of the concentrate, as determined with a Mineral Liberation Analyser (MLA), is given in Table I. The main sulphide minerals present in the concentrate were pyrrhotite (Fe<sub>1-x</sub>S), pentlandite ([Ni,Fe]<sub>9</sub>S<sub>8</sub>), and chalcopyrite (CuFeS<sub>2</sub>); together accounting for 50.1% of the mass of the concentrate. The metal sulphides in sub-samples showed a degree of variation with respect to phase compositions (Rambiyana, 2015). Attaching a fixed set of conditons to a degree of oxidation is therefore problematic.

# **Procedure**

Roasting tests were conducted in a rotating-tube furnace (Figure 1). This reactor provided good gas-solid mixing and contact for the duration of a test and readily dissipated heat from the exothermic reactions. The furnace was fitted with a quartz work tube, 100 mm in internal diameter and 1150 mm long. The work tube was externally heated, which resulted in a hot zone of 550 mm. The tube was fitted with lifters to ensure good gas-solid mixing and contact. The roasting tests were conducted under isothermal conditions at temperatures ranging from 400°C to 650°C and a residence time of 20 minutes. The work tube was purged with air at a flow rate of 42 NL/min. Roasting was conducted with the reactor run in continuous mode.

Table I							
Mineral composition of the Merensky concentrate (bulk modal analysis)							
Mineral	Mass %						
Base meta	ll sulphides						
Pyrrhotite (Fe <sub>1-x</sub> S)	22.9						
Pentlandite ([Ni,Fe] <sub>9</sub> S <sub>8</sub> )	16.0						
Chalcopyrite (CuFeS <sub>2</sub> )	11.2						
Pyrite (FeS <sub>2</sub> )	2.0						
Bornite (Cu <sub>5</sub> FeS <sub>4</sub> )	0.1						
Other sulphides	0.2						
Gar	ngue						
Enstatite (Mg <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> )	30.6						
Other	16.9						



Figure 1 - View of the rotating-tube furnace (RTF)

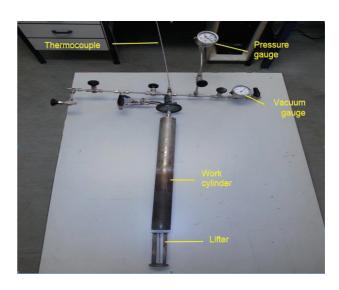


Figure 2 - View of the angular reciprocating capsule (ARC)

The sulphation reactions were tested in an angular reciprocating capsule that was heated in a horizontal splitshell furnace. This capsule rotated about its longitudinal axis, but alternated between clockwise and anticlockwise (Figure 2). The capsule had an internal diameter of 44 mm, a working zone of 120 mm, and a volume of 954 cm<sup>3</sup>. It was also fitted with lifters. The temperature of the bed was measured with a K-type thermocouple. Tests were carried out on 50 g samples held at 500°C under controlled atmospheres (air at 1 and 2 bar) for one hour. The pressure in the capsule was recorded for the duration of the tests. The capsule provided 0.0148 moles of oxygen for every 1 bar of pressure. Smelting tests were conducted in a vertical-tube furnace. The mullite work tube had an internal diameter of 80 mm and a hot zone of 150 mm. Unroasted concentrate, concentrate roasted at 550°C, and concentrate roasted at 650°C were smelted in alumina crucibles. A flux consisting

of 10 g  $Al_2O_3$  and 10 g CaO for every 100 g of concentrate was added to the charge. The charge was mixed well and smelted at 1500°C for 30 minutes. The sample was furnacecooled.

### Analytical techniques

The products of roasting and smelting were examined and analysed by an array of techniques. These included X-ray diffraction analysis (XRD); scanning electron microscopy (SEM), using energy dispersive spectrometry (EDS); quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN); and quantification of the amount of ferromagnetic material. XRD analysis was performed with a PANalytical X'Pert Pro powder diffractometer in  $\theta$ - $\theta$  configuration with an X'Celerator detector and variable divergence and receiving slits. The radiation was Fe-filtered Co-Ka ( $\lambda$ =1.789 Å). Phases were identified by means of X'Pert Highscore Plus software. SEM-EDS was performed with a Mineral Liberation Analyser to identify phases and analyse their compositions. QEMSCAN-EDS was used to create mineral maps of the samples. The percentage ferromagnetic material was determined with a Satmagan 135 (Rapiscan Systems). This instrument measures the ferromagnetic signal from a sample and correlates it with magnetite content.

