

PROCEEDINGS OF THE 7<sup>TH</sup> INTERNATIONAL

# SLAG VALORISATION SYMPOSIUM

SHIFTING GEARS TO A CLIMATE-NEUTRAL  
& RESOURCE EFFICIENT SOCIETY



**KU LEUVEN**

MATERIALS ENGINEERING

# PROCESS ORIENTED CHARACTERISATION OF COPPER SLAG PROCESSED BY FLOTATION IN VIEW METALS RECOVERY

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## Introduction

It is estimated that about 2.2 to 3 tonnes of copper slags are generated per each tonne of copper produced. Typically, copper slag contains around 1% Cu and 40% Fe, with the balance being mainly SiO<sub>2</sub>. There are minor amounts of other valuable metals as well<sup>1</sup>. Currently, these slags are treated mainly via pyrometallurgical routes with the aim to produce copper rich phase that is reintroduced back to the process and a slag to be discarded. Flotation stands as an alternative option<sup>2</sup>. Despite all the slag re-processing options being industrially validated, the final discarded slags are still rich in Cu and do contain other economic metals such as Mo, Ni and Co. This require a constant strive to improve the concentration processes, a necessity which is in phase with the integrated and optimized tailings management strategies<sup>1</sup>. Furthermore, new environmental legislations impose obligation to reduce the volumes of discarded slags and limits on slag constituents, meaning that, besides process improvements, new technologies enabling by-products recovery with little or no residue generation need to be developed. The objective of the current study was to realize a process oriented characterisation on representative samples from specific streams from the slag flotation plant belonging to Aurubis Bulgaria and to evaluate grades and form of occurrence of the economically important metals. Coupled to this an assessment of a combined hydrometallurgical approach to recover Cu, Mo, Co and Ni was targeted.

## Materials and Methods

Six process streams from the slag flotation plant adjacent to Aurubis Pirdop copper smelter were sampled. These streams are referred as: 1. Autogenous Mill Hydrocyclone Overflow (AMHO); 2. Ball Mill Hydrocyclone Underflow (BMHU); 3. Slag Flotation Feed (SFF); 4. Rougher Flotation Tailings (RFT); 5. Final Flotation Concentrate (FFC); 6. Final Flotation Tailings (FFT). They were analysed by a field emission gun scanning electron microscope (FEG SEM, Zeiss Sigma 300) equipped with two Bruker XFlash 6|30 X-ray

detectors for energy-dispersive X-ray spectroscopy (EDS) analysis. The same system Zeiss Mineralogic was used for an automated mineralogy as to derive modal mineralogy and microstructure. Mineral abbreviations adopted throughout the text are taken from Whitney and Evans (2010)<sup>3</sup>, except for glassy phase (GPh) and mixed phase (Mix). Chemical assays were done either by XRF, ICP-AES or ICP-MS depending on the analytical lab location. Subsequently, a combined hydrometallurgical approach to recover Cu, Mo, Co and Ni from the FFT was performed through sulphation roasting followed by water leaching. In the first step, a 50 g sample from the FFT was thoroughly homogenised in a ceramic crucible with a pre-determined amount of 96% sulfuric acid. The crucible was placed inside an inductive oven for roasting for a specific duration. The sample was then left to slowly cool at room temperature before to be leached with water at pulp density of 10% in an agitated 500-mL glass reactor coupled to a water bath. Leaching duration was kept at 30 minutes, temperature at 50°C and stirring speed at 350 rpm. A vacuum filtration was finally performed to separate the pregnant leach solution from the residue, the latter being washed with deionized water and dried at 65°C. The effect on metal extraction of the process duration, amount of sulphuric acid, and temperature of the sulphation roasting were investigated.

