NICKEL, COPPER AND COBALT DISTRIBUTION AND EQUILIBRIA IN ANGLO PLATINUM FURNACE SLAGS

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ABSTRACT

The base metals (nickel, copper and cobalt) are recovered as part of the smelting and refining process operated by Anglo Platinum in South Africa. This study focuses on the losses of these metals to furnace slag, as well as the effect of changing furnace feed and hence slag properties, and the use of a modelling program to predict base metal distribution between slag and matte.

A combination of electron microbeam and Mössbauer techniques were used to characterize the base metal distribution in the slag, and the variation of losses with depth in the slag bath.

Initial modelling predictions assuming bulk matte-slag equilibrium underestimated base metal dissolution into the slag, and the values so obtained did not resemble measured values. Subsequent modelling with pO_2 calculated from the Mössbauer results showed that the tapped slag is more likely to be in equilibrium with entrained matte and/or overlying concentrate.

INTRODUCTION

Three smelters are operated by Anglo Platinum in the North West and Limpopo Provinces of South Africa to process platinum-bearing ores. More than eighty per cent of worldwide platinum group element reserves are found in South Africa [1] and the base metals (nickel, copper and cobalt) are recovered as part of the platinum-producing process. The metals are mined from the Bushveld Complex, mainly as sulphide minerals contained in the platinum ores – the Merensky reef, the Platreef and the UG-2 chromitite reef. After mining, the base metals pass through the concentrating, smelting and converting process route and are finally recovered from the nickel-copper converter matte by electrowinning at the Rustenburg Base Metals Refinery [2].

The history and present function of the two electric furnaces at Waterval Smelter have been described in the literature [3, 4]. The furnaces are rated at 39 MVA (34 MW). Both are 8 x 26 m in size, and current passes between three pairs of Söderberg electrodes, situated down the length of the furnace. The interdependence of slag composition, conductivity, viscosity, and liquidus temperature in electric furnaces of this type has been emphasised – these must be carefully controlled [5].

Blended ore concentrate is dried in the flash driers, mixed with limestone flux, and then fed into the furnaces. Up until 2001, molten converter slag was returned to the furnaces, but latterly this practice has been phased out to coincide with the commissioning of two Ausmelt converters to replace the six older Peirce Smith converters. Matte from the six-in-line furnaces is tapped into ladles and granulated in water, after which it is stored prior to being used as converter feed. Furnace slag is tapped continuously and granulated in water. This is then collected by rake classifiers, dewatered and stored before treatment in the Slag Plant, where a portion of the slag is milled and floated, and the concentrate returned to the furnaces. The nature of matte losses experienced in the Slag Plant has been documented [6].

Slag and matte from two of the electric furnaces were sampled over a period of time where converter slag return to the furnaces was discontinued. This altered the Mg/Fe ratio of the slag and resulted in higher smelting temperatures. The slag pO_2 also dropped, making conditions less oxidising. These factors altered the levels of base metal dissolution in, and therefore losses to, the slag, as will be described below. The results presented here originate from only one of the furnaces, for reasons of brevity – very little difference was observed between the two furnaces of the study.

The object of this investigation was to establish the distribution of base metals in furnace slag in order to optimise recovery. The study focuses, therefore, on the losses of the base metals, as entrained and dissolved phases, to furnace slag, as well as the effect of changing furnace feed and operation conditions. In addition, the viability of using a modelling program to predict base metal distribution between slag and matte has been assessed, and recommendations are made to improve the outcome.

METHODOLOGY

Sampling

The furnaces were sampled once a week for four weeks over the periods of interest. Matte was sampled from the ladle after tapping, and tapped slag was taken as cuts across the rake classifiers after granulation in water. Samples were also taken from sounding bars dipped into the furnace, and these provided an insight into the variation of slag and entrained matte composition with depth in the furnace.

