Partitioning of PGEs in nickel converter matte phases: Direct observations by electron microscopy and electron probe microanalysis

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ABSTRACT

A recent study investigated the mineralogy and basic mineral chemistry of PGE-containing nickel converter matte phases as a function of their iron-endpoints from actual fast cooled production samples. Important findings from the study indicate that the formation of stable phases and their associated microstructures are influenced by the amount of iron present in the bulk composition. Stable phases include the formation of alloy phases into which the PGEs preferentially partition as compared to the copper–sulphide, nickel–sulphide and oxide phases. It follows then that careful analysis must be paid to a more comprehensive understanding of PGE partitioning into the respective phases and the formation of particularly the host alloy phases.

A combination of analytical techniques were applied to characterise nickel–sulphide, copper–sulphide and alloy phases with respect to the relatively low iron-endpoint of 0.15 wt.%. Representative analytical sub-samples were characterised using electron probe microanalysis and electron transparent samples were characterised using field emission scanning electron microscopy (FEG SEM) and transmission electron microscopy (TEM).

The partitioning coefficients of palladium, platinum, rhodium and iridium between alloy and nickel–sulphide phases are indicated at 2.2, 43.4, 2.2 and 7.4, respectively. In comparison, the partitioning coefficient of specifically rhodium between nickel and copper–sulphide phases is indicated at 1.29. The characteristic partitioning behaviour of PGEs in converter matte phases can be described as a strong function of parent sulphide matte chemistry, crystallization sequence and the role played by nickel as facilitator during alloy crystallization. High resolution bright-field TEM images suggest that PGEs are probably incorporated within the alloy structure in solid solution. It has been proposed that uneven cooling rates, heat dissipation, substitutional solid solution chemistry and fractional crystallization could possibly be responsible for the variety in composition and phase morphology, in particularly related to the formation of alloy phases.

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1. Introduction

The effect of changes in the iron-endpoint during Peirce-Smith converting on subsequent matte mineralization can provide significant opportunity for the optimal control and monitoring of nickel converter blow conditions. An important focus in this regard is to further unlock the dependency between iron-endpoint control, resultant fast cooled microstructures, their genesis and potential impact to the integrated processing of nickel converter matte phases as an intermediate product. A previous study by Thyse et al. (2010) indicated in particular, a lack of sulphide phase-specific PGE distribution data for the respective iron-endpoints

studied. Furthermore, the partitioning behaviour (as related to fast-cooling) of PGEs during converter matte phase-specific crystallization sequences, transformations and morphological changes, appears to be a poorly understood process. It therefore becomes relevant to relate PGE partitioning to the formation of stable phases, as the subsequent microstructures form an integral part to the processing characteristics of their host phases. Of particular relevance to this study is that of Schouwstra (2000), in discussing a model for the slow-cooling process indicated that an ingot is a non-equilibrium system, with crystallization taking place according to the principles of fractional crystallization.

The aim of this study was therefore to investigate the partitioning of trace, minor and major concentrations of PGEs (Pd, Pt, Rh, Ru, Ir and Os) between nickel–sulphide, copper–sulphide and alloy phases from an actual fast cooled (water granulated) production

sample with reported iron-endpoint of 0.15 wt.%. This in turn would result in a more comprehensive understanding of varying PGE partitioning, compositional and external morphologies, related in particular to alloy formation.

2. Analytical techniques

A combination of analytical techniques was applied to methodically characterise nickel–sulphide, copper–sulphide and alloy phases. Electron-transparent sub-samples were characterised using a high resolution JEOL JSM-7001F FEG SEM equipped with a number of detectors. An extremely small probe diameter at accelerating voltage of 15 kV and probe current of 90 μA proved optimal for phase-specific analysis.

It became relevant to quantify the PGE distribution between phases. For this purpose, electron probe microanalysis was performed on representative analytical sub-samples with a Cameca SX50 microprobe equipped with four wavelength dispersive spectrometers and an energy dispersive spectrometer. The system was calibrated with reference standards of pure Fe, Co, Ni, Cu, Pb, Pd, Pt, Rh, Ru, Ir and Os and a pyrrhotite (FeS) reference was used for S. The analysis was performed exclusively on wavelength dispersive spectrometers and conducted in a semi-sequential manner on three of the spectrometers that were suitably equipped to detect the element suite of interest. An accelerating voltage of 30 kV was used with a beam cup current of 30 nA. A counting time of 20 s on peak and 10 s on each of two background positions was employed. The following lines were measured; $K\alpha$: S, Fe, Co, Ni, Cu; $L\alpha$: Ru, Rh, Pd, Ir, Pt, Pb; $M\alpha$: Os. Matrix correction was based on the ZAF procedure in the SAMX Analysis software. Detection limits are as follows in parts per million: S (300), Fe (200), Co (200), Ni (700), Cu (700), Pb (1200), Pd (600), Pt (800), Rh (700), Ru (700), Ir (800) and Os (800). The analytical precision was limited by the two micron beam diameter and the heterogeneity of the analysed phases.

