

Characterisation and recovery of non-ferrous metals met in a copper-slag processed by flotation

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ABSTRACT

Detailed process oriented characterisation on representative samples from plant survey of the slag flotation plant belonging to Aurubis, Bulgaria has been realised in order to evaluate the mineralogical occurrences of Cu, Ni, Mo and Co bearing phases. The slag subjected to flotation consisted in majority of fayalite, magnetite-iron oxides and a glass-like phase. Ni and Mo have been found to be closely associated to magnetite and fayalite. The tailing from the slag flotation has been subjected to sulphation roasting followed by water leaching as a hydrometallurgical means to recover the remaining Cu, Mo, Ni and Co. Based on the various sulphation roasting conditions (acid dosage, duration, temperature) copper, nickel and cobalt were brought to solution to a different extent. Molybdenum was the most difficult to be rendered soluble due to its close association with iron, suspected to form an insoluble compound with it. Sulphation roasting performed at 350°C has secured the best extraction degree for Cu, Mo and Co, while maximum recovery of Ni has been documented when roasting was done at 150°C.

Keywords: Copper slag; characterisation; SEM; roasting; metals leaching, hydrometallurgy 16(2), 153–65.

1. Introduction

The largest part of copper production is realized through processing of sulphide bearing polymetallic ores that are first concentrated by flotation and subsequently, the concentrates are subjected to series of pyrometallurgical steps such as smelting, conversion, refining with concomitant indispensable management of the associated slags [1]. The European Copper Institute defines copper slags as “Substance produced at high temperature in a liquid state, by melting mixtures of metal oxides and non-ferrous metals (from primary sources such as copper ores, matte or anodes) or by oxidizing metals (from copper rich materials such as metals, alloys or metal oxides)”.

A slag from copper refining contains relatively high amount of copper as oxides or sulphides and various amounts of other non-ferrous metal oxides [2]. As a rule, slags are stored inside purposely built infrastructures (dumps), occupying large surface area, requiring operational costs for safe disposal and monitoring. Therefore, studies on reutilization and recycling of slags are being initiated aiming at cost-efficient management of these technogenic wastes and their possible valorisation. It is estimated, that about 2.2 - 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 SiO₂. There are minor amounts of other valuable metals as well [3]. Currently, the slags are treated mainly via pyrometallurgical routes using electric or flash smelting furnaces with the aim to produce copper rich phase that is reintroduced back to the process and a slag to be discarded [4]. Flotation stands as an alternative option to deal with the slags being generated. Before being send to flotation the slag is left for cooling. After the concentration process a concentrate is generated and returned to the flash smelting furnace. In such a way important metals such as Co or Zn are continuously recycled from slag to concentrate. Some of them however are inevitably lost with the flotation tailings. From an economic point of view, the reported levels of metals recovery by flotation are considered as adequate ones [4]. Nevertheless, despite all the slag re-processing options being industrially validated, the final discarded slags are still rich in copper and do contain other economic metals such as molybdenum, nickel and cobalt. This requires a constant strive to improve the concentration processes, a necessity which is in phase with the integrated and optimized tailings management strategies [3]. 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 efficient by-products recovery with little or no residue generation need to be developed.

Based on the above, the objective of the current study was to realize a process oriented characterization on specific streams from the slag flotation process 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 copper, molybdenum, cobalt and nickel from the final flotation tailings (fayalite) was targeted.

2. Materials and methods

2.1. Sampling

The flowsheet of the slag flotation plant adjacent to Aurubis, Pirdop copper smelter is shown in Figure 1. For the aim of the current work, six process streams were sampled using two different sampling set-ups.