## Results and Discussion

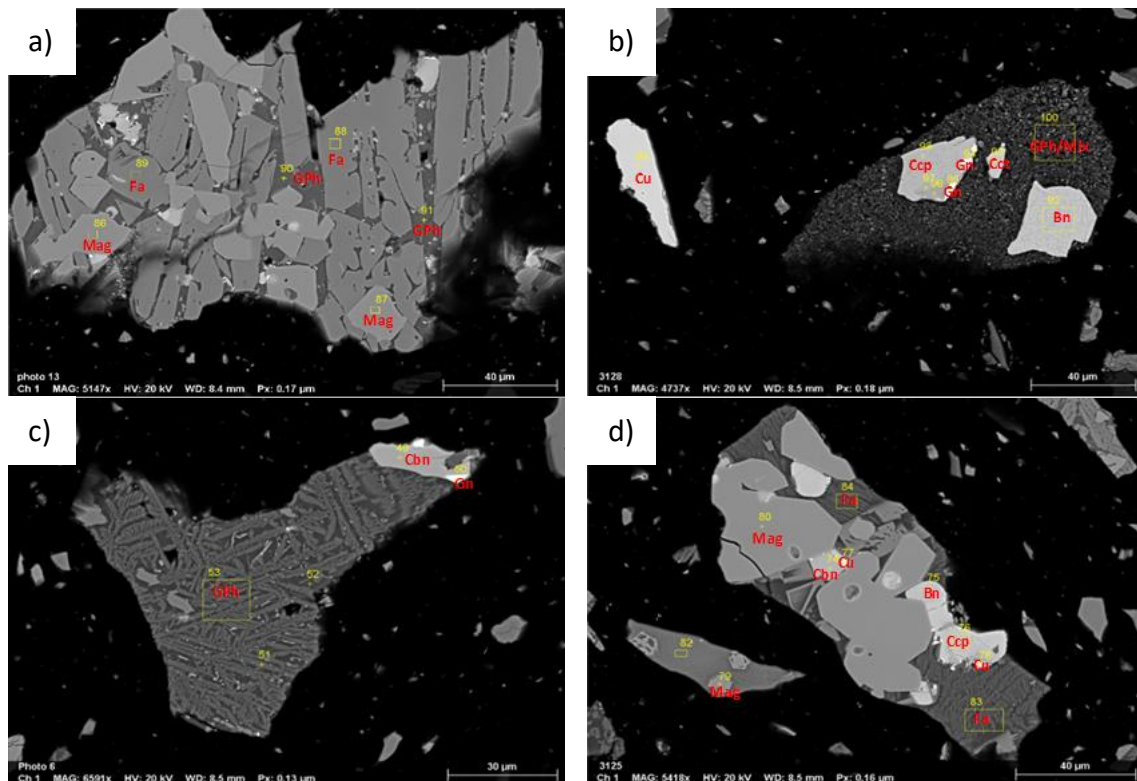
The concentrations of Fe (56%) and Si (11%) determined by SEM inside the AMHO and in SFF streams correspond well a fayalitic copper slag. These streams show a Cu grade of nearly 2.5%, a content which further increases within the flotation to around 22%, while it drops down to 0.5% in the RFT and FFT. The Cu concentration in the BMHU is about 10%, suggesting Cu preferable associations with the coarser size fractions. According to the SEM analyses, Mo is present nearly at same amount inside all the tested streams (from 0.05 to 0.08%), while when Ni is detected, it does not exceed 0.01%. No cobalt was identified in the samples. However, these figures are to be used as a rough estimation only, due to the low detection limits of the SEM especially for Mo, Ni, and Co. Indeed, ICP-MS analyses show about 0.03% of Co and 0.2% of Mo for the AMHO, the RFT and the BMHU. Likewise, according to these results, Ni content increases from zero to 0.02% for the former two streams, while the BMHU shows 0.04%. Furthermore, ICP-AES analysis indicates that Co and Ni are in majority concentrated in the FFT, respectively at 0.07% and 0.12%. The Mo content for this stream drops from 0.2% to 0.08%. The Fe and Cu concentrations, 45% and 0.4% respectively, are almost the same as the ones obtained by the SEM analyses. The mineralogical composition of the slags coming from the EDS-SEM using the element-to-mineral conversion method is given in Table 1.

