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Factors affecting nickel recovery from slags produced during platinum smelting

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Nickel is recovered as a by-product of the platinum-producing process operated by Anglo Platinum. The metal is mined mainly as sulphide minerals contained in platinum ores. These pass through the concentrating, smelting and converting process route and nickel is finally recovered by electrowinning. Smelting of the concentrated ore in the electric furnace produces a melt with a high slag to matte ratio. The resulting furnace slag is granulated and later milled and floated to recover matte. A project was initiated to investigate the distribution of nickel in the slag in order to improve recovery. Slag samples were examined using a combination of chemical and mineralogical techniques. The granulated slag was found to consist mainly of a silicate glass phase, which reflects the composition of the molten slag in the furnace. Nickel occurs as free matte granules, as matte phases locked inside the glass, and in the glass phase itself. Whereas nickel in the matte is as sulphide, most of the nickel in the glass phase appears to be oxide- bound (i.e. in solid solution). Milled slag as flotation feed showed recovery-limiting features such as free matte with oxidized surfaces and unliberated matte inclusions in the slag. The biggest nickel losses, assuming no tapping problems, are in the glass phase solid solution. Only around 40% of nickel would be recovered from the slag, even under ideal conditions. Spoon and pot slag samples were also examined to see if casting and crushing would improve recovery. Although larger and therefore more easily recovered matte phases formed, nickel partitioned into crystalline silicate phases, limiting the maximum theoretical nickel recovery to 70%.

Introduction

Nickel is recovered as a by-product of the platinum-producing processes operated in the Rustenburg area of South Africa. 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 concentrating, most of the nickel in the ore concentrates occurs as sulphide minerals, predominantly pentlandite $(Fe,Ni)_9S_8$ and nickel-bearing pyrrhotite ($Fe_{1-x}S$).

At Anglo Platinum the 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[1]. A mineralogical project was initiated towards the end of 1999 to investigate the distribution of nickel in furnace slag with a view to improving recovery of this metal. Due to ever-changing smelter practice (see below) and the recent installation of a slag cleaning furnace, the project has been ongoing and has proved useful in monitoring the trends in nickel losses to slag over the past three years. Parallel investigations have been run to identify slag plant recovery problems and to assess the benefit, if any, of slow cooling the slag as distinct from granulation.

Smelting of platinum-bearing ores at Anglo Platinum

At Anglo Platinum's Waterval Smelter, where most of this investigation was carried out, concentrate (containing on average 3 to 4 per cent nickel) from the concentrators is dried in the flash-driers, mixed with a limestone flux, and then fed into one of two six-in-line electric resistance furnaces. The power rating of the furnaces is 34 MW each, heat being generated by current passing through the slag layer between pairs of the six Soderberg electrodes. Smelting of the concentrate in the electric furnaces produces a melt with a high slag to matte ratio. The resulting matte (which runs at around 16 per cent nickel) is used as feed for the converting process. The slag, varying in nickel content from 0.1 to 0.5 per cent, is tapped continuously and granulated in water. The slag granules are collected in rake classifiers, and later milled and floated in the slag plant to recover entrained matte, and hence reduce PGE (and base metal) losses.

Sampling methodology

During the initial campaign samples of granulated slag were collected from the classifiers on a weekly basis at the two electric furnaces. Further samples were taken during 2001 and 2002 to monitor the changes in slag composition and mineralogy produced by changes in ore composition and the reduction of revert material, predominantly converter slag, being returned to the furnaces.

Sampling to establish the effects of slow cooling on nickel recovery from the slag involved taking pot and spoon samples at the same time as collecting granulated slag from the classifier. Samples of flotation feed, flotation concentrates and tailings were also collected early in 2000, and again in 2003, in order to identify recovery problems at the slag plant.

Analytical techniques

All the granulated slag samples were screened initially to obtain a size distribution. Crushed spoon and pot, as well as granulated slag, samples were split and pulverized for chemical analysis and X-ray diffraction (XRD), and also prepared as polished sections. These were examined using the ore microscope, imaged on the JEOL JSM-5400 Scanning Electron Microscope (SEM) and analysed by means of wavelength dispersive X-ray spectroscopy (WDS) on the JEOL 733 Superprobe. The standards used were normal oxide or silicate standards, that specifically used for nickel determination was nickel oxide (NiO).

Modal analyses of the granulated slag samples were run on the Optimas Image Analyser, and those of the spoon and pot slag were determined by random microprobe analysis. Slag plant feed, concentrate and tails samples were examined on the SEM, and also on the QEM*SEM and Minerals Liberation Analyser (MLA), where bulk modal analyses, as well as sulphide size and liberation, were carried out.