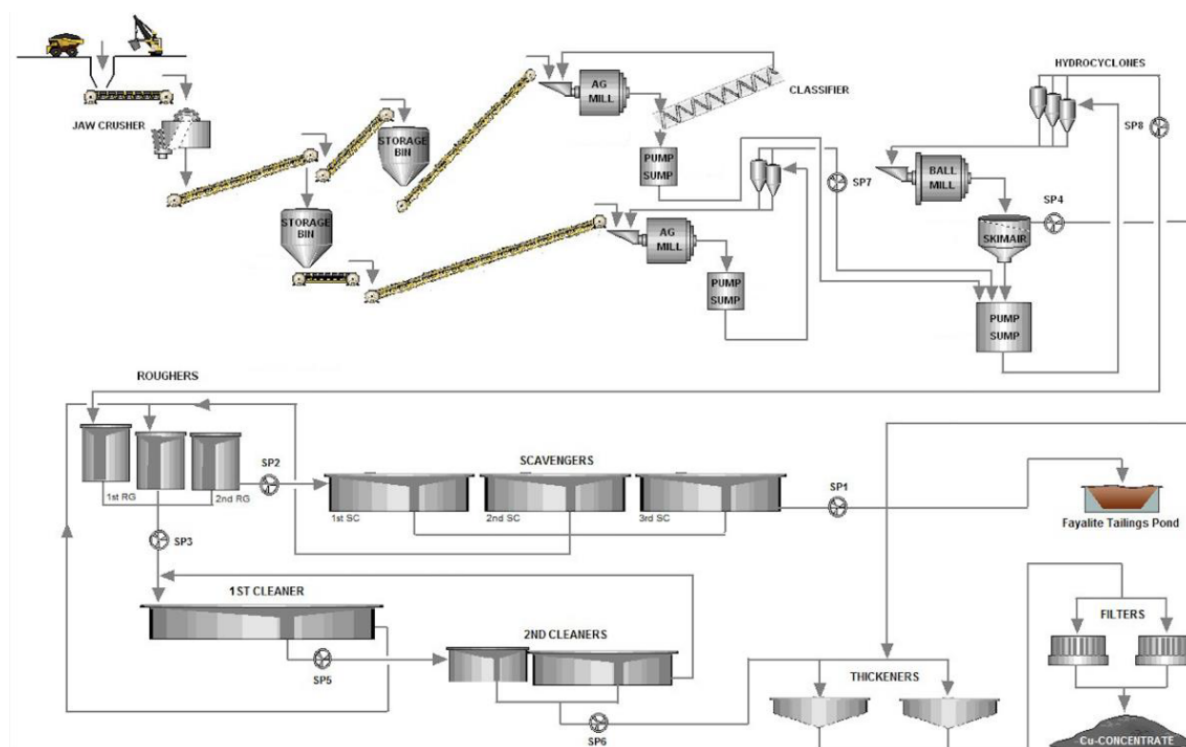


Fig. 1. Flotation plant flowsheet employed at Aurubis, Bulgaria

The first batch of samples (feed, tailings and concentrate) were collected via a Courier analyzer (Outotec, Espoo, Finland). This system takes representative samples from the flotation streams by cutting the respective flows in a 10 minutes' interval and recovers about 20-30 g per single passage. About 1 kg composite sample was prepared by this way. The second methodology consisted of a plant survey, where representative samples were gathered following established protocols. The six streams being sampled are referred further as: 1. Autogenous Mill Hydrocyclone Overflow; 2. Ball Mill Hydrocyclone Underflow; 3. Flotation Feed; 4. Rougher Flotation Tailings; 5. Final Flotation Concentrate; 6. Final Flotation Tailings.

2.2. Chemical and mineralogical analysis

Polished sections were prepared for mineralogical observations using 1 g of sample embedded in a mixture of 0.4 g carbon powder, 15 cm³ epoxy resin and 2 mL hardener. The polished sections were observed and analyzed 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. The operating conditions of the system were 20 kV acceleration voltage, and 8.4 to 8.5 mm working distance. Chemical assays were done either by ICP-AES or ICP-MS depending on the analytical lab location. All reagents used were of analytical grade.

2.3. Sulphation roasting - water leaching

The objective of the sulphation roasting was to render the targeted metals as soluble sulphates and thus to facilitate their subsequent water leaching. The sulphation is a step-wise process passing via oxidation of the metals, followed by a reaction with SO_3 to form metal sulphates. To this end, 50 g of sample from the final flotation tailings were thoroughly homogenized inside a ceramic crucible and a pre-determined amount of 96% sulfuric acid was then added. The crucible was introduced inside an inductive oven for roasting. After roasting time elapsing, the samples were left to slowly cool at room temperature. Further on, the calcine was leached with water at pulp density of 10 % in an agitated 500-mL five-neck 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 several times with deionized water and dried at 65 °C in a laboratory cabinet. Sulphation roasting parameters such as process duration, amount of sulphuric acid and temperature have been varied.