**Table 1:** Mineralogical composition of the slags (wt%)

Bn	Cbn	Cct	Ccp	Cu	Other Cu sulphides	Fa	Gph	Mag	Mix	Qz
1.8	0.29	0.17	0.22	0.37	0.44	56.4	10.48	22.8	6.6	0.18

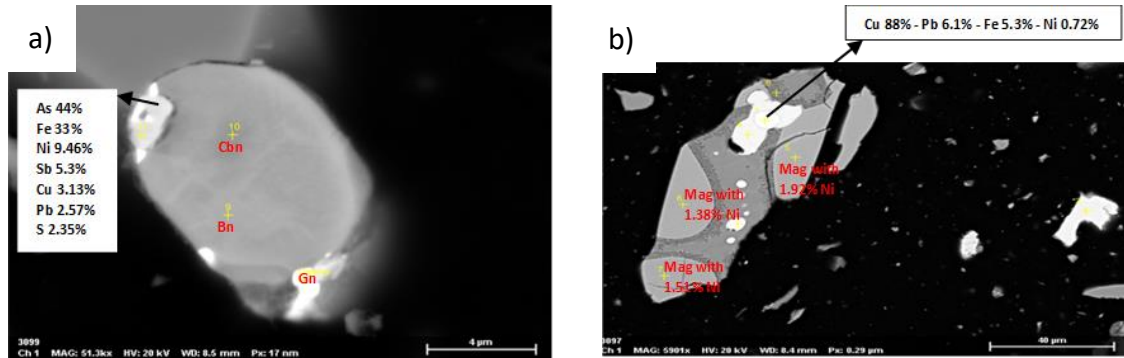
The average chemical composition of the FFT obtained by XRF through a Courier analyser inside the plant is (in wt%): 47.00 Fe, 28.00 SiO<sub>2</sub>, 2.75 Al<sub>2</sub>O<sub>3</sub>, 2.00 Zn, 1.50 CaO, 1.00 Na<sub>2</sub>O, 0.75 MgO, 0.55 S, 0.50 K<sub>2</sub>O, 0.48 Cu, 0.40 Pb, and 0.06 As. These assays corroborate well with the SEM findings apart for the zinc (2.00% instead of 0.84%). The granulometric analysis indicated d90 of ~200 µm, while d50 was slightly below 50 µm.

Figure 1 illustrates the mineralogical phases detected in the SFF sample. Likewise expected for slags, the principal mineral phases are found as microcrystals, coarse crystals and glass-like structures with eutectic skeletal/dendritic crystals<sup>4</sup>. The major mineral phases being detected are the fayalite with content of 56.43%, magnetite-Fe oxides in 22.85% and a glassy phase in 10.48%. Among the observed copper-bearing minerals, one finds bornite at 2%, chalcocite at 0.17%, chalcopyrite at 0.22%, and cubanite at 0.02%. They constitute, together with metallic copper at 0.37%, the matte that has not sedimented during copper refining step. As a rule, metallic copper is formed in the absence of oxygen when sulphide minerals become entrapped within the glass phase and start to crystallize as temperature goes down. They occur most frequently as either inclusions or emulsions inside the fayalite-glass phase<sup>4</sup>. What can be very well appreciated in Figure 1b is that these particles are spherical in shape and are met as elongated to spindle-shape drops of various sections<sup>4</sup>. The size of the above mentioned copper-bearing minerals ranges from a few to hundred microns.



**Figure 1:** SEM micrographs of slag flotation feed.

Nickel was rarely detected or was virtually absent in the EDS analyses of selected particles from the SFF either because of very low content or due to the extremely small size of the particles where it is present. As can be seen from figure 2b, Ni is most frequently observed as association with magnetite, where it reaches 1.9%, but could also be met as coating on copper-bearing minerals or placed along to arsenic or arsenopyrite, where is most abundant (nearly 10%). Arsenic and nickel spectra show also presence of Fe, Sb, Cu, S and occasionally Pb. Cobalt was not detected.