Mineralogy and composition of the samples

Granulated slag samples

These samples are made up of black, vitreous, rounded granules, usually between 200 µm and 3 mm in diameter.

Averaged bulk chemistry results for the granulated slag are shown in Table I.

Most of the slag consists of an amorphous glass phase, compositionally a Mg-Al-Ca-Fe-Cr silicate, which also contains trace amounts of sulphur, titanium, nickel and copper. Minor to trace phases such as spinel ($FeO.Cr_2O_3$ invariably containing some Al and Mg) are found in the main glassy phase*. Crystals of olivine ($(Mg,Fe)_2SiO_4$), and matte inclusions also occur in the glass. In certain samples, pure matte and/or sulphide-bearing spinel-silicate granules form, but the most common occurrence of entrained matte is as smaller inclusions in the glass phase. Back-scattered electron (BSE) images of typical granulated slag are shown in Figures 1 and 2. In terms of modal abundance, all the samples consist of 98 to 99 per cent glass phase, with the combined matte and spinel phases making up only 1 to 2 mass per cent of the sample.

Nickel is found in major amounts in entrained matte (sulphides and alloy), and also in the silicate glass and spinel (oxides).

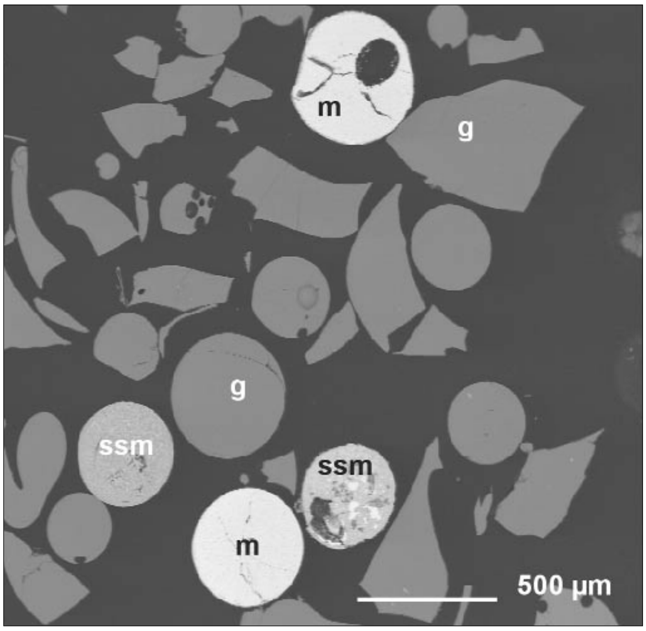

Figure 1. BSE image showing a 'dirty' granulated slag that may have resulted from tapping problems. Most of the slag consists of silicate glass (g), but matte granules (m) and spinel-slag-matte granules (ssm) are also present

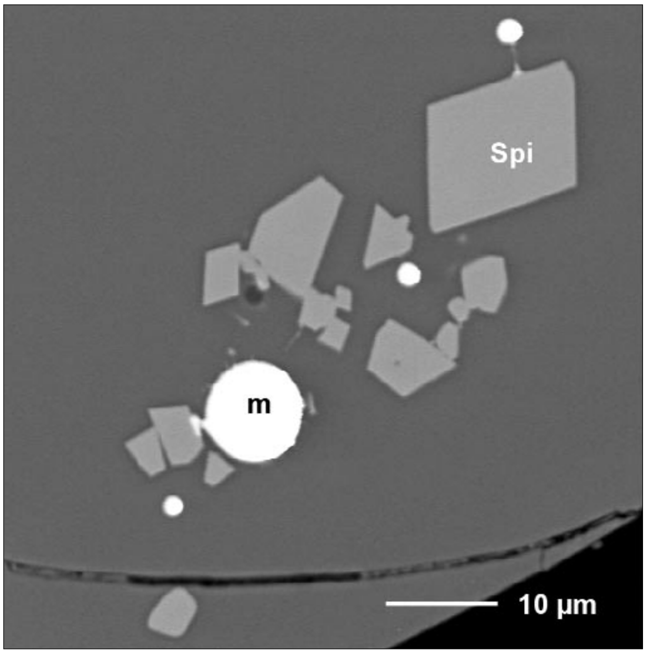

Figure 2. Higher magnification BSE image of a silicate glass granule in furnace slag. Primary spinel (Spi) has crystallized and a number of matte inclusions (m) have formed

Table I
Bulk chemical analysis results (in mass %) averaged for both furnaces for granulated slag sampled in 1999 and 2002