Analytical Techniques

The samples were analysed in bulk using base metal fusion and ICP-MS, and LECO for sulphur (combustion). A novel combination of techniques was used to quantify the base metal distribution in furnace slag. Wavelength dispersive X-ray (WDX) analysis of the slag silicate phase on the electron microprobe was combined with whole slag chemistry to provide information on the levels of dissolved metals in the slag. Entrained matte phases in the slag were analysed by energy dispersive X-ray (EDX) area acquisition, and the process was automated by use of the Latti method. This is a computer-controlled scanning electron microscopy (CC-SEM) technique which has not been used before for pyrometallurgical research [7]. The results of these analyses, run on selected samples, allowed the composition of matte droplets in the slag to be related to their size. The pO_2 of the slag was calculated using Mössbauer Spectroscopy to determine Fe^{3+}/Fe^{2+} ratios, and FactSage modelling provided predictions of base metal slag/matte partitioning.

The use of the microbeam and Mössbauer techniques has previously been described in detail [8].

Modelling

The modeling program used for the equilibrium calculations was FactSage [9]. The slag-matte systems were modelled using the Equilib Module. Normalised matte compositions (Fe, Ni, Cu, Co and S) were entered, followed by major elements as determined by electron microprobe analysis of the slag silicate phase. Temperature ranges of 1300 – 1550°C were selected to include the range of tapping temperatures recorded at the smelter, and pressure was set at 1 atm.

RESULTS AND DISCUSSION

Base Metal Levels and Partitioning in Matte and Slag

Furnace matte spoon samples solidify to produce a number of sulphide and alloy phases. The most common of these are synthetic pentlandite ($(Fe,Ni,Cu)_9S_8$), troilite (FeS), bornite (Cu_5FeS_4) and minor Fe-Ni-Cu alloy. None of these phases are present in the molten matte.

When the tapped slag is granulated in water, the rapid quenching produces a product consisting almost entirely of silicate glass, in which trace amounts of nickel, copper, cobalt and sulphur are dissolved. Small entrained matte droplets are preserved as sulphide spheres. Although slag from these furnaces commonly contains minor amounts of slag spinel ($(Cr,Fe,Mg,Al)_3O_4$), this phase was present only in trace amounts in the samples examined in this study, due to relatively low chromium levels in the feed. At smelting temperatures the silicate and sulphide phases in the slag are liquid but separate – the quenched slag samples are assumed to reflect the molten nature of the slag.

Little variation is evident in furnace slag and matte compositions within the sampling periods. The results of chemical analysis of the furnace matte samples are shown in Table 1, where the earlier samples produced during converter slag return are compared to those produced after this was discontinued. Here, and throughout, these are referred to as CSR (converter slag return) and NCSR (no converter slag return).

Table 1: The average compositions (in mass %) of matte as determined by chemical analysis. The standard deviations (s.d.) of the results are also shown. For comparison purposes the results have been normalised after removing contaminants from entrained slag and refractory. CSR = converter slag return, NCSR = no converter slag return.

	Matte	Fe	Co	Ni	Cu	S
CSR	Bulk	43.99	0.52	17.87	9.44	28.19
	s.d.	1.37	0.03	0.91	0.75	0.33
NCSR	Bulk	41.60	0.38	17.26	11.04	29.72
	s.d.	0.34	0.02	0.78	0.58	0.46

The compositions of the silicate glass phases as determined on the electron microprobe are shown in Table 2. The slag also contains sodium and titanium in trace amounts. Cobalt levels were so low in the NCSR slags that this element was only analysed in two samples, using microprobe trace analysis. Oxygen is not measured using this technique, and the oxide levels are calculated by stoichiometry – it can be argued that sulphur should be reported as the element, but conventionally it is presented as the oxide.

Table 2: Electron microprobe analysis results (in mass %) for the glass phase in the furnace slag samples. Each analysis is an average of twenty-five (CSR) or forty (NCSR) positions on the glass phase. A grand average is included in the table (G. ave) as well as standard deviations (s.d.).