#### **Results**

# Roasting mechanisms

Roasting tests focused on two temperatures, 450°C and 650°C. These temperatures were chosen based on data published in the literature for the pertinent systems Fe-Ni-S and Fe-Cu-S. Rates of oxidation are too slow at temperatures below 400°C, while particles sinter and stick to the wall of the work tube at temperatures above 700°C. Tests were run in air at temperature for residence times ranging from several minutes to 25 minutes. Most tests were run with the sample passing through the kiln in 20 minutes. The phase chemistry of the roasted samples was analysed using SEM-EDS and XRD. By combining the conditions of roasting and phase chemical results with phase diagrams and thermochemical data, the mechanisms for the oxidation of the three primary sulphide minerals in the PGM concentrate were postulated.

# Pyrrhotite (Fe<sub>1-x</sub>S)

Pyrrhotite reacted with oxygen to form iron oxide. This reaction was rapid compared with the oxidation of the base metal sulphides. In the 400—650°C temperature range pyrrhotite disappeared within 20 minutes. Chemical thermodynamics predicts that oxidation should result in the formation of Fe<sub>2</sub>O<sub>3</sub> (haematite) (Muan and Osborn, 1965: Figure 12). However, Fe<sub>3</sub>O<sub>4</sub> (magnetite) formed as an intermediate phase. These observations are consistent with the assumption that in the temperature range 400-650°C,

the oxidation of  $Fe_3O_4$  to  $Fe_2O_3$  is relatively slow and that the oxidation rate increases with temperature. At temperatures below 500°C oxidation did not proceed much beyond Fe<sub>3</sub>O<sub>4</sub>. As temperatures increased from 500°C to 650°C, increasing amounts of Fe<sub>2</sub>O<sub>3</sub> formed and less Fe<sub>3</sub>O<sub>4</sub>. The reaction occurred at the interface between pyrrhotite ( $Fe_{1-x}S$ ) and the iron oxide. The reaction might proceed by means of a shrinking core but, given that the pyrrhotite is porous, it might occur at several loci within each particle.

As the conversion of Fe<sub>3</sub>O<sub>4</sub> to Fe<sub>2</sub>O<sub>3</sub> also occurred during the oxidation of the base metal sulphides, it is discussed in more detail in a subsequent section of this paper. This 'duplex layer' has been observed in other studies on the roasting of base metal sulphides (Xia, Pring, and Brugger, 2012).

### Chalcopyrite (CuFeS<sub>2</sub>)

Chalcopyrite particles in the initial stages of oxidation had

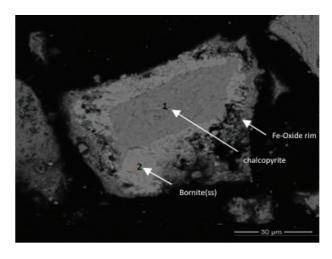


Figure 3 - Backscattered electron (BSE) image of bornite(ss) around a core of chalcopyrite. 1 - Cu<sub>0.9</sub>Fe<sub>0.98</sub>S<sub>2</sub>; 2 - Cu<sub>4.73</sub>Fe<sub>0.94</sub>S<sub>4</sub>

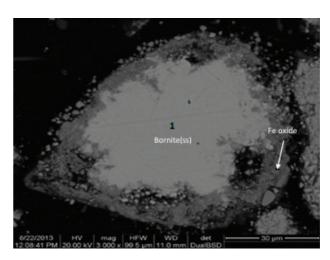


Figure 4 - Backscattered electron (BSE) image of bornite(ss) occupying a core that was formerly chalcopyrite. 1 - Cu<sub>5.77</sub>Fe<sub>0.24</sub>S<sub>4</sub>

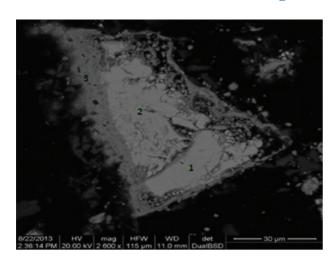


Figure 5 – Backscattered electron (BSE) image of a particle of mss and iron oxide after oxidation (formerly pentlandite). 1 - Ni<sub>0.69</sub>Fe<sub>0.18</sub>S; 2 - Ni<sub>0.78</sub>Fe<sub>0.12</sub>S; 3 – Fe oxide rim