Slag	MgO	Al_2O_3	SiO_2	CaO	S	Cr_2O_3	FeO	Ni	Cu	Total
F1 1999	17.97	4.33	47.27	9.71	0.46	1.33	20.70	0.17	0.09	102.03
F2 1999	16.40	3.88	45.95	9.51	0.47	0.98	24.13	0.15	0.08	101.55
F1 2002	22.55	4.62	49.30	7.22	0.21	1.16	12.20	0.08	0.06	97.39
F2 2002	22.00	4.56	48.65	10.02	0.22	0.97	11.50	0.07	0.05	98.02

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*The word spinel in this paper denotes a member of the spinel mineral family, which includes chromite, chrome-spinel, magnetite and various intermediates. It does not refer to the specific mineral, spinel, which is $MgAl_2O_4$

Table II
Averaged electron microprobe results (in mass %) for the glass phase of the furnace slag sampled in 1999 and 2002

Slag	MgO	Al_2O_3	SiO_2	CaO	SO_3	Cr_2O_3	FeO	NiO	Cu_2O	Total
F1 1999	17.87	4.59	46.91	9.59	0.77	0.90	18.48	0.13	0.06	99.30
F2 1999	15.61	3.95	44.85	8.82	1.04	0.77	23.95	0.15	0.08	99.22
F1 2002	22.83	4.62	50.66	6.87	0.55	1.07	12.06	0.08	0.12	98.85
F2 2002	22.36	4.54	49.62	9.53	0.57	0.92	11.41	0.07	0.11	99.11

The entrained matte consists of very fine-grained intergrowths of synthetic pentlandite ($(Fe,Ni,Cu)_9S_8$), troilite (FeS) or pyrrhotite ($Fe_{1-x}S$) and copper-iron sulphides interspersed with tiny spinel crystals. Sometimes copper metal is present as well as tiny base metal alloy plates.

The results of electron microprobe analysis of the glass phase are shown in Table II. When compared to the sample chemistry these results imply that most of the nickel in the slag is actually chemically bound in the glass phase, rather than present as entrained matte sulphide. There are exceptions—for example, where a relatively large amount of free matte granules have been produced due to tapping problems and, to a lesser extent, where high levels of spinel have captured matte in composite matte-spinel-slag granules.

The olivine crystals, which were detected in the glass phases of all the slag samples, are present only in trace amounts, and probably represent areas of localized slower-cooling of the slag. Nickel levels in this phase run at 0.2– 0.3 mass per cent NiO.

The most common spinel in the granulated slag is primary recrystallized chromite, which is found in the glass phase and shows much higher chromium content (68–70 per cent Cr_2O_3) than feed chromite does (41–44 per cent Cr_2O_3). Nickel varies from 0.1 to 0.2 per cent in this type of spinel. Other spinel types are magnetite (Fe_3O_4) and partially assimilated feed or refractory chromite. Neither of these makes any significant nickel contribution to the slag.

Slag plant samples

The mineralogy of the slag plant samples is essentially the same as that of the granulated slag described above. The slag milling specification is 50–65 per cent passing 75 μm after which the slag is fed into the flotation circuit. Screen size analysis results for flotation feed samples are shown in Table III. Two of the feed samples taken in 1999 were over milled. The more recent feed samples are all within specification, but there seems to be more coarse material than usual in sample 2003/4, which could tie in with the losses described overleaf. The liberation of matte in the flotation feed samples is reported as 80 per cent liberated, 10 per cent middlings and 10 per cent locked, but the common tiny sulphide inclusions are too small to be detected using this technique. Free matte usually occurs as pentlandite-copper sulphide matte, which is often surrounded by an oxidized rim (Figure 3).

The loss of matte to flotation tailings late in 1999 was mainly due to its being locked in silicate or surrounded by an oxidized rim. Recent examination also shows the presence of oversized free matte particles in the tailings—these may not have floated due to their mass.

Slow cooled slag samples

Pot and spoon samples of furnace slag were examined and were found to have cooled to produce a crystalline intergrowth in which matte sulphides ‘grew’ to larger sizes at the expense of the tiny unrecoverable matte inclusions normally seen in the glass phase of the granulated slag. Phases that form upon slow cooling are olivine, pyroxene and spinel as well as a residual matrix, out of which the sulphides normally solidify (Figure 4).

One such slowly cooled sample was subjected to microprobe phase analysis and compared to a slag granulated at the same time. The results of phase analysis are presented in Table IV. From the results it can be seen that nickel is not only present in the entrained matte phases of the spoon sample, but is also found in the silicate and oxide phases.