CSR	MgO	Al_2O_3	SiO_2	CaO	SO_3	Cr_2O_3	FeO	CoO	NiO	Cu_2O
1	15.86	3.73	45.66	5.89	1.06	0.87	26.54	0.070	0.152	0.095
2	15.88	3.83	45.25	7.64	0.98	0.92	23.77	0.098	0.175	0.082
3	14.21	4.15	42.65	13.68	1.06	0.55	22.44	0.070	0.122	0.068
4	16.49	4.07	45.86	8.08	1.08	0.73	23.05	0.069	0.174	0.084
G. ave	15.61	3.95	44.85	8.82	1.04	0.77	23.95	0.077	0.156	0.082
s.d.	0.98	0.20	1.49	3.37	0.04	0.17	1.81	0.014	0.025	0.011
NCSR	MgO	Al_2O_3	SiO_2	CaO	SO_3	Cr_2O_3	FeO	CoO	NiO	Cu_2O
1	21.09	5.11	48.04	9.80	0.69	1.42	11.95	0.014	0.088	0.065
2	20.72	5.35	47.83	9.42	0.75	1.61	12.75		0.094	0.065
3	20.40	5.17	47.59	9.61	0.59	1.30	13.17		0.098	0.062
4	20.58	4.98	47.24	10.46	0.69	1.42	12.69	0.016	0.098	0.054
G. ave	20.70	5.15	47.68	9.82	0.68	1.44	12.64	0.015	0.095	0.062
s.d.	0.2.9	0.15	0.34	0.45	0.07	0.13	0.51	0.001	0.005	0.005

The higher Fe/Mg ratio of the CSR slag is due to the high-iron composition of the converter slag. Also notable are the higher dissolved base metal levels and the lower chromium content of the CSR slag. The higher levels of dissolved base metals are predominantly due to higher slag pO_2 – this is dealt with in more detail later in this paper. Chromium and magnesium levels were lower in feeds prior to 2000 due to different concentrate blends and a lower UG-2 component in the feed.

The dissolved nickel and copper levels in the slag silicate are plotted against sulphur content in Figure 1. No relationship between the two is obvious, which suggests that dissolution is primarily oxidic. This is confirmed by FactSage calculations.

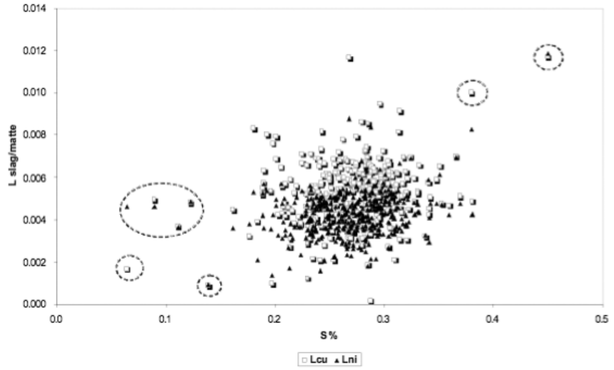

Figure 1: The distribution of dissolved nickel and copper with sulphur content of the slag silicate phase. The plot is a composite of all the NCSR slag samples. All the outliers, such as those ringed, originate from one sample and probably indicate some degree of microcrystallinity.

Entrained Matte in Slag

The average compositions of entrained matte phases in the slag samples are shown in Table 3. The results produced using the Latti technique are normalised, but the method was also tested against standards with excellent results. The sulphide component of the flash drier product (furnace feed) for the later slag samples was calculated from a combination of electron microprobe and CC-SEM results – feed was not sampled during the earlier campaign.

Table 3: Results, in normalised mass %, of averaged EDX area scans on entrained matte in two of the slag samples. The averages were calculated on over 100 (CSR) and 500 (NCSR) phases in each sample. The (normalised) compositions of bulk matte and feed from same-day samples are shown for comparison.

Sample	Sulphide	S	Co	Fe	Ni	Cu
CSR	Entrained matte	32.7	1.1	37.0	21.1	8.1
	Bulk matte	27.9	0.5	43.0	18.7	9.8
NCSR	Entrained matte	31.8	0.7	32.5	24.2	10.8
	Bulk matte	29.5	0.4	41.4	17.7	11.0
	Feed sulphide	37.4	0.2	38.0	14.0	10.3

The relationship between the size and composition of the entrained matte droplets is shown in Figure 2.