3. Results and discussion

3.1. Material characterization

The chemical composition of the selected streams as determined by the SEM-EDS is given in Table 1. The concentrations of iron (56 %) and silicon (11 %) inside the autogeneous mill hydrocyclone overflow and in feed streams correspond well a fayalitic copper slag. These streams show a copper 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 rougher and final flotation tailings. The copper concentration in the hydrocyclone underflow from the ball mill is about 10 %, suggesting copper preferable associations with the coarser size fractions. According to the SEM analysis, molybdenum is present nearly at same amount inside all the tested streams (from 0.05 to 0.08 %), while when nickel 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 analysis presented in Table 2 show about 0.03 % of cobalt and 0.2 % of molybdenum for the autogenous mill hydrocyclone overflow, the rougher flotation tailings and the ball mill hydrocyclone underflow. Likewise, according to these results, nickel content increases from zero to 0.02 % for the former two streams, while the underflow stream shows 0.04 %. Furthermore, ICP-AES analysis indicates that Co and Ni are in majority concentrated in the final flotation tailings, 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 are almost the same as the ones obtained by the SEM analysis. The mineralogical composition of the slags coming from the EDS-SEM using the element to mineral conversion method is presented in Table 3.

Table 1.

Chemical composition of selected streams as given by the SEM analysis

Stream	Concentration (wt %)																			
	O	Na	Al	Si	S	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Sn	Sb	Pb
1	24.00	0.13	2.15	11.91	0.62	0.73	1.29	0.03	0.01	0.00	56.50	0.00	0.00	2.32	0.16	0.02	0.05	0.00	0.00	0.03
2	22.65	0.11	2.13	10.41	0.80	0.67	1.22	0.06	0.01	0.00	51.73	0.00	0.01	9.90	0.17	0.03	0.05	0.01	0.00	0.03
3	24.00	0.18	2.02	11.46	0.78	0.72	1.79	0.05	0.01	0.00	56.18	0.00	0.01	2.42	0.19	0.02	0.08	0.00	0.00	0.04
4	24.32	0.14	2.55	12.62	0.24	0.87	1.65	0.05	0.01	0.00	56.70	0.00	0.00	0.53	0.18	0.02	0.05	0.00	0.00	0.03
5	17.55	0.12	1.60	7.60	5.11	0.48	1.23	0.04	0.01	0.00	43.59	0.00	0.01	22.21	0.21	0.08	0.06	0.00	0.01	0.07
6		0.00	0.00	16.72	0.59	0.00	0.00	0.00		0.00	47.00	0.00	0.00	0.48	0.84	0.06				0.40

Table 2.

Chemical composition of 4 out of the 6 streams as determined by an ICP-AES

Stream	Concentration (wt %)				
	Fe	Co	Cu	Ni	Mo
Autogenous Mill Hydrocyclone Overflow (1) *		0.03		0.02	0.19
Ball Mill Hydrocyclone Underflow (2) *		0.02		0.04	0.19
Rougher Flotation Tailings (4) *		0.03		0.02	0.20
Final Flotation Tailings (6) **	45.24	0.07	0.41	0.12	0.08

*ICP-MS at Aurubis, **ICP-AES at GeMMe (University of Liège)

Table 3.

Mineralogical composition of the slags as determined by the EDS-SEM following an element-mineral reconciliation (wt%)

Bornite	Cubanite	Chalcocite	Chalcopyrite	Copper	Other Cu sulfides	Fayalite	Glass	Magnetite	Mixed phases	Quartz
1.8	0.29	0.17	0.22	0.37	0.44	56.4	10.8	22.8	6.6	0.18

The average chemical composition of the final flotation tailings obtained through the Courier stream analyzer inside the plant is presented in Table 4. These assays corroborate well with the SEM findings apart for the zinc. The granulometric analysis indicated d90 of around 200 µm, while d50 was slightly below 50 µm.

Table 4.

Chemical composition of the final flotation tailings as determined by XRF (wt%)

Cu	S	Fe	CaO	MgO	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	Pb	As	Zn
0.48	0.55	47.00	1.50	0.75	28.00	2.75	1.00	0.50	0.40	0.06	2.00

Figure 2 illustrates the mineralogical phases detected in the flotation feed sample and Table 4 reports on the respective data coming from SEM-EDS spots analysis. Likewise expected for slags, the

principal mineral phases are found as microcrystals, coarse crystals and glass like structures with eutectic skeletal/dendritic crystals [5].

