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Fundamental process equilibria of base and trace elements in the DON smelting of various nickel concentrates

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Abstract

The converter-less nickel matte smelting technology (DON) adopted more than 20 years ago in Boliden Harjavalta smelter has been since that applied successfully to the processing of large number of nickel sulphide concentrates of various Ni-to-Cu ratios and MgO contents. The operational point of the technology is far from the conventional primary nickel smelting in the smelting-converting route. Therefore, a careful scouting of distribution equilibria of the base and trace elements in the smelting conditions of DON process has been conducted, in order to obtain quantitative information about the equilibria and thermodynamic properties of the nickel mattes at low iron concentrations, less than 10 wt-% [Fe] in matte. The series of investigations has included novel experimental and analytical techniques for increasing the reliability and sensitivity of the phase equilibria as well as the element distribution observations carried out in typical high-grade nickel matte smelting conditions.

Key words: Nickel matte; Iron silicate; Magnesite; Precious metals; Platinum group metals.

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Introduction

An access to high-MgO raw materials for nickel smelting directed Outokumpu in late '80s to development of a new primary smelting technology for nickel matte, based on the flash smelting concept. The fundamental novel idea was the expansion of slag volume generated in the smelting step, by oxidation the feed mixture to much lower iron concentrations in the produced matte than the conventional practice [1]. This involved a new flow sheet, closing internal circulation of the slag and matte between the converting and slag cleaning thus improving the metal value recoveries, in particular that of cobalt, and lowering environmental impact of the nickel matte smelting. The elimination of converters and the entire converting step had several side effects to the industrial operation, including e.g. lower fugitive emissions and smaller CAPEX [2]. It also required modifications in the refinery flow sheet [3]. The current operational practices will be described elsewhere in this Conference [4].

Fundamentals of nickel smelting are much less scrutinised than those of copper smelting [2-5]. In 1995 only limited information existed, about the fundamentals of matte-slag equilibria, when the direct nickel matte smelting was taken into industrial use, and the data on properties of trace elements at low iron concentrations in the matte below 15 wt-% Fe were non-existent. In high-iron mattes, the previous focus had been in nickel losses to slag and recoveries of selected trace elements, typically cobalt [6].

The knowledge in early '90s upon nickel mattes in the converting was largely based on a review of Kellogg [7] and the prior experimental data. Font et al. [8] and Henao et al. [9] presented new experimental data on the slag-matte-gas equilibria in MgO crucibles and about selected trace elements. The scope was in conventional matte making and its conditions. Certain details on trace elements in nickel matte converting related to platinum group element distributions were studied [10]. For helping to understand the coupled phenomena in converting, process dynamics modelling has also been used [11-12].

This presentation gives an overview on the recent studies of the slag-matte equilibria carried out with a novel experimental technique, allowing accurate observations about phase equilibria, their assays and the distributions of minority elements deporting them between matte to be recovered and slag where many elements will be discarded at low concentrations to various slag products.

Experimental

The experimental technique was based on gas equilibration of small matte-slag samples on a solid substrate in flowing CO-CO₂-SO₂-Ar mixtures of controlled compositions. The experimental conditions were selected so that sulphur dioxide pressure in the furnace in all conditions was $P(\text{SO}_2) = 0.1 \text{ atm}$. This was a modification of a technique used earlier in many geochemical applications [13], and adopted by Jak et al. [14] for metallurgical

slags and slag-metal equilibria. The experimental set up as well as the techniques used for confirming the state of equilibrium reached in the experiments of this work have been presented earlier in detail in the literature [15-17].

The experimental breakthrough in the analytical techniques for the trace elements was the use of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) directly from the polished sections, without separating the different phases of samples prior to the phase composition analyses. Combined with the electron microprobe X-ray analysis (EPMA) it allowed accurate chemical analyses in the whole range from several wt-% to sub-ppm concentrations. The technique used also involved a statistical evaluation of the composition of each phase so that 8-10 points were measured on well-quenched domains of the sample and in addition to the average composition, its standard deviation will also be reported [15]. Those were the first metallurgical slag samples analysed with LA-ICP-MS technique and a lot of effort was put on the possible systematic errors arising from samples, from different composition domains than the geological specimens studied earlier [18].