**Figure 2:** SEM micrographs of flotation feed: mineralogical forms in which nickel is found.

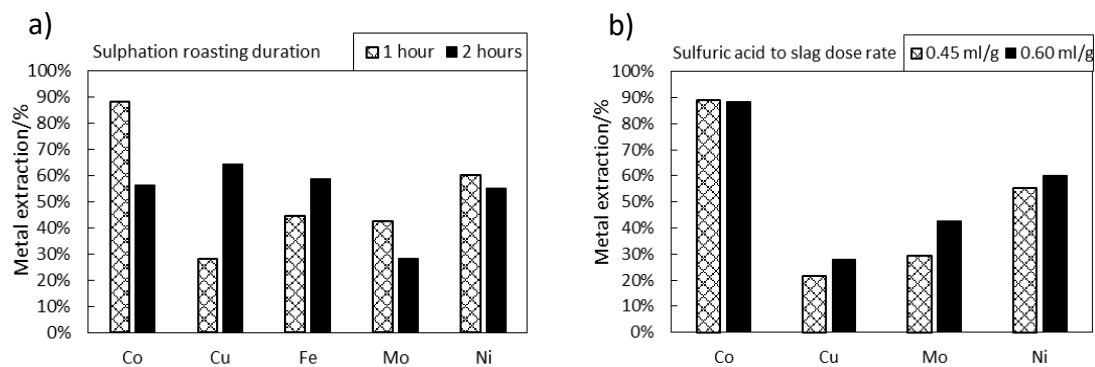
To quantify the degree of Mo associations with fayalite and magnetite, selected particles from the feed were subjected to automated mineralogy. It has been observed that about 17% (2164 counts) of the fayalite holds Mo. With 4788 counts, magnetite is not as abundant as fayalite (12410 counts), however about 27% (1303 counts) of the magnetite bears Mo. Fe is distributed throughout the glassy iron silicate phase. Mo distribution is closely bound to the Fe content in the slag, which is logical since during pyrometallurgy, the molybdenum coming with the mining concentrates is subjected to oxidation and associates magnetite. Mo is present as complex precipitated oxides and silicates where it forms separate phases of Fe-Mo-O type with low silica content such as  $\text{FeO} \cdot \text{MoO}_2 - \text{Fe}_3\text{O}_4$ <sup>5,6</sup>.

Through combining the available assays from XRF, SEM and ICP it has been possible to perform data reconciliation and thus to ultimately yield the mineralogical composition of the FFT – Table 2. The major phases being identified follow the ones met in the slag flotation feed. The lower content of copper-bearing minerals is a direct consequence of the high copper grade in the FFC. The increase of Ni in the final tailings could be explained by its elevated concentration inside magnetite and residual copper-bearing minerals, taking into account its preferential association with the former and assuming that the later are difficult to float due to nickel presence on particle surfaces.

**Table 2:** Mineralogy of the final flotation tailings (wt%)

Fa	Mag	Gph	Qz	Bn	Ccp	Cu	Cbn	Po	Sp	Apy	Gn
60.06	21.77	10.81	0.25	0.14	0.07	0.02	0.01	0.01	< 0.01	< 0.01	< 0.01

The results of the sulphation roasting and subsequent water leaching tests on the FFT are presented in figures 3 and 4. The effect of roasting duration was studied at 350°C and a ratio of concentrated acid to FFT equal to 0.6 mL/g. Figure 3a shows that Cu extraction increases substantially when roasting duration was increased from one to two hours possibly due to the slower sulphation kinetics of the copper-bearing phases or the rapid formation of ferrites due to the relatively high iron content. The Fe extraction follows the same evolution, although to a lesser extent, while the extractions of Co, Mo, and Ni decrease with roasting time. A possible reason for the Mo extraction decrease could be its volatilization with time or its oxidizing to a non-soluble form. From the results presented in Figure 3b for a 350°C roasting, it can be seen that while 33% excess acid does not affect Co dissolution – 0.45 mL/g being the stoichiometrically required amount –, Cu and Ni were improved by about 5% and Mo by about 15%.