compositions at the iron-rich end of the bornite solidsolution series. Chalcopyrite occupied a core that shrunk as bornite(ss) developed around it (Figure 3). Iron oxide (Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>) formed on the surface of the bornite(ss). The disappearance of chalcopyrite was rapid. Further oxidation proceeded by the reaction of oxygen with iron and sulphur in bornite(ss), which retained its structure but became increasingly depleted in iron and (somewhat less) in sulphur (Figure 4). It was difficult to accurately determine the change in bornite(ss) phase compositions radially with SEM-EDS, as the particles were too fine. It is therefore not clear whether the chalcopyrite disappeared before bornite(ss) started to oxidize. Cu-rich end-members of the bornite(ss) were not detected with chalcopyrite cores in a particle. Reactions were faster at higher temperatures. Chalcopyrite disappeared after roasting for 20 minutes at 450°C and 650°C. However, the bornite(ss) was richer in copper at higher temperatures and richer in iron at lower temperatures after 20 minutes. This empirical evidence is in disagreement with the phase relations in the system Fe-Cu-S (Rambiyana, 2015). An intermediate solid solution (iss) was found to be stable at temperatures above 400°C, occupying a region of the phase diagram between CuFeS2 (chalcopyrite) and the bornite(ss). The presence of iss could not be confirmed in this study.

# Pentlandite ([Ni,Fe]<sub>9</sub>S<sub>8</sub>)

An initial rapid reaction resulted in pentlandite losing iron through oxidation to  $Fe_3O_4$  and transforming into the *mss* (monosulphide solid solution) phase, which became progressively depleted in iron through further oxidation. An individual particle could exhibit variable compositions of the *mss* phase (Figure 5). More  $Fe_3O_4$  (magnetite) formed and was oxidized to  $Fe_2O_3$ . The Ni-rich *mss* finally became unstable and underwent a structural change to heazlewoodite (*ss*). This agrees with the work of Zamalloa and

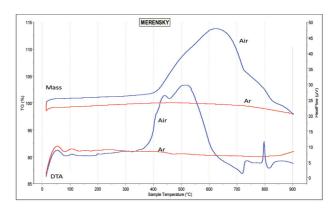


Figure 6 – TG-DTA curves of Merensky concentrate roasted in air and argon (heating rate 5°C/min)

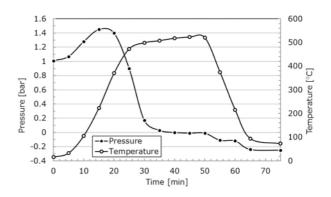


Figure 7 – Change in pressure and temperature in the angular reciprocating capsule during the roasting of Merensky concentrate

Utigard (1996), who identified (Ni,Fe) $_{3\pm x}S_2$  (heazlewoodite) in particles roasted at 747°C. This reaction sequence was observed at all temperatures above 400°C. Pentlandite disappeared after 10 minutes at all temperatures above 400°C. Heazlewoodite (ss) appeared after 20 minutes at temperatures above 650°C.

# The absence of sulphates

The formation of sulphates during roasting is undesirable as sulphates retain sulphur. Sulphate formation can, however, be avoided by considering the thermodynamic relations depicted in the predominance diagrams of Fe-Ni-S-O and Fe-Cu-S-O. High partial pressures of  $SO_2$  and  $O_2$  tend to stabilize the metal sulphates  $FeSO_4$  and  $Fe_2(SO_4)_3$ . To avoid the formation of sulphates during roasting of base metal sulphides,  $pSO_2$  should therefore be kept low (<1%). However, higher partial pressures of  $SO_2$  may be established inadvertently – fixed beds of fine particles promote high  $SO_2$  partial pressures within the bed, as  $SO_2$  is unable to diffuse rapidly to the free surface of the bed. Examples include particulate beds contained in crucibles or boats used in thermogravimetry and in work utilizing muffle furnaces. Disturbing the bed frees the 'trapped'  $SO_2$ . This was

accomplished in the rotating-tube furnace by the action of the lifters in the work tube. Compressed air was also forced in at the feed end of the work tube and extracted by means of an extraction duct inserted at the discharge end. A high  $pO_2$  and a low  $pSO_2$  were therefore maintained in the tube. No sulphates were detected in any of the products from tests conducted in the rotating-tube furnace. Roasting of concentrate in a thermobalance and the angular reciprocating capsule, however, produced metal sulphates, as indicated by a gain in mass shown by the thermobalance (Figure 6). The sample started to gain mass from approximately 350°C, and the gain became significant between 400°C and 620°C (Figure 6). It is at these temperatures, under high SO<sub>2</sub> partial pressures, that metal sulphates can be expected to form. At temperatures greater than 620°C the sample lost mass. This loss is associated with the decomposition of sulphates, which are thermodynamically unstable at high temperatures. The temperatures for the thermal decomposition of ferrous sulphate, copper sulphate, and nickel sulphate are reported in the literature (Kolta and Askar, 1975). The two peaks in the TG curve — one at 725°C, the other at 830°C — indicate the decomposition of different sulphates at their respective thermal stability limits.