The major mineral phases being detected are the fayalite (Fe_2SiO_4) with content of 56.43 %, magnetite-Fe oxides (Fe_3O_4) in 22.85 % and a glassy phase presented in 10.48 %. Among the observed copper bearing minerals, one finds bornite (Cu_5FeS_4) at 2 %, chalcocite (Cu_2S) at 0.17 %, chalcopyrite (CuFeS_2) at 0.22 % and cubanite (CuFe_2S_3) at 0.02 %. They constitute, together with metallic copper at 0.37 %, the matte that has not sediment during copper refining step. All chemical formulae are based on [6]. 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 [5]. What can be very well appreciated in Figure 2b is that these particles are spherical in shape and are met as elongated to spindle-shape drops of various sections [5]. The size of the above mentioned copper-bearing minerals range from a few to hundred microns.

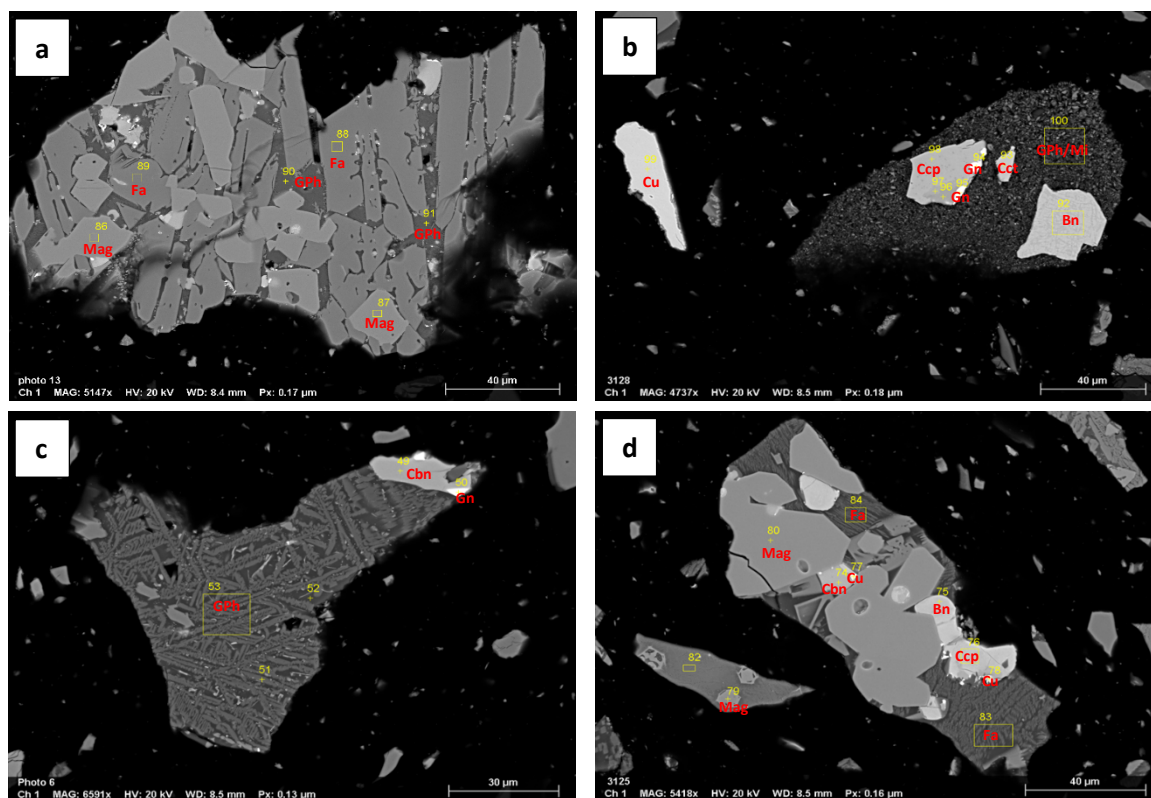


Fig. 2. SEM micrographs of slag flotation feed. Abbreviations after [7]: Fa-fayalite, Cct-chalcocite, Ccp-chalcopyrite, Cbn-cubanite, Bn-bornite, Mag-magnetite, Gn-galena. GPh stands for glassy phase, Cu for copper and Mix for a mixed phase.

Table 4.

EDS analysis (%) of selected particles from the flotation feed. Point locations - in Figure 2.