Discussion

Nickel losses to furnace slag tailings can occur in several ways—by dissolution in the silicate glass, by the inclusion of sulphides in the glass that are not liberated for flotation, by entrapment in spinel-rich slag and incorporation into non-floatable granules, and by matte being tapped with slag leading to free matte inclusions. The latter should be recovered in the slag plant but sometimes they are not—this will be discussed more fully below.

Nickel partitions into the silicate and oxide phases in the slag and can also be entrained as very small sulphide inclusions—these forms of nickel are unlikely to be recovered. The dissolution of nickel in furnace slag has been shown to be both oxidic and sulphidic[2]. In addition, the amount of nickel that will partition into the slag varies with the composition and temperature of the slag, the total chemistry of the system and the pO_2 present during smelting[2–5].

In the light of this knowledge it is interesting to note that the amount of nickel present in solid solution in the slag glass phase has fallen (from 0.14 to 0.08 per cent) over the last three years, at the same time that magnesium has increased at the expense of iron. This effect may not be solely due to compositional changes, however, since the furnaces have to be run at higher temperatures to smelt the increasingly magnesium-rich slag and nickel dissolution in the slag is inversely related to temperature.

Recently a higher UG-2 component in the furnace feed has produced increased chromium levels in the slag. Since only a limited amount of chromium can dissolve in the slag, this results in the crystallization of primary chrome-bearing spinel, which tends to accumulate between the matte and slag. The spinel increases slag viscosity locally and impedes matte fall. Tapping into a layer or pocket of this type can entrap matte into granulated slag. Depending on

Table III
Screen size analysis (in mass %) of slag plant flotation feed samples sampled in 1999 and 2003

size (µm)	1999/1	1999/2	1999/3	1999/4	1999/5	2003/1	2003/2	2003/3	2003/4
+ 212	9.7	9.2	1.0	0.0	5.1	6.8	8.8	5.6	14.3
+ 106	23.9	25.3	11.3	1.3	16.1	22.7	22.7	16.8	23.1
+ 53	25.4	27.3	25.4	10.8	27.1	21.5	24.3	23.2	21.1
+ 25	19.4	18.6	23.2	26.0	22.8	12.8	14.0	14.8	12.4
- 25	21.6	19.6	39.1	61.9	28.9	36.2	30.2	39.6	29.1
% - 75 µm	54	52	78	95	65	62	55	66	52

Table IV
Electron microprobe analysis results (in mass %) for the phases in the spoon (slow-cooled) and granulated slag samples taken in 2001

Type	Phase	MgO	Al_2O_3	SiO_2	CaO	SO_3	Cr_2O_3	FeO	NiO	Cu_2O	Total
G.S.*	Glass	20.53	4.52	48.24	8.17	0.71	1.17	15.40	0.11	0.08	98.93
	Spinel	11.70	9.82	0.85	0.36	0.00	55.81	19.60	0.12	n.d†	98.26
Spoon	Olivine	44.49	0.06	39.77	0.30	0.00	0.70	14.40	0.20	0.00	99.89
	Pyroxene	21.01	2.55	52.26	9.53	0.00	1.86	12.10	0.03	0.00	99.34
	Matrix	1.32	14.19	48.81	9.58	0.99	0.07	21.34	0.02	0.03	96.35
	Spinel	10.74	8.41	1.87	0.61	0.06	54.88	21.44	0.12	n.d.	98.13

*G.S. = granulated slag.
†n.d. = not determined

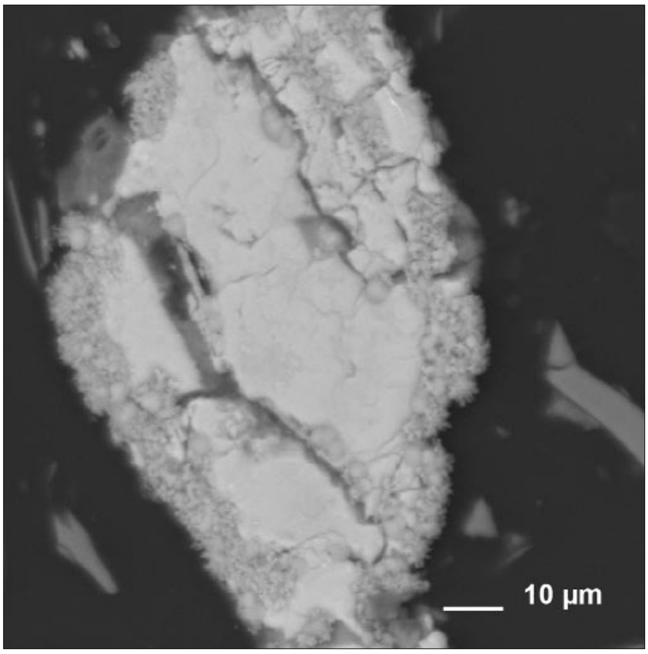

Figure 3. A free matte particle in a feed-to-float slag mill sample. The matte is rimmed by an oxidized layer which may not respond to flotation. BSE image