Sulphates were also formed in the angular reciprocating capsule, as high  $SO_2$  partial pressures were established by maintaining a closed system. The pressure in the capsule increased while the capsule was being heated to temperature (Figure 7). The initial increase in pressure can be attributed principally to the thermal expansion of gas (air) in the freeboard. The pressure dropped when the temperature exceeded approximately  $200^{\circ}$ C, and the final recorded pressure was lower than the pressure in the system at the beginning of the test. From these measurements, and from an understanding of the conditions that promote sulphate

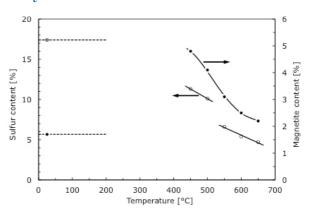


Figure 8 – Sulphur and magnetite contents in the concentrate as a function of roasting temperature (roasting in air for 20 minutes)

formation, it can be concluded that oxygen was withdrawn from the gas phase and reacted with the sulphides to form sulphates.

# Sulphur removal and the formation of iron oxides

The primary objective of roasting is to lower the levels of sulphur in a concentrate. A second objective is the preferential oxidation of iron in the base metal sulphides so that the iron can be removed in the slag phase during smelting. Iron is oxidized to either  $Fe_2O_3$  or  $Fe_3O_4$ . Where possible, magnetite formation should be avoided as iron-bearing spinels form a viscous intermediate layer between the matte and slag layers during smelting. This viscous layer results in increased levels of matte entrainment in, and PGM losses to, the slag. The build-up of  $Fe_3O_4$  or other spinels during smelting also reduces furnace capacity (Jones, 1999).

The amount of either  $Fe_3O_4$  or  $Fe_2O_3$  in the product is also linked to temperature (Muan and Osborn, 1965). The unroasted concentrate contained 17.4% sulphur. The degree

Table II											
Compo	sitions of p	hases sho	own in Fig	gure 9 (wt	%)						
	A†			B‡		C (insert in B)		D			
	1	2	3	1	2*	1	2	Matrix	Digenite*	Silicate	Spinel#
S	37.6	34.5	31.6	26.7	21.3	_	_	28.23	21.3	_	_
Fe	58.6	40.0	35.8	_	_	2.0	2.4	_	_	15.0	60.2
Ni	3.8	20.8	16.4	73.4	_	62.0	70.7	71.77	_	1.4	8.7
Cu	_	4.7	16.3	_	78.7	26.0	26.2	_	78.7	_	_
Pt	_	_	_	_	_	10.0	_	_	<u> </u>	_	_
Pd	_	_	_	_	_	_	0.8	_	_	_	_
Mg	_	_	_	_	_	_	_	_	<u> </u>	4.2	
Al		_	_	_	_	_	_	_	l –	6.0	9.9
Si	_	_	_	_	_	_	_	_	_	19.1	_
Ca	_	_	_	_	_	_	_	_	<u> </u>	21.5	_
0	_	_	_	_	_	_	_	_	_	32.8	21.2

<sup>\*</sup> These phases are digenite(ss) with Cu<sub>9.3</sub>S<sub>5</sub>

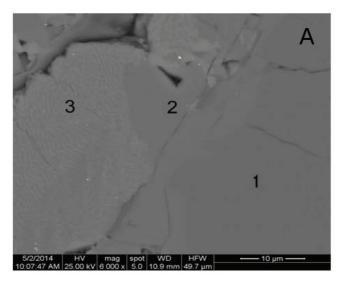
 $<sup>^{\</sup>dagger}$  A phase assemblage of (1) Fe $_{0.9}$ Ni $_{0.5}$ S (pyrrhotite[ss]), (2) (Fe $_{0.6}$ Ni $_{0.3}$ Cu $_{0.06}$ ) $_{9}$ S<sub>8</sub>(pentlandite[ss]), and (3) Cu $_{9}$ S<sub>5</sub> (digenite) in a matrix of pentlandite(ss) is postulated