Point	O	Na	Mg	Al	Si	S	K	Ca	Ti	Cr	Fe	Co	Ni	Cu	Zn	As	Mo	Sb	Pb
49						32.31					41.91			22.76	3.03				
50						11.72													88.28
51	37.49	0.64		4.05	19.19	0.01	0.85	12.25	0.29		22.73			1.17		1.33			
52	40.82	1.76	0.75	8.31	23.50	0.40	4.12	4.69			9.22			1.24					5.21
53	37.41	1.14		5.00	19.38	1.35	1.99	8.64			22.40			1.75	0.65				0.30
74						30.76					40.62			28.61					
75						28.02					22.44			49.54					
76	13.61			1.65	3.02	18.67		1.56			30.71			30.78					
77			0.00			2.20					8.29		27.56	4.61		4.49		52.86	
78														100					
79	26.72								0.66		72.62								
80	26.39			2.41					0.84		69.76			0.60					
82	31.72	0.59	0.34	2.69	13.33	0.28	0.9	1.28	0.35		48.52								
83	40.68	1.19		6.84	20.49	0.45	3.55	10.98			15.34			0.49					
84	34.96	1.11		5.25	15.54	2.36	2.75	7.42			26.37			4.24					
86	25.87	0.46		2.39	2.26	0.19		0.18	0.66	0.14	66.21			1.63					
87	27.35	0.22		1.78	4.04	0.24			0.55		64.34			1.49					
88	32.02	0.80	0.48	1.29	12.51		0.79	1.12			48.75			2.25					
89	30.05		0.52	1.62	12.67	1.60	0.68	1.91			46.06			2.37	2.52				
90	37.57	0.92		5.69	18.94	0.51	1.71	13.54			19.45			1.68					
91	38.16	0.90		6.46	16.08	0.99	2.36	13.77			18.79			2.49					
92						21.02								70.46					
93						22.29								77.71					
94						12.95													87.05
95						11.52													88.48
96						34.83					35.66			29.51					
97						31.27					25.15			43.59					
98						27.42					18.21			54.37					
99														100					
100	30.23	1.65	0.65	3.92	17.95	1.19	2.10	3.63			34.55			4.13					

The perusal of the data depicted in Table 4 shows that nickel was rarely detected, or was virtually absent, 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 3 (b), Ni is most frequently observed as association with magnetite, where it reaches 1.9 %, but could be also 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 iron, antimony, copper, sulfur and occasionally lead (data not shown). Cobalt was not detected.

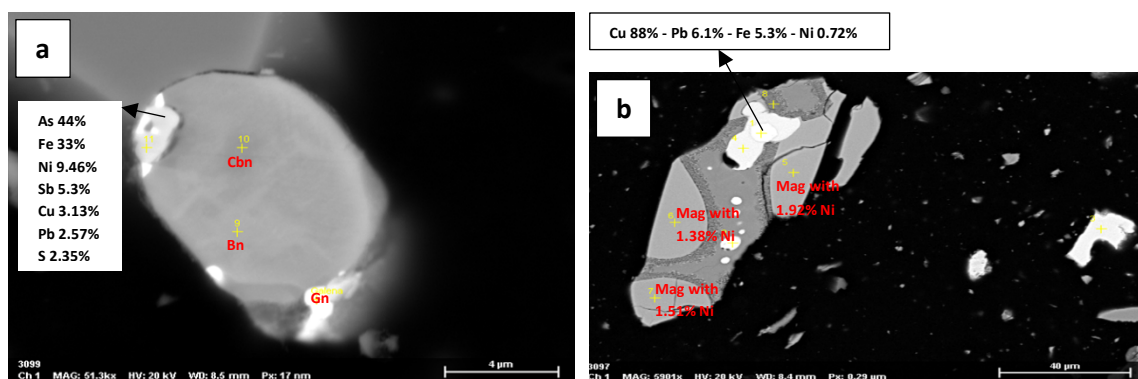


Fig. 3. SEM micrographs of flotation feed showing the mineralogical forms in which nickel is found. Abbreviations after [7]: Cbn-cubanite, Bn-bornite, Mag-magnetite, Gn-galena.

To quantify the degree of Mo associations with fayalite and magnetite, selected particles from the feed were subjected to automated mineralogy - Table 5. It could be noted, that about 17 % of the fayalite holds Mo. Magnetite is not as abundant as fayalite, however about 27% of the magnetite bears Mo. Fe is distributed throughout the glassy iron silicate phase. It can be observed, that Mo distribution is closely bound to the Fe content in the slag, which is logical since during copper 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.