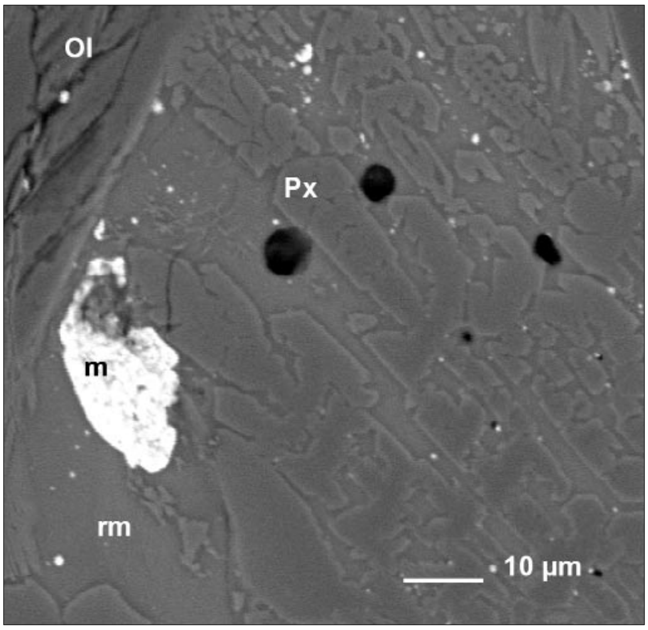

Figure 4. BSE image of an area of slow-cooled slag in spoon sample. Relatively large matte particles (m) have formed in the residual silicate matrix (rm). Olivine (Ol) and pyroxene (Px) crystals are also evident

the ratio of finely intergrown matte to slag and spinel in the resulting granules, these may not be recovered by flotation.

Nickel recovery at the slag plant sometimes appears unacceptably low. Losses are unavoidable, however, because (in a ‘clean’ slag) most of the nickel is present in oxide or silicate phases, either in solid solution or as tiny sulphide inclusions.

Problems that could be avoided are those of inconsistent grind size of feed-to-float samples and the loss of free matte in the system. When feed samples are too coarse there may be insufficient liberation of matte, and when overgrinding occurs too much slag may float with the matte. The problem of free matte not being recovered could again be linked to coarse feed size, but it is more likely to be a result of oxidation rims forming around matte particles.

Slow cooling of the furnace slag, as distinct from granulation, leads to the formation of coarser matte particles, which would probably increase recovery at the slag plant. There is again a limitation, however, in that approximately 40 per cent of the slow cooled slag consists of olivine, and nickel partitions into this silicate in the same way as it would in a natural system[6]. In the case of this particular sample nickel, recovery would not exceed 70 per cent.

The processing of cast slag, as distinct from granulated, would involve the introduction of a crushing circuit which may not be economically justifiable. Additionally, there is evidence that cast slag tailings would not be as environmentally stable as granulated slag tailings[7].

It could be argued that the amount of nickel reporting to slag is so low compared to the levels present in furnace matte, that the efforts required to increase recovery from slag may not be justified. Given the high slag to matte ratio produced from the electric furnaces, however, nickel losses to slag can represent a substantial amount. Every effort must therefore be made to limit nickel losses of the type described in this paper during future operation.

Conclusions

The low recovery of nickel from furnace slag is to a certain extent unavoidable because of the oxide dissolution in slag that occurs under current furnace operating conditions. Losses that could be addressed, however, include those due to spinel formation, slag tapping problems and control problems at the slag plant.

Lowering the chrome content of the feed can reduce the amount of spinel forming inside the furnace. Given that chrome levels will of necessity increase as more UG-2 is mined, methods of increasing chromium solubility in slag are being investigated in other project work. Lower spinel levels, if these can be achieved, should lead to lower matte entrainment in the slag.

Tapping problems, which can lead to relatively high levels of free matte granules within the slag, are usually unavoidable, but sometimes could be controlled by more careful tapping practices.

The slag plant milling operation should also be more stringently controlled in order to produce consistent grind size for feed-to-float, and wet-storage of feed-to-float material should be avoided.

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