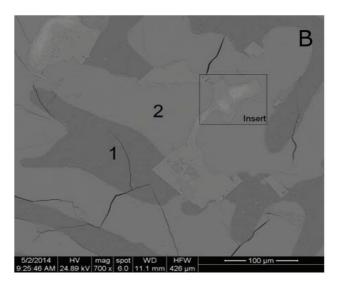
<sup>†</sup> The phase assemblage comprises (1) heazlewoodite(ss) and (2) digenite(ss), which is intergrown with heazlewoodite(ss) in a macro- and micro-texture

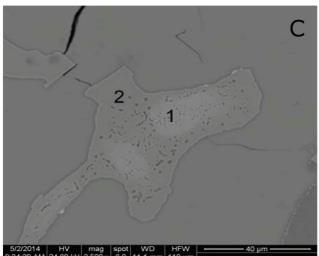
<sup>#</sup> The spinel composition matches the following stoichiometry (Fe<sub>0.7</sub>Ni<sub>0.3</sub>)(Al<sub>0.7</sub>Fe<sub>1.3</sub>)O<sub>4</sub>

Compositions of phases shown in Figure 10B (wt%)										
	1	2	3	4	5*	6#	7	8		
Fe	1.46	1.76	2.22	15.94	62.95	38.56	1.65	2.31		
Ni	3.19	5.36		1.73	7.97	15.01	15.15	3.98		
Cu	95.35	88.96	94.58					93.72		
Mg				4.56	2.21	6.30	5.47			
Al				5.98	9.96	21.09	6.25			
Si				20.97			20.67			
Ca				23.40			23.81			
Cr						2.44				
0		3.88	3.20	27.42	16.91	16.60	27.99			

<sup>\*</sup> A spinel, (Mg<sub>0.16</sub>Ni<sub>0.24</sub>Fe<sup>2+</sup><sub>0.61</sub>)(Al<sub>0.64</sub>Fe<sup>3+</sup><sub>1.36</sub>)O<sub>4</sub>







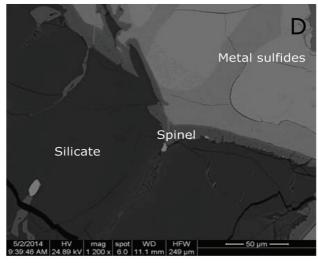
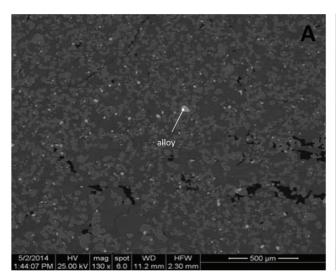


Figure 9 – Backscattered electron (BSE) images of phases observed in the smelted samples. (A) matte from unroasted concentrate; (B) matte from concentrate roasted at 550°C; (C) insert appearing in (B); (D) matte and slag from concentrate roasted at 550°C. (Phase compositions are given in Table II)

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<sup>\*</sup> A spinel,  $(Mg_{0.38}Ni_{0.38}Fe^{2+}_{0.24})(Al_{1.15}Cr_{0.07}Fe^{3+}_{0.78})O_4$ 



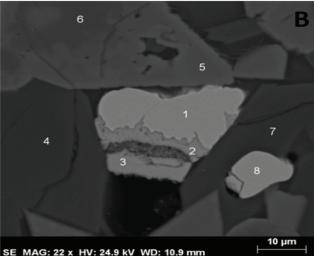


Figure 10 – Backscattered electron (BSE) images of the smelted concentrate roasted at 650°C. (A) Typical microstructure, (B) Typical phase assemblage at higher magnification (phase compositions are given in Table III)

of desulphurization increases with increasing temperature, as reactions are faster at higher temperatures and, for the same duration of oxidation (20 minutes), the extent of desulphurization is higher. Since the concentrate sample consisted of different proportions of pyrrhotite, pentlandite, and chalcopyrite, the overall degree of desulphurization reflects the joint extents of oxidation of these different sulphide phases. At 550°C the sulphur content in the roasted concentrate dropped to 6.5% (a decrease in sulphur content of approximately 60%), while at 650°C it dropped to just over 5% (a decrease of 70%).

The magnetite content also decreased with temperature (Figure 8). Oxidation produced both  $Fe_2O_3$  and  $Fe_3O_4$ . At approximately 400°C, after 20 minute of roasting, the magnetite content was at its highest and decreased steadily with increasing temperature. Thermodynamics predicts that haematite is the stable form of iron oxide in air, in the temperature range used in this study (Muan and Osborn, 1965. The presence of magnetite therefore reflects non-equilibrium conditions.