A 200 kV JEOL JEM-2100 LaB$_6$ TEM equipped with an Oxford Instruments XMax 80 SDD EDS detector was used for high resolution imaging and compositional analysis on specially prepared electron-transparent samples.

Equilibrium solidification paths were generated with MTDATA supported by the Mtox matte database (Gisby et al., 2007), for the iron-endpoint of interest. The database contains assessed thermodynamic descriptions for the matte system Co–Cu–Fe–Ni–O–S and thus allows calculations of the equilibrium properties of the phase assemblages from metal saturated mattes and solid sulphide to oxide saturated systems. In addition, a comparative examination is provided with respect to the equilibrium compositions of MTDATA alloy phase assemblages beside mineralogically observed alloy structures in order to present a comprehensive understanding of alloy exsolution, compositional and morphological varieties.

3. Converter matte characteristics

Quantitative X-ray diffraction analysis and subsequent mineralogical examinations with respect to iron-endpoint 0.15 wt.%, yielded the following results (in order of decreasing relative abundance) with heazlewoodite (Ni$_3$S$_2$ – 63.7 wt.%) forming the dominant phase, a tetragonal form of chalcocite (Cu$_2$S – 17.9 wt.%), PGE-containing nickel–copper (NiCu) – dominant alloy phase (14.2 wt.%) and a spinel phase (NiFe$_2$O$_4$ – 4.2 wt.%). Osmium-dominant phases could not be quantified; instead volume-% estimation diagrams set the relative abundance below one percent. Phase-specific scanning electron and transmission electron-induced energy dispersive X-ray microanalysis supported by backscattered

electron and bright-field images has been provided for the respective phases in the previous study (Thyse et al., 2010).

The accurate measurement of the composition of the nickel–sulphide, copper–sulphide and alloy phases using electron probe microanalysis became particularly important for this study. It was furthermore important to have identified most of the phases by then as it assisted in reliable standardisation.

Electron probe microanalysis (all percentages are in weight% unless specifically otherwise noted) of twenty-two heazlewoodite grains on various particles confirm the presence of nickel–sulphide phases. Table 1 contains the compositional ranges, averages and standard deviations for the principal, major, minor and trace elements distributed in the analysed nickel–sulphide grains.

The standard deviations as shown in parenthesis are widely used to indicate how much dispersion there is within the electron probe microanalytical data set from the average analysis. The PGEs distributed in nickel–sulphide grains are reported in detail in Section 4.1

Microanalysis of eighteen chalcocite grains on various particles confirms the presence of copper–sulphide phases. Table 2 contains the compositional ranges, averages and standard deviations for the principal, major, minor and trace elements distributed in the analysed copper–sulphide grains. The particular PGE distributed in copper–sulphide grains is also reported in Section 4.1.

The analysis of eighteen alloy grains on various particles indicates the presence of NiCu-dominant alloy phases. Table 3 contains the compositional ranges, averages and standard deviations for the principal, major and minor elements distributed in the analysed NiCu-dominant grains. The PGEs distributed in NiCu-dominant grains are reported in detail in Section 4.2.

In addition, the respective phases were characterised using a JEOL JSM-7001F FEG SEM with EDS, from which compositional images (mixed backscattered and secondary electron signal), were acquired by high-resolution phase-specific assemblage and element mapping. Fig. 1 provides a comparative examination with respect to the characteristic intimate intergrowth relationship between the nickel–sulphide, copper–sulphide and NiCu-alloy phases.

Table 1
Compositional ranges, averages and standard deviations of electron probe microanalysis with respect to nickel–sulphide grains.

Element	Detection limit (ppm)	Grains below [*]D.L.	Grains analysed	Compositional range	Average analysis (ppm)
Ni	700	None	22	60.52–71.08	66.56 (3.30)
S	300	None	22	17.66–26.80	23.34 (2.22)
Cu	700	1	21	0.97–13.84	5.49 (3.98)
Co	200	None	22	0.20–0.68	0.48 (0.11)
Pb	1200	1	21	0.13–0.30	0.21 (0.05)
Fe	200	None	22	0.03–0.26	0.09 (0.05)

Standard deviations in parenthesis.
[*] D.L. – Detection limit.

Table 2
Compositional ranges, averages and standard deviations of electron probe microanalysis with respect to copper–sulphide grains.

Element	Detection limit (ppm)	Grains below [*]D.L.	Grains analysed	Compositional range	Average analysis (ppm)
Cu	700	None	18	65.92–76.57	71.32 (3.05)
S	300	None	18	19.22–20.76	20.12 (0.46)
Ni	700	None	18	3.92–15.23	8.42 (2.84)
Fe	200	None	18	0.05–0.73	0.13 (0.16)
Co	200	None	18	0.11–0.28	0.16 (0.04)

Standard deviations in parenthesis.
[*] D.L. – Detection limit.