The composition of the entrained matte droplets in the tapped slag differs from that of bulk matte, being nickel-rich, sulphur-rich and iron-depleted in comparison. Most of the droplets are under 10 µm in size, and no obvious compositional trend is evident in the 2–100 µm size range. Very few droplets larger than 100 µm were present in the tapped slag, but analysis of these indicates higher Fe/Ni ratios than the smaller droplets. The results for iron and nickel in Figure 2 are displayed in Figure 3 with 95 % confidence intervals. The plot shows that a significant trend towards bulk matte composition only occurs at larger droplet sizes, and that nickel and iron appear to substitute for each other in the entrained matte. No significant trends were observed for copper or sulphur.

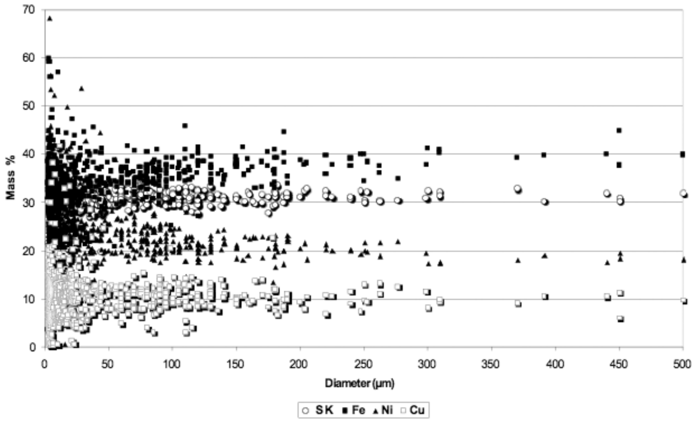

Figure 2: The variation of entrained matte droplet composition with size. The greater spread at small sizes is probably an artefact due to phase separation on cooling and the fact that the analysis were run on two-dimensional sections

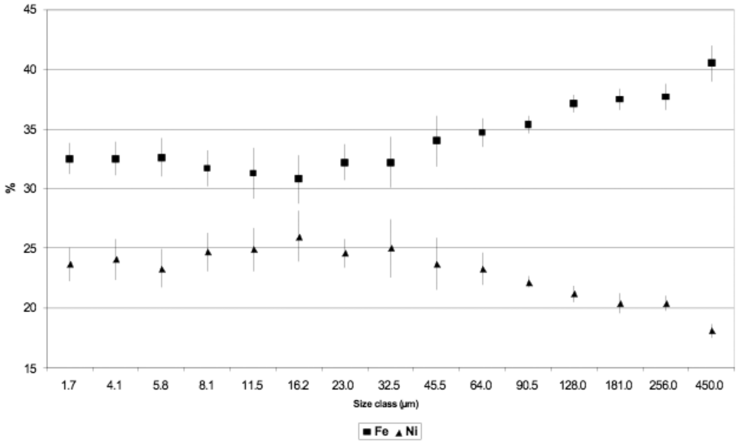

Figure 3: The mean values and 95% confidence intervals of the nickel and iron contents of entrained matte droplets plotted against size class mid point. A significant increase in Fe/Ni only takes place in the larger droplets

Recently, sounding bar results from both furnaces have suggested that the composition of settling matte droplets approaches that of bulk matte below tapping levels. Sounding bar samples are similar to dip samples in that interpretation of results must be made with caution. Some degree of slow-cooling (crystallisation) is always evident, but neither chemical analysis nor microprobe area scans were able to detect major differences in slag silicate composition with depth in the bath. This agrees with earlier work on the furnaces [10]. SEM-EDX analysis results for entrained matte phases are shown in Table 4. During this sampling period, the depth of the bulk matte surface was around 150 to 155 cm, and the lowest slag tapping level would have been 130 cm. The 145–150 cm sample shown in the Table, therefore, was taken below normal slag tapping level.

Table 4: The averaged results (in normalised mass %) of SEM-EDX area analysis of entrained matte in selected sounding bar samples, with same-day bulk matte for comparison

Depth (cm)	S	Fe	Co	Ni	Cu
78–88	29.2	35.5	0.5	27.7	7.3

95–105	30.9	38.9	0.4	20.1	9.7
145–150	31.1	41.4	0.4	18.8	8.3
Bulk matte	30.9	42.4	0.4	16.6	9.6

Entrained matte phases in the furnace slag are scarce, so CC-SEM analysis proved invaluable. The high Ni/Fe ratio as compared to bulk matte and feed sulphide composition suggests that there is preferential entrainment of nickel-rich sulphides from the concentrate, possibly because the surface tension of the molten sulphides varies for different sulphide compositions [11].