# **Smelting**

When concentrate is smelted, PGMs are collected in the matte phase. The principal aim of partially roasting the concentrate before smelting is to decrease the matte fall, thereby resulting in a higher PGM concentration in the matte phase. It is thus important to know how a roasted concentrate will behave on smelting. Bench-scale smelting tests were therefore conducted on the roasted concentrate, using alumina crucibles. The smelting tests were evaluated according to the matte fall (as a percentage of material charged to the crucible), the deportment of Ni and Cu to the matte, the collection of PGMs in the matte (if this could be measured accurately on a small scale), as well as the composition of the matte.

Since roasting lowered the sulphur concentrations in the concentrate by approximately 60%, from 17.4 % to 6.5 % at 550°C, while the concentration of magnetite formed decreased from approximately 4.8% to 3.1% as the temperature increased from 450°C to 550°C, it was decided to do the smelting tests only on the roasted concentrate samples of lower magnetite content, i.e. the samples that were roasted at 550°C and 650°C. Matte was collected from the smelting of fresh concentrate, while matte associated with an alloy phase was collected from smelting of concentrate roasted at 550°C (Figure 9). Smelting of the concentrate roasted at 650°C produced only an alloy. In all three tests the matte or alloy collected in fine beads and prills, which did not fall under gravity to the bottom of the crucible. The viscosity of the slag was therefore too high to facilitate the coalescence of matte or alloy into a button within 30 minutes. Dispersed matte hindered the direct measurement of matte fall. Matte fall was subsequently estimated at 45% for the unroasted concentrate and 15% for the concentrate roasted at 550°C, using a least-squares regression of concentrate and matte compositions within the framework of a mass balance. These values are lower than the matte falls calculated from all sulphides that can possibly report to the matte: 52% for the unroasted concentrate, 21% for the concentrate roasted at 550°C, and 17.6% for the concentrate roasted at 650°C.

Although matte (from the unroasted and 550°C roasted concentrates) and alloy (from the 650°C roasted concentrate) did not coalesce, the compositions of matte and alloy beads and prills as well as the slags could be determined. The matte from the concentrate roasted at 550°C comprised  $Ni_3S_2$  (heazlewoodite),  $Cu_9S_5$  (digenite),  $Cu_{1.97}S$  (djurleite), and  $Cu_2S$  (chalcocite) (Table II). The PGM-containing alloy was associated only with nickel-copper-iron alloys (Figure 9C). Some nickel was lost to the slag (estimated in a mass

balance calculation to be less than 10% in silicates and spinel). Copper was not detected in any of the phases in the slag.

The formation of a Cu-rich alloy in the smelted product of the concentrate roasted at 650°C was unexpected (Figure 10). With 5% residual sulphur in this roasted product, up to 10% matte was expected to form. The alloy was entrained in an iron-rich spinel in a silicate matrix of variable composition (Table III).

### **Conclusions**

- ➤ It is possible to selectively oxidize the iron in sulphides that are present in a Merensky concentrate, leave the nickel and copper in sulphide phases, and produce a matte on smelting. This was achieved by roasting the concentrate at 550°C for 20 minutes
- ➤ The oxidation of the iron-containing sulphide phases at temperatures between 500°C and 650°C proceeded as follows:
  - Pyrrhotite oxidized to magnetite, which in turn oxidized to haematite. The extent of haematite formation increased with roasting temperature
  - Chalcopyrite oxidized to form a bornite(ss) phase, with compositions close to the Fe-rich end member at 550°C and a Cu-rich end member at 650°C
  - Pentlandite oxidized to monosulphide solid solution (*mss*). The *mss* composition tended towards the NiS (millerite) end-member of the solution with oxidation at higher temperatures.
- ➤ Roasting at 550°C lowered the sulphur levels by at least 60%, from 17.4% to 6.5% total sulphur, and at 650°C, sulphur was lowered by 70%, from 17.4% to 4.9% total sulphur
- ➤ The magnetite content of the calcine roasted at 550°C was double that of unroasted concentrate
- ➤ As long as the oxygen partial pressure in the rotary furnace remained high (close to that of air), metal sulphates did not form
- ➤ Smelting tests revealed that concentrates roasted at 550°C for 20 minutes produced matte and a greatly reduced matte fall. The iron levels in the matte were below 3.5%. The sulphur content of this matte was just above 20%, compared to a sulphur content of more than 30% for matte from unroasted concentrate
- ➤ The matte produced from roasted concentrate resembled the converter matte in composition.

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