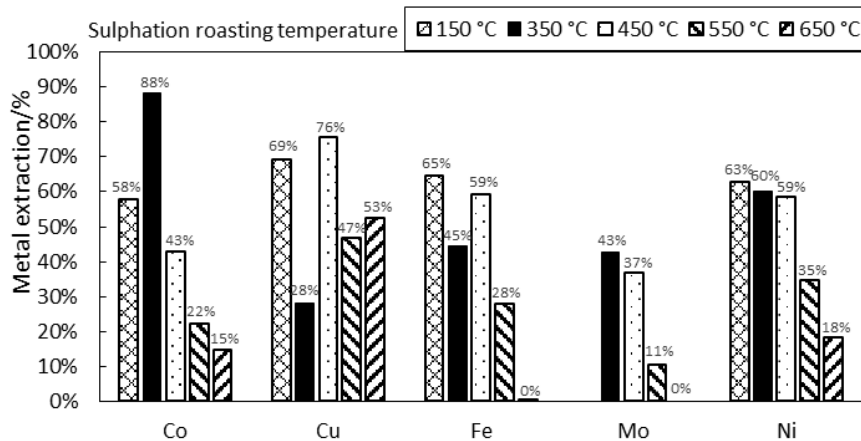


**Figure 3:** a) Effect of sulphation roasting duration; b) Effect of sulphuric acid dose rate

The relatively low Mo extractions are not surprising since there is strong evidence that at least part of the Mo in the FFT is associated to magnetite in the form of a stable iron oxide spinel compound from the  $\text{FeO} \cdot \text{MoO}_2 - \text{Fe}_3\text{O}_4$  series and that these complex compounds exhibit very low degree of leaching. The liberation of Mo from such a compound requires highly oxidative conditions and a roasting temperature below 800°C but sufficiently high enough to produce the soluble form of molybdenum trioxide and insoluble hematite.<sup>5,6,7</sup> Whereas Mo need to be oxidised to its highest state to make it amenable to leaching, Co need to be reduced from  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$ . An extended roasting time from 1 to 2 hours seems to favour the oxidation of cobalt and hence the reduction in cobalt extraction.

Figure 4 shows that, for a sulfuric acid to slag ratio kept at 0.6 mL/g and 1-hour roasting duration, increasing the roasting temperature in the range 150-650°C is leading to decrease in Mo and Ni solubility. Cobalt reached its highest extraction level (88%) when roasting was done at 350°C and then decreased at higher temperatures. The dissolution of Fe and Mo is approaching nearly zero when roasting was carried out at 650°C. Mo extraction level follows a similar trend to that of Fe due to their close associations in the

tested slags. The drop in Mo extraction at higher roasting temperatures could be due to oxidation and sublimation effects at elevated temperatures<sup>8</sup>. Likewise, transformation from water-soluble sulphates to non-soluble oxides could be suspected for the rest of the metals of interest. The observed decrease in the extraction level could be also due to increased decomposition of sulphuric acid with temperature and hence its limited availability at higher temperature ranges.



**Figure 4:** Effect of sulphation roasting temperature

## Acknowledgements

The presented results are part of the Master thesis of Ms Silvana Bertoglio elaborated within the Erasmus Mundus Master on Georesources Engineering EMerald. Aurubis A.D. is gratefully acknowledged for supporting this project.

## Conclusions

The process oriented characterization realized on selected streams belonging to the slag flotation plant adjacent to Aurubis Pirdop copper smelter has shown that the copper slag consisted in majority of fayalite, magnetite-iron oxides and a glass-like phase. The nickel met in the slag flotation tailings is mainly associated to the iron-bearing phases. Cobalt was virtually no detectable within the limits of the instrumentation being used. Mo is to be found predominately inside the magnetite and to less extent in the fayalite. The sulphation roasting of slag flotation tailings realised under the optimal conditions facilitates bringing metals of interest in solution. Within the 150-650°C range, the best metal recoveries were respectively achieved at 150°C for Ni (63%), 350°C for Co (88%) and Mo (43%), and 450°C for Cu (76%). Above 450°C all the investigated metals show drop in their leaching recovery.

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