Data is available on thermal profiles through the slag of South African PGE-producing furnaces [5]. Present-day tapping practice in the furnaces precludes slag tapping to less than 20 cm above the matte-slag interface and to less than 30 cm from the overlying concentrate. Given that slag tapping temperatures are normally at least 100°C above those of matte, this means that the entrained matte in the tapped slag samples would be at a higher temperature than that of the bulk matte, and that the slag samples studied would not actually have been in equilibrium with bulk matte.

Base Metal Equilibria and Modelling

The reactions involved for dissolution of the base metals in the slag are shown below, and the equilibrium constants for these are given in Table 5. These constants are taken from the FactSage database, using liquid reference states for the matte and slag species.

$$\mathrm{Cu} + 0.25\ \mathrm{O_2} = \mathrm{CuO_{0.5}} \qquad K = a_{\mathrm{CuO_{0.5}}} / [a\mathrm{Cu}\ (p_{\mathrm{O2}})^{0.25}]$$
$$\mathrm{Ni} + 0.5\ \mathrm{O_2} = \mathrm{NiO} \qquad K = a_{\mathrm{NiO}} / [a\mathrm{Ni}\ (p_{\mathrm{O2}})^{0.5}]$$
$$\mathrm{Co} + 0.5\ \mathrm{O_2} = \mathrm{CoO} \qquad K = a_{\mathrm{CoO}} / [a\mathrm{Co}\ (p_{\mathrm{O2}})^{0.5}]$$

The extent of dissolution of the metals in the slag depends on the metal activities in the matte (a_{Cu}, a_{Ni} and a_{Co}), the partial pressure of oxygen, and the activity coefficients of the metal oxides in the slag.

Table 5: Equilibrium constants for base metal dissolution. The equilibrium constants are given in the form ln K = A/T + B, where T is the absolute temperature. Reference states are the pure liquids for the metal and oxide species

Reaction	**A (K)**	**B (-)**
$\mathrm{Ni} + 0.5\ \mathrm{O_2} = \mathrm{NiO}$	23018	-8.015
$\mathrm{Cu} + 0.25\ \mathrm{O_2} = \mathrm{CuO_{0.5}}$	7408.3	-2.663
$\mathrm{Co} + 0.5\ \mathrm{O_2} = \mathrm{CoO}$	25511	-7.384

The prediction of the partial pressure of oxygen was based on two buffers – $\mathrm{Fe_{matte}}$ in equilibrium with $\mathrm{FeO_{slag}}$, and equilibrium between $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$ in the slag. The relevant reactions are:

$$\mathrm{Fe} + 0.5\ \mathrm{O_2} = \mathrm{FeO} \qquad K = a_{\mathrm{FeO}} / [a_{\mathrm{Fe}}\ (p_{\mathrm{O2}})^{0.5}]$$
$$\mathrm{FeO} + 0.25\ \mathrm{O_2} = \mathrm{FeO_{1.5}} \qquad K = a_{\mathrm{FeO_{1.5}}} / [a_{\mathrm{FeO}}\ (p_{\mathrm{O2}})^{0.25}]$$

The results of Mössbauer Spectroscopy allowed $\mathrm{Fe^{3+}/Fe^{2+}}$ to be calculated. The average for the CSR slag samples was 0.114 and for the NCSR 0.039. This shows that the slags produced during converter slag return to the furnaces were considerably more oxidising. The predicted partial pressure of oxygen for the two buffers is shown in Table 6. The activity of iron is very different in the entrained matted droplets and in the bulk (tapped) matte, resulting in different partial pressures of oxygen for the Fe/FeO buffer when presuming equilibrium between FeO in the slag, and Fe in respectively entrained and tapped matte. The calculated extents of dissolution of nickel, copper and cobalt in the slag are reported in Table 7.