An indication of the consistence of the two direct analytical methods is the good agreement for such elements present at concentrations above the detection limits of both the methods. An example is shown in Fig. 1 where cobalt concentrations of various iron silicate slags by LA-ICP-MS and EPMA are plotted as a function of iron concentration in the nickel matte at 1350-1450 °C. The agreement between two independent techniques is good, and the obtained standard deviation of the results is ± 0.01 wt-% between the different techniques.

Figure 1. A comparison of EPMA and LA-ICP-MS data of cobalt concentration in iron silicate slags at nickel matte saturation containing about 0.5 wt-% Co in different iron concentrations of the sulphide matte.

The experimental series consisted of equilibration experiments at 1350-1450 °C for gas-matte-slag samples in fused quartz crucibles and with constant Ni-Cu ratios of 0, 2:1 and 4:1 (w/w). The studied sulphide mattes were synthesised *in situ* in the equilibration furnace from pure Cu₂S, FeS and Ni₃S₂ powders. They initially contained 1 wt-% of each trace element which were distributed between the slag, matte and gas phases during the high-temperature equilibration period. The main process between the gas, iron silicate slag and nickel-copper matte was the adjustment of iron distribution by two independent system variables, based on the overall reaction (1):

Thus, the prevailing sulphur and oxygen pressures as independent variables define the distribution of iron between the nickel matte and slag, as well as ‘the matte grade’ defined in this study as iron concentration of the sulphide matte. As a parallel reaction within the slag, iron oxides distribute between the oxidation stages as

but the advancement of reaction (2) was not considered experimentally, as EPMA is sensitive to the elements only and no information about their oxidation states can be obtained.

Results

The slag assay in matte-slag equilibrium at silica saturation was examined as a function of the matte grade and magnesia concentration. The EPMA results of iron concentrations at 1400 °C from 3 to 12 wt-% are plotted on an isothermal constrained Gibbs triangle $\text{FeO}_x\text{-MgO-SiO}_2$ in $P(\text{O}_2) = 0.01$ Pa in Fig. 2. The oxygen pressure range in the two mattes with $[\text{Ni}]:[\text{Cu}] = 2$ and 4 (w/w) had no major impact to the silica saturation boundary, as can be seen in the graph. It shows about 1 wt-% higher silica solubility in contact with matte than the assessed copper- and nickel-free iron silicate slag system in the Mtox database [19] used in the calculations.

Figure 2. Experimental slag composition of silica saturation at 1400 °C superimposed on a calculated isothermal section of the system by MTDATA and Mtox database, vers. 8.2 [19]; CPX = clinopyroxene, HAL = halite (wüstite, MgO), OLI = olivine, OX_LIQ = slag, TRI = tridymite.

Figure 3. Liquidus contour projection as a function of SiO_2 concentration with MgO as parameter: silica solubility increases along with MgO-concentration; the calculated boundaries at $\text{MgO} = 0$ (---) and 9 wt-% (—) are based on Mtox database (vers. 8.2) and MTDATA software.

The experimental liquidus composition data allow also estimation of the temperature dependency for the silica saturation boundary at fixed magnesia concentrations, Fig. 3. The used magnesia concentrations in the two experimental series with $[\text{Ni}]:[\text{Cu}] = 4$ and 2 (w/w) are not completely overlapping, in particular at the highest MgO concentration. The experimental technique used and the small differences in the initial MgO compositions causes the recognisable scatter in the liquidus line projection shown in Fig. 3.

The solubility of sulphur in the slag was studied as a function of temperature, iron concentration of matte and MgO concentration of the slag. MgO concentration of the slag has a clear effect on the sulphur solubility, as can be seen in Fig. 4. It is clearly also equally affected by the iron concentration of the matte in a fixed atmospheric point, which also reveals the activity of iron in the system. This indicates that the nickel-to-copper ratio has relatively small impact to the iron activity of matte in the current composition range.