Table 5.

Molybdenum distribution in associated minerals met in flotation feed

	Fayalite counts	Fayalite %	Magnetite counts	Magnetite %
With Mo	2164	17	1303	27
Without Mo	10246	83	3485	73
Total	12410	100	4788	100

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 final flotation tailings - Table 6. The major phases being identified follow the ones met in the flotation feed. The lower content of copper-bearing minerals is a direct consequence of the high copper grade in the final flotation concentrate. 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 latter are difficult to float due to nickel presence on particle surfaces.

Table 6.

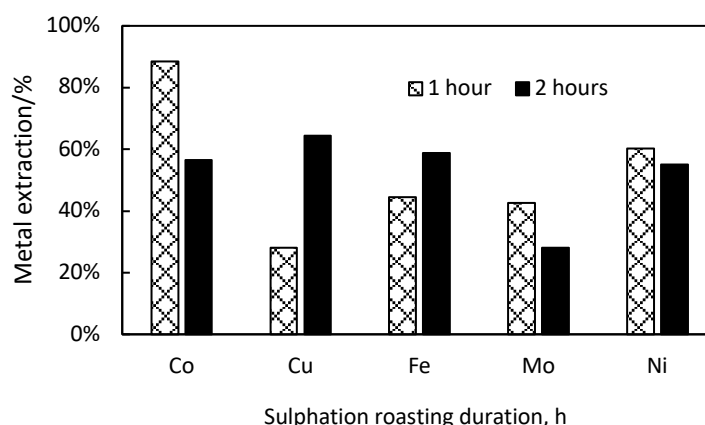
Mineralogy of the final flotation tailing

Phase	(%)	Phase	(%)
Fayalite	60.06	Bornite	0.14
Magnetite	21.77	Chalcopyrite	0.07
Glass	10.81	Copper	0.02
Quartz	0.25	Pyrrhotite	0.01
Cubanite	0.01	Arsenopyrite	< 0.01
Sphalerite	< 0.01	Galena	< 0.01

3.2. Sulphation roasting of the fayalite tailings and water leaching of the calcine

3.2.1. Effect from sulphation roasting duration

The extraction efficiency of Co, Cu, Fe, Mo and Ni was studied for roasting done at constant temperature of 350° C and two different durations (1 and 2 hours). The ratio of concentrated sulfuric acid to slag flotation tailings was kept at 0.6 ml/g. It can be observed from Figure 4, that Cu extraction increases substantially when roasting duration was increased from one to two hours. The Fe extraction follows the same evolution, although to a lesser extent, while the extractions of Co, Mo, and Ni decrease with roasting time prolongation. The observed trend for the Cu extraction could be explained by the slower sulphation kinetics of the copper bearing phases, requiring longer time to be converted to sulphates in comparison to that for the rest metals. Another explanation could be the rapid formation of ferrites due to the relatively high iron content. Mo extraction decreases with roasting duration with one possible reason for this being the Mo loss due to volatilization with time or its oxidizing to a non-soluble form. Since the main focus of the test was the recovery of Co, Mo and Ni, a one hour sulphation was considered as optimal duration.

**Fig. 4.** Effect of sulphation roasting duration on Co, Cu, Fe, Mo and Ni extraction

3.2.2. Effect from sulfuric acid concentration

Further on, the concentration of the acid used as roasting agent was evaluated as process parameter. The stoichiometrically required amount (calculated as 0.45 mL/g) was compared to one

supplied at 33% excess. The results shown in Figure 5 indicate that while cobalt dissolution is not affected by the excessive acid supply, cobalt and nickel extractions were improved by about 5% and 15% respectively.