Table 6: Matte activities and predicted partial pressure of oxygen (pO_2) for the Fe^{3+}/Fe^{2+} and Fe/FeO buffers

	Matte	**Activities (liquid reference)**				**pO_2 (atm)**	
		Fe	**Ni**	**Cu**	**Co**	**Fe^{3+}/Fe^{2+}**	**Fe/FeO**
CSR	Bulk	0.184	0.141	0.0452	0.0041	9.7×10^{-5}	1.2×10^{-9}
	Entrained	0.012	0.035	0.0075	0.0012	9.7×10^{-5}	3.1×10^{-7}
NCSR	Bulk	0.106	0.110	0.0344	0.0023	6.7×10^{-6}	1.6×10^{-9}
	Entrained	0.010	0.036	0.0101	0.0007	6.7×10^{-6}	1.8×10^{-7}

Table 7: The predicted dissolved base metal content for slag in equilibrium with bulk and entrained matte for the buffers in Table 6. Calculation for T = 1500°C; a_{FeO} = 0.210 (CSR) and 0.139 (NCSR) – liquid reference. Figures in italics indicate the closest values to those measured, as shown in Table 2.

	Slag/matte equilib.	**NiO %**		**Cu_2O %**		**CoO %**	
		Fe^{3+}/Fe^{2+}	Fe/FeO	Fe^{3+}/Fe^{2+}	Fe/FeO	Fe^{3+}/Fe^{2+}	Fe/FeO
CSR	Bulk	8.569	0.031	0.528	0.032	4.907	0.018
	Entrained	2.114	0.120	0.088	0.021	1.385	0.078
NCSR	Bulk	1.164	0.018	0.177	0.022	0.586	0.009
	Entrained	0.378	0.062	0.052	0.021	0.176	0.029

Modelling with the pO_2 calculated from the Mössbauer results, therefore, shows that the tapped slag is more likely to be in equilibrium with entrained matte or overlying concentrate than with bulk matte.

Process Optimisation

To summarise, the losses of base metals to Anglo Platinum furnace slags are of two types – losses by predominantly oxidic dissolution in the slag, and losses as unsettled entrained sulphide matte. Since the slags are not treated further by pyrometallurgical reduction, losses by dissolution in slag are not recoverable. A limited amount of furnace slag is currently milled and floated in the Slag Plant where at least the coarser entrained matte particles should be recovered, but a great deal of the slag is dumped. Given these facts, it is obvious that the best approach to reducing base metal (and associated PGE) losses to slag lies in process optimisation to minimise the dissolution of base metals, and to maximise the settling of entrained matte.

Nickel (and probably cobalt) losses to slag were higher when converter slag was being returned to the furnaces (Table 8). The main reason for this was the more oxidizing conditions introduced with the slag feed, as demonstrated in the higher pO_2 values determined by Mössbauer Spectroscopy. The relative amounts of dissolved to total percentages shown in the Table explains the low recovery of base metals by milling and flotation in the Slag Plant.

Table 8: The averaged relative amounts of dissolved base metals in slag calculated from microprobe results and chemistry. The figures show dissolved metals as a percentage of the total element content in slag. Cobalt was not determined for the earlier samples.

	Dissolved Ni (%)	**Dissolved Cu (%)**	**Dissolved Co (%)**
CSR	71	76	
NCSR	56	78	50

Because of the increase in pO_2 shown above, as well as magnetite build-up in the furnaces, adding converter slag is contra-indicated. The production of reducing conditions by carbon addition is not currently practical due to the design of the furnace off-gas system. Loss of entrained sulphide to tapped slag can be controlled by careful tapping practice and level control, and also by blending feed materials to limit slag chromium content. When this rises above 2%, spinel crystallizes and this can impede matte fall, causing matte to be tapped out with the slag. It may also be advisable to reconsider the position of the feed ports above the furnace and the particle size of the feed materials.

CONCLUSIONS

The combination of electron microbeam techniques with bulk chemistry and Mössbauer spectroscopy has provided important insights into base metal distribution in the furnaces, and the reasons for lower than expected recovery by flotation. Modelling of slag losses does not predict dissolved metals in slag accurately when the data fed in is bulk matte (rather than entrained matte) composition.

ACKNOWLEDGEMENTS

The authors would like to thank Anglo Platinum for permission to publish this work, and all the staff at Head Office and Smelters, and at Anglo Research, who have assisted with this project.

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