The distribution coefficient of a component Me was defined in this study as ratio of its concentration in the nickel matte divided by that in the slag, i.e.

$$L^{m/s}(\text{Me}) \equiv [\text{wt-\%Me}]_{\text{matte}}/(\text{wt-\%Me})_{\text{slag}}. \quad (3)$$

Figure 4. Sulphur solubility in DON slags at iron concentrations of the matte from 3 to 12 wt-%; the slags with a similar MgO-level at 1400 °C have been plotted on the same graph and no impact of the [Ni]:[Cu] ratio of nickel matte can be seen (open symbols [Ni]:[Cu] = 2, closed [Ni]:[Cu] = 4).

The above referred fact that iron activity in nickel-copper-iron sulphide mattes at constant iron concentration is not strongly a function of the [Ni]:[Cu] -ratio is also seen in the behaviour of the distribution coefficient of iron at low iron concentrations, Fig. 5. Magnesia concentration of slag, affecting the iron activity of the slag in each oxygen pressure [17] and thus the matte composition in each equilibrium condition has been used as parameter in Fig. 5. The de-ironisation of nickel mattes proceeds thus in a similar way from mattes with a high and low copper concentration, over a wide range of [Ni]:[Cu] ratios, down to 2-3 wt-% iron. The removal of iron from the nickel-copper mattes occurs at high iron concentrations essentially without major slagging of copper or nickel, and independently of the copper concentration of the matte, as scrutinised in industrial converter blows already by Browne [20].

Figure 5. Distribution coefficient of iron between matte and slag as a function of iron concentration at 1400 °C with MgO-concentration of the slag as parameter (open symbols [Ni]:[Cu] = 4, closed 2; $\square$ 8-9 %, $\diamond$ 4 and $\circ$ 0 % MgO).

The thermodynamic properties of nickel and copper in the matte vary when it is de-ironised in the smelting, and, as a consequence, when the Ni-Cu ratio of the feed mixture of the smelter fluctuates along with time. This causes changes in their matte-to-slag distribution coefficients. That feature at 1400 °C is demonstrated in Figs. 6a and b for nickel and copper at (MgO)=0, and in Fig. 7a, and b for nickel, at three magnesia concentrations of the slag.

Figure 6. Distribution coefficient of nickel and copper between nickel matte and slag at 1400 °C with different MgO concentrations in the slag (11-12 wt%, 6-7 wt% and 0 wt%: ●, ● and ○; [Ni]:[Cu] = 2).

MgO additions to the slag favour the distribution of copper and nickel to the sulphide matte. The effect is small but clear in all studied concentrations of magnesia. The distribution coefficient is affected slightly also by the used boundary condition of this study, when (Fe):(SiO₂) ratio of the slag decreases with increasing MgO, as pointed out earlier, e.g., by Takeda [21] and Strengell et al. [16].

As suggested earlier (e.g., Teague et al. [6]) the reason of more favourable distributions between matte/metal and slag is the increase of the activity coefficient of less basic oxides, by formation of stronger MgO-SiO₂ bonds in the slag when magnesia is added.

Figure 7. The effect of [Ni]:[Cu]-ratio of matte on the distribution coefficient of nickel at (MgO) = 0 (a) and 8 wt-% (b) at 1400 °C, as a function of iron concentration of the matte (open symbols [Ni]:[Cu] = 4, closed 2).

The distribution coefficients of the trace elements cobalt and gold between the nickel-copper mattes as a function of its iron concentration and slag are shown in Figs. 9 and 10, respectively. The nickel-to-copper ratio of nickel sulphide matte in these studies was [Ni]:[Cu] = 4 (w/w). As can be concluded from Fig. 10, the solubility of palladium from the nickel mattes containing 1 wt-% Pd in the iron silicate slag is very low (< 1 ppm).

MgO clearly affects low concentrations of cobalt in iron silicate slags when upper iron concentration range of this study is concerned, see Fig. 8. Below ≈ 3 wt-% iron in the matte, the impact of magnesia cannot be found any more. The MgO-free data obtained are in good agreement with Toscano & Utigard [22].

Figure 8. The effect of MgO concentration in slag on the distribution of cobalt between nickel matte and iron silicate slag at 1400 °C in silica saturation; (wt-% MgO) = 0, 4 and 8 and [Ni]:[Cu] = 4.

The PGM and PM distributions measured in copper (Cu-Fe) and nickel (Cu-Ni-Fe) matte-metal equilibria suggest that nickel mattes are more favourable collectors of precious and platinum group metals than copper mattes, as shown in Fig. 9. Nevertheless, the obtained distribution coefficients in both the cases are very high.

Figure 9. A comparison of matte-slag distribution coefficients for gold and platinum in copper and nickel matte-slag systems at 1350 °C and 1400 °C, respectively; [Ni]:[Cu] = 4 in the studied nickel sulphide matte.

The presence of basic oxides in the slag affects the distributions of the precious and platinum group metals very much. As Fig. 10 indicates, the impact of MgO on the distribution coefficient of gold is about factor of 5 larger when its concentration in silica saturated iron silicate slag is increased from 0 to about 8 wt-% (MgO). We did observe a similar trend in the distribution behaviours of palladium and platinum, as well [17]. Also here, increasing silica concentration of the iron silicate slag has a positive influence on the distributions [21].

Conclusions

Due to the absence of data on nickel-copper-iron mattes in low iron concentrations, below 15 wt-% [Fe] and in the operational window of DON process, an experimental program was carried out for measuring base metal and trace element distributions. The variables used were iron concentration of the matte, its nickel-to-copper ratio, magnesia concentration of the slag and temperature. Magnesia of the slag in these conditions, in a fixed atmosphere, has a clear impact to iron concentration of matte, as a feedback from iron activity of the slag [17].

Figure 10. The effect of iron concentration in nickel sulphide matte and MgO concentration in the iron silicate slag on the distribution coefficient of gold at 1400 °C in silica saturation; [Ni]:[Cu] = 4, $P(\text{SO}_2) = 0.1$ atm.

The common substance in nickel sulphide concentrates' gangue, MgO [24-25], improves favourably recoveries of the base metals to the sulphide matte. A particularly large impact of MgO was found to be on those elements, which are weak oxide formers, as typically the precious and some platinum group metals.

A comparison of the current observations at silica saturation with the computational phase diagram Fe-O-MgO-SiO₂ based on Mtox database [19] indicates a good agreement. This suggests that the assessed data of Mtox database reproduces reliable phase property data for the industrial nickel matte smelting slags in DON smelting conditions in the flash smelting furnace (FSF) [26].

Font et al. [8] presented distribution data for selected trace elements in MgO crucibles at 1300 °C (i.e. in olivine saturation). They compared their observations as a function of $P(\text{SO}_2)$, with mattes of different [Ni]:[Cu] ratios and iron concentrations, including the limiting 'binary' matte systems Cu₂S-FeS and Ni₃S₂-FeS. Their results indicate the effects of prevailing $P(\text{SO}_2)$ on the dissolution of the base metals into iron silicate slags. The impact of MgO on the distributions is not visible, due to olivine saturation where silica concentration of the slag still is a free variable, as indicated in Fig. 1, and was less accurately controlled in those experiments.

As atmospheric SO₂(g) links together the sulphur and oxygen pressures in the equilibrium systems. The high-SO₂ environments thus represent higher oxygen pressures in a fixed matte composition, according to reaction

where sulphur pressures in the slag-matte equilibria are controlled by the matte and its assay. Therefore, in the environments of flash smelting, when slag and matte are formed below the reaction shaft, on the FSF settler bath surface, from the oxidation products the settler reactions generate essentially pure sulphur dioxide gas and the local prevailing $P(\text{SO}_2) \approx 1$ atm [23]. This is also the universal boundary condition for the sulphide matte and slag forming reaction process in the flash smelting furnace settlers, independently of the oxygen enrichment.

The results by Font et al. [8] imply that the matte-slag distribution coefficients for As and Sb increase when iron concentration of copper-nickel matte decrease, and the highest values for As, Bi and Sb were always obtained in copper-free mattes. This pattern, based on the present experimental observations, is more complicated if the effect of magnesia on the slag assay and its silica will be taken into account. There seems to be no data concerning the non-saturated magnesia-bearing iron silicates.

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