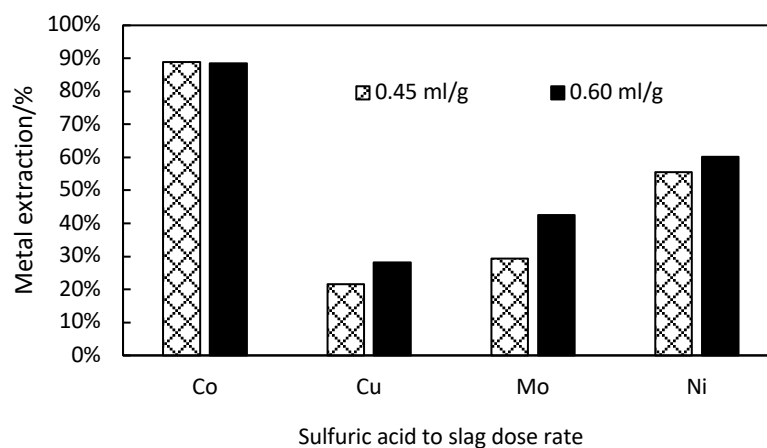
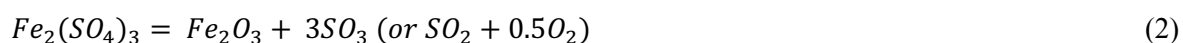


Fig. 5. Effect of sulphuric acid dose during roasting on Co, Cu, Mo, and Ni extraction

3.2.3. Effect of sulphation roasting temperature

Sulphation roasting temperature was varied in the range 150-650 °C in order to follow its effect on metals extraction. Sulphuric acid to slag ratio was kept at 0.6 mL/g and roasting duration - 1 hour. The results are shown in Figure 6. Increasing the roasting temperature is leading to decrease in Mo and Ni solubility. Cobalt shows its highest extraction level when roasting was done at 350 °C, reaching 88 % recovery which then decreases at higher temperatures. Copper and iron extractions drop at minimum at 350 °C before raising at 450 °C and after that dropping down again, although copper extraction showed a slight increase at 650 °C. The dissolution of iron and molybdenum is approaching nearly zero when roasting was carried out at 650 °C. Molybdenum extraction level follows a similar trend to that of iron 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 [8]. Although neither oxygen nor air was injected inside the furnace, since this latter was not completely sealed, one could not exclude oxidation to occur. Likewise, transformation from water-soluble sulphates to non-soluble oxides could be suspected for the rest of the metals of interest. For example, the decomposition temperatures for copper and iron sulphates are close respectively to 650 °C and 480 °C [9].



The observed decrease in the extraction level could be also due to increased decomposition of sulphuric acid with temperature increase and hence its limited availability at higher temperature ranges.

To sum up, among the investigated roasting temperature, 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%). Needless to say that within the 150 – 550 °C interval, iron extraction was always above 30 %, which has to be accounted in the downstream recovery of metals.

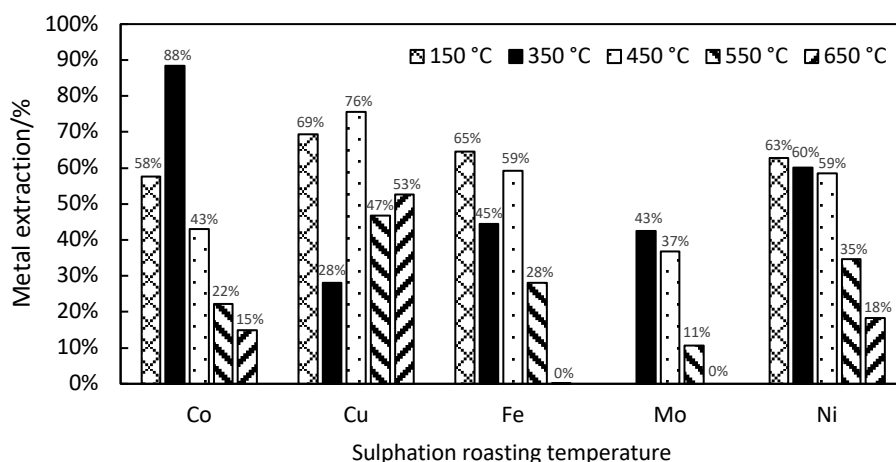


Fig. 6. Effect of sulphation roasting temperature on Co, Cu, Fe, Mo and Ni extraction

4. Conclusions

The process oriented characterization realized on selected streams belonging to the slag flotation flowsheet has shown that the Ni met in the slag flotation tailings is 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. Sulphation roasting of the flotation tailings followed by water leaching is relatively straightforward to realise. The sulphation roasting realised under the optimal conditions facilitates bringing the metals of interest in solution. It has been found, that the different roasting temperatures do have influence on metals leachability. While Co and Mo were best leached after roasting at 350 °C, roasting at 150 °C seem to be an optimal one for Ni. With increase in roasting temperature above 450 °C all the investigated metals show drop in their leaching